On the Manufacturing of SFF Based Tooling and Development of SLS Steel Material

A Doctoral Thesis within Woxéncentrum,
Department of Production Engineering,
KTH

by
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Abstract

Despite significant progress over the last few years, the application of metallic materials to Solid Freeform Fabrication (SFF) technology has not reached a wider acceptance as a competitive manufacturing method yet. One reason for this is that the technology still struggles with limitations concerning manufacturing time, precision, the selection of available materials and their properties.

This thesis addresses this situation, both with an overview of the different process approaches, and with an experimental investigation of the potential for the development of new liquid phase sintering steel-base materials. In the overview, different approaches to the SFF of metals are described, arranged and evaluated according to the form of the added material. It is concluded that a principal source of the limitations is to be found in the strong coupling between material and process approach. However, it is also concluded that while the limitations hamper the usage of Solid Freeform Fabrication for several purposes, there is still potential for significant progress by the application of established knowledge regarding metallic material and processes to SFF.

The experimental part proceeds from these conclusions in a direct approach to investigate the conditions for a potential steel material system for application in the two-step SLS process approach. This work has been carried out in a step-by-step procedure where the conclusions from each set of experiments forms the background for the next.

First, a vacuum furnace process is developed to provide a stable atmosphere for the furnace consolidation of steel alloys by liquid phase sintering. This is followed by the investigation in regards principal limitations for this application and ways to address those, within a material system, consisting of a base material steel powder combined with copper, and iron. The applied powder mass density was significantly increased by the addition of small sized particles to the base powder. However this increases the inter-particle friction that becomes a critical issue in the application of powder layers. Furthermore the possibility for the formation of metallic bonded green bodies by means of melting the copper fraction in the powder composition is investigated and confirmed experimentally. However this option brings up the issues of laser penetration in the powder layers, and the draining of liquid phase from areas unexposed to the laser. Finally, the liquid phase sintering to full density, and the possibility to enhance the diffusion, and thus the dissolving rate of the liquid phase, in the base material by the addition of ferrophosphorous to the liquid phase is addressed.

**Keywords:** Solid Freeform Fabrication, Metallic materials, Selective Laser Sintering, Liquid phase sintering, Powder density, Particle size range, Inter-particle friction, Green bodies, Laser energy absorbance, Secondary heating, Self diffusion, Dissolving rate.
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Preface

“The most beautiful thing we can experience is the mysterious. It is the source of all true art and science.”

Albert Einstein

The research associated with this present thesis has been carried out at the Department of production engineering at the Royal Institute of Technology, KTH, under Woxéncrum’s program for lean and agile production. There are several persons who has inspired, encouraged, or in other ways influenced me, and my work, over the time of research, and during the writing of this thesis. First of all I must acknowledge my advisors present, and in the past, Prof. Bengt Lindberg and Prof. Torsten Kjellberg, who has been supporting and supervising my research over these past years, a task that may not have been easy at all times. From Woxéncrum, I am obliged to the directors, past and present, Peter Gröndahl and Thomas Lundholm, who has supported this project all the way until the completion of this thesis. The support and contributions of other sponsors such as Karlskogainstitutet and Leif Jonsons Minnesfond should neither be forgotten.

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Finally my thanks go to my friends and family for enduring support over the years. Last of them, and perhaps least is size, -but never in importance, to my nieces and nephews for reminding my what is really important in life.

Stockholm, May 2004
1. Introduction

"We have a habit in writing articles published in scientific journals to make the work as finished as possible, to cover up all the tracks, to not worry about the blind alleys or describe how you had the wrong idea at first, and so on. So there isn’t any place to publish, in a dignified manner, what you actually did in order to get to do the work.”

Richard Feynman

This thesis addresses the limitations and possibilities of the metallic approaches of Solid Freeform Fabrication, SFF. The work has essentially been divided into two parts, one theoretical and one experimental. The background and argument for the experimental work is provided in the theoretical part. This part, consisting of published as well as unpublished material, includes a description of the general nature of SFF technology with a brief outline of its role as a strategic time saving tool for the manufacturing industry as well as a systematic view of different approaches to SFF based metal tooling. This part of the thesis is intended to give an overview of the SFF landscape, and thus presented in general terms. However, rather than pinpointing one specific source of reference where the reality is a general understanding and conclusions from several sources, the principal background material has been presented in the beginning of each section, in the manner of: “Based on [],[]…”.

The experimental part consists of previously published material, put in the context of the development of the foundation for a steel alloy material system for a variety of applications, though mainly addressing tools. This part takes a direct approach to the problem and includes a primary process modification, investigations concerning a suitable material system and the effect of powder particle composition parameters interacting with alloy composition.
Introduction

Initially and for a long time the development within this area of the SFF world has been aimed at the manufacturing of different tools; prototype tools as well as production grade tools, moulds and dies. But in a wider perspective, it is very possible that other application areas of metallic SFF will prove more advantageous and eventually become more important. It is therefore important to keep in mind, that even though “tools” is the primary term used in the thesis, the expected applications are expanded to include a multitude of other applications. The limitations and possibilities of SFF technology in the aspect of making tools can easily be applied to other potential uses of SFF technology. Just like the technology itself easily could be applied to a multitude of applications apart from tooling.
1.1 The Reader’s Guide to the Thesis


This thesis takes a holistic approach to the manufacturing of Solid Freeform Fabrication based metallic objects and the development of Selective Laser Sintering steel material. It is essentially divided into two parts. The first part begins by presenting a background perspective on Solid Freeform Fabrication technology. This provides the fundamental arguments behind the topic and direction of this research project. This is followed by a summary of the performed experimental research, and finally discussion and conclusions. The second part consists of previously published original papers arranged in a logical order. See Fig. 1.1.

Fig. 1.1. The principal structure of this thesis.

The introduction chapter includes, apart from this guide, some sections regarding terminology and concepts, (sections 1.2-1.4,) which are not directly connected with SFF technology or this research project. However these sections contribute with a perspective on the meaning of these terms and concepts, and how they are used in the thesis. The nature, application areas, development trends, and principal constraints of SFF technology are described in chapter 2. Chapter 3 is an extended summary of a previously published paper. However, since this paper is describing some of the SFF technologies from a particular perspective, this summary is placed in the
Introduction

descriptive part of the thesis, instead of in connection with the rest of the previously published material, which are experimental work. The approach to the experimental research is presented in chapter 4. The research project as such is presented in a series of published original papers in part 2 of the thesis. However to facilitate for the reader and put each paper in their right context, summaries of the papers with comments are included as chapter 5 in the first part of the thesis. This is intended to make it easier to follow the arguments and the development of the project in a continuous perspective, as well as relate the earlier works to more recent developments in the global SFF community. The findings and conclusions of this thesis are discussed in chapter 6.
Introduction

1.2 “Artefacts”, “Technology”, “Manufacturing” and “Tools”

“You must speak straight so that your words may go as sunlight into our hearts”

Cochise, Chokonen Apache Chief

Mankind is a manufacturing species. Since the earliest history of man, and probably even before that, humans and hominids have been manufacturing objects by the shaping of materials. The skill in development and fabrication of artefacts has been an essential part, not to say the essential part in the success story of our species. Over history, the manufacturing of artefacts and the technology used to manufacture these artefacts has been an important part in the development and survival of civilizations. Today people are more dependent on artefacts, technology, tools and manufacturing systems than ever.

The term “artefact” is of Latin origin, formed by “ars” art/skill, and “factum” to make, to do. The artefact is thereby a term used to distinguish a man-made object from naturally occurring objects. Technology, on the other hand has Greek roots, consisting of “tékhne” skill, art or craft, and “logos” (roughly) systematic knowledge of. Thus “technology” is the systematic knowledge of methods and materials used in the arts and crafts to achieve specified objectives. “Manufacturing” also originates in Latin, composed of “manu” hand, and “factum”. Still, this does not mean that all manufacturing is done by hand. On the contrary, “hand” in the original


context is more likely to suggest something controlled by human will, a voluntary, planned action, with, or without tools. The term is thus used to distinguish “man-made” from the production by natural causes. With the development of more and more complex tools and more advanced production systems, the meaning of “manufacturing” has widened and has come to the more general meaning of the entire industrial making of articles or materials for sale, especially in large quantities. In this thesis however, the term “manufacturing” is used as the conscious, planned shaping of material into artefacts. “Tool” is of Old English, Norse and Germanic origin. The original Germanic term “towlam” is derived from “tow-“ whence, from what². A “tool” is thereby an object or design used to achieve a specific result. In this perspective a computer is a tool for data storage and calculations, just as the software is a tool to make the computer perform these tasks. These are not less tools than a hammer or a wrench. In this text, however, the term “tool” does not usually refer to computers, software, hammers, wrenches or even SFF equipment. The term is primarily used for formative tools like moulds and dies which is the common use of this term within the field of SFF and related technologies. See Fig. 1.2.

Fig. 1.2. Manufactured objects, (artefacts,) in this case the pots and plant pins, are tools in the production (~ to bring forward) of an otherwise natural occurring object of beauty, the Phalaenopsis orchid. However, the author’s knowledge in horticulture is much too small and unsystematic to call this case of growing pot-plants a “technology”.


1.3 Shaping

“I choose a block of marble and chop off whatever I don’t need.”

François-Auguste Rodin, when asked how he managed to make his remarkable statues

(Based on [1])

Materials can be shaped in one, or combinations of, four basic principles: additive, subtractive, formative and net shaping.

- Net shaping: is to give a material the desired shape in a single process step, for example by casting-, or injection moulding methods. This usually requires a mould or die to transfer the shape to the material, and thereby, is the system as flexible as the tooling. The single process step makes this approach well suited for automatic manufacturing in high volumes and for the manufacturing of complex shapes.

- Formative shaping: is to modify the shape of a material by the application of pressure, such as bending and forging. Usually applied for minor shape modifications and is often combined with other shaping operations. Being of limited flexibility this approach is rarely used to give materials complex shapes.

- Subtractive shaping: is to give a material the desired shape by removing material, for example milling, turning and EDM (Electro Discharge Milling). Being a fairly flexible approach by nature, and since automation of these types of processes began in the 1940s, this has been a competitive approach for high volume manufacturing, as well as for the manufacturing of complex shapes.

- Additive shaping: is to give the material the desired shape by the successive adding of material. Apart from the occasional artistic use, this approach has not been widely used in manufacturing. However, this has begun to change with the appearance of Solid Freeform Fabrication technologies. Extremely flexible in regard to shape, this shaping principle is more difficult to make competitive for volume production. See Fig. 1.3.
Apart from this, there could be a philosophical discussion whether the joining of pieces together is a form of shaping, which it perhaps could be, dependent on the parts and the nature of the joints. If the pieces were small, somewhat generic and joined with permanent bonds into a part, entirely different from the original pieces, that would be a form of additive shaping. But if the individual pieces are significant parts of the finished product, or are not permanently joined, it would simply be “joining” and closer related to assembly than shaping. Of course, if the joints themselves are permanently integrated in the part such as in welding or brazing, then the forming of the joint itself might be considered an additive shaping process, but only if one considers the actual joint a “part”.

Of course most industrial shaping of materials is a combination of two or more of the mentioned principles. Even net-shaped objects often need to be milled or drilled at critical points and even injection moulded parts have to be cut loose from gating system. Still, it is usually desirable to keep the need for shaping operations of an object at a minimum.

*Fig. 1.3. Additive layered manufacturing of ceramics, a native manufacturing technique from the Southwestern part of the United States. From R. Vernam, "Morning Star A little Pueblo Girl" No. 3300F The Platt & Munk CO., Inc.*
1.4 The Time Factor

“Time is at once the most valuable and most perishable of all our possessions.”

John Randolph

(Based on [2], [3], [4] & [5])

The impact of the industrial revolution started an avalanche of supply and demand that has been growing ever since. Today, as product lifecycles are shortening, companies are under increasing pressure to develop new products at an increasing pace. More than ever before is the ability to reach the market with the right products at the right time a matter of vital importance for the survival of a company. According to survey by McKinsey & Co, [2], [3], a 6-month delay in product release to the market, may cause a 33% loss of profit over the products life cycle, whereas a 50% overdraft in development budget only causes a 3.5% loss of profit.

This effect is widely felt in the manufacturing industry. Product development time is always costly and has to decrease. However, the constant drive to reduce product development time, fulfil plans and meeting deadlines puts a tremendous pressure on the people involved in design and manufacturing. Meeting time-to-market goals at the expense of product quality is as disastrous in a long-term perspective as the failure to deliver on time. Instead new strategies for improved, more efficient product development have to be adopted. New strategies require new tools and methods. Since the product development process, from the concept idea to the launch on the market, includes several steps and usually involves a number of different people, it is essential that the communication between these people, as well as each different step in the development process, is as rapid and effective as possible. For this purpose, several different methods and tools been have developed, one of them is Solid Freeform Fabrication, SFF.
2. The Nature of Solid Freeform Fabrication

2.1 Definition

The area of Solid Freeform Fabrication (SFF), Rapid Prototyping (RP), Rapid Tooling (RT), etc. is a tangled mass of concepts and abbreviations, which are not entirely standardized. For the purpose of this thesis and throughout the previous research the following definition of the SFF technology, formulated by the author, has been used:

“SFF, Solid Freeform Fabrication, is the collective name given to a family of technologies aiming at the automatic manufacturing of solid three dimensional objects directly from a computer model by the successive addition of material, without the use of specialized tooling and with a minimum of conventional post processing.”

Other definitions are possible, however the terminology of the area is, further complicated by the common use of the term Rapid Prototyping as a general term for the technologies in this area. This use of terminology is hardly satisfactory, partly since there are today many other uses to SFF technology while there are other competitive non-SFF methods for Rapid Prototyping. Partly because SFF based manufacturing does not necessarily have to be rapid, even though that may be a principal reason to choose this type of manufacturing technique.

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5 "Rapid prototyping is the name given to a host of related technologies that are used to fabricate physical objects directly from CAD data sources. These methods are unique in that they add and bond materials in layers to form objects. Such systems are also known by the general names solid freeform fabrication and layered manufacturing" [7]

"Rapid Prototyping Defined
What is rapid prototyping? Some say that it is a process that creates parts in an additive, layer-by-layer manner. In the Wohlers Report 2000, the definition is "A special class of machine technology that quickly produces models and prototype parts from 3-D data using an additive approach to form the physical models."

http://wohlersassociates.com/Max01TCT.htm
With this applied definition of SFF technology, a wide array of quite different processes can be included in the family, but still there are some common traits in the available SFF processes today:

- Firstly, all processes require, by definition, a digital model of the solid. This model is in most cases represented in the STL format, which has established itself as the de facto standard for the communication of solid models for SFF purposes, since the earliest days of the technology. For further discussion of the computer software aspect of SFF technology see section 2.4.1.
- Secondly, the actual building process is in all commercial processes, and in most research approaches, performed by the layer-wise addition of material. This has prompted the suggestion of Layered Manufacturing (LM) as an alternative term for SFF. See Fig. 2.1.
- Thirdly, apart from the different welding based technologies, most SFF processes were originally developed for polymer materials.
- Finally, dependent of process route and material, there are usually some finishing operations required, (such as removal of support structure, removal of unsintered powder or uncured resin, polishing, etc.).

Fig 2.1. Additive layered manufacturing. However, ancient Egyptian pyramid construction methods as seen above, or Native American pottery techniques (Fig1.3.), are hardly to be considered as parts of the SFF family. Drawing provided by courtesy of Nalle Malmborg.
2.2 The SFF Family
(Concluded from [1], [7], [9], [13], [14] & [15])
Since the birth of SFF technology in the latter half of the 1980’s, a number of new approaches and different processes have been developed. As each process is marketed by it’s own brand name, it has not always been easy to understand the similarities and differences between the different approaches. In order to systematize this confusing state, a series of unofficial group names has been established. These names are usually identical to the name of the first established process of each family, which of course is a source of confusion on its own. For example: the processes that are building objects by the curing of a liquid polymer resin are usually called “SLAs”. Still the abbreviation “SLA” stands for “StereoLithography Apparatus”, and it is the name used by 3D Systems Corporation for one of their lines of products. As an alternative to this, trying to clarify the scope further, new process group names such as StereoLithography (SL) and Selective Curing (SC) has been suggested, gaining varying popularity, and adding some extra terms to be confused with the rest. Still, for the time being, the traditional names applied to the different groups of SFF technologies are generally recognized and will continue to serve their purpose until another, more precise, terminology is generally accepted by the international SFF community.

Apart from the selective curing of photopolymers in SLA, there are a handful of other groups that should be described in this brief introduction to the SFF family. This introduction is by no means intended to be a complete list of available methodologies, but serves as an example for the purpose of basic orientation.

- SLS is the name used for the powder-based processes where the powder is selectively fused by the heat of a laser. The term stands for “Selective Laser Sintering” and originates as the name DTM Corp. (now 3D Systems) used for their particular process approach. In this thesis SLS is used exclusively for DTM’s approach, the similar approach to metallic SFF, used by EOS Gmbh is termed DMLS, Direct Metal Laser Sintering.
- FDM, stands for “Fused Deposition Modelling”, and applies to the approach where the objects are being built by the extrusion of thin filaments of semi-melted material (mostly thermoplastic). Since Stratasys Inc exclusively distributes this approach to the world market; the use of this term is one of the least controversial.
The Nature of Solid Freeform Fabrication

- 3D printing, originates from MIT (Massachusetts Institute of Technology), and is licensed to a number of companies. The basic principle is that powder is being joined together by the addition of liquid binder in a manner not unlike the inkjet technique of a common desktop printer.
- LOM, is the term most widely used for the techniques that are manufacturing by the lamination of cut-outs from paper or other polymer sheet material.
- Inkjet is one term used for the various techniques where a wax, or wax-like thermoplastic is being printed layer by layer with inkjets, forming the final object.

This is one example of how the SFF family could be arranged, other systematisations are plausible, but this system is recognizable throughout the world to day. Which systematisation is most suitable depends on for which purpose it is applied, and what the system is intended to illustrate. See Fig. 2.2.
<table>
<thead>
<tr>
<th>Process</th>
<th>Principle</th>
<th>Material</th>
<th>Building process</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLA</td>
<td>Liquid polymer</td>
<td>Selective curing by exposure to light</td>
<td></td>
</tr>
<tr>
<td>SLS</td>
<td>Powder</td>
<td>Selective fusing by the heat of a laser</td>
<td></td>
</tr>
<tr>
<td>FDM</td>
<td>Polymer filament</td>
<td>Extrusion and fusion of filaments</td>
<td></td>
</tr>
<tr>
<td>3D Printing</td>
<td>Powder</td>
<td>Selective adding of liquid binder</td>
<td></td>
</tr>
<tr>
<td>LOM</td>
<td>Polymer sheet</td>
<td>Joining of stacked cut-outs</td>
<td></td>
</tr>
<tr>
<td>Inkjet</td>
<td>Thermoplastic</td>
<td>Layer-wise “printing” of material</td>
<td></td>
</tr>
</tbody>
</table>

*Fig. 2.2. Basic SFF processes, pictures from [7].*
2.3 Areas for SFF Application: Rapid Prototyping, Rapid Tooling and Rapid Manufacturing

"Airplanes are interesting toys but of no military value,"

Maréchal Ferdinand Foch, Professor of Strategy, École Supérieure de Guerre

"...is of no industrial relevance..."

The Board of ProViking, a Swedish Foundation for Strategic Research program, in response to a project proposal regarding metallic SFF

Even though most SFF systems originally were developed for prototyping purposes in quite poor materials, the application area for SFF technology have spread far beyond the visualisation of 3D models and basic prototyping. Today the use of SFF manufactured parts is established as an integrated part within the product development process in many branches of the manufacturing industry, see Fig. 2.3.1. However, despite the high flexibility and freedom of part geometry inherent in SFF, this technology, as it is today, is naturally not necessarily the answer to all manufacturing situations. For the time being, SFF exists alongside more traditional manufacturing methods, where the respective advantages and drawbacks should be weighed against each other in pursuit of the most advantageous manufacturing solution in each particular situation. In the perspective of the product development process the different applications of SFF technology could be arranged to fall under one of the following topics: Rapid Prototyping, Rapid Tooling, or Rapid Manufacturing.

Fig. 2.3.1. SFF technology has found applications in the different phases throughout the product development chain, from visualisation of the original idea in the form of concept models, over prototypes and tools to manufacturing of products for direct use on the market.
2.3.1 Rapid Prototyping
(Based on [5], [6] & [7])

The single most important element of new product development is effective communication [5]. From the presentation and visualisation of new concepts to the discussion of specific engineering changes, much time can be saved and misunderstandings be avoided by the use of efficient tools for communication. Engineering drawings may provide critical information such as dimensions and views, but for complex objects, three-dimensional representations are usually necessary [5]. These can be provided on a computer screen or a printout by most modern 3D CAD software, but still this is not enough for most people. Humans are after all physical beings, and are much better equipped to comprehend physical objects by the combination of seeing, moving, sensing and touching, than from mere images. Models and prototypes have been used for this purpose by product developers, manufacturers and sales people for hundreds of years. In combination with drafts, renderings, and more recently computer representations, models and prototypes have been proven a most powerful tool for communication.

Rapid Prototyping, RP, was developed for the rapid manufacturing of accurate prototypes. RP is in the strictest context not as much a technology as it is a strategy, where prototypes of the appropriate type and quality are brought in and used for communication and evaluation, as an integrated part of the design process. These prototypes should be automatically fabricated, preferably directly from the CAD file. This could be done by milling or high-speed milling, but also, with advantage, especially for complex shapes, be manufactured by Solid Freeform Fabrication, SFF.

Since it was first developed and integrated with 3D CAD solid modelling in the late 1980s, SFF technology has proven to be a most flexible and powerful tool for the making of rapid prototypes. With the uncoupled relationship to geometries that comes with additive shaping, and the automatic building from a digital representation of the CAD file, the application of SFF to RP has been so successful that RP is often used as a synonym for SFF. However, this use tends to neglect milling as an option for RP purposes [6]. This can be a serious mistake since milling still can be more advantageous in respect to both speed and accuracy for certain geometries and materials. This thesis is however oriented within SFF technology and does not cover milling even though they are sometimes complementary or competing technologies.
However important, visualisation and communication are not the only means to enhance the product development process. Throughout the whole process chain there are several steps that could be shortened in time. One essential issue is to have the right information at the right development stage. This requires relevant testing, and to carry out these tests there is need for prototypes that share the relevant properties with the intended product. Dependent on which these properties are, this could call for different properties of the prototype and thus different rapid prototyping systems in different situations. However as the product development progresses, there is often a point where intent manufacturing process and material becomes necessary to receive the relevant information. By then, direct RP is no longer sufficient, and different technologies are needed.

2.3.2 Rapid Tooling
(Based on [2], [3], [4], [5], [6], [7], [8] &[9])
Rapid prototypes can only enhance the product development up to a certain phase. As the functionality of a design manufactured of a certain material becomes the issue, using the complete manufacturing process with intent material is often necessary. Testing the quality of a product or the entire process chain usually requires proper tools for the manufacturing. However, with high prices and long lead times using production grade tooling is often not an option; faster and cheaper tools are usually needed.

This has brought the need for Rapid Tooling, RT, which like RP, in reality is a strategy using rapidly made tools as means to reach the market with high quality products at the right time, and right manufacturing process. One important use is verification of part design and quality in regards to intent material and manufacturing process. Furthermore, apart from that these tools could, if deemed satisfactory, serve as “bridge tooling”, used to produce parts that are launched on the market while the high volume production tools are manufactured. Similar to RP, RT can be achieved by using milling or high-speed milling, or be SFF based. Also like RP, RT is often used as a synonym for SFF based tooling, but for this application, milling is often an even stronger competitor in the pursuit of speed and accuracy for certain geometries.

When RT is based on SFF, there is a further distinction to be made: direct or indirect tooling. Since the objective of the thesis deals with metal applications of SFF technology, different approaches to SFF based metal tooling will be covered in extension later in the text. However, this leaves room for a brief introduction.
With a direct RT approach, tools are built directly, in a single, or multiple steps, based on the CAD-file of the actual tool. There are a variety of methods, which build in polymers as well as metal materials. The indirect approach, on the other hand, bases the manufacturing of the tool on a prototype of the final object or a prototype of the tool, which is used as a master for the shaping of the tool. See further paper A, section “Tooling from SFF patterns”. Likewise to direct tooling, both polymer and metallic materials are used.

For RT considerations, milling should not be neglected. Actually, all the new developing SFF based tooling approaches are really not competing against each other; they are rather competing with each other, and against CNC powered milling. Being several decades older than SFF, CNC milling is a well-established technology, well distributed over the market and well known to the customers and users. Until recent years, milled tools required several months to be delivered, even for prototype tooling. However as demand and competition for rapid delivery has increased and milling technology developed, the necessary time has been reduced significantly. In a survey of 300 US toolmakers, DTM corp. determined an average delivery time for machined prototype injection mould tooling to be 39 days, whereas some could manage in only 10 working days. Apparently many companies have not fine-tuned their workflow aiming at rapid delivery of prototype tools, and there should be room for significant improvements there [5].

With this potential for improvement, SFF based RT applications will probably be facing a stiff competition for a long time ahead. However, the primary advantage of milling is very much based on the technology’s relative maturity, whereas SFF is still very underdeveloped. Based on fundamentally different shaping principles, the additive and the subtractive, SFF and milling, will at each step of their respective development be facing fundamentally different limiting factors and possibilities. When it comes down to the actual processing, it is the complexity of the tool geometry and the requirements for material properties, which are the primary factors determining which type of process is more rapid. Tools of complex shapes are time consuming to mill, both because the complexity often means that much material has to be removed, and because complex shapes requires complex tool paths. The additive manufacturing of SFF technology has a much more uncoupled relationship to the geometry and is thus not hampered by the shape in the same way. However, the additive process is, dependent on method and material, not always fast in itself, and just like
removing much material is time consuming in milling, adding much material is time consuming in SFF. Since tools often are quite large blocks of massive material this makes an additive approach time consuming for many tooling applications. This issue is a serious constraining factor for SFF based tooling in many potential applications.

Furthermore, with increasing demand for material properties of the tool, demands on tooling processes change as well. Many currently available metal SFF tooling approaches require secondary processing, (such as removal of support material, surface milling, blasting, polishing, etc.) to complete the tool. Similarly, secondary treatments could be needed for milled tooling as well, and all post processing consumes precious time. In reality, it is the time from order to tool-in-production that matters. When evaluating the competitiveness of each RT approach, it is important to take the whole process chain into account. For the time being, SFF based approaches have the upper hand when it comes to prototype tooling of complex shapes which are difficult to CNC program, or where the cutter has difficulties to reach, whereas milling is advantageous for most other applications. See Fig. 2.3.2.a and Fig.2.3.2.b.

**Fig. 2.3.2.a.** (Above) Inserts for an RT die for die casting of aluminium covers for a grinding machine from Atlas Copco tools.

**Fig. 2.3.2.b.** (Left) The inserts assembled with mother tool and base plate.
From a customers point of view, the situation of different competing technologies are all for the better. While it forces process developers and service providers to bring out the best in their respective technologies it also encourages the user companies to re-evaluate their tooling and prototyping approaches. This, in turn, is helping companies to discover new ways to reduce time to market.

2.3.3 Rapid Manufacturing
(Based on [3], [5], [7], [9], [10], [11] & [12])
As SFF based manufacturing has developed and improved regarding quality, precision and material properties, more and more applications beyond prototyping and tooling have emerged. In analogy with RP and RT, this use of SFF technology has been termed Rapid Manufacturing, RM. This terminology is, however somewhat ambiguous. While RP and RT frequently are used as terms for prototyping or tooling based on SFF technology they are, in reality strategies to improve the product development process, which could include SFF technologies or more conventional processes, RM is a term used exclusively for making functional parts by means of SFF technology. No one would call the direct milling of a functional part “Rapid Manufacturing”, whereas the equivalent method for making a prototype or tool could very well be RP or RT. This confusing situation is quite unsatisfactory, and there have been suggestions for alternative terminologies. For RM, tool-less manufacturing has been suggested as one alternative, however considering the linguistic roots and general understanding of the word “tool”, this term is hardly satisfying either. For the time being, and in this thesis, RM will be used for SFF based manufacturing of functional parts, well aware of the inconsistency of terminology this is.

Meanwhile, RP is established as a useful tool to facilitate communication and visualisation for the manufacturing process by the design-for-manufacturing (DFM) principle, and RT can be used for the verification of the designs of part and tools for this purpose, RM bypasses much of the limitations inherent in conventional manufacturing processes. Without the geometric constraints of conventional tooling, the restrictions with DFM are very much loosened and a whole new level of flexibility in manufacturing is possible. Furthermore, while the freedom of design is increased, the cost of tooling has been omitted, and thus has the option for competitive, customised production been realised. The combination of these benefits makes it possible for the designer to combine several parts
into one, which leads to faster, easier assembly, lower inventory and increased reliability, while maintaining the part price on a competitive level, [10].

In respect to this, and in the perspective of the minimal set-up times, as compared to the delivery and set-up time of tooling, -even Rapid Tooling, it is reasonable to say that the SFF based approach to manufacturing has earned the name of “Rapid Manufacturing” by it’s own merit. In a long-term perspective, the flexibility of the SFF based approach could enable manufacturing to be decentralised in geographical as well as time perspective, thus parts could be made wherever and whenever they are demanded, [10]. At present, the available systems are developed for prototyping purposes, and there are some important limitations for full exploitation of the RM possibility for a number of manufacturing purposes. However as the success of the pioneering companies starts to create a demand for development, the barriers formed by limitations in speed, volume, materials and accuracy will surely be overcome.

The application of SFF for the manufacturing of functional parts has proven useful, in particular for manufacturing in small series and for the making of unique products for the individual customer. SFF manufactured functional parts include parts for space shuttles, Formula 1 cars and fighter jets [10], all indeed made in very small series. However the ongoing development of the available systems is pushing the numbers for break-even cost between SFF based manufacturing and conventional methods to increasingly greater figures, [11], [10]. For individual objects the advantage is more obvious. As mentioned previously, the additional cost for tooling would in most cases manifold the price of a unique product. Applications of unique parts include parts for the international space station, custom fit hearing instruments and teeth aligners, as well as artistic objects and models for surgery.

**Fig. 2.3.3.** SFF manufactured medical models based on CAT scan, or CT scan images can be a tremendous help for surgeons in the planning of an operation. This 3D Printing manufactured model features the tumour as well as nerves and vital veins in different colour, thus further improving the visualisation. From "Magasin Vinnova" NR1-2001, Vinnova 2001.
New direct manufacturing applications to SFF technology is constantly being found, and since these new applications spread the knowledge of this technology to more people, even more new applications is likely to be found in the future. In this perspective it would not at all be surprising if the metallic approaches of SFF technology eventually would find their most important applications in the field of RM.

2.3.4 Castings

(Based on [3], [7], [10] & [13])

This is an area for SFF application that dependent on use could be classified as RP, RT or RM. In similarity with RP, RT and RM, SFF technology was introduced in the foundries as a time saving method to enhance the creation of accurate patterns and moulds, especially for complex shapes. This application has found several uses in such remote areas as automotive, aviation and jewellery industries, the latter especially for the capacity to produce unique individual designs with fine details and a high resolution. SFF manufactured parts can, for example, be used as masters for sand or investment castings. However, since the masters are removed as the moulds are completed, there is, apart from the occasional surface imprints, insignificant influence on the castings’ quality from the SFF origins. Another approach is the actual building of the mould by an SFF technique. These moulds have properties equivalent to conventionally made moulds, and similarly to SFF based investment casting. The quality of such a casting is primarily determined by the casting technique and material. If correctly handled, application of SFF technique to metal casting has a minimum influence of the outcome.
2.4 The Three Pillars of SFF

(Concluded from [14])
Apart from the list of common traits in the SFF family mentioned above, all processes as well as the entire SFF technology could be viewed as resting on three pillars. A more scientific description would be that the development of each process, as well as the whole technology is enabled by, but is also being constrained by, three basic limiting factors. These pillars, enabling technologies, or limiting factors, whichever term is preferred, are [14]:

- The digital model and software development
- Materials technology
- Process technology

These factors are closely linked together and it is not possible to take full advantage of progress in any of the scientific areas if both the others does not match that progress.

2.4.1 The Digital Model and Software Development

(Based on [5], [13], [14] & [16])
The SFF technology was initiated as a mean to visualize, “print”, CAD models. With this origin, it is only natural that much of the initial research dealt with software development. However, as the use of SFF has expanded into prototypes, functional prototypes, casting patterns, tooling, and small series manufacturing, the demands on the products have shifted, and other critical issues and constraints have come into focus for further development.

Since the development of early StereoLithography, the first true SFF process, the STL file (STereoLithography file) has been established as de facto standard for the communication of digital solids for the SFF technology. Its principal advantages are that it has been readily available since the beginning, it is easy to apply, and generic enough to be adopted by most major CAD vendors. However, since the STL format translates all surfaces into triangles in a digital space, with each triangle defined by three corners and a normal, there will be a trade-off between accuracy and size of the geometric description, [13]. Several alternative formats have been suggested to replace the STL file but until this date none have reached any significant impact.
An algorithm, will in turn, slice this faceted interpretation during the preparation of the build file, determining the shape of each layer of material. Since each layer is of uniform thickness and angled outer surfaces are not possible in most commercial SFF techniques, this will make another approximation of the objects outer surface. The precision of this approximation is dependent on layer thickness, and this is, in turn, determined by process parameters, material properties and the acceptable size of the build file. Despite these additive approximations, the STL file is considered adequate for visualization applications. However the increased demands for precision and surface quality makes the adequacy of this format is unclear when it comes to functional parts and high quality patterns. Still, as the recent rapid development in computer and communication technology has made large digital files less of an issue, the precision and adequacy is far more constrained by process and material variables than by the digital model.

Another constraint of the STL format is that it has a limited possibility to communicate certain features to the build file. Some features can however be added, recent developments have included SFF equipment that builds multicoloured prototypes, but other features, such as surface quality or material, have not been possible to include yet. For example, one of the more promising future developments of SFF technology will be the possibility to build graded material properties into the products. To make this practical, it is necessary that these properties should be included into the digital model in order to be interpreted into a material, or a combination of materials by the SFF equipment. Since 50 bytes are required to represent each triangle in a binary format of the STL file, there is hardly enough space to also include such a complicated representation in the STL format. This is one reason why it is likely that the STL representation eventually will be replaced. But this change of de facto standard is mainly constrained by the development progress in process and materials technology for SFF. When that time comes, when materials and process development has made the STL format obsolete, then the most likely replacement, as it appears today, would probably be the STEP format. Standard for Exchange of Product model data, STEP, is an open format ISO standard. Apart from excellent communication and accurate representation of solid models, STEP is more efficient when it comes to data storage and has the possibility to include diverse engineering information, such as strength, dimension tolerances and surface finish [17]. However, with the current technology, STL files serve their purpose satisfactory, and until the other
The Nature of Solid Freeform Fabrication

constraining factors has been overcome, further developments in this field would have little impact.

Apart from the digital format, other software development targets are, for example process speed and precision. These variables are very process specific, and the progress is usually accompanied by simultaneous developments of the process hardware or material. With respect to this, it is hardly surprising that most significant progress in this field is done by the machine vendors themselves and their (cooperation) partners.

2.4.2 Materials Technology
(Based on conclusions from [7], [10], [17] & [18])
Since the first applications of SFF products were for visualization, prototyping and casting patterns, it was natural that the first processes were developed for polymer materials. Since polymer oriented SFF has proven itself useful and is established for several applications a demand for more, new and better polymer materials has developed, and is expected to grow even more as RM spreads to a wider market. In the present situation the limited selections of materials is a principal constraining factor for a wider application not only to RM, but also to more functional testing of RP. However, there is ongoing development in progress in this field, and powerful commercial interests are involved, so it could be expected that the development of new polymer SFF materials closely will follow the pace of demand by commercially viable markets, software and process development permitting.

However, to enable expanding use of SFF for functional prototyping, tooling and other, even more demanding purposes, there is as distinct need for improved and more diverse material properties of the products, and the focus has been shifting towards metals and ceramic materials. These materials are fundamentally different from polymers and cannot be expected to behave in polymer-like manner in a process developed for polymer materials. Even if, as in the case of the welding based processes, the process has been developed with the particular material in mind, there are many issues of successive addition of these very potent but demanding materials, which need to be controlled. After all, within the actual process of materials addition lays an inherent strong coupling between the material properties and the process. Thus, the challenge is to coordinate the materials behaviour and the SFF processes, in such a manner that they can be used to make products with the desired properties. Dependent on the original process, there are different approaches to this. From small
software-based modifications, where the actual processing of the material takes place outside the SFF equipment, to complete redesigns and the establishment of entirely new processes.

In the design of products of most conventional materials, the intended manufacturing process has long been a highly significant issue. The selection of material for any manufactured product as well as the design of a new material is a trade-off between desirable material properties of the final product and the desirable material properties for the intended manufacturing method. Different manufacturing methods put different demands on the material. For example: for milling purposes a material should be rather soft and have good chipping properties, or for hot working, materials should be ductile and without hot brittleness. Likewise materials are optimised in respect of casting, welding and other, manufacturing processes. Therefore, it is unlikely that materials designed to yield specific material properties when used in a conventional manufacturing process would give similar desirable results when used in a manufacturing method so entirely different as an SFF process. Instead, new materials that are optimised in respect to the different SFF process approaches will have to be developed. Highly dependent of the specific SFF process approach, this is a challenge of varied difficulties and possibilities. Without the constraints of conventional manufacturing processes, it is possible to use unconventional materials and exploit a different set of phenomena from materials science. On the other hand have the different SFF process approaches their own demands for material properties, that will impose a different set of constraints, and direct the potential for material and process development. For example, the approach to how the material is transported to, and fused with the part will control the materials’ shape and restrain the physical properties. The experimental part of this thesis will provide a good example of how these constraints can influence and direct the evolution of a material system for SFF application.

However, the materials science and the technology of the most interesting materials are mature by comparison to SFF. Therefore, the challenge today is largely to find which properties and phenomena to exploit, and to transfer established materials technology to SFF processes. The first SFF materials beyond the original polymers, have been highly constrained by the process technology, but further progress in SFF materials and process technology will possibly liberate the future designer not only from manufacturing constraints in geometry, but also offer the opportunity to focus the material properties entirely on product quality.
2.4.3 Process Technology

(Based on conclusions from [1], [4], [8], [11], [12] and others)

Process technology is the connecting link that combines the digital design with the intent material into the desired shape and properties of the product. The applied process technology as such, is to a high degree specialized applications of traditional technology, and the novelty of the SFF processes is actually the particular combination of applied computer, process and materials science. As mentioned previously, most commercial processes were originally designed for the manufacturing of visualization models in polymer materials. As the use of the products and material scope has widened, the demands on the process technology as well as the controlling software has increased. These demands are developing principally along five lines: lower prices, user friendliness, higher speed, better precision, and better materials, with priorities dependent on each particular application and target niche on the market. The development of each SFF process technology will be shaped by these demands, the original process concept, the progress in software development and the constraints and possibilities occurring in the new materials. Obviously, most of the development of the commercial processes is tied to each particular machine vendor, and for the independent researcher there are small possibilities to make any significant impact apart from developing entirely new processes.

From the perspective of the basic shaping principle, none of the current SFF approaches appears to have the potential to take full advantage of all the technological possibilities. For example, since the material is successively added, nothing contradicts the option to vary the material composition during build-up, thus manufacturing objects with graded properties. If such a process could be developed, it would enable the future designer to optimise the parts only with respect to functionality. Optimised geometry as well as material properties, not only in the part as a whole, but optimised material properties for maximum performance at every single point in the part.

Still, the SFF manufactured products are getting more and more competitive, and the development of technology for SFF application of metallic and ceramic materials is progressing. This makes the demands on the process technology escalating, and it is not likely that all the current processes will survive in their present form and applications. Which are the processes that will survive, and for which applications will be determined by the development during next few years.
2.5 Con straining Factors for Tooling and Metallic Materials SFF

“This telephone has too many shortcomings to be seriously considered as a means of communication. The device is inherently of no value to us,” From a Western Union internal memo, 1876.

(Based on conclusions from [3], [8], [10], [17] & [18])

Since it emerged during the last decades of the 20th century, Solid Freeform Fabrication (SFF) technology has been gaining importance as a strategic tool for the competitive manufacturing industry. As with all technologies, SFF is about making things possible. SFF technology has made it possible to automatically manufacture objects, with no or little concern to geometry. However, to this date, the use of these objects is, limited by among other things, properties of available materials. A principal challenge facing the industry, as well as academia, is to overcome these limitations. A first step has been the introduction of metallic material applications of SFF. However, as metallic materials were integrated in contemporary SFF processes, these materials were adapted to each technique, which has led to new limitations in metallic material properties. To have full benefit of SFF technology for manufacturing in metallic materials, the gap must be bridged between the material properties offered by existing processes and the needs these are expected to fulfil. Otherwise, new processes, which are less coupled to materials used, must be developed. With both of these issues the question is not really if they will be fulfilled but when, how, and by whom. The answer may very well determine the future of the entire manufacturing industry.

Among the earliest and long considered most promising applications of metallic materials in SFF technology is tooling, and the advantage for product verification and small series production has been proven [8]. This has increased the expectations and demand for further development in this field. However despite extensive research and development efforts over the last few years, this application of SFF technology has not yet taken off. Presently, there are three principal limiting factors hampering the capacity of current metal-based SFF for tooling purposes. Much of the ongoing development in the SFF community worldwide is concerned with overcoming these from different perspectives, dependent on the limitations in each process. It is not unlikely that the pursuit for improved SFF based
tooling processes and materials technology will open new doors and carry metal SFF towards a wider area of applications. In general the limiting factors are: build time, precision (in respect to geometry and resolution, as well as surface quality), and the selection of available materials and their properties.

**Build time:** The most common reason for using SFF technology for tooling is to save time, but dependent on the process used, the additive manufacturing of metal objects is not always rapid, and speed often comes at the price of precision.

**Precision in respect to geometry, resolution and surface quality:** In difference to concept models (another important use of SFF technology), tools are (functionally) required to have exact measures of high precision, as well as high resolution to detail and best possible surface control. Several metal SFF processes require extensive finishing work, such as grinding or polishing, and sometimes even electric discharge machining or milling (see chapter 3 and paper A). This need is of course dependent on the final use of the product, however, every additional process step between the actual building and the tool-in-production consumes precious time, and reduces the benefits of using SFF technology. If a process is too slow, or if the tools become too expensive, these drawbacks could overshadow the other advantages of additive manufacturing, such as the possibility to insert conformal cooling channels for optimised cooling, reduced cycle time and increased lifetime of the tools. Therefore, it is vital for the competitiveness of any SFF tooling approach to develop towards higher build speed, trueness to geometry, and minimized need for post-processing of the product.

**The material properties and selection of available materials:** Both the selection of materials and the material properties are limited compared to the wide expectations for competitive tooling materials. The perfect material for tooling purposes should be hard, tough, have maximum resistance to abrasion, high resistance to corrosion and be resistant to softening at high temperatures. There are not one such material in existence! Instead, tooling materials are designed to optimise the performance of the tool in respect to the specific application and the method for the manufacturing of the tool. For most production tool applications, different varieties of steel are the primary choice of material, and if SFF technology to is to be a competitive alternative for tooling.
purposes, it should produce material properties equivalent to, or surpassing the conventional tool steels qualities for the intended tool application.

The wide array of different tool steel qualities makes a tool material system with the capacity for a wide variation of properties most desirable. Stretching from the equivalence of cold-working steels, optimised in respect to strength, abrasive resistance and toughness. Over steels for the forming of plastics, optimised with respect to tool size, kind of plastic, forming method, surface texture, number of parts and resistance to corrosion. To the equivalence of hot-working steels, optimised in respect to resistance to high temperature softening, high temperature strength and hardness, combined with toughness and resistance to wear and heat transfer properties. Such a flexible material system would most likely also allow for optimisation of material properties, beyond actual tooling applications and thus expand the competitiveness of metal SFF further. It could even possibly convince a few sceptics. Therefore it is hardly surprising that different varieties of conventional tool steel are used as reference by both vendors and users of commercial SFF metal tooling techniques, and likewise it is only natural that several of these metal tooling approaches also have been addressing steel in various forms as the primary choice of material.

However, tool steels usually are optimised, not only in respect to tooling performance, but also in respect to the manufacturing method for the tool. For SFF application there are quite different manufacturing conditions to take into account compared to conventional manufacturing. For example, most conventional tool steels are wrought material and delivered in annealed condition to facilitate milling and electric discharge machining to the desired shape. In an SFF based tooling system, neither hot forming nor milling properties is a priority, and other properties relating to the SFF process are of higher significance. (Unless, of course, the SFF process has such poor precision and surface quality that extensive post-processing is necessary.) More to the point, the conditions associated with additive manufacturing will primarily be determined by the most significant and critical part of such a process: the actual addition of the material. Which conditions, and thus which potential, there are for competitive SFF based tooling and manufacturing in metallic materials is thereby determined by each process approach to materials addition and their respective inherent constraints.
3. Systematic View of SFF Metal Tooling Approaches

The area of SFF based metal tooling is covered in extension in the previously published material by Paper A, “Systematic View of SFF Metal Tooling Approaches”. However, since this paper is describing some aspects of SFF technology and is logically connected to the previous chapter it is presented in an extended summary at this point instead of being summarized together with the other published material. Moreover, since there is an ongoing rapid development and continuous progress in the areas of commercial processes and materials for SFF technology, the publication of this systematic perspective was postponed until 2002 in order to ensure that the material should be valid and reasonably up to date for this thesis.

The variation within the SFF family is also reflected within the metallic applications by a number of different process approaches. However, since the SFF technology is defined as the manufacturing of solid objects from a digital representation by the successive addition of materials, and the digital representations are more or less standardized and considered satisfactory for today’s technology, the critical point and greatest source of variation is in the addition of the material. There is much development in progress in the area of metal SFF, and it is extremely difficult, if not impossible to predict exactly which are the process approaches that will be the most important in the future. It is however possible to make a qualitative evaluation of the capacity of each process approach. Paper A surveys different process approaches with the object of forming a better understanding of the characteristics and fundamental differences between the principal metallic applications of SFF technology. This survey is based on the perspective of solution to the addition of material, which will be used as basis for a qualified estimation of the constraints for metal SFF application inherent in each approach. Focusing on metallic materials, the added metal can occur either in solid, liquid, gaseous phase, or in combinations of these. See Fig 3.1.
Fig. 3.1. Overview of SFF metal tooling approaches arranged according to shape of the added material, with examples on each process approach.

**Adding from Gaseous Phase:** The possibility to develop a process that builds the objects by adding material from a gaseous phase has been the subject for some research projects. By the nature of gases, the bonding takes place at a molecular or even atomic level, and has the theoretical capacity for extremely controlled material composition as well as surface quality. Still, with the size of added units, even with extremely rapid process control system, this approach would be too slow and costly for objects much larger than fibres and semiconductors, such as metal tooling and functional parts.

**Adding from Liquid Phase:** In this overview this group includes the approaches in which the material is in liquid shape at the moment of addition to the object. There are two principal solutions to this: the added material could either be a powder spread out in advance of melting, or fed to a pool of melted metal. In the first case, the applied powder bed, acts as a support during the building, thus allowing a higher degree of flexibility in geometries. In addition to what is mentioned in Paper A, it should perhaps
also be mentioned that this solution also offers the potential to successively change material composition, but only in the z- (building-) direction. The second solution, on the other hand, offers the possibility for variation of materials in x-, y- and z-direction during the processing. This is however at the price of severe difficulties to build overhangs above a 45° angle. One solution to this is the addition of 5-axis process capacity, however it has been suggested that this also could be achieved with advanced process control software.

In these solutions, is the metal melted upon addition. The build speed achievable in each process is thus, among other things, dependent on the transfer of energy to the metal. This is a crucial point that under some conditions may be a serious limiting factor for the building speed. Another limiting factor is the precision and surface quality. Since pure metals are melted in one step forming a liquid drop of low viscosity, there is little possibility to control the shape of this drop before, and during, solidification. Dependent on the drops’ immediate environment the parts’ surface will either be similar to sand cast material, or have a surface pattern shaped by solidified metal droplets. The best possible resolution and precision will eventually be determined by the size of the melt, however small melts most likely will mean long building times. The melted droplets are usually very small in comparison to the solid base, and thus the solidification is very rapid. This means that the solid metal is likely form a very fine grain structure, which usually is very positive for the strength and toughness of the material.

The SFF processes based on addition of material in liquid shape seem like a very promising family, but with a load of constraints that limits the practical applications. There will always be a trade-off between build speed, precision and post processing, such as milling. Currently, this approach is most advantageous for certain niche applications, such as the manufacturing of near net shape objects in titanium for the aviation industry, where the alternative is milling these thin-wall structures from large solid block of metal or for parts that has small demands on surface quality. These technologies are hardly competitive in the making of large solid pieces of metal, but for minor material additions, such as the repair or modification of moulds or dies, they have a significant competitive edge. It is hard to see how this would change in the immediate future as long as the difficulties with surface quality remains. However with improved multi-material capacity, and the opportunity for surface coating, the suitable
niche applications of these technologies are likely to increase and become more and more competitive.

**Adding from Solid Phase:** The additive building using solid metallic material units requires some sort of joining operation. This joining must include a controlled phase transformation of either the building material itself, or of some other additional component activated in the process. However, solid metals in the shape of powder can be integrated within a polymer based SFF processes, and thus exploit the binding during the phase transformations active in those. In this type of approach, the polymer materials function merely as a binder of the metal powder, while the metallic consolidation is accomplished by subsequent furnace processing. In this perspective, it seems only natural that the most successful metallic applications of polymer based SFF technology has been of those processes where powder is the original form of building material. In the metallic application of these processes are the geometries formed by the selective joining of particles in each powder layer, as well as with the previous layer using a polymer binder.

A principal difference in the capacity of the two most important commercialised process approaches to this is based in the different ways to distribute and activate the polymer binder. Both the process cycles start by the spreading of a powder layer over the building space. In one 3D printing based approach, the binder is “printed” on the surface of the applied layer, and penetrates the powder by capillary action, forming, what in powder metallurgy is known as a green body, upon curing. This approach has, alike all 3D printing based processes, the capacity to be a very rapid process. There are, however, some constraints with this approach. The resolution and precision is determined by the penetration and infiltration of the liquid binder in the powder mass, and it is thus hardly possible to control how much powder and which of the particles will be joined together by every individual drop of binder. This is a limiting factor for the precision and resolution for all 3D printing based processes.

In a different SLS based approach, powder is coated with a layer of binder material, which is melted by the scanning laser, and glues the particles together to a green body. Since binder is activated by the temperature variation by the scanning laser, the potential speed of this process approach is determined by (apart from the powder spreading procedure): the scanning software, the laser power and the heat transfer in the powder. This usually means that SLS based approaches are slower than their 3D printing
based counterparts. The precision and resolution is determined by the amount of powder joined by the melted binder. However, this is easier to control than the penetration of liquid in a particle mass, thus alike the polymer based process, the green bodies formed by this SLS approach has a higher potential for precision and resolution, compared to those formed by the 3D printing approach.

Apart from the proposed examples of process differences, there are several traits that are in common for the binder activated metal powder type of process approach. The green bodies have to be manually broken out and of the powder mass and rinsed from unbound powder. Thus the preparation of the green bodies for furnace processing is dependent on the skill of the operator to turn out good results. It is an obvious weakness for any automated manufacturing process to be dependent on the operator’s skill and craftsmanship for every single piece made. The strength of the binder also limits the size of parts and features that can be practically handled in the form of a green body, just like the particle size place a limit on the potential resolution.

The furnace procedure of these process approaches consists of debinding, sintering and infiltration. The binder burnout usually requires the green bodies to be packed in a supporting material to maintain the geometric shape of the parts. During sintering the part will undergo some shrinkage and dependent on the part geometry there is a risk of cracking of thin sections surrounding holes or hollow areas filled with support powder. The voids between the particles in the sintered steel framework are filled by infiltration with a metal of lower melting temperature, thereby forming a massive metal object. For infiltration with their respective steel powder, both commercial systems use copper alloys. Dependent on the infiltrant’s melting temperature and powder particle size, the sintering and infiltration could require one or two furnace cycles. Since the furnace cycle includes heating and the cooling time of furnace, and crucible, a complete furnace cycle can take around 24 hours. For most tooling applications, surface structure and quality is of critical importance. The use of infiltration gives a composite material with inhomogeneous properties, which cannot be etched for polishing or specific surface feature purposes. For tooling, this often requires further processing such as grinding or polishing on critical surfaces. Therefore, infiltration is a limiting factor for this process approach.
Despite the inherent constraints, 3D Systems’ (DTM’s) SLS based tooling approach is among the most successful and widely used SFF based tooling systems today. It is commercially used for prototype tools and small series manufacturing. However, with the current material processing system of sintering a framework of steel powder and infiltration with copper alloy it is unlikely that any groundbreaking progress beyond this point is possible. Meanwhile, the additive joining of solid phase particles, followed by a separate furnace consolidation, has a relatively uncoupled relationship between SFF processing and material. If the need for infiltration could be avoided, much progress towards a wider selection of more durable materials with production grade tooling, and a wide array of other applications for SFF technology with metallic materials would be possible.

**Some Hybrid Approaches:** Apart from the adding in gaseous, liquid or solid phase there are some hybrid approaches to metallic applications of SFF technology. This overview will describe two of those (three in Paper A): one major competitor on the international market, and one between research and commercialisation.

*Direct Metal Laser Sintering, DMLS,* by EOS Gmbh, has become one of the most important processes in the SFF world, outside North America. In the perspective of SFF processing, DMLS and SLS are very similar; both build their parts from powder material, spread out in layers and joined by the heat of a scanning laser. But in difference to 3D Systems’ metal approach, DMLS melts a fraction of the metal powder, joining the particles by liquid phase sintering into metal objects of close to full density. Thus this is a hybrid approach that adds material in both liquid and solid state. EOS method relies on both a much more powerful laser, (280 W compared to 3D Systems’ 100 W) and a specific blend of metal powders consisting of base material and a lower melting material. EOS markets a variety of different powder materials with different properties addressing building speed, strength, surface quality and resolution. The combination of a powerful laser with powder of different materials with different melting temperatures does indeed provide the possibility for consolidation into a solid metallic material. However, the finished part material will thus become a highly segregated metallic compound with inhomogeneous properties.

It is widely considered that the fewer the process steps and the less the manual work, the faster the process will be. This would make DMLS, being an almost fully automatic, single-step process the fastest SFF metal process
on the market. In fact it is, however within a strictly limited area. DMLS does indeed build solid metal objects directly in the machine, however the objects are not entirely completed when removed from the equipment. Firstly, the surface is characterised by the powder, to close porosity and smooth surfaces, shot peening is used as an integrated part of the process. Secondly, DMLS builds from a 20 mm steel base plate. This has either to be removed by conventional machining or, which is common for tooling applications, be machined to be a part of the tool itself. Even if both the shot peening and the machining of the base plate are additional process steps, they are of minor importance as speed limiting factors, compared to the actual building process. Since DMLS requires the melting of a part of the powder compound, there is much energy that has to be transferred to the metal powder by the laser, and this takes time. Compared to 3D Systems’ approach, where the laser melts only a small amount of polymer binder, the actual building process is much slower in DMLS. True, the SLS metal materials does require about 24 hours of furnace processing, but for any part that would take more than 40 hours in DMLS, 3D Systems’ SLS approach would most likely be a faster alternative. Still, the direct formation of metallic bonds in the SFF equipment makes the DMLS parts much stronger during the breaking out and rinsing from unsintered powder. This is a significant advantage compared to SLS, since the outcome of the process is much less dependent on the manual skill of the operator.

In today’s European market, EOS’ DMLS and 3D Systems’ SLS are the principal competitors for metallic SFF applications. DMLS appears to have the advantage for smaller parts and finer features, but is hardly competitive for parts taking more than 40 hours to complete. However the applications of both processes are constrained by their materials. While DTM’s process cannot complete a part in shorter time than the furnace process, DMLS building speed is constrained by the absorption of laser energy. Which of these, if any, will emerge the winner of the future market will be determined by the further development of materials and processes.

Direct Metal Fabrication, DMF, was originally developed by Rockwell Science Centre to be used on a DTM Sinterstation. DMF powder is a three-component blend consisting of a parent alloy, which is the target structural material, a lower melting temperature version of the parent alloy, and a polymer binder. The green bodies are built by common SLS procedure, but the furnace procedure consists of only two parts, debinding at lower temperature, and sintering, where the temperature is raised to melt the lower melting temperature alloy. Liquid phase sintering consolidates the
parts. Rockwell claims to have reached final densities of 95 – 99 %, with strengths equivalent to as-cast material. Furthermore, the technique has been successfully applied to a variety of materials. In the spring of 2000, DTM (now 3D Systems) and Rockwell announced the cooperation for the development of materials according to DMF principles, but today, three and a half years later, no results from that cooperation has reached the market yet. The reason for this is unknown, however it seems like DMF has faced some serious difficulties. Anyhow, DMF or not, consolidation of metal parts by liquid phase sintering may be one of the few possibilities to reach full density objects of homogenous metal alloys from a powder based SFF approach.

**Tooling from SFF Patterns:** In connection to the SFF family there is a group of indirect tooling approaches that uses SFF models as patterns or masters to make tools or metal objects. Hardly fulfilling the criteria for an SFF process, (automatic additive shaping of solid three dimensional objects) this group is in reality not a SFF technology, and the shaping process should rather be considered net shaping. Still, the parts are based on SFF patterns and are for some applications competitive alternatives to true SFF tooling, which is why it is covered in Paper A. However at this point, these methods have little to add in relation to the perspective of metal applications of SFF technology, and thus provides nothing of relevance to the experimental part of this thesis, which was the primary motive for this extended summary of Paper A at this point.
4. Research Approach

4.1 Scope, Aim and Delimitations

"Research is the act of going up alleys to see if they are blind."

Plutarch

A fundamental question in all technological research should be, “What is the potential impact?” This implies that research efforts should be aimed for the highest possible impact, and by doing so limit the scope to where this effect could be achieved. From a purely academic standpoint, the desired impact is the advancement of technological science. Meanwhile, the desired industrial impact is the practical application of the research results. Since research in general, and technological research in particular, is future oriented, the impact can never be taken for granted, the researcher can only make his, or her, contributions, academic and industrial, within the selected area of research. After that it is up the academic and industrial world to exploit or neglect the respective contributions. The most successful technological research, however, manages to combine academic advancement with industrial application. The research area addressed in this thesis is the potential and limitations for the metallic material application to SFF technology. This is a comparably young field of research, where many aspects and interacting phenomena within additive manufacturing of metals are largely unknown. To identify some of these, describe how they affect the outcome, and suggest solutions to the constraints they impose on the process, would be a noteworthy academic contribution. However, to fulfil the ambitions of technological research this academic contribution should be oriented to where the outcome may reach the widest industrial application.

Considering the possibilities offered by an additive manufacturing approach, both by the inherent freedom of geometry and the potential to vary the material composition, it can be concluded that metallic applications of SFF technology is an area of great potential for numerous manufacturing purposes. One particularly interesting area is the manufacturing of tools, which has been the primary target of development for some time, but also in a not so distant perspective for a multitude of other possible applications. However, in respect to the current situation in the developing SFF world, it appears that while several, commercial and research, metallic application systems exists, mainly targeting the
manufacturing of prototype and short run tools, the applications of this technology are still hampered by constraints primarily in material and processes. Different technologies have been commercialised and are available on the world market, but while there are a growing number of users, the vast majority of potential users have not yet found metallic SFF to be a competitive alternative to conventional manufacturing methods. In consequence, the highest potential impact of research in metallic applications of SFF technology apparently would be where the results from research not only could enhance SFF based tooling, but also open opportunities for many other new applications for a critical number of potential users. This last observation implies that the highest possible impact in a near perspective could be achieved by improving the capacity of a SFF technology that is well established on the market.

However, the inherent limiting factors will eventually constrain the potential for long-term developments within contemporary SFF metal applications. The full potential of the additive manufacturing approach to metallic, and ceramic, materials will not be reached with the current available systems. To reach that ultimate goal, new processes, which are more uncoupled to materials used, must be developed.

Since most of the potential users of SFF based tooling are likely to have tool steel as their point of reference, the SFF tooling materials will be evaluated by their performance as compared to tool steel. Homogenous steel-based SFF tooling materials with the capacity for heat treatments would therefore not only improve the capacity for SFF manufactured tools, they would also bring the technology closer to the customers’ point of reference and thereby make it appear less alien to the potential user. Apart from tooling, different steel alloys are commonly used to manufacture a vast variety of objects of different shapes and complexities.

Therefore, a flexible, SFF applicable steel material system would not only have potential use for tooling purposes, but would also offer opportunities for functional prototyping and manufacturing of complex geometries in different steel alloys. Furthermore, such a material system should be applicable to SFF tooling processes that are established on the market, and have the capacity to make tools with precision and surface quality comparable to other commercial SFF tooling systems currently available on the market. (The term “homogenous” is, in this text, referring to solid non-porous steel alloy, with phase structure corresponding to as-cast material of the specific alloy composition, with respect to possible heat treatments.
Research Approach

This term is used to mark the difference from the composite or highly segregated materials used in some commercial metal SFF applications, such as the DMLS, DTM/3DSystems’ SLS or ProMetal.

For this thesis, the research is aimed at the making of tools and high performance parts, in a homogenous steel material. More specifically, it aims at forming a foundation for the application of different steel alloys with a wider variety of material properties for different tooling purposes and other possible applications. With the primary target set at production grade steel parts, this work aims to investigate the possibility establish a technology platform for building SFF parts in solid homogenous steel alloys. Based on a qualified estimation of the capacity and constraints of contemporary metallic applications of SFF technology, 3D Systems’ SLS process, allowing a high degree of freedom of geometry, good building speed, and fair surface quality, combines a comparably uncoupled relationship between the additive manufacturing process and the material, with a widespread acceptance on the world market. SLS was therefore found to be promising for this approach.

In respect to the maturity of contemporary materials technology as compared to SFF, it can be expected that much progress can be made by the adaptation of established materials knowledge to SFF and SLS applications. Since the SLS approach uses a secondary furnace cycle for the metallic consolidation, all the material is heated for a prolonged time simultaneously. This ensures minimal thermal tensions in the product, and provides the conditions for homogenisation of the material. The parts in SLS are built from layers of loosely applied powder, and therefore there is need for enhanced sintering to reach full density. This can be provided with the aid of a lower melting material, by liquid phase sintering, but in order to achieve a homogenous material this liquid phase must be dissolved into the base material, forming an alloy. For this purpose copper is especially interesting. Not only is copper known to have excellent properties for liquid phase sintering of iron base alloys, it also dissolves up to approximately 8% at sintering temperatures.
Research Approach

Therefore, the primary scope of the research associated with this thesis aims at investigating the possibilities and limitations for exploiting the phenomena in the iron-copper system for a liquid phase sintering approach to the establishment of a foundation for a new SLS based steel material system. Are such material systems possible for application in commercial SLS equipment? Which are the limitations? Based on established knowledge in conventional metallurgy science, as well as on experimental work, the research described in this thesis has investigated the principal parameters regarding material characteristics, process variables and related phenomena.
4.2 Scientific Method

"Everything should be made as simple as possible, but not simpler."  

*Albert Einstein*

The topic of the experimental research is metallic applications in the SLS process, more specific, the possibilities and limitations for the development of a material system for the manufacturing of objects in homogenous steel alloys. The experiments have thus been focused on the process conditions and variables interacting with powder material behaviour in the perspective gaining the desired outcome.

Powder metallurgy is a complex area of materials science with a multitude of variables that can be hard to quantify, and much of the conventional practice has been based on trial and error procedures. However, over time this has led to a substantial amount of established materials technology with a solid scientific base, though primarily oriented around the practice of the conventional powder metallurgical manufacturing processes. The SLS process, on the other hand, is by comparison young and has only been subjected to research for a limited amount of time, but shares one trait with powder metallurgy in the aspect of having many variables with some uncertainty regarding their respective influence, especially in relation to new material systems. In the combination of powder metallurgy and SLS processing there will naturally occur some interaction between material parameters and process conditions, which will have a significant effect on the outcome of the process. Since there are factors of uncertainty, regarding which parameters are the most important, and how they are affected by the process conditions as well as their internal relationship, this combination is hard to determine in measurable terms.

In this perspective it is clear that any attempts to simulate this process approach would be futile until the entangled web of material parameters and process variables is somewhat more disentangled. Likewise, it would hardly have been productive to focus the attention to any particular variable or parameter until a fundamental influence on the process behaviour has been established. Instead an over-grasping approach to the problem was deemed more promising.
In difference to the natural and social sciences where the subject is being “re-searched”, technology and the technical sciences, strives to find new, and preferable better ways to do things, and thereby create new knowledge. Thus reproducible experiments, with a predicted outcome, are, if combined with a description of relevant parameters and their respective influence, sound technological science. In the current situation the principal research task is to explore a new possibility, and therefore would a successful attempt to manufacture parts of homogenous steel by SLS, be a technological and scientific confirmation of this possibility. Complimentary investigations of the principal relevant parameters would further enhance the scientific quality of the research from a technological perspective. However, as with all scientific truths, the technological sciences are preliminary true, and the effect of a specific procedure as well as the different parameters may, and perhaps should, be subjected to revision in respect to further advancement of knowledge. The investigation of SLS manufactured parts of homogenous steel is no exception to this principle.

Meanwhile the materials science is mature by comparison to SFF, with a firmly established knowledge base, the principal challenge at this stage has been to identify the most important phenomena and variables for this application and investigate how they affect the process conditions. Since the selected process approach includes a number of subsequent procedures, each dependent on the previous, the primary experimental strategy has been holistic. This means a full process has been performed, from powder composition, over SLS processing, to the completion of the furnace cycle, while observing the behaviour and outcome of each procedure. The powder composition has been selected and composed according to common powder metallurgy practice in the aspect of SLS process conditions, for example powder handling and powder spreading behaviour. Materials behaviour and process results have been interpreted in the perspective of established powder metallurgy science and previous research in the SLS process. This interpretation has been the basis for conclusions regarding what phenomena to address and what parameters to modify for the following experiments.
In difference to the descriptive research of the theoretical part, the experimental research is thus normative and holistic, which perhaps is not in accordance with the principles taught by some schools in the philosophy of science or experimental planning. It would most likely have been possible to formulate one or more hypotheses, or to set up a carefully designed plan of the experimental order, but in respect to the complexity of the process in relation to the amount of established knowledge in adjacent areas, and the cost and time consumption of each experiment the above described strategy has been deemed more productive.
5. Survey of Experimental Research

"A theory is something nobody believes, except the person who made it. An experiment is something everybody believes, except the person who made it.”

Albert Einstein, attributed

It is a natural conclusion that today’s metal applications of SFF technology still are quite immature and that metal SFF technology has not quite reached a stable phase in technology development yet. With a biological analogy to stem cells, SFF could be classified as a “stem technology”, still adapting to a variety of applications. However, this situation leaves several openings for development with the possibility to influence the future of this technology. With the potential impact of metal SFF technology on the manufacturing industry, such developments may find a widespread use and could be essential in the future of manufacturing industry.

The theoretical part of this thesis states that while the inherent limitations of current processes will eventually enforce the specialization of the different approaches. In anticipation of new more powerful process developments, significant improvements of materials and process aspects of the current technology can be achieved by importing and adapting established materials and process knowledge to SFF technology. With the objective of SFF based production grade parts and tooling, this hypothesis has been applied to contemporary metal application of SLS technology investigating the possibilities and limitations for the development of a solid steel material system. The work so far has resulted in the publication of seven different scientific papers. Of these have five been presented at “The Annual Solid Freeform Fabrication Symposium” at the university of Texas at Austin in 1999, 2000 2001, 2002, and 2003, and two more presented at the RAPDASA international conferences in South Africa: in Stellenbosch 2001 and in Bloemfontein 2002.
Survey of Experimental Research

**Paper A**, “Systematic view of SFF Metal Tooling Approaches” presented in Bloemfontein 2002, surveys the most important commercialised approaches to metallic application of SFF technology from the perspective of the shape of the material during the additive manufacturing process. This provides the background for a qualified estimation of the strengths and inherent constraints of the respective process approach.

**Paper B**, “A Vacuum Furnace Process for DTM’s RapidSteel 2.0 material”, presented in Austin 1999, addresses a process limitation that affects both the RapidSteel 2.0 and the possibility for further processing of a homogenous steel material.

**Paper C**, “SLS Application of the Fe-Cu-C System for Liquid Phase Sintering”, presented in Austin 2000, is a primary investigation of some of the phenomena associated with the development of a liquid phase sintering material system for SLS purposes.

**Paper D**, “Limits of Loose Metal Powder in the Sinterstation” presented in Austin 2001, addresses the most significant limiting factor for successful liquid phase sintering found in paper B: the density of the applied powder mass.

**Paper E**, “Investigation of Size Range Composed Powder for SLS Based Liquid Phase Sintered Tooling” presented in Stellenbosch 2001, applies the findings from paper D to a liquid phase sintering material system similar to the ones subjected to the primary investigation in paper C. Furthermore is the potential to exchange the use of binder material to the metallic bonding of the powder particles during SLS processing subjected to a primary investigation. (This paper was republished by the SME, in 2002, as “Technical Paper CM02-218.”)

**Paper F**, “Investigation of the Liquid Phase Sintering of Size Range Composed Powder for SLS Application” presented in Austin 2002, further investigates the constraints and phenomena encountered in paper E. Apart from trying a different method to introduce the melting fraction in the powder blend, has the metallic bonding of green bodies and the sintering behaviour been subjected to further investigation.
Survey of Experimental Research

*Paper G*, “A Generic System for Homogenous SLS Steel Materials” presented in Austin 2003, concludes the experimental research by addressing the issues of internal friction in the powder mass, limitation of the maximum soluble amount of liquid phase material and the low dissolving rate of copper in the base material, thus confirming the possibility to manufacture parts, made from homogenous steel alloy, in a two-step SLS based process.

The development work of the new steel material system is not finished by the conclusions of the experimental research included in this thesis. There still are some issues to address, primarily concerning the forming of stable green bodies during SLS processing. However these issues cannot be included with the current experimental set-up and must, regrettable, be left for further research. At this stage has the most significant constraints identified and addressed, as the possibility for the homogenous, SLS based, steel material system has been experimentally confirmed for all principal parts of the process.
5.1 **Paper A**

The survey of principal approaches to the application of SFF technology presented in paper A, provides a critical background for the approach to the experimental research of this thesis. This is why paper A was the subject for an extended summary in chapter 3, and will thus not be subjected to a second summary here. However, despite the comparable recent publication of paper A, the rapid development of the SFF universe have added some noteworthy points that call on to be commented.

5.1.1 **Comments to Paper A**

As was indicated in the extended summary in chapter 3, DTM’s SLS technology is now marketed by 3D Systems. This is due to an acquisition of DTM by 3D Systems in 2001. This was first labelled a merger but has led to a complete shutdown of, and move from, the original DTM facilities during 2002. As one result 3D Systems gained a dominating position, especially on the American market, but included with this acquisition were some costly SLS patent litigations with EOS. These legal issues have remained unresolved and may in the long run have a negative influence on the development of two of the more widely accepted applications to metallic SFF technology worldwide.

Despite the litigations both companies have continued to develop their respective technologies since the publication of paper A. 3D Systems launched their Laserform ST-200 material in 2002, and followed with Laserform A6 steel material in late 2003 [19]. Laserform ST-200 is basically a further development of Laserform ST-100 however with the principal advantage of a higher achievable green strength. This makes the SLS processed parts easier to handle during breakout and rinsing, which in turn makes smaller features practically achievable. However this has come at the price of lower powder packing density, which also means that the final material composite will consist of lower fraction steel, and the material properties are influenced accordingly. The Laserform A6 steel material has included the stronger binder system, but the principal building material of the two older Laserform materials, 420 stainless steel powders, has been replaced by A6 tool steel powder [19]. To further enhance the

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6 During the completion of this thesis a press release was issued announcing that an agreement between 3D Systems and EOS had been reached, settling all litigations [23]. If this indeed is the case, this is good news for all involved as well as the whole international SFF community.
tooling material properties, and possibly to improve lose powder packing, fine tungsten carbide particles has been added to the powder composition [20]. This makes Laserform A6’s composition quite similar to another 3D Systems material, 3D Keltool, and it is very possible that this has been the source of inspiration. Laserform A6 Steel Material claims, apart from the improved green strength, and the increased abrasive resistance that comes with the tungsten carbide, the possibility to be heat-treated to HRC 39 and even the possibility to be textured and etched. Whether the last option is a result of including a new infiltrant material or just possible with a special etching medium remains unclear at present. As a tooling material Laserform A6 seems to be a significant improvement, and one might wonder how much further the development could advance with the current process technology. (3D Keltool has not seen much development during the last few years.) However this material is considerable more brittle than its predecessors, and apparently is not corrosion resistant, therefore Laserform A6 might not be well suited for a number of other possible applications.

Meanwhile, the material and process developers at EOS have not been idle either. At the EuroMold 2003 exhibition a new machine, EOSINT M 270, was presented. This machine addresses some of the limitations known in the previous equipment, and in the perspective of SFF processes used in paper A, is the new laser system of particular interest. The laser used is a so-called fibre laser, which in combination with a variable focus system is claimed to give improved building speed and system productivity. This is probably due to the new type of laser which apparently has a higher energy absorbency in the material compared to the older system. Another interesting development on the material side that is being launched in early 2004, is the new DirectSteel H20 material. Alike 3D Systems new Laserform A6, this is also a tool steel material, but in accordance with the DMLS principle builds the part in one single process step. The DirectSteel H20 is claimed to reach hardness up to HRC 42 and a tensile strength up to 1200 MPa [21], which is within the lower range of conventional tool steels [17], [18].

In addition to the mentioned processes in the section regarding solid phase adding processes, there are two interesting process developments that deserve some attention, however they do not alter the conclusions. One is an entirely new SFF process and the other an exciting material development.
Ultrasonic Consolidation (UC) is a technology developed by Solidica, Inc., where a 25 mm wide 0.1 mm thick aluminium tape is used as the building material. The tape is fused with under laying material by means of ultrasonic welding, and any excess material is removed by CNC milling [10], [22]. Being the first approach to successfully address aluminium for additive manufacturing this process has some weaknesses compared to other SFF metal tooling approaches but also advantages compared to conventional machining. The UC in combination with the removal of excess material limits the possibilities for overhangs, and thus in a SFF perspective is a serious constraint regarding geometry. However Solidica’s primary target niche is the manufacturing of tools, and with the common requirement for draft angles, the difficulties to produce overhangs may not be a problem for that particular application. Furthermore Solidica has declared the intention to include a support material system within the next few years. This system is supposed to consist of a second tape made of lower temperature melting point material, which will be melted away after a completed building process. For the time being, and in the current form, UC’s primary competitor is milling from solid blocks of aluminium. In that situation UC has one primary advantage in the superior capacity to form thin, deep slots and sharp corners, thus decreasing or eliminating the need for EDM, which is usually required for these features. Another interesting feature of Solidica’s approach is the possibility to embed structures of different materials (such as powders, fibres and meshes) in the material, and thus manipulate the mechanical properties of the part, or to encapsulate optical fibres, sensors or printed circuits. In the future development of SFF technology these last possibilities, and the high potential for a large building space, may prove to be the key factors were UC remains to have a competitive edge, even though Solidica also has plans to include other metallic materials in their building capacity.

Meanwhile other technology vendors are also pursuing the possibility to add aluminium among their building materials. However aluminium is a very reactive material and a thermodynamically stable oxide layer always covers aluminium that has been in contact with air. This has been a principal obstacle to overcome, but researchers at the University of Queensland seem to have at least partially succeeded with this in a two-step SLS based approach [23]. An aluminium-magnesium powder blend (approximately 2 wt% Mg) is used to form green bodies with the aid of a polymer binder by common SLS procedure. After removal from building platform and rinsing from loose powder, the green bodies are sintered in flowing nitrogen at atmospheric pressure. For support while the polymer
binder is burned off, the green bodies are embedded in aluminium oxide powder with a small addition of magnesium. Aluminium nitride will form in preference to the present oxide in a nitrogen atmosphere at the right temperature (540 °C) provided that the oxygen partial pressure is exceedingly low. The magnesium, functioning as an oxygen scavenger when added in the powder compositions, achieves this requirement. The green bodies formed are thus aluminium particles joined by a rigid aluminium nitride skeleton. After the skeleton has been formed, the system is heated to the infiltration temperature, where the infiltrant, typically a eutectic aluminium alloy with a melting point sufficiently below the melting point of the base material, is melted and absorbed into the aluminium nitride skeleton.

Still at the research phase, this approach seems like a most promising approach to SFF based aluminium prototyping and manufacturing in the current situation. However, the material is not homogenous aluminium and it does not have material properties equivalent to aluminium. Meanwhile the most advantageous infiltrant alloy has not yet been determined, the aluminium nitride skeleton is not only rigid but also quite brittle, and even though the tensile strength is comparable to conventional aluminium alloys, the strain at failure is less than 1%. Nevertheless, the success so far is a fine illustration of the advantage of a process approach with an uncoupled relationship between material and process. If this approach does reach the market, the prospect for a widespread application seems very good. See Fig. 5.1.1.

![Fig 5.1.1. A laser sintered and infiltrated aluminium part with hollow sections Photo by K. Newall 3D Systems Inc. [23].](image)
5.2 Paper B

5.2.1 Summary

Paper B addresses an obvious and significant limitation of DTM’s RapidSteel 2.0 material (R.S.2.0) process. Released in 1998, R.S.2.0 a powder-based stainless steel bronze infiltrated composite material, was a significant improvement from RapidSteel (1.0), which it replaced. The R.S.2.0 was processed in several steps. The binder-coated particles (~45µm) were applied in the Sinterstation by the standard procedure. The scanning laser selectively melts the binder, which on solidification glues the particles together into solid but brittle “green bodies”. The green bodies were packed in a crucible embedded with supporting aluminium oxide powder, to be sintered and infiltrated by two subsequent furnace cycles. During the first furnace cycle the binder was burned off and material sintered forming metallic bonds between the particles. The sintered “brown” parts were repacked in the crucible, together with bronze infiltrant and again embedded, but with a finer grit aluminium oxide powder for the infiltration cycle.

The furnace cycle was found to be the crucial part of the entire process. The process specified a 30/70-hydrogen/nitrogen atmosphere. Hydrogen being an expensive, highly reactive and, in combination with oxygen, explosive gas requiring a special furnace, was a critical issue. But vacuum furnaces are successfully used in conventional powder metallurgy, for a variety of metals, especially for stainless steel, and are also quite common for brazing, an operation not unlike infiltration. Paper B describes the experimental work to develop a vacuum furnace process for R.S.2.0 and the outcome of that work. A dependable furnace cycle consisting of sintering and infiltration cycles was found and has since then been applied for all use of R.S.2.0 at KTH. The vacuum furnace process proved to be efficient for sintering, with slightly higher shrinkage than the original furnace process, and has been advantageous for the infiltration, were infiltration rates up to 99.8% of the porosity has been achieved.

5.2.2 Comments to Paper B

The hydrogen/nitrogen furnace atmosphere is not uncommon in powder metallurgy; among other things it is efficient in reducing metal oxides, which has a strong negative effect on sintering behaviour. However, this kind of furnaces do not have much other use, and the high price of hydrogen in combination with the long time running furnace cycles makes
the furnace processing for this type of application expensive. Vacuum furnaces also have the potential reduce some metal oxides in a clean and stable atmosphere, and are commonly used in for a variety of heat treatment operations. Additionally, in cases of powder metallurgy involving highly reactive materials, (such as titanium, tantalum and beryllium), high temperature materials, (such as tool steel and refractories), and corrosion resistant materials, (stainless steel), vacuum is the most reliable atmosphere, [24]. For the development of a foundation for the application of a variety of steel materials, including tool steels and stainless steels, it is essential to use a reliable type of furnace, which is likely to be used in the final process. Since it is most desirable to minimize the number of steps in manufacturing processes, it would also be a significant advantage if the option of including heat treatments in the furnace processing existed. In difference to the hydrogen/nitrogen furnace, vacuum furnaces provide this possibility, and in combination with an atmosphere well suited for the most interesting materials. This makes the vacuum furnace an obvious choice to include in this development approach.

Since the publication of Paper B, there has been some further build-up of knowledge and experience. In difference to what is suggested in paper A, the non-existent gas pressure as such is probably of less importance in comparison to thermodynamic effects on the material’s surface. The results, however, remains the same: Improved infiltration conditions and a slightly higher shrinkage, which on the other hand, also could be explained by the individuality of different SLS equipments. Furthermore is the probable cause of the uneven coloration of the infiltrated samples probably not increased pore closure due to the vacuum atmosphere as was suggested in the conclusions of paper A. If so, the infiltration rate would probably been lower. Individual fluctuations in the infiltrant’s wetting of the surface of the part is a more likely explanation, especially as similar behaviour also has been observed on parts sintered in the conventional type of furnace. Still, this does not alter the expectation regarding the potential for liquid phase sintering to full density in a vacuum furnace, even though the non-existent gas pressure in the pores may not be the most crucial advantage.

Another point that is raised in paper A is the effect of no heat-conducting atmosphere in the vacuum furnace. Further experience has shown that this has to be considered while packing the crucible and could be a serious drawback when building certain geometries. Heat is in the vacuum furnace transferred to the part by heat radiation and conduction in the crucible’s walls and bottom. If the part has insufficient contact with the crucible’s
bottom or walls, a steady state for the heat conduction through the aluminium oxide support powder may be established without the part reaching sintering or infiltration temperature. Most moulds and dies however have at least one large flat surface, on which the part can rest in the crucible during furnace procedures.

DTM has recognized the drawbacks of R.S.2.0, dependence on hydrogen/nitrogen furnace atmosphere, and others, and has made some important improvements with the new LaserForm ST-100 material (which replaced R.S.2.0 in January 2001) and the further material developments under 3D Systems. These materials are based on smaller particle steel materials, (~ 20μm stainless steel 420, and tool steel A6), which does not only allow the parts to be built by thinner layers, reducing the stair stepping effects common in layered manufacturing techniques, but also improves the surface finish and resolution, and finally allows the material to be completed by sintering and infiltration in one single furnace cycle. The smaller particles are much more reactive, and starts sintering already at ~700 °C, well before the bronze starts to melt. During the furnace cycle the temperature is kept at ~700 °C until firm interparticle bonds are formed and the temperature is raised to infiltration level where the melted bronze is being absorbed in the steel material matrix.

The issue of hydrogen/nitrogen atmosphere has been addressed in a different manner. The newer materials are processed in an electric kiln type oven with nitrogen atmosphere, which is less expensive, simpler to operate, and provides more consistent thermal control. DTM also did appreciate the infiltration advantage of vacuum furnaces, but the higher price associated with buying that equipment has been deterring.
5.3 Paper C

5.3.1 Summary
Despite the progress made by both DTM and EOS there is still no homogenous heat treatable tool steel material for either system. A basic investigation of a possible such material system is presented in Paper C. In principle and conventional powder metallurgy practice, a steel material could be densified and reach homogeneity by the use of Liquid Phase Sintering, LPS. This technique consists of sintering of a base material in the presence of a lower temperature melting material, which provides a diffusion medium for the base material. Apart from the lower melting temperature, the liquid phase also should have good wetting properties on the base material and the base material should have good diffusivity through the liquid phase. In order to form a homogenous material, the liquid phase material should also be soluble in the base material.

Copper have excellent wetting properties on iron base materials, considerably lower melting temperature and is soluble up to approximately 8%. There has also been reported a swelling effect of copper dissolving into iron, and this combination has thus been used in so-called zero-shrink powders. However copper’s rate of diffusion into iron is larger than iron’s diffusion rate into copper and this could cause pores, known as Kirkendall porosity. Still the rate of copper diffusion can be controlled by the presence of carbon in the liquid phase. Interestingly enough, the suitable fractions of copper and carbon are within the limits for improved tensile properties. This material system is heat treatable [25].

The research presented in paper C is a basic investigation of two different commercial powders from this material system, regarding Sinterstation as well as furnace behaviour. The powders selected in this investigation are sampled from Höganäs’ Distalloy grade powders, Distalloy DH-1 and Distalloy ACu. “DH” stands for “Direct Hardening”, this powder can reach a tensile strength of 750 MPa after a single pressing and sintering in conventional powder metallurgy, but tensile strengths of 1000 MPa has been reached after carbotnitriding. Within this family of powder grades there are tool steel powders that reaches tensile strengths of 1050 MPa after pressing and sintering, with close to zero dimensional change. Distalloy ACu is commonly employed in press ready powder mixes to balance the copper levels and improve dimensional tolerances [26]. Since it has been concluded that contemporary materials science, including powder
metallurgy, is mature by comparison to SFF, the first step was to investigate a commercial powder for some of the basic principles and phenomena that are active in this material system and how they affect the behaviour in a SLS approach. For the purpose of this investigation Distalloy DH-I was picked to sample a composition with a low fraction of copper and Distalloy ACu sampled a composition with excess copper, both samples were processed with and without the presence of carbon.

Due to the low original powder packing in the green bodies, no sample was sintered to full density. This facilitates comparison of the sintering behaviour, and some encouraging phenomena were observed. Prolonged presence of liquid phase, be it due to excess copper level or the presence of carbon, does carry the sintering further. However, the distribution of liquid copper on the surface of the base material does effect particle growth during sintering. Copper swelling effects were recognized and a surface smoothing effect was noted on the macro particle structure.

5.3.2 Comments to Paper C

The Höganäs powders are optimised with respect to conventional powder metallurgy, where pressing properties and the strength of pressed green bodies is of great importance. These properties are of complete irrelevance to SLS based processing, and that optimisation is likely to have negative influence on the properties desirable for SLS purpose. For example: rough particles of a ductile material are known to give a high green strength in compressed powder which is desirable in conventional powder metallurgy. Meanwhile rough particles also are known to have poor loose powder packing properties, which is highly undesirable for an SLS based process. However, the purpose of the investigation described in Paper C was to find critical issues to address in the continued research and to monitor the effects of carbon and copper on the sintering behaviour. With the high fraction of porosity of a loosely applied powder mass, and the massive shrinkage, which is necessary to reach full density, it is only natural that the powder density must be the primary subject for the continued research. Consequently, this is the topic for paper D. In further conclusion, it was found that this material system holds many interesting phenomena, that if properly managed, could make this the basis of a useful material system for production grade tooling, with the potential for further development toward other steel materials. Still, this is entirely dependent on the possibility to form green bodies of sufficient particle packing, to reach full density during sintering.
5.4 Paper D

5.4.1 Summary

The issue of the loose metal powder density in the Sinterstation is essential for the successful SLS application of a powder composition for LPS consolidation. This issue is addressed in Paper D. However, the principles and limiting factors for applied powder density may be applicable to other systems as well.

A powder mass was densified by the successive addition of smaller sized powder particles. Optimal compositions in respect to apparent powder densities were experimentally determined, and the application behaviour as well as the acquired densities were monitored and compared to apparent densities. It was concluded that the principal limiting factors for the density of applied metal powders in the Sinterstation were, apart from particle shape and powder availability, the small sized powder’s tendency to form suspension in the air and, even more important, the inter-particle friction caused by Van der Waal’s and electrostatic forces, effective in very small particle powder. With a practical upper limit for particle size in the Sinterstation application, this means that composition with more than two size range components are unlikely to be successfully applied in this type of equipment. Thereby, the theoretical upper level of relative powder packing is determined to 86%, of the density of the solid material. In this investigation, the highest relative density achieved was 68.6%, and considering the tight size range tolerances at this level, any density above 70% would be an impressive achievement.

5.4.2 Comments to Paper D

Firstly it should be mentioned that there were a few insignificant misprints in the original publication of this paper that have been edited for the purpose of this thesis. Furthermore, in addition to the described experimental procedure, it should be mentioned that the powder layer thickness is 0.1mm for all experiments.

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7 Section 2, line 21, the original publication read “Sinter station” this has been edited to “Sinterstation, which is the correct name of the process equipment. Moreover section 3.4.1, text to Fig. 7, line 8-9, the original text read “Tap density; is given by the manufacturer, to 3.8 - 4.5 g/cm^3,...” These figures are not correct, however of no importance to the experiments or conclusions in the paper. This has been edited to the correct figures of 3.0 - 3.5 g/cm^3.
Since the green bodies in the SLS approach are shaped by loosely applied powder layers the particle packing density of these layers is of vital importance. The most significant effect, provided that parts can be sintered to full density, is the shrinkage during sintering. Powders of high particle packing density have a low fraction of porosity and thus a smaller shrinkage. The concluded theoretically achievable maximum particle packing density in the Sinterstation, 86%, would if sintered shrink 5% provided uniform shrinkage in all directions. However, it is hardly practically possible to reach 86% in the applied powder, and the highest density achieved in the Sinterstation 68.6%, would at the same conditions shrink 12%. This may seem rather high, especially in respect to maintaining shape and dimensional control. On the other hand, in the manufacturing of cemented carbide cutter inserts linear shrinkages up to 18% are not uncommon, while keeping within satisfactory tolerances.

Apparently there are other factors apart from the magnitude of shrinkage that determines the shape and dimensional control. Since small sized particles are more reactive, and thus prone to sintering, and sintering is further enhanced by the presence of a liquid phase, it is more than likely that the arrangement of particles in the green body, and distribution of the liquid phase during sintering are extremely important factors. Therefore, the arrangement of particles, both of steel material and copper in the applied powders were the subject of special attention in the following research.

These arguments are all based on the assumption that the spherical particle shape is the most advantageous for loose powder packing properties. However some recent research in the packing properties of certain lens shaped chocolate candies, have indicated that even higher packing densities are achievable using ellipsoids [27]. The packing experiments with the ellipsoid candies were averaging 68.5% density, while an identical set up for spherical ball bearings averaged 63.5% density [27]. This is explained by the fact that an ellipsoid can rotate out of a position where a sphere would be completely fixated by it’s adjacent neighbours and thus be able to move into an even closer packed arrangement. This is apparently due to a combination of shape and low friction surface of the particles. Whether it has anything to do with the well-known fact that you will always find room for more sweets remains undetermined. The experiments found that ellipsoids in disordered packing had an average number of contact points of 9.82, considerably larger than 6.4, which is the average number for spheres
[27]. For sintering purposes are both close packing and a high number of contact points much desirable. But on the other hand, the present research has determined that the most important limiting factor for powder packing densities is the internal friction in the powder mass. Friction increases with surface, and if the small sized particle mass would increase it’s surface further by ellipsoid particle shape, it is not unlikely that the internal friction would increase beyond practical limits. Still, this is a noteworthy possibility that could be subjected to future research. For the time being, this research has been limited to commercially available metal powders, and the author does not know of any commercially available ellipsoid metal powders within the designated size range. (But it might be possible to modify the shape of spherical powders in the direction by milling. See further paper E.)

Since copper will act as the liquid phase in the proposed material system, copper should be carried by the smaller sized particles, to fit into the voids between the larger particle base material powders. Which leads to another important issue for future research whether the dissolvable amount of copper into the steel will be enough liquid to wet all surfaces and serve as a liquid phase, throughout the whole process until full density. The dissolving rate of copper into steel alloys can be controlled by addition of carbon (see paper C), though this increases the wetting angle and thus decreases the wetted surface and sintering rate of the powder particles. This will, if the process is realizable, be a question for optimisation. The most immediate following research, in paper E, will target the composition of the steel-copper powder blend, how to combine the small size copper particles with base material and other possible additions to achieve best possible distribution of particles and liquid phase during sintering.

Another issue of importance to the powder mass’ density is the additional components, besides the metallic particles. If a powder is size range composed for maximum density, then every other non-metallic addition will decrease the density of that powder compound. Therefore, it is desirable to minimise all additions besides the metallic components. Carbon may be necessary to control the dissolving rate of the copper into the steel base material and may be added in the form of graphite powder. How much will be a question for optimisation. In 3D Systems’ process approach, the powder is joined together to a green body with a binder. This implies that a binder also will be necessary for this type of powder, and since the binder fraction usually is about 4% of the powder mass, and the binder materials are very much lighter than metal powder, this would
occupy a large volume in the powder mass. However, since smaller particles are much more reactive, there could be a possibility to activate the smallest particles to start diffusion bonding by the heat of the laser. If that were possible it would greatly increase the capability of this approach to the making of solid steel objects in the SLS process. This is another topic investigated in paper E.
5.5 Paper E

5.5.1 Summary

Paper E consequently addresses the issues raised in papers C and D. Two different types of iron base powders, pure iron and stainless steel 420, has been combined with a copper coated iron powder and investigated with the objective of SLS behaviour and the outcome of the furnace sintering process. A primary issue has been to compose the different powder components according to size range in order to achieve a maximum applied powder density in the Sinterstation and in the green bodies. This would, ideally, provide optimal conditions for the formation of green bodies and liquid phase sintering to full density while dissolving the liquid phase into the base material and reach homogeneity. The object of this research was to investigate this possibility and monitor the behaviour during the different process steps.

The base material powders were quite different regarding both particle shape and alloy composition. The pure iron powder was coarse an uneven, similar to sponge iron, whereas the stainless steel had a smooth, spherical shape, typical for gas atomised powders. For increased densification, and in the function of a copper carrier, was a small sized powder of copper coated iron selected. Further additions of very fine graphite powder and binder material were included in the powder composition for the relevant experiments. The copper carrier powder had a coarse and uneven or agglomerated shape. In combination with the base materials this led to a decrease in powder mass density instead of the anticipated increase. The prepared metal powder compositions were therefore de-agglomeration milled separately in a cemented carbide mill until the measured increase in powder mass density reached a steady state. During the milling both the pure iron powder and small sized copper carrier powder were plastically deformed, whereas the stainless steel appeared not to have been affected.

A noteworthy increase in the loose powder blend’s density was achieved by the milling operation. This effect did however not transfer to the application in the Sinterstation. Contrary to the loose powder density increase observed in paper D, these powder compounds showed a significant decrease in powder density when applied in the Sinterstation. This can be explained by the coarse shape of the small-sized particles, which aggravates the orientation of particles and increases the inner friction of the powder mass. However since the high inner friction in the powder
compound obstructs the orientation of particles for powder packing density, it is also counteracting the segregation of different powder grades within the powder mass. Consequently, there were no observations of powder segregation in any of the experiments. The additions of fine graphite powder to the pure iron compound, as well as binder material to both compounds, further diminished the density of applied powder in the Sinterstation. The final densities reached, after milling and non-metallic powder additions, were below the levels where full density can be expected after sintering.

The adverse effect on density by the non-metallic addition was expected, and in respect to this, a second series of powder samples had been prepared without the binder material. These samples were used to examine the possibility to form metallic bonds between the particles by laser activation of the powder mass. Since reactivity of powders increases with the specific surface of the powder mass it was considered plausible that some bonding, either by surface diffusion, or possibly even the melting of a fraction of the powder, could be possible.

Both sets of samples were processed in the Sinterstation. The binder joined samples formed porous and brittle green bodies as was expected due to the low powder density. More encouraging was the outcome of the binder-less powder samples. Bonds were indeed formed, however this also included a curling of the newly formed layers. As the next powder layer was spread over the building area, the newly formed green “flakes” easily were caught and pushed out of position by the powder spreading mechanism. This made the connection between the layers somewhat random and no cylindrical green bodies were formed. However this also made the confirmation of the metallic bonding easy by the examination of the elasticity of the connections between layers and plastic deformation (i.e. bending) of the “flakes”.

The green samples were sintered together in a crucible according to the previously established procedure. The polymer bonded green bodies were packed in support powder, whereas the metallic bonded samples were sintered without any support material. All the polymer bonded green samples experienced a significant shrinkage, and among those, did the pure iron samples undergo the largest. In the perspective of the experiences from carbon addition to the iron-copper liquid phase sintering system in paper C, this was interpreted as a result of prolonged sintering due to the presence of carbon in the liquid phase. The disorganized geometry of the metallic
bonded green bodies, made it impossible to obtain any meaningful estimations of the shrinkage of these samples. However the most significant conclusion to be drawn from the sintering of these samples was that they were sintered, apparently with maintained geometry, without supportive powder, which suggests an interesting possibility for the further research.

5.5.2 Comments to Paper E

The issue of the coarse, agglomerated small particle sized copper carriers highlights the importance of knowing the background of powder data, especially for small sized powders. The data sheet from the powder manufacturer gives the particle size range based from a Fisher Sub Sieve Sizer, which actually estimates the surface of a powder mass and interprets that into spherical particles. A large powder surface will be interpreted as small particles. Coarse particle shape will therefore have an estimated size range that is considerably smaller than the size in reality is. This makes size range data more precarious for small sub-sieve\(^8\) powders, and other information, for example on how the powder has been manufactured, can be very helpful. (The carbonyl iron powders used in paper D are manufactured by gas precipitation and are thus of a spherical shape as also can be seen in the pictures.)

The milling of the powder blends apparently deformed the coarser shaped particles which made a higher powder mass density possible. However there does not seem to have been any significant decrease in the internal friction in the powder mass, possibly the effect was contrary, but that is impossible to tell. From the pictures it seems like the particles are flatter but still in reality as coarse as previous to milling. The increase in powder density that was encountered after milling may be interpreted as caused by the increased potential for orientation of a flattened shape that was implied in [27]. However when applied in a Sinterstation the powder mass’ internal friction dominates and thus the additional densification effect is omitted. Regardless of the interpretation of the cause for the encountered effect, the milled powders’ behaviour is a strong indication of the crucial importance of internal friction in the powder mass. The milling may also be of some importance for the behaviour during sintering. It is well known that coarse particles are more reactive and have a faster shrinkage during the initial phase during sintering [24]. Plastic deformation can be expected to have a

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\(^8\) Sub-sieve powders: powders that are small enough pass through a 325 mesh sieve screen and thus cannot be sifted [24].
similar effect on the powder particles. It is quite possible that the combined effect of these two phenomena has been more critical for the extremely large shrinkage of the pure iron samples during sintering, than the effect of dissolved carbon in the liquid phase. Furthermore is it likely that at least a part of the carbon was consumed for deoxidising the powders during the processing in the vacuum furnace.

The most important conclusions to be drawn from paper E is:

1. That even with a bimodal powder blend is the internal friction within the powder mass of great importance. For the spreading of powder layers as well as the formation of green bodies during SLS processing, and thus the behaviour during sintering. However there were no observations of segregation of the powder fractions, which also can be ascribed the inner friction.

2. Any non-metallic additions to the powder composition decrease the density and should therefore be kept at a minimum.

3. It is possible to form metallic bonded green bodies of a size range composed powder with a fraction of very small particles (or seriously deformed particles).

The combination of point two and three, in respect to point one, is the principal topic of paper F. Furthermore is the formation of the metallic bonded green bodies and its correlation with the sintering behaviour investigated.
5.6 Paper F

5.6.1 Summary

The research behind paper F addresses the topics that were raised by the conclusions from the preceding papers. Once again were two different base powder materials selected, a tool steel, Anval 9044, and a stainless steel, Anval 2205, both in the size range -45μm. However this time both powders were gas atomised and therefore had the characteristic spherical shape and free flowing behaviour. These powders were combined with a pure copper powder and an addition of small sized carbonyl iron powder for increased densification.

Determining the fraction of copper added was a matter of balance between the constraints of reasonable process time, due to the copper’s dissolving rate into the base material, and the need for sufficient particle wetting during liquid phase sintering. Calculations showed that with this base material particle size, and acceptable process temperatures, full homogeneity cannot be reached at maximum copper solubility (9%) within reasonable sintering times. But, with a slight decrease in copper content, a homogeneous solution of 8% copper can be reached at 1200 °C within four hours. The process temperature was set to 1200 °C, to avoid chromium evaporation, which can be expected at temperatures above 1233°C, during the vacuum furnace processing for the stainless steel base material.

This determined the copper fraction. A fixed composition of copper and each base material powder was combined with carbonyl iron powder for increased density. However this copper powder also had the all-to-familiar deviation from the stated particle size range. This had the effect that powder densities acquired did not reach the levels that could have been hoped for, and the copper was not as widely distributed in the powder mass as perhaps would have been desirable. Furthermore, it is reasonable to suppose that the copper particles’ roughness has increased the internal friction of the powder and thus has had an adverse effect on the powder particle arrangement during the spreading of new layers.

Initially, one powder composition based on each different steel alloy powder was prepared. The fractions were approximately 75% base material, 8% copper and 17% carbonyl iron. To ensure the reduction of inherent metal oxides was a small fraction (0.1%) carbon added. However when applied for a few test runs in the Sinterstation, the stainless steel
powder composition preformed in a manner symptomatic of too high inner friction. Therefore was a second composition prepared on the same base, but with the fraction of 77% Anval 2205, 15% Carbonyl SM, 8%, copper and finally, 0.1% carbon. The original 75% base material powder compositions reached an applied powder density in the Sinterstation of barely 61% whereas the modified 77% base material composition was applied at 64.6%.

Four different test series were performed with varied laser energy exposure. The first two with the Anval 2205 based compositions, 75% and the 77%, whereas the 75% tool steel, Anval 9044, composition was used for the latter two. The general principle of laser exposure was to successively increase the energy impact, but a variation of fill scan laser powers and speeds combined with different outline laser powers and speeds were used.

In all experiments were metallic bonded green bodies formed, and there was an observed increase in strength of these green bodies with the exposure to increased laser energy. With the increased strength followed, however, an increased curling tendency of the layers. Since the strength of the bonding within of each layer was considerable higher than the strength of the bonds in between layers this could lead to separation between layers. This could nevertheless be controlled, if the bonds to the previous layer, and within that layer itself, were rigid enough to withstand the strain. Another observation of increased laser energy exposure was an increased roughness of the outlines of each scanned layer.

One principal purpose of paper F has been to investigate the formation of the metallic bonded type green bodies encountered in paper E. Observations of the behaviour of the laser exposed powder surface as well as SEM micrographs provided some clues of which mechanisms are active in the bonding process. As it appears, exposed powder slightly raised above the surrounding surface, instead of sinking, which might perhaps rather have been expected when powder particles bond together. This is an indication of that some rearrangement of the particles takes place due to the exposure to the laser. SEM micrographs of the green bodies revealed that a substantial fraction of the powder had melted. This apparently is the principal source of the metallic bonding, and also provides a most reasonable explanation for the curling of the exposed layers. The melted material that wet and bond to the particles, will upon solidification shrink, and thus produce the strain that causes the layer to curl. In respect to the micrographs displaying both very small particles in the carbonyl iron size.
range, and large base material particles remaining, and since copper is the component with the lowest melting temperature, the melted fraction was identified as being the copper. Furthermore, by appearance from the series of SEM pictures, the smallest sized particles did arrange closer opening wider pores with increased laser energy exposure.

The green bodies were sintered in a vacuum furnace according to previously established procedure and at 1200 °C temperature, for four hours according to calculations. All samples were sintered and underwent some shrinkage, however none to full density. The stronger, more rigid green bodies also proved to be more stable and maintained their shape better, including geometry, whereas the more brittle ones had a tendency to sag under their own weight. The porosity was mainly oriented in parallel with the lasers’ scanning direction and along the layers. Furthermore, there was a tendency for this porosity to be larger and coarser when samples had been exposed to more laser energy during the formation of green bodies.

From the observations and outcome of the experiments it was concluded that the issues regarding powder packing and arrangement play an important role for the formation of green bodies and therefore also the whole process. The inter-particle friction is dependent on the particles’ mass and surface. Therefore would it be likely that an improvement could be achieved by using a larger size range for base material powder. Not only to accommodate the available size range of copper within the suitable size range ratio, but also to decrease the adverse effect of inter-particle friction on the powder packing and arrangement. This could, in turn, improve the wetting conditions for copper during the formation of green bodies. A denser packed powder mass would have less distance between particles, and with a larger sized steel particle size range there would be less surface to wet and bond with the melted copper. Less particle surface to wet and bond would allow the available amount of liquid phase act more efficiently as a metallic binder.

The oriented porosity encountered in the sintered samples was likewise explained by laser exposure and limited liquid phase. The exposed powder particles will, provided sufficient laser absorbance of the material, reach the momentarily highest temperature in the powder mass. The melted material, i.e. the liquid phase, will predominantly wet the heated particles. Thus the formed drops of liquid phase will be adhered onto the laser-exposed particles, and therefore drained from the adjacent areas. Since this principle is applicable in three dimensions this also provides an explanation
for the weaker bonding and porosity in between the layers as compared to within each layer.

While it is unlikely that the powder will be optimally arranged and packed to achieve maximum theoretical density within the practical boundaries of this technology, there are some issues to address before a fully dense homogenous steel material is possible.

1. Powder composition: apart from particle size ranges, shapes and inter-particle friction, powder mass behaviour is also dependent on the mass of the base material particles not being too small and dominated by the inter-particle friction. However, too large particles would lead too thick layers and thus hamper laser penetration and bonding to the previous layers.

2. Sintering time and temperatures: to reach homogeneity in the material, the time and temperatures must allow the liquid material to reach an even distribution throughout the largest base material particles. With larger base material size range the diffusion times would increase, and since there are upper practical limits for sintering times as well as temperatures this could be a limiting factor for the acceptable amounts of liquid phase and particle sizes.

3. The fraction of melting phase: with the evident draining of melting material during the formation of green bodies, there were apparently not sufficient liquid phase to sinter the samples to full density. However, the amount of copper cannot be increased if homogeneity is to be reached. A different strategy using a second melting material may be required to address this issue.

5.6.2 Comments to paper F
Prior to the actual commentary of this paper, there were a few misprints in the original publication that have been edited for the readability of the thesis.

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9 In the section 3, “Calculations”, line 28, original publication read: “However s slight…” has been corrected to “However a slight…”. In section 4.2 “Formation of Green Bodies”, figures 6 and 7, were both numbered “6” in the original publication, has also been corrected. Finally, in the same section, “Test A Amal 9044,” second line, originally “…is the curling severe …” corrected to: “…is the curling severe …”. 
Much of the commentary regarding the experiments and their outcome has been included in paper F, and therefore also in the somewhat extensive summary. However there are a few points that should be subjected to some further attention.

The introduction of metallic bonding for the green bodies is a reduction of the uncoupling in the relationship between material and process. This uncoupled relationship was one of the principal reasons for choosing the SLS based two-step approach for this research. However since the final and most important metallic consolidation and homogenisation takes place during the furnace process, there still is a significant uncoupling in the relationship between the SFF processing and the final outcome of the process. Furthermore, a polymer binder material would normally require a support material to maintain the parts’ shape during the sintering process. Since it apparently is not likely to achieve full density in the powder packing of the green bodies, a substantial shrinkage seems unavoidable when sintering to full density. The support material would in that case resist the shrinkage during liquid shape sintering of holes and deep cavities, and most likely cause cracking in the parts. The binder material as such would also decrease the metal particle density in the powder composition. This, in turn, hampers the possibility to reach both full density in the material and a homogenous solution of the liquid phase material. In respect to all this, may the increased coupling by the metallic bonding be, however less desirable, an acceptable accommodation to technical realities.

Rearrangement and orientation of particles is known to happen during the initial phase of sintering, and it is reasonable to expect that this would be an active mechanism in this case also. For very small sized powders this phenomenon is especially relevant, [25], where the surface diffusion strives to straighten the points of contact between particles. Since there is a significant amount of small sized carbonyl iron particles in these powder compositions this is, at least in part, a reasonable explanation for the observed elevation of the scanned surface compared to the unexposed areas. Furthermore, since there evidently is a liquid phase active on some particle surfaces there would possibly be an initial and uneven liquid phase sintering during the metallic bonding of green bodies. This could in combination with the initial particle rearrangement provide a full explanation for the raising of the scanned layer above the surrounding unexposed powder. Regardless of the scientific explanation, this may pose a problem for the initial layers during the building of green bodies. If the elevation of the scanned layer is high, and the powder mass has a high
internal friction, the green layer can get caught and moved out of position by the “wedge” of powder in the advancing front during the spreading of a new layer. This effect has also been observed, mostly in combination with the curling effect of enhanced metal bonding, during the formation of the first layers of a green body.

The melting of a fraction of the powder may be a bit surprising with the low laser energy applied for these experiments. Even more so in respect to the conclusion that copper is the melted powder fraction. Copper is known to have a particular low absorption coefficient for carbon dioxide lasers which are used in the Sinterstation, see Fig. 5.6.2.a. However, the absorption coefficient is considerably higher for iron, and even more for steel, so it is quite possible, even likely, that the laser has heated the base and fill materials and that the copper was melted by heat conduction from these particles. This theory is supported by the fact that the melted material has wetted and bonded to the base and fill material particles (Fig. 5.6.2.b.). If this is the case, the formation of metallic bonded green bodies in this application is a process quite similar to brazing.

\[\text{Fig. 5.6.2.a. Laser absorption coefficients by wave lengths of Nd:YAG and Carbon dioxide lasers in iron, steel and copper, [28].}\]

\[\text{Fig. 5.6.2.b. Paper F, test 2. Green body surface, laser power 35w scan speed 400.}\]

The coarsening of the porosity and particle arrangement that was observed with increased laser energy exposure is most likely in part an outcome of initialised sintering, with both liquid phase and surface diffusion. However for these samples there was also an apparent tendency of copper to be absorbed deeper into the particle matrix. This could be explained if the heat has penetrated deeper into the layer and thereby has spread the melted copper over more particles and, further down bonded to the previous layer. That is, of course, desirable, for the strength of the green body, but in
combination with the draining of copper, which also was observed in the same samples, the overall benefit is somewhat dubious. Even more so in the perspective of the coarsening of the outline that also was experienced at prolonged laser exposure. Apparently, the heat from laser exposure also to a large extent spreading sideways along the powder surface, and at least at the available laser powers and applied powder compositions, more so than penetrating into the layer.

Something that was not discussed in the paper was the possible effect of the carbon addition to the liquid phase. The reason for this is found in the assumption that all of the carbon was consumed during deoxidation of the power. This assumption was made for the calculation determining the added amount of carbon. However, if this were not the case, the copper’s wetting of the particles would have been restricted, which in turn would enhance the concentration and thus draining of copper to the most heated areas. This is worth considering for future experiments.

The limitations in the formation of green bodies, and thus the outcome of the whole process, are a complex combination of different interacting phenomena. These could be addressed in different manners, and each be subjected to extensive research, however, at this stage it is deemed more productive to focus on some crucial issues that could determine the potential for success. The inter-particle friction in the powder mass is apparently resisting the denser arrangement of all particles. One way to address this is to use larger and heavier particles for base material. It is likely that the increased particle mass could overcome the adverse effect of the inter-particle friction and allow the powder a denser packing arrangement. However, larger base material particles would require either longer process time or higher temperatures in the furnace to allow diffusion to homogeneity in the parts. Another issue that cannot be overlooked is that while the powder particle arrangement is unlikely to receive an ideal packing density, the soluble amount of copper apparently insufficient to liquid phase sinter the green bodies to pore-free parts. These are the principal issues addressed in paper G.
5.7 Paper G

5.7.1 Summary
The original publication of paper G does not cover all the research carried out regarding this particular approach to achieve a homogenous material. Paper G does cover the principal part, but some additional investigations further into this matter were conducted, however neither time nor space allowed that part of the research to be included in paper G. A survey of that part will nevertheless be included as a complementary part in this summary.

Paper F identified some principal constraining issues regarding size range distribution and inter-particle friction as well as the fraction of melting phase material in the powder composition. Since these issues are connected to the performance during SLS as well as during the furnace process, the possible solutions are subjected to certain constraints to meet the expected demands on the process. This is especially crucial for stainless steels, which is why a stainless steel, Anval 2205, was selected for this investigation.

It has previously been found that the small sized carbonyl iron and copper particles has a strong influence on the overall powder behaviour. Despite a 75% fraction of ~45μm base material powder, the powder mass behaviour became dominated by inter-particle friction and favourable particle packing arrangement was not possible. The inter-particle friction is dependent on the particle mass/surface ratio. To reach an improvement in this ratio, a larger particle size range was selected for this investigation. The larger particle size range also made it possible to chose a more narrow size range interval for the particles and thus further improve the particle arrangement conditions. Furthermore, the new, larger, size base material particles are better disposed for a high-density particle arrangement with the deviant size ranges of the available copper particles previously encountered. The base material powder selected was 75 – 45μm Anval 2205, however the same principle can be applied to a vast number of different steel alloys. The increased particle size imposes some constraints to the further process variables, however these will be addressed in due course.

The applied amount of copper as liquid phase material has, despite being on the very limit of copper solubility at process conditions, been found insufficient to liquid phase sinter the material to full density. Furthermore
would the larger sized base material particles require exceedingly longer processing times to completely dissolve the copper to homogeneity. These criteria, in combination with the previously determined upper limits for process temperatures, eliminates the option to increase the amount of copper, instead a second melting material is required.

Liquid phase sintering is a fast process, provided that sufficient amount of liquid is available. Copper is dissolved into steel by self-diffusion, which ensures a comparably slow process. Hence the crucial issue is to reach homogeneity, and thus the dissolving rate of copper into the steel base material. At process temperature is the base material alloy arranged in Face Centred Cubic γ-phase, austenite, which is a slow alternative environment for copper self-diffusion. However, being iron based and with a melting temperature of 1168°C, ferrophosphorous is a particularly interesting for introduction as a second melting phase. Even more so in the perspective of that phosphorous has a very strong stabilizing effect on Body Centred Cubic α-phase that also provides a more self-diffusion friendly environment. By comparison, calculations showed that 8% copper would require 369.42 hours to dissolve into a homogenous distribution in 75μm spherical particles of γ-phase. Meanwhile the same operation would only require 204.32 seconds(!) in α-phase.

Even though phosphorous is well known to have a very fast diffusion rate in steel alloys, the ideal conditions assumed in the calculation cannot be expected at real process conditions. Still the potential improvement is so big that even a partial phase transformation could tilt the balance towards the possibility to reach homogeneity within acceptable process times. Therefore it is the hypothesis of this investigation that the combination of copper and ferrophosphorous can be used to liquid phase sinter SLS formed green bodies to full density and homogeneity. If this can be successfully achieved with the selected stainless steel material it should also be possible for a wide variety of different steel alloys, thus confirming this anticipated technological possibility.

The first round of experiments was therefore performed with a powder composition consisting of a fixed fraction copper and ferrophosphorous as melting components, the base material and carbonyl iron was combined to maximize powder particle density. The amount of copper was set to 8% according to established practice in previous research. The added amount of ferrophosphorous was adjusted to yield a final phosphorous content of 0.8%, which in conventional powder metallurgy is reported to give
improved material properties. Composition for maximized powder packing density was performed according to standard procedure. The proportions for the primary experiments were 75.88% Anval 2205, 11.0% Carbonyl SM, 8.0% Copper and 5.12% ferrophosphorous. With this composition the particles did arrange themselves in the Sinterstation to densities between 65.8% and 67.4% of the theoretical.

The powder was exposed to a series of increasing laser powers and decreasing laser scanning speeds. Usable, however fragile, green bodies were received, when the settings were on the limit of machine capacity. However the machine used in this and the previous experiments is a rather old Sinterstation 2000, equipped with a 50W laser, though the measured maximum laser power was 41.5W. It has previously been concluded that the copper is melted by secondary heating form the base material particles, and since these particles are considerably larger in this powder composition, it would require more energy to heat the particles to the melting temperature of copper. If the ferrophosphorous is not melted by direct laser exposure, even more energy would of course be required to reach the melting point of the second liquid phase. This problem is not crucial at this stage, more modern models of DTM/3DSystems SLS equipment uses much stronger lasers (100W), and for this particular investigation the most important part is the liquid phase sintering and dissolving of the liquid phase during the furnace process. For the credibility of the full process approach it is satisfactory to have determined that metallic bonded green bodies indeed were formed.

The green bodies were sintered in a vacuum furnace according to standard procedure. The sintering time was set to four hours, well between the calculated values for diffusion times for the stipulated amount of copper to homogeneity of α- and γ-phase. This is to allow enough time for the dissolving process of copper, even with an incomplete phase transformation. However, should the hypothesis not be correct, would the failure to reach homogeneity show as a clear pattern in the analysis of the samples.

During sintering the samples underwent some shrinkage, and a tendency for sagging of large overhangs was noted. Microscope inspection revealed that while some porosity remained, predominantly oriented between the layers, the material was on the whole very close to full density. The existence of porosity is hardly surprising in the perspective of the less than
perfect conditions during the formation of green bodies, however the low fraction of porosity must be considered encouraging.

The principal issue of reaching homogeneity was displayed by scattering analysis of the most important elements. It is evident that a complete homogeneous distribution of all elements has not developed. Instead the elements were somewhat oriented according to phase patterns, as they would normally be in as-cast material and in respect to heat treatments, see Fig.5.7.1.a. If the copper had not completely dissolved into the base material there would have been clear gradient of copper distribution made visible by the analysis of the investigated area. That is evidently not the case, however there are areas of heightened copper and silicon concentrations in the samples. These areas are also very low in iron and chromium, which is why they can be identified as former pores which has contained a larger amount of copper than could be absorbed in the surrounding material. As previously been stated is liquid phase sintering a rapid process whereas copper dissolving into steel, even α-phase, is by comparison a slow process. If one pocket between steel particles is slightly larger and contain slightly more copper, that copper will require longer time to dissolve. If other copper containing pockets around the same steel particle are being closed and the emptied on copper, the steel particle will have grown and thus greatly expanded the diffusion distances necessary to complete the dissolving process of remaining copper. Consequently the time for complete homogenisation in the material has been further prolonged. This is one possible explanation for the existence of the pockets of concentrated copper.
Fig. 5.7.1a. Paper G, distribution analysis of important elements display a fairly even distribution over the sample area of 58.9 x 44.6 μm. However some tendencies of segregation in phase structures are visible.

Mechanical and electrochemical properties, such as tensile strength, hardness, and corrosion resistance were not tested. This was because of the limitations in the process of formation of green bodies, does not permit the manufacturing of parts with sufficient quality to give any conclusive results of such measurements. But the alloy composition and distribution does suggest that the mechanical properties could be well comparable to conventional steels. The issue of corrosion resistance is a bit more uncertain. The base material stainless steel would even in this diluted state still carry sufficient chromium, and both minor copper as well as phosphorous additions are known to increase the corrosion resistance. However, there is some remaining porosity that could activate crevice corrosion, and the remaining areas of excess copper are possible points of galvanic corrosion. These points of hazard are on the other hand originated in the less than perfect formation of green bodies, and the conditions for corrosion resistance would most likely change for the better with improved quality of the green bodies. One obvious way to address this would be to investigate the effect of an increased laser power, however this is not possible with the current experimental set-up.

Small pores could most likely be closed with an increased addition of liquid phase, which in this case would be more ferrophosphorous. This was investigated in an additional series of experiments that were not included in
the published version of paper G. However, to have a better insight into the relevant phenomena active in this process, this part of the investigation will be included in this summary.

A new powder blend was composed with 76% Anval 2205, 8% copper, 8% ferrophosphorous, and 8% carbonyl iron. After several attempts it was found that this composition had instable powder application behaviour and was therefore found less suitable for SLS application. A new composition was prepared of 75% Anval 2205, 8% copper, 8% ferrophosphorous, and 9% carbonyl iron. This new powder blend displayed more stable application behaviour and the particles were arranged in 64.0 – 64.3% packing densities.

The powder was SLS processed over several runs, however the process cycles were frequently subjected to automatic shutdowns, due to overheating according to the SLS process program. But since the process parameter in some cases were set identical to more successful previous process runs there might be other reasons which caused these failures. These inconsistencies makes the results of the SLS processing less credible, but on the other hand was that not the principal object of this investigation. Nevertheless, despite these problems, and the occasional formation of green “muesli” instead of green bodies, some useable parts of green bodies were formed, and subjected to furnace processing. Green body surface and powder mixture can be seen in Fig. 5.7.1.b.

![Fig. 5.7.1.b. Second powder composition, green body surface with some loose powder mixture, x500.](image)

The parts were treated with identical furnace conditions and parameter settings as the previous experiments described in paper G. There was a noteworthy increase in the sagging of parts from the previous powder composition. Apparently the additional amount of liquid phase from ferrophosphorous has affected the metallic bonds to become less rigid during sintering. Another possibility, that does not eliminate the first, is
that the laser quality has deteriorated during this research, which eventually has gone beyond a critical level. Irrespective of the reason for the sagging, is it clear that the improved conditions for the formation of the green bodies will be required for further progress along this particular thread of research. The liquid phase sintering has had a smoothening effect on the part’s surface on a micro-scale. However the amount of liquid phase has not been sufficient to make any significant impact on surface roughness or the SFF-familiar stair-step effect under the current conditions, see Fig. 5.7.1.c.

![Fig. 5.7.1.c. Top view of sintered mesh sample x20. The stair-step effect of layered manufacturing is clearly visible. There has evidently been a liquid phase sintering surface smoothening between the individual particles. However, the effect is apparently not sufficient to have any significant influence on the part’s overall surface quality. The porosity does not look good though.](image)

Looking deeper into the material it is evident that complete pore closure has not occurred, however the pores’ inner surfaces have apparently been affected by liquid phase sintering. At this stage, in respect to the conditions during the formation of green bodies, it can only be concluded that the pores had been too large to close with the present amount of liquid phase. See Fig. 5.7.1.d.

![Fig. 5.7.1.d. The surface and interior of a sintered body reveals significant remaining porosity, however the shape of the pores suggests that they once have been subjected to liquid phase sintering. Therefore it is concluded that the amount of liquid phase has not been enough to reach complete pore closure under the present conditions.](image)

The phase structure has become more explicit with the increased addition of ferrophosphorous, and that has made the tendency to segregate the elements into different phases become evident. The surfaces of the parts appear to contain an excess of oxygen, calcium and aluminium that can
only be explained by contamination, *Fig. 5.7.1.e*, and *Fig. 5.7.1.f*. In a broad perspective, apart from aluminium and oxygen, are the various elements distributed as could be expected. The elements are dispersed over the whole material surface, but where certain elements have a preferred orientation to certain phases, and others, in consequence, are less present in these same areas. Among the liquid phase components, the phosphorous displays a stronger tendency towards formation into phase structures, while copper appears to be more even dispersed over the whole structure, see *Fig. 5.7.1.e*. However there is one familiar exception in some small pockets of extremely elevated copper concentration, see *Fig. 5.7.1.f*. The shape of these pockets appear to be a confirmation rather than contradiction of the previous suggestion that this distribution pattern originates in pores filled with copper in excess to what could leave the area by diffusion within the process time.

*Fig. 5.7.1.e*. Dispersion analysis from the surface of a sintered sample, fairly even distribution of present elements, however with significant presence of aluminium, calcium and oxygen.
Looking deeper below the surface of the material we find that the contamination with aluminium and calcium has decreased to insignificant levels, however there still remains more oxygen than could be desired, Fig. 5.7.1.g, and Fig. 5.7.1.h. Apparently the deoxidation reaction during the furnace process was insufficient to remove all oxygen in the powder components. The amount of silicon seems also to be of a level more consistent with the alloy composition of the powder components. Other elements have arranged in a similar manner as was displayed on the surface. The phosphorous has oriented into phase structures in apparent combination with molybdenum and chromium. As could be expected, these structures are lower in iron copper and nickel, Fig. 5.7.1.g, and Fig. 5.7.1.h. No copper pockets were found in these sample areas, but that does not eliminate the possibility that they exist, the findings from the surface, existing porosity, and the previous experiments rather suggests that they do.
Fig. 5.7.1.g. Dispersion analysis in the interior of a sample, no apparent contamination, however the oxygen level is more than would be desired. A clear tendency to segregate into different phase structures.

Fig. 5.7.1.h. Dispersion analysis in a different sample area. Similar behaviour and phenomena as displayed in Fig 5.7.1.h.
Since some of the copper evidently remains in pockets of particular high concentration, it is obvious that the concentration of the copper dispersed in the bulk of the material must be smaller than the average. SEMQuant analysis of the material composition at a number of points confirms this; see Appendix 1 for the most relevant points. (Since the primary interest is focused on the bulk material, measuring points in the bulk, inside the samples, are considered relevant for this investigation.) However, the separation into phases makes an overall quantitative distribution analysis of all the alloy components difficult, and the measurements will not give exact numbers valid for the whole sample. To somewhat balance the difference in the composition of the various phase structures is the average alloy composition calculated for five different relevant measuring points. However the oxygen fraction found by the analysis is most likely remains from insufficient deoxidation of the powder particles’ surface oxide. To facilitate the evaluation of the material composition is the oxygen therefore not included in the calculation of the average material composition, and the resulting difference in total alloy composition is compensated for. See Tab. 5.7.1.a. For comparison is the average composition of the material as calculated from the materials in the powder components’ and their respective proportions in the powder blend displayed in Tab. 5.7.1.b. It is however important to remember that the SEMQuant measurements cannot take the proportions of the different phases, the particulate inclusions or even possible concentration gradients within each phase into account. Thus despite the quantitative measurements are the figures only useful for qualitative observations.

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<td>Ti</td>
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Tab. 5.7.1.a. The composition of the material according to the SEMQuant analysis.

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<tr>
<td>Si</td>
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<td>0.56 %</td>
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<tr>
<td>Ti</td>
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Tab. 5.7.1.b. The composition of the material according to the calculations from material data sheets.
Apart from the low copper concentration, the most striking difference to the expected alloy composition is the extremely high content of nickel. The powder composition suggests a fraction of 3.88% whereas the SEMQuant average is found to be 9.28%. If this is caused by some contamination, extreme unfortunate selection of measuring points, or faulting analysis procedure has not been possible to determine. However this gives a perspective on the credibility of exact numbers of the quantitative analysis, and adds a degree of uncertainty in the interpretation of the experimental results. Aside from the components that would make up the dominant fractions of the material, iron, chromium and copper, most alloy components have in general been found in higher concentrations than the expected average. For iron and chromium is the difference comparably small and could serve as an illustration of the uncertainties regarding the quantitative analysis as well as indicate reasonable levels for compensation factors. However if compensation factors would be applied it would not be sufficient to explain the deviating copper and nickel concentrations.

The encountered pockets of particular high copper concentrations can explain the low average copper concentration; meanwhile the issue of the mysterious nickel must remain unresolved. However nickel is well known for its γ-stabilizing properties, and it is most likely that such high amount could have hampered the anticipated phase transformation. This leaves the question whether the phosphorous in reality induced any phase transformation, which, in turn facilitated the diffusion through the base material. The found concentration of copper would easily dissolve into the base material within the process time regardless of α- or γ- phase, and copper is in itself γ-stabilizing in steel alloys. Since no apparent concentration gradients are made visible by the distribution analysis, one possible explanation is that the phosphorous indeed did bring about a limited phase transformation. However, this was eventually reversed as the dissolving copper brought the combined concentration of copper, nickel and other γ-stabilizing alloy components to a critical level and reached domination over the phosphorous and the other α-stabilizing components. A small indication that this could have been the case, may be provided by the fact that chromium and molybdenum has oriented to the phosphorous rich phase, and neither element is known to have rapid diffusion in γ-steel.

The undissolved copper is oriented to points of high concentration, and since there is no indication of the original size of these pockets, it is hardly possible to estimate the magnitude of copper diffusion away from these points. However, it is clear that the copper in the green bodies were not
oriented in the rounded shape displayed by the distribution analysis. Thus it can be concluded that there has been significant reorientation of copper by diffusion in solid phase. Theoretically the argument holds, however experimentally the copper concentration neither confirms nor contradicts the possibility for enhanced diffusion by phase transformation. Rather, it indicates that there may be other issues that are more critical to address in this matter.

5.7.2 Comments to paper G and the complementary investigation

Once again there were some misprints in the original publication of the paper that has been edited for the readability in this thesis.\(^\text{10}\)

The larger base material particles allowed a more favourable powder particle arrangement than in the previous experiment (paper F), not only by the heavier particles overcoming the forces of internal friction, but also because the size range intervals between base material and copper were more suitable. However the copper particles still are large in comparison to the optimal size range, as well as the ferrophosphorous and carbonyl iron, and larger copper particles also means a smaller number of particles for the same fraction of copper. With fewer particles there will be less copper dispersion in the powder blend regardless of how well blended the powder is. Thus smaller sized copper particles would most likely have a better dispersion in well-blended powder. That in turn would allow for a more efficient binder function and probably also reduce the conditions for copper concentration in the remaining porosity.

This brings about the issue of the drainage of the liquid phase, and the consequent concentration of copper to laser exposed areas. Since the copper is melted by indirect heating from iron and steel particles, it is only natural that the copper melts onto the surface of the laser exposed, and thus

\(^{10}\) In section 1, “Introduction” line seven, the original print is “…development in theses areas…” is edited to “…developments is these areas…” In section 2.1, Fig.4, original print reads “…coarse and uneven. Particles.” This is of course edited to “…coarse and uneven particles.” In the same section, Table 3, “15.23 µ” has been edited to “15.23 µm”. Section 2.3 “Furnace process conditions” fourth paragraph line three the original print is “…base material been changed the to 44µm - 75µm,…”, has been edited to “…base material been changed to 44µm - 75µm,…”. Section 3.1 “Powder composition” line 21 the original print is “…range between 65.8 % and 67.4,…” has been edited to “…range between 65.8 % and 67.4 %,…”. 
heated, particles. Hereby the copper is drained towards the surface of the exposed powder layer with the adverse effects on green strength and risk of producing areas of unnecessary high copper concentration. However with a smaller sized, well-dispersed, copper powder it is likely that the smaller drops of melted copper will adhere to the closest heated iron or steel particles. The 8% fraction of copper in combination with small sized particles makes larger volumes of interconnecting melted copper drops less likely, which should reduce the draining phenomenon.

However, to establish metallic bonds with the previous layer requires that sufficient heat to melt the designated powder fraction penetrate through the upper powder layer into the next. The increased base material particle size range in paper G made the limits of energy transfer from laser to particles clear. It is obvious that a larger particle requires more energy to reach the desired temperature than a small one, and this was illustrated by the problems with forming stable green bodies in this series of experiments. Furthermore was the possibility to melt the ferrophosphorous and thereby improve the quality of the green bodies at the available laser power, either by indirect heating or by direct exposure, laid aside. Even though the difference in melting temperature between copper and ferrophosphorous is barely 100 °C, and phosphorous additions has been known to make copper more susceptible to carbon dioxide laser wave lengths, did the ferrophosphorous powder remain intact until the furnace processing. A logical way to address this would be to increase the laser power to levels common used in the SLS systems currently on the market. This, in combination with finely dispersed smaller sized copper particles, could make a crucial difference in improving the conditions for formation of green bodies and the subsequent liquid phase sintering and diffusion to full density in a homogenous material.

However the actual laser power used in this last series of experiments is not entirely certain. Originally was the laser power 50W, more recent measurements has given 41.5 W as maximum available laser power. But in connection to the observations during the last set of experiments was the laser power measured again, and this measurement suggested an unstable behaviour, with output power ranging between 21.5W to 45W.

Apart from the unexpected high content of nickel the material analysis found some elements from apparent contamination on the surface of the samples. However, during the furnace process, the samples were placed on the surface of an aluminium oxide powder bed, and apart from that this is
an obvious source for aluminium contamination was the oxide powder not entirely clean, just like the furnace and crucible. This is an obvious source of contamination and the small levels found at the surface of the samples are probably insignificant.

The levels oxygen, and thus oxide inclusions found inside the material is quite a different matter. By necessity is the powder exposed to oxygen and thus subjected to oxidation during the handling of the powder. These oxides can be reduced by reaction with carbon during vacuum furnace processing as has been mentioned in previous experiments and papers. Since this series of experiments addressed stainless steels there was a concern to avoid the reaction between excess carbon and chromium, forming chromium carbide. Since the level of oxidation in the powder after manual handling was impossible to predict, and both the carbonyl iron and the ferrophosphorous contains some amount of carbon, no additional carbon was added to the powder. Apparently was the available fraction of carbon insufficient to reduce all oxides, but this issue is by comparison easy to come to terms with.

As was mentioned in paper G and in the comments, has the mechanical and electrochemical properties not been measured in this investigation, since the results from such an investigation would not be conclusive. The issue of corrosion resistance has been discussed in the comments, however there are some points regarding the mechanical properties that might need some further comments. In general, small additions of copper and phosphorous are known to have a positive influence on both mechanical properties and corrosion resistance. Dissolved copper will have a solution hardening effect, and the hardening can be further enhanced by aging and precipitation hardening. (Though this could be a source of galvanic corrosion in stainless steel.) The amount of phosphorous added to the first set of experiments was based on fractions that have been reported to give the best improvement in mechanical properties from conventional power metallurgy. In this perspective would it be reasonable to expect an improvement in mechanical properties even by comparison to the commercial 2205 stainless steel. However in this application has the original alloy composition of the stainless steel been diluted, and in respect to this as well as the additions to the alloy are the mechanical properties difficult to predict, regardless of inclusions and porosity.
In respect to the apparent constraints it is obvious that the work to investigate a new steel material system is not finished by the experiments presented in, and in connection with paper G. There still are several issues to address, primarily dependent of the limitations in the formation of stable good quality metallic bonded green bodies. Apart from the obvious difficulties, this is a fine illustration of the hazards brought by the close coupling of material and process technology that comes with this type of approach to additive manufacturing. Even though this particular model has decreased the dependence by the subsequent liquid phase sintering in the furnace process. The performed research has reached a situation where the encountered limitations cannot be addressed within the current experimental set-up and must therefore be left for further research. However the possibilities to form metallic bonded green bodies by conventional SLS equipment, and to liquid phase sinter them to full density has been experimentally confirmed, or perhaps in a more accepted scientific terminology, has not been falsified. The dissolving and diffusion of liquid phase components to homogeneity has neither been falsified, and though the experimental results are not entirely conclusive there is good scientific reason to maintain this possibility as a principal hypothesis. Further research into this possibility should include the use of a more powerful laser, in the level of the contemporary commercial systems, smaller sized copper particles, and a base material with a confirmed lower nickel content.
6. Discussion and Conclusions

“Success is just a matter of attitude.” Darcy E. Gibbons

In the descriptive part of the thesis was an overview of Solid Freeform Fabrication technology in its present state and situation presented. From this, it is clear that additive manufacturing methods such as SFF technology has many advantages for the manufacturing of complex shapes and artefacts in small numbers. It is furthermore clear that we are only in the beginning of finding out the true potential and limitations to this new approach to automatic manufacturing. For example, since the material is added to the artefact successively, there is, in principle, nothing that contradicts the possibility to vary the material composition in order to optimise the performance of every single part of the object. However at this stage, we are far from achieving this complete liberation from both geometrical and material constraints and it is a long way of research and development before it can be reached.

A most common consequence of the additive manufacturing approach is a stronger coupling between process and material technology than is usual in conventional manufacturing techniques. Since most contemporary commercial SFF processes originally have been developed for prototyping purposes it is most likely that a whole new family of additive processes are required in response to the increasing number of new applications beyond the actual prototyping. For the future development of SFF technology, it would be most desirable that the approach to this next generation processes is aimed at minimizing the coupling between material and process technology.
In **Paper A**, from the overview of the present metallic SFF applications, it was concluded that while there is a variety of approaches to SFF metal tooling, and a number of these are commercialised, the development and application of metal-based SFF is still hampered by constraints and limitations in material and process approaches. These constraints and limitations are made visible by:

- **Prolonged build time,** either by a time-consuming process approach or by the need for subsequent processing operations, such as removal of supports, furnace processing, milling, polishing etc. The effect of these delays is dependent on the part and its application.
- **Restraints in geometry, precision and resolution.** Some approaches cannot build, or requires support structure to build certain geometries. Whereas some have difficulties with building the geometry to exact measures, or with reproducing finer features. Most approaches, dependent on application, need some post-processing, for example polishing, peening or blasting. Even if these restraints in most cases are possible to overcome, they are hampering the application of the respective processes.
- **Limited selection of materials or limitation in quality of the part made in the material.** The commercial metal SFF processes that are best suited for tooling applications in respect to precision, resolution and build speed, are also quite limited in respect to material selection and material properties.

In respect to this situation, it is clear that there is a high potential for significant impact from further research and development in the area of materials and processes for metal materials in SFF. Since there is a number of processes developing and competing for acceptance on the market, it is likely that more impact could be achieved by the development of improved material systems for commercialised process systems, which are well established on the market. Seeing that materials science is mature by comparison to SFF, it appears that the application of established materials knowledge to SFF purposes could make much progress for this technology. For this reason, DTM/3DSystems’s SLS approach was selected for the development of a tool steel material system, with the possibility to expand to the application of other steel qualities. The research has been based on experimental application of established powder metallurgy to the Sinterstation system. The work includes both a process modification and the investigation of powder parameters, relevant for this application. The conclusions of the experimental research so far are hereby:
Paper B.: Vacuum furnaces provide a reliable atmosphere and can successfully be used for sintering as well as infiltration of SLS materials. However, heat transfer can be limited by supportive powder and the lack of convective furnace atmosphere. Therefore heat conduction through the crucible wall should be ensured, or the objects should be directly exposed to heat radiation.

Paper C.: Iron-copper-carbon is a material system with potential for liquid phase sintering. If sintered to full density, this system could form a homogenous material and have heat-treating capacity. The same basic principle could most likely be applied to a whole series of SFF steel materials. However the achievable particle packing density determines the possibility for successful SFF application, where the absolute minimum for successful sintering is 50% solid material.

Paper D.: Increased powder packing densities can be achieved by the addition of smaller sized particles to a powder mass. With respect to the practical limitations, the theoretically highest possible relative density is 86%. But in this investigation, the highest relative density achieved was 68.6%. Being well over 50%, this indicates that liquid phase sintering to full density is not at all impossible. However, if a green body of this porosity would be sintered to full density, a significant shrinkage would be unavoidable. If such a shrinking material would be sintered with supporting powder, any hollow features filled with support powder would not have the freedom to shrink sufficiently, and thus the shrinking part would crack. This makes supportive powder and hollow features incompatible with LPS to full density.

Paper E.: Particle shape is another important variable in the SLS application of sub-sieve powders. Primarily because the shape also affects the size measurement, which may cause the powder appear more small-sized than in reality is the case. Secondly because rougher particles claim a larger volume in relation to mass compared to spherical particles, and thirdly because a rougher surface increases the inter-particle friction which resists the densified particle packing arrangement. Any non-metallic particles such as graphite powder or organic binders added to the powder composition may decrease the metallic particle density and should therefore be kept at a minimum. The solution to this, and the issue of shrinkage during LPS to full density in combination with supporting
Discussion and Conclusions

powder, could be provided by the confirmed possibility to use a fraction of
the powder for metallic bonding of the green bodies.

The function of the supportive powder in the conventional SLS approach
with organic binders is two-fold. To support and retain the shape of the
green body while the binder is burned off and metallic bonds are formed
between the powder particles, and to keep the infiltrant contained in the
brown part during infiltration. Since metallic bonds can be formed already
in the Sinterstation, binders are no longer necessary. With stable metallic
bonds, followed by liquid phase sintering, the supporting powder would
also lose its motivation, and thus there would hardly be anything physical
to hinder the shrinkage of any shape, to full density. However this option
comes at the price of stronger coupled relationship between material
physics and process approach.

A principal idea of the iron-copper steel material approach is to dissolve
the copper into the steel base material upon reaching full density. A critical
aspect of this is whether the copper will remain for a sufficient time for
LPS to reach full density, or if the copper will dissolve prematurely,
leaving a severe porosity. This is of course to a large extent dependent on
the amount of porosity, the amount of copper, and the rate of copper
dissolving into the steel base material. This is why this have been a critical
subject for investigation in the research of this potential material system.

**Paper F:** Inter-particle friction plays an important role whenever small
sized particles are a significant fraction in a powder composition. The
combined effect of the copper and carbonyl iron powders brought too much
inter-particle friction to the powder, which hampered the densified particle
arrangement. However the inter-particle friction of a powder mass is
dependent on the particle mass/surface relationship. Therefore is this an
indication that secondary factors, apart from the physical fitting, of particle
geometries may also play an important role in determining the size range
combinations for increased powder packing density of powders in the
Sinterstation. In the present investigation these conclusions suggests that
the inter-particle friction by the applied small sized fractions requires larger
base material particles (more particle mass in comparison to surface area)
to allow increased density particle arrangement. Larger base material
particles does, on the other hand require thicker powder layers which in
turn calls for increased laser energy impact to penetrate.
Discussion and Conclusions

The metallic bonding of the green bodies is apparently a result of secondary melting of copper particles in contact with heated iron and steel particles in the fill and base materials. Since copper particles melt onto the surface of heated particles this causes drainage of liquid phase material from unexposed areas in the powder mass. If a body of melted copper is in contact with more than one solid particle these particles will be subjected to local LPS. That, in combination with the solidification shrinkage has a particle orienting effect within the green body layer.

The draining of liquid phase material from areas unexposed to the laser hampers sintering to full density. A copper fraction equivalent to the full solubility at the furnace process temperature was found to be insufficient to reach full density at the present conditions. The process temperatures are limited to avoid adverse effects on the base material, such as grain coarsening, melting or evaporation of a fraction of the original alloy. For most interesting steel qualities, this settles the process temperature to about 1200 °C. Therefore is copper not sufficient as a single soluble, liquid phase material, and a second similar material is required.

The need for a sufficient amount of liquid phase to overcome the inherent porosity imposes large fractions of liquid phase material. This makes the dissolving rate of the liquid phase materials into the base material a critical issue in the pursuit of a homogenous material. The increased particle size range required to overcome the inter-particle friction stresses this issue further. To reach homogeneity the processing times must allow for the liquid phase material to be evenly distributed throughout the largest base material particles by means of diffusion. Since copper diffuses through iron and steel by self-diffusion this could push the processing times beyond what is practically acceptable.

**Paper G.:** Increased base material particle size did improve the applied powder density, though the large particles also increases the time to dissolve the full soluble amount of copper into the base material beyond practically reasonable limits. However ferrophosphorous was found to have an excellent potential as a second liquid phase material. Primarily for general liquid phase sintering properties for this type of alloys. Secondarily, for the potential to cause a phase transformation from austenite, with slow self-diffusion properties, to ferrite, which has a lot faster self-diffusion properties. This could reduce the dissolving time for copper most significantly, even with an incomplete phase transformation.
The increased base particle size led to an increase in layer thickness. In combination this required an increased laser energy exposure to form metallic bonds. The green bodies formed at the limit of the present equipment’s capacity were nevertheless very fragile and many samples were sintered as fragments. The copper was melted by indirect heat exposure at 1086 °C but the laser effect was insufficient to melt ferrophosphorous at 1168 °C. Further research into this material system would require an improved laser capacity. Despite the limited quality of the green bodies were samples sintered close to full density.

A tendency for sagging of large overhangs can be attributed to the additional liquid phase material. This effect was emphasised by an increase in liquid phase powder that was unaffected by laser exposure. It is not unlikely that one reason for this sagging effect is to be found in the melting and wetting of the base and fill materials by the ferrophosphorous. Liquid phase sintering has caused a surface smoothing effect between particles on a micro-scale, but the amount of liquid phase and the original porosity in the green bodies have so far resisted this effect to appear on a macro-scale. If this issue remains unresolved the finished parts from this process approach will have a serious limitation in regards to surface quality, or require some post processing.

Material analysis of the samples revealed some obvious cases of contamination, such as high levels of aluminium and calcium on, and directly under the surface. Furthermore does high levels oxygen suggest that an additional reduction agent such as carbon would decrease the amount of metal oxides and thus further improve sintering behaviour. More mysterious is the appearance of nickel in levels far above what could be expected from the alloys of the combined powder components. Nickel stabilises austenite and thus opposes the desirable phase transformation towards ferrite structure, expected from the addition of phosphorous to the alloy. Therefore this unexpected nickel may have had an adverse effect on the actual diffusion properties in the base material. However, with some exceptions have the different elements reached as even distribution in the material as could be expected in respect to the different phase structures apparent in the material. This segregation tendency becomes clearer with increased levels of phosphorous added to the material.

One crucial exception to the overall even alloy distribution is certain pockets of particular high copper concentration encountered in the material. This is attributed to uneven copper distribution in the green bodies (caused by, for example draining and random cases of particle orientation). A
combination of smaller copper particles, well distributed in the powder mass, and deeper laser penetration into the layers is a likely way to address this issue. However this brings about the difficult question whether there in reality was a phase transformation austenite to ferrite and possibly reversed back. Complete homogeneity was not reached, but there can be other reasons for that, this has already been discussed in the comment to paper G. Granted that the apparent nickel is not caused by an analysis error, that contribution has most likely had a negative effect. On the other hand has the elements distributed fairly well under the present circumstances, which would suggest that better results are likely to attain without such high nickel levels. While the outcome of the present experiments cannot entirely confirm this possibility, the principle of the generic system for homogenous SLS steel material has not at all been falsified either. Contrary, conclusions to be drawn from the latter experiments regarding increased ferrophosphorous addition, rather suggest that the issue to focus for the future research in this particular niche of SFF technology would be the formation of high density, robust green bodies. If that issue cannot be resolved, this approach to building solid steel parts by SLS would be difficult to attain.

However the full process, from the selection of powders for the composition, over SLS processing to the establishment of an optimal furnace cycle for the specific material composition is evidently an extremely complex matter with a large number of connected variables. This research and development can therefore only be carried out one step at a time basing every new step on the conclusions drawn from the preceding. The previous research has strictly speaking not proven the possibility, only failed to prove the impossibility of such a material system and process. At this stage, the safest conclusion is that this approach still appears possible, and that an eventual success is not unlikely. However in regard to the pace of development within this industry, it could be questionable whether the outcome of this materials research would reach the anticipated wide impact, before the ongoing materials and processes development would push it into more narrow niche applications or even worse, make it obsolete.
6.1 Further Research

Obviously the research of this approach to expanding the metallic capacity of SFF technology is not at all finished with the completion of this thesis. As has been suggested on several places throughout the text, there are some more issues to address before this proposed material system is ready to be exploited. The obvious first step should be a further investigation into the formation of metallic bonded green bodies; the penetration of laser energy in the powder layer, and the interaction with other relevant parameters is of crucial importance for the outcome of the process. In addition to that the melting of the different liquid phase material particles; the copper and the ferrophosphorous, bonding between the layers, and how to minimize the draining of liquid, as well as the curling of the layers are also of significant importance. In relation to this will smaller sized copper particles be very interesting, partly in respect to melting properties but mostly to achieve a better distribution of copper over the surface of the base material particles.

For the dissolving process of the liquid phases, it will of course be essential to ensure the correct alloy composition of the applied steel powders and to avoid the contamination of the samples. The origin of the excess nickel in the samples in Paper G remains illusive, however to be able to address this possibility in a conclusive manner such surprises must be avoided. Moreover was there apparently more oxides in the powder than could be reduced by the present carbon in the furnace process, and another topic of research should be to determine how much additional carbon is needed to ensure sufficient deoxidation.

Finally when these and other occurring parameters, whose importance is yet to be discovered, are sufficiently researched, future work will be aimed at expanding this application to a wider array of commercially interesting steels.
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SYSTEMATIC VIEW OF SFF METAL TOOLING APPROACHES

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ABSTRACT
The present work surveys the principal approaches of metallic materials to SFF technology. This survey has arranged the different process approaches in respect to the shape of the added material: gaseous, liquid, solid or hybrid. From this perspective has the inherent constraint in the different process approaches been estimated together with a qualitative evaluation how this affects the long-term development potential of the respective process. It is concluded that while there are several metal-SFF processes available, there is still much need for further development. In a short term perspective in respect to the speed, process precision, and available materials of the most widely accepted commercial processes, but in a longer perspective also of new processes, that if possible are more uncoupled in the relationship between process and material. The solution to these development challenges may very well determine the future of the entire manufacturing industry.

INTRODUCTION

The Solid Free Form Fabrication Family
The area of Solid Freeform Fabrication (SFF), Rapid Prototyping (RP), Rapid Tooling (RT), etc. is a tangled mass of concepts and abbreviations, which are not entirely standardized. For the purpose of this paper has the following definition of the SFF technology has been used: "SFF, Solid Freeform Fabrication, is the collective name given to a family of technologies aiming at the automatic manufacturing of solid three dimensional objects directly from a computer model by the successive addition of material, without the use of specialized tooling and with a minimum of conventional post processing."

With this definition a wide array of quite different processes can be included in this family, but still there are some common traits in the available SFF processes today:

- Firstly, all processes require, by definition, a digital model of the solid. This model is in most cases represented in the STL format, which has established itself as the de facto-standard for the communication of solid models for SFF purposes, since the earliest days of the technology.
- Secondly, the actual building process is in all commercial processes, and in most research approaches, performed by the layer-wise addition of material. This has prompted the suggestion of Layered Manufacturing (LM) as an alternative term for SFF.
- Thirdly, apart from the different welding based technologies, most SFF processes were originally developed for polymer materials.
- Finally, dependent of process route and material, there are usually some finishing operations required, (such as removal of support structure, removal of unsintered powder or uncured resin, polishing, etc.).
A number of different processes, new, and variations on similar process approaches have been developed. Since each process is marketed by its own brand name, it has not always been easy to understand the similarities and differences between the different approaches. In order to systematize this confusing state, a series of unofficial group names has been established. These names are usually identical to the name of the first established process of each family, which of course is a source of confusion on its own. For example: the processes that are building objects by the curing of a liquid polymer resin are usually called “SLAs”. Still the abbreviation “SLA” stands for “StereoLithography Apparatus”, and it is the name used by 3D Systems Corporation for one of their lines of products. As an alternative to this, trying to clarify the scope further, new process group names such as StereoLithography (SL) and Selective Curing (SC) has been suggested, gaining varying popularity, and adding some extra terms to be confused with the rest. Still, for the time being, the traditional names applied to the different groups of SFF technologies are generally recognized and will continue to serve their purpose until another, more precise, terminology is generally accepted by the international SFF community.

Apart from the selective curing of photopolymers in SLA, there are a handful of other groups that should be described in this brief introduction to the SFF family. This introduction is by no means intended to be a complete list of available methodologies, but serves as an example for the purpose of basic orientation.

- SLS is the name used for the powder-based processes where particles in a powder bed are selectively fused by the heat of a laser. The term stands for “Selective Laser Sintering” and originates as the name DTM Corp. used for their particular process approach. In this survey SLS is used exclusively for DTM’s approach, the similar approach to metallic SFF, used by EOS GmbH is termed DMLS, Direct Metal Laser Sintering.
- FDM, stands for “Fused Deposition Modelling”, and applies to the approach where the objects are being built by the extrusion of thin filaments of semi-melted material (mostly thermoplastic). Since Stratasys Inc exclusively distributes this approach to the world market; the use of this term is one of the least controversial.
- 3D printing, originates from MIT (Massachusetts Institute of Technology), and is licensed to a number of companies. The basic principle is that powder particles are being selectively joined together by the addition of liquid binder in a manner not unlike the inkjet technique of a common desktop printer.
- LOM, is the term most widely used for the techniques that are manufacturing by the lamination of cutouts from paper or other polymer sheet material.
- Inkjet is one term used for the various techniques where a wax, or wax-like thermoplastic is being printed layer by layer with inkjets, forming the final object.

This is one example of how the SFF family could be arranged, other systematisations are plausible, but this system is recognizable throughout the world to day. Which systematisation is most suitable depends on for which purpose it is applied, and what the system is intended to illustrate.
Scope
The variation within the SFF family is also reflected within the metallic applications, with several different process approaches. However, since the SFF technology is defined by the manufacturing of solid objects from a digital representation, by the successive addition of materials, and the digital representations are more or less standardized for today’s technology, the critical point and greatest source of variation lays in the addition of the material. There is much development in progress in the area of metal SFF today, and it is extremely difficult, if not impossible to predict exactly which are the process approaches that will be the most important in the future. It is however possible to make a qualitative evaluation of the capacity of each process approach. This paper will survey different process approaches with the object of forming a better understanding of the characteristics and fundamental differences between the principal metallic applications of SFF technology. Since the capacity of the building process as well as the properties of the manufactured parts is, to a large extent, determined by the form of the material upon addition, this will be the criterion for the systematisation of metallic SFF processes in this survey. This perspective will be used as basis for a qualified estimation of the constraints for metal SFF application inherent in each approach. Focusing on metallic materials, the added metal can occur either in solid, liquid, gaseous phase, or in combinations of these.

ADDING FROM GASEOUS PHASE
(Based on [1] and links)
The possibility to develop a process that builds the objects by adding material from a gaseous phase has been the subject for some research projects, for example Gas Phase Deposition (GPD) of University of Texas, Laser Assisted Chemical Vapour Deposition, (LCVD) of Georgia Institute of Technology, and Selective Area Laser Deposition (SALD) of University of Connecticut. By the nature of gases, the bonding takes place at a molecular or even atomic level, and has the theoretical capacity for extremely controlled material composition as well as surface quality. The processes have been used to manufacture objects with high demands for purity and molecule/atom arrangements, such as coatings, fibres and semiconductor material, but the possibility for graded materials also exist. Still, with the size of added units, even with extremely rapid process control system, this approach would be to slow and costly for objects much larger than fibres and semiconductors, such as metal tooling. In the field of nanotechnology, on the other hand, building by adding at atomic or molecular level is a natural approach, and such processes has the subject of research at labs such as IBM and Institute for Molecular Manufacturing.

ADDING FROM LIQUID PHASE
(Based on conclusions from [2], [3], [4], [5], [6], [7] and [8])
Liquid shape seems to be an obvious alternative to add material for SFF purposes, and it is hardly surprising that several processes are using this approach. In this overview this group includes the approaches in which the material is in liquid shape at the moment of addition to the object by the SFF equipment. But in between those, there is one further distinction that should be made: by the solution of material transportation to the point of fusion. The material could either be a powder spread out in advance of melting, or fed to a pool of melted metal.
Thanks to the applied powder bed, which acts as a support during the building, the first solution has the advantage of a higher degree of flexibility in geometries (see Fig. 1). This methodology is used in “Electron Beam Melting”, EBM, (by Arcam), and “Selective Laser Melting”, SLM, (by F&S Gmbh, in cooperation with Fraunhofer Institute for Laser technology). Both these technologies are targeting the manufacturing of steel moulds, and both are at the brink of commercialisation.

Fig 1. Sample part from the EBM process, by Arcam. The applied powder bed allows this process approach the liberty to include complex geometrical features, such as in this case a caged ball. However, the drop of liquid metal and the connecting powder particles determine the surface quality thus limiting the achievable smoothness.

The second solution, on the other hand, offers the possibility to add different materials during the processing, and thereby to build with graded materials. Another difference is that the material does not necessarily have to be added in the shape of powder, it could just as easily be a wire fed into the melted pool. All this is however at the price of that no overhangs above a $45^\circ$ angle are possible without the addition of extra support, or 5-axis process capacity. (See Fig. 2.)

Among the processes that has emerged from this approach there are a few that have reached commercial applications, and a handful more still in the research phase. The commercialised processes include Laser Engineered Net Shaping, LENS, by Optomec, Controlled Metal Build-up, CMB, (by Albrecht Röders Gmbh), LasForm (by Aeromet), and Direct Metal Deposition, DMD, (by Precision Optical Manufacturing, POM). The commercialisation of the last two is principally in the form of service providers.

Fig. 2. The LENS process in progress, the powder is continuously fed into the pool of melted material, allowing a variable material composition within each layer, but also limits the freedom of geometry.

A hybrid approach, which adds material by liquid phase sintering and thus combines liquid with solids at the point of addition, has been quite successful in the commercialisation. It is called Direct Metal Laser Sintering, DMLS, (by EOS Gmbh). This approach will be covered more extensively later in this text.
In all these techniques, the metal melted upon addition. This comes by the transfer of energy, in the mentioned processes, either by an electron beam or by a laser. The build speed achievable in each process is thus, among other things, dependent on the transfer of energy to the metal. Since lasers transfer energy by lightwaves, the efficiency, and thus build speed, of those processes in each material, is determined by the energy absorbance of the specific wavelength of each type of laser. An electron beam on the other hand, does not have that same limitation, but is generally more difficult to control.

In contrast to polymers, pure metals melt in one step forming a liquid of comparably low viscosity. Since liquids by their nature assumes the shape of the vessel, and the additive approach of these SFF techniques makes a particular “vessel” for each drop of material impossible, it has proven very difficult to have complete control of the surfaces. The best possible resolution and precision will eventually be determined by the size of the melt and its adjacent particles. This precision thereby influenced by the nature of powder addition. In a distributed powder bed, the melted drop rests surrounded by powder particles, which will bind to the droplet, whereas if the material is fed into the melt, there are usually no adjacent particles. This does not mean that the material fed process necessarily has higher resolution and precision. Since nothing surrounds the droplet, it will be more difficult to control. Furthermore, the feeding material itself could also add some limitations. If the material is being fed in the shape of powder, the friction between powder and feeding device would put a constraint on how small an amount of powder that is possible to feed through the device into the melt, and thereby setting a lower limit on the size of the melted droplet, resulting in a limitation on the achievable resolution and precision.

How important each of these mentioned constraints are, is very difficult to say, as there are apparently many factors interacting with each other. Still, in a wide perspective, it is hardly surprising that a finishing processing operation, such as milling or EDM, is, almost always a necessity, (dependent of the use of the object). In the CMB process, the milling has been integrated as a part of the SFF process, so that each applied layer is milled to accurate measures (hence the name “Controlled” in “Controlled Metal Build-up”).

From liquid phase, the droplet will solidify into solid metal, which in most SFF processes is pore free, or nearly pore free. The melted droplets are usually very small in comparison to the solid base, and the solidification is very rapid. This means that the solid metal will form a very fine grain structure, which usually is very positive for the strength and toughness of the material. Since solidification in most metals means shrinkage, there will be residual tension in each newly applied layer. This does however not necessarily mean a continuous build-up of tension in the whole object. Each layer is applied on top of the previous and thereby the heat of each new layer will affect the all the previous layers, which are thus stress relieving annealed. Still, since complex geometries are a most common use for SFF technology, each layer does not have identical shapes and therefore all the stress is not always relieved.

The SFF processes based on addition of material in liquid shape seem like a very promising family, but with a load of constraints that limits the practical applications. There will always be a trade-off between build speed, precision and post processing, such as milling. Currently, this approach is most advantageous for certain niche applications, such as the manufacturing of near net shape objects in titanium for the aviation industry, where the alternative is milling these thin-wall structures from large solid block of metal. Other applications are the reparation of dies or moulds, or the modification of old ones, for the making of new products. These technologies are not competitive in the making of large solid pieces of metal, but for
minor material additions they have a significant competitive edge. It is hard to see how this would change in the immediate future, however with improved multi-material capacity, and the opportunity for surface coating, the suitable niche applications of these technologies are likely to increase and become more and more competitive.

**ADDING FROM SOLID PHASE**

(Based on conclusion from [2], [3], [4], [10] and [11])

In this survey, the different metallic applications of SFF technology are being viewed by the metals’ physical shape at the moment of addition to the geometric shape. Gaseous and liquid metals can be transformed from their original state to solid material by a change of temperature or pressure, but the additive building using solid material units requires some sort of joining operation, and may therefore not seem like an obvious first hand choice for SFF purposes. However, in the shape of powder, solid metals can be integrated, and used as building material within established polymer based SFF processes. In this type of approach, polymer materials are used as a binder of the metal powder and the metallic consolidation is accomplished by subsequent furnace processing. Therefore, only minor modifications have been necessary to develop metallic applications of original polymer based SFF processes, which is a principal reason why addition from solid phase has been applied for several process approaches of which a few has reached commercialisation.

However, many of the metallic modifications of polymer-based processes are seriously constrained by the nature of material transportation and addition in each original process. If the original process builds from filaments, sheets or liquids, the powder particles must be combined with enough polymer to resemble that original form of material: filaments for FDM based, sheets for LOM based, and at least a paste-like compound for SLA based processes. This means that there has to be a large fraction of polymer in the material for all mentioned process approaches. To transfer the polymer dispersed metal powder particles to a solid metal object, does require the removal of this polymer, which will cause substantial shrinkage with the risk of loosing precision and geometry in the process. In this perspective, it seems only natural that the most successful applications of established polymer based SFF technology has been of those processes that originally builds from powder material, DTM’s SLS and MIT’s 3D Printing, (licensed for the development of the metallic application to ProMetal). In the metallic application of both these processes are the geometries formed by the selective joining of particles in each powder layer, as well as with the previous layer using a polymer binder. Unlike processes based on FDM, SLA or LOM, there is no need to alter the materials powder shape, only for a small amount of binder to join the particles at points of contact. Alike their parent processes none of the metallic modifications has the capacity to build with graded materials.

The principal difference in the capacity of the two above mentioned commercialised process approaches is in the different ways to distribute and activate the polymer binder. Both process cycle starts by the spreading of a powder layer over the building space. In the 3D printing based process, the binder is “printed” on the surface of the applied layer, and penetrates the powder by capillary action, forming what in powder metallurgy is known as a green body upon curing. Since the binder is distributed in liquid phase, and the curing is a spontaneous reaction, the 3D printing approach has the capacity to be a very rapid process, just like the original prototyping process.
Further, dependent on the type of binder, the joining does not have to involve contraction of the binder during curing, thus it is possible to avoid curling of the layers during the building of green bodies, which could be an advantage for the building of very complex, or large objects.

Fig. 3. Parts by ProMetal, a metallic application of 3D printing. Particles are joined by the “printing” of a liquid binder on the powder bed, thus enabling a rapid building process but limiting the precision and resolution of this approach.

There are however also serious constraints with this approach. Just like in the original prototyping process, the resolution and precision is determined by the penetration and infiltration of the liquid binder in the powder mass. This is in turn dependent of the binder’s viscosity, wetting properties and the arrangement of the individual particles. It is thus hardly possible to control how much powder and which of the adjoining particles will be joined together by every individual drop of binder. This is a limiting factor for the precision and resolution for all 3D printing based processes.

In the metallic application of SLS, powder is coated with a layer of binder material, which is melted by the scanning laser, and that upon solidifying glues the particles together to a green body. Since binder is activated by the temperature variation by the scanning laser, the potential speed of this process approach is determined by: the scanning software, the laser power and heat the transfer in the powder. If any conclusion of the capacity of metallic approaches can be drawn from the original polymer based processes, SLS is a slower approach than 3D printing. Since the particles are coated, the binder distribution is secured in the powder layer. However when the binder melts and joins particles together the material in these joints will contract with the risk of curling thin layers.
The precision and resolution is determined by the amount of powder joined by the melted binder. However, the speed and power of a laser beam is easier to control than the penetration of liquid in a particle mass, and in a uniform powder mass it is to a large extent predictable, thus alike the polymer based process, the green bodies formed by SLS approach has a higher potential for precision and resolution, compared to those formed by the 3D printing approach. (See Fig. 4.)

Fig. 4. Part made by SLS. This approach is more limited in terms of building speed, compared to 3D printing based approaches, but is less constrained in regards to precision and resolution. With the development of Laserform ST-100, the 20μm powder has made it possible to sinter and infiltrate the parts in a single furnace cycle, thus saving much process time. It is uncertain whether this is possible for a 3D printing based process.

Apart from the proposed examples of process differences, there are several traits that are in common for this type of process approach. Both mentioned processes form their green bodies from layers in an applied powder mass. The unbounded powder serves as a support material during building, offering great freedom in building geometry, including conformal cooling channels for tooling purposes. However, the green bodies have to be broken out of the powder mass and unbound powder removed. This work has to be done manually. Since the green bodies usually are weak and brittle, this work, as well as the preparation of the green bodies for furnace processing, is dependent on the skill of the operator to turn out good results. Even if some damages to the green body can be mended, this part of the process of making metallic objects is critical, and it must be considered a weakness for any automated manufacturing process to be so dependent on the operator’s skill and craftsmanship for every single piece made.

The furnace procedure of these process approaches consists of three parts, binder burnout, sintering and infiltration, and could, dependent on powder and infiltrant material be carried out in one or two furnace cycles. The binder burnout usually requires the green bodies to be packed in a supporting material to maintain the geometric shape of the parts. This packing must provide an even support for the whole part to avoid distortions. During sintering the part will undergo some shrinkage and dependent on the part geometry there is a risk of cracking of thin sections surrounding holes or hollow areas filled with support powder. Infiltration is used to fill the voids in the sintered steel framework with a metal with lower melting temperature, thereby forming a massive metal object. For infiltration in the commercial systems, both approaches use a copper alloy in combination with their respective steel powder, which is a material combination with well-known infiltration properties, however also with a swelling effect of the original part. Compensation factors for these size fluctuations and other variations during processing, must be determined experimentally for the individual process equipment, but are reproducible for most part geometries. Since the furnace cycle includes heating and the cooling time of the furnace, and the crucible loaded with parts and supportive powder, a complete furnace cycle can take around 24 hours.
For most tooling applications, surface structure and quality is of critical importance. The use of infiltration does not only limit the choice of material to certain combinations, thus limiting the possible material properties, it also gives a composite material with inhomogeneous properties, which cannot be etched for polishing or specific surface feature purposes. Therefore, infiltration is a limiting factor for this process approach. The surface quality achievable for this type of sintered and infiltrated tooling is determined by the size of metal powder particles used in the building process, and the imprints from the support powder. This often requires further processing such as grinding or polishing on critical surfaces especially for injection moulding or pressure die-casting.

Despite the inherent constraints, DTM’s SLS based tooling approach is among the most successful and widely used SFF based tooling systems today. It has been successfully used for more than 100 000 cycles of injection moulding plastic parts, and more than 100 parts of pressure die-cast aluminium. Thus it is satisfactory for prototype tools and small series manufacturing. With the current system of sintering a framework of steel powder and infiltration with copper alloy it is however unlikely that much further progress beyond this is possible. Apart from the use of sintering-infiltration material system, has the SFF metal process approach, by the additive joining of solid phase particles, followed by a separate furnace consolidation, a relatively uncoupled relationship between SFF processing and material. If the need for infiltration could be avoided, much progress towards a wider selection of more durable materials with production grade tooling, and a wide array of other applications for SFF technology with metallic materials would be possible.

**SOME HYBRID APPROACHES**

(Based on conclusions from [2], [3], [4], [12], [13], [14] and [15])

Apart from the adding in gaseous, liquid or solid phase there are some hybrid approaches to metallic applications of SFF technology. This overview will describe three of those: one major competitor on the international market, and two in different stages between research and commercialisation.

**Direct Laser Metal Sintering, DMLS**, by EOS GmbH, has become one of the most important processes in the SFF world, outside North America. The reason why EOS has not entered the North American market, which is the largest and most important in the world for this type of technology, is the close similarities between DMLS and SLS, which would make an introduction a complicated legal issue of possible patent violations. In the perspective of SFF processing, DMLS and SLS are indeed very similar; both build their parts from powder material, spread out in layers and joined by the heat of a scanning laser. But while DTM’s metal approach uses a binder to join the particles into green bodies, DMLS melts a fraction of the metal powder, joining the particles by liquid phase sintering into metal objects of close to full density. Thus this is a hybrid approach that adds material in both liquid and solid state.

EOS method relies on both a much more powerful laser, (280 W compared to DTM’s 100 W) and a specific blend of metal powders consisting of base material and a lower melting material combination that expands upon solidification thus reducing stress in each new applied layer. EOS markets two different materials, DirectMetal, which is bronze based, and DirectSteel, which is an iron based compound, where DirectMetal is faster to build and DirectSteel is stronger and more stable at higher temperatures. Both materials are available in 20 and 50 μm powder, where the smaller particle powders have a superior resolution and surface finish, but the larger particle powders are more than twice as fast to build [2].
Injection moulded tools made with 20 μm powder has been reported satisfactory for production without further polishing.

The combination of a powerful laser with powder of different materials with different melting temperatures does indeed provide the possibility for consolidation into a solid metallic material. However, the relatively short dwelling time at an elevated temperature provided by the scanning laser is not enough for homogenisation. The finished part material will thus become a highly segregated metallic compound with inhomogeneous properties. This constraint is built in the basic principle for the DMLS process and would therefore be most difficult to completely overcome.

Since the different powder materials are just blended there is no guarantee that they are evenly distributed throughout every applied powder layer. Perhaps this could partially explain the "cracks" that sometimes appears parallel to the layer direction in DMLS parts. During liquid phase sintering, the wetted surfaces are joined and moves toward each other by enhanced diffusion through the liquid phase. If the lower melting material is not evenly distributed in the powder layer, there may be points with insufficient wetting. As the wetted, liquid phase sintering material contracts it will pull away material from dry areas and porosity is formed. This could possibly provide some explanation to why parts built with above 95% density still appears to have open porosity while in conventional powder metallurgy porosity closes at 90-95% density [15].

It is widely considered that the fewer the process steps and the less the manual work, the faster the process will be. This would make DMLS, being an almost fully automatic, single-step process the fastest SFF metal process on the market. In fact it is, however within a strictly limited area. DMLS does indeed build solid metal objects directly in the machine, however the objects are not entirely completed when removed from the EOSINT M equipment.

Fig. 5. DMLS part, a base plate is necessary to anchor the part and resist the effects of thermal tensions during the building process. Shot peening is used as an integrated part of the process to improve surfaces and close porosity.

Firstly, the surface is characterised by the powder used, to close porosity and smooth surfaces, shot peening is used as an integrated part of the process. This is included in the compensation factors and has no negative impact on part precision, apart from the risk of deforming very thin parts and sharp corners. Secondly, DMLS builds from a 20 mm steel base plate. This has either to be removed by conventional machining or, which is common for tooling applications, be machined to be a part of the tool itself. (See Fig. 5.)

Even if both the shot peening and the machining of the base plate are additional process steps and therefore extra time consuming, they are of minor importance as speed limiting factors, compared to the actual building process. Since DMLS requires the melting of a part of the powder compound, there is much energy that has to be transferred to the metal powder by the laser, and with respect to the powders energy absorption of the laser wave length, this takes time. Compared to DTM’s approach, where the laser melts only a small amount of polymer binder, the actual building process is much slower in DMLS. True, the SLS metal materials does require about 24 hours of furnace processing, but for any part that would take more than
40 hours in DMLS, DTM’s SLS approach would most likely be a faster alternative. To some extent this limitation has been integrated in DMLS philosophy, and sintering is only recommended where it is most advantageous, i.e. the most complex shapes. That also explains why the base plate is often integrated as a part of moulds and tools.

Still, the direct formation of metallic bonds in the SFF equipment makes the DMLS parts much stronger during the breaking out and rinsing from unsintered powder. This is a significant advantage compared to SLS, since thinner sections and smaller, more complex conformal cooling channels are possible and the outcome of the process is much less dependent on the skill of the operator. On the other hand, DMLS build files may include both inner and outer support structure and variation of scanning parameters to save build time, thus requires significant skill from the operator working at the computer.

In today’s European market, EOS’ DMLS and DTM’s SLS are the principal competitors for metallic SFF applications. Both have been successfully applied for prototype tools and small series manufacturing of injection moulded, as well as pressure die cast parts. DMLS appears to have the advantage for smaller parts and finer features, but is hardly competitive for parts taking more than 40 hours to complete. How large those parts are, is currently determined by the choice of powder material. However the surface quality and resolution of EOS 50 µm powder might not measure up to the 20 µm powder of DTM’s LaserForm ST-100 material. The applications of both processes are constrained by their materials. While DTM’s process cannot complete a part in shorter time than the furnace process, DMLS building speed is constrained by the absorption of laser energy. Which of these, if any, will emerge the winner of the future market will be determined by the further development of materials and processes.

**Direct Metal Fabrication, DMF**, was originally developed by Rockwell Science Centre to be used on a DTM Sinterstation. The SFF processing is thus identical to SLS, and the principal difference lays in the consolidation of green bodies to solid metal objects. DMF powder is a three component blend consisting of a parent alloy which is the target structural material, a lower melting temperature version of the parent alloy, and a polymer binder which chars on burnout leaving a thin carbon coating that serves as a sintering aid and reduces the melting temperature of the metal particles. The green bodies are built by common SLS procedure, rinsed from unsintered powder, and loaded in the furnace. The furnace procedure consists of two parts, debinding at lower temperature, and sintering, where the temperature is raised to melt the lower melting temperature alloy. Liquid phase sintering consolidates the parts.

Rockwell claims to have reached final densities of 95 – 99 %, with strengths equivalent to as-cast material. Furthermore, the technique has been successfully applied to mild steel, stainless steel, tool steel, nickel based super alloys and copper alloys. Consolidation of metal parts by liquid phase sintering may be one of the few possibilities to reach full density objects of homogenous metal alloys from a powder based SFF approach. In the spring of 2000, DTM and Rockwell announced the cooperation for the development of materials according to DMF principles, but today, two years later, no results from that cooperation has reached the market yet. It is possible that DMF experiences some difficulties to maintain geometry and precision during the large shrinkage, or that the process is dependent on supporting powder during the furnace cycle, which constrains the freedom of building geometry. Anyhow, DMF or not, liquid phase sintering in a secondary furnace process could become a part of a future process approach for a variety of metallic materials.
Another possible way to consolidate metallic parts to full density, while avoiding infiltration, as well as liquid phase sintering, is to combine SLS with Hot Isostatic Pressing, HIP. This approach has been the subject for some research at the University of Texas, but has not yet reached commercialisation. The basic principle of this process is to build parts utilising SLS to form a gas impermeable skin at the parts’ surfaces, the powder in the interior of the part is left unsintered. The encapsulated part is post processed by containerless HIP to full density. Machining can be applied if necessary. SLS/HIP has been developed to take advantage of the freedom of geometry in SLS in combination with in-situ HIP encapsulation. This includes the ability to perform containerless HIP without adverse container-powder interactions, reduced pre-processing time, and fewer post-processing steps compared to conventional HIP of canned parts.

This approach bypasses the need for a base plate, lower melting temperature material and infiltration, to build full density, homogenous metal objects with great freedom of geometry. The combination of SLS and HIP requires several process steps: SLS, HIP and finishing operations, it is unlikely to find a wide spread use except for some niche applications, where the demand for material and geometry are high, and as a complimentary alternative to conventional HIP of canned parts [23].

TOOLING FROM SFF PATTERNS

(Based on [2], [3], [16], [17] and [18])

In connection to the SFF family there is a group of tooling approaches that uses SFF models as patterns or masters to make tools or metal objects. Thereby hardly fulfilling the criteria for an SFF process, (automatic additive shaping of solid three dimensional objects) this group is in reality not a SFF technology, and the shaping process should rather be considered net shaping. Still, the parts are based on SFF patterns and are for some applications competitive alternatives to true SFF tooling, as well as conventional milled tooling, which is why they will briefly be covered in this overview. Since it is mainly concerned with metallic applications of SFF technology, aiming at the manufacturing of tools, this overview will sample two different approaches to SFF pattern based tooling: powder metal and spray metal tooling.

The pattern based powder metal approach to SFF tooling has applied in several different processes, 3D Keltool, from 3D Systems, EcoTool, developed by Danish Technological Institute and TNO Institute of Industrial Technology, and Wiba Tool, developed by Wiba and IVF Industrial Research and Development Corp., to mention a few. All approaches starts with a pattern, usually made by polymer based SFF. Where EcoTool’s pattern is a parting line block over which the powder binder slurry is poured, 3D Keltool and WibaTool makes a master of the desired part and cast a silicon mould against that master. 3D Keltool being the oldest and most developed of these examples, will illustrate the basic principles of the powder application of a pattern based approach to metallic tooling applications of SFF technology.

The master patterns are finished to desired surface and cast in silicon rubber to create a set of moulds. A mixture of specially composed metal powder, a combination of tool steel and tungsten carbide particles, and binder is poured, packed and cured into green bodies in the moulds. Green bodies are removed from the silicon rubber moulds, processed in a hydrogen furnace atmosphere, where the binder is decomposed, and the part is sintered and infiltrated to form a solid metal composite material. Because of the net shaping of green bodies and, in the case of 3D Keltool, the fine particles in the metal powder composition, this type of approach can offer excellent surface quality and fine features, where fingerprints can be duplicated. However, removing the brittle green bodies from the silicon moulds can be quite precarious,
with the risk of breaking chips and thin structures. Furthermore, the final result is dependent on the outcome of every single process step, and since several steps are in the form of physical duplications of a pattern formed by the previous step, whatever shortcomings and limitations that occur in each step will be added to the final result and can hardly be compensated for. In the case of EcoTool, where SFF manufactured parting line blocks are used as patterns, is one step and one pattern interpretation shorter, but the systematic limitation remains the same, and the separation of green body and pattern is still a jeopardy.

The 3D Keltool Process

![Diagram of the 3D Keltool Process]

Fig. 6. The 3D Keltool process, but the principle also applies to other pattern-based SFF tooling processes. This approach exhibits a high capacity for the reproduction of the patterns’ surface and minute details are possible. However, the removal of the pattern as well as the transfer mould limits the freedom of geometry and the multiple interpretations of the patterns make any dimensional inaccuracies additive.

Since the tools according to this principle are net shaped from patterns, and the sintering of metal powder implies some shrinkage, conformal cooling channels are highly unlikely to ever successfully be built into the tools in this type of process. The pattern-based shaping only allows complexity on the outer surface of the geometry, and while the sintering green bodies shrink, any additional built-in piping could hardly shrink, and would therefore cause distortions in the tools during the sintering.

Another net shaping approach to SFF-based tooling is to build the tool by spraying metal over a pattern, which has been applied in, for example, the RSP Tooling (Rapid Solidification Process) and Ford's Sprayform tooling approach. In their current form both processes spray deposit molten metal over a ceramic pattern, which usually has been shaped from a SFF master. However, goals have been set to eliminate the interpretation to of the master to ceramic, and make it possible to use the SFF pattern directly, either as a polymer, or by building ceramic SFF parts. Apart from the thermal impact on the patterns, this approach has a comparable uncoupled relationship to building materials and nearly any tooling alloy can be used. Metal spraying has a high deposition rate, and with only the separation of the tool from the pattern, milling to the appropriate outer shape in addition to the cooling time, the overall turnaround time from design to production tooling can be as short as a few days. The rapid making of the tools in combination with the freedom of material gives this approach special advantage for large dies, for example for sheet metal stamping, provided that satisfactory masters are available.
Alike the powder based approach, spray metal tooling has excellent capacity for minute
details down to reproducing fingerprints. However, in difference to the moulding of powder,
sprayed metal building can easily integrate conformal cooling channels in a tool. The building
process is interrupted, cooling tubes are inserted, and metal is sprayed over the channels to
desired thickness.

Pattern based tooling using powder is competitive for injection moulding and small series
metal castings on today’s market. However, constrained by the pattern transferring to the
green body and with development potential hampered by the material, this approach appear
unlikely to remain so, in a prolonged perspective. Spray metal tooling is still developing, and
is now on the brink of commercialisation. It seems promising for certain future applications,
especially larger tools, but being dependent on several subsequent process steps, the final
result cannot possible become more accurate than the combined outcome from every single
one of them. For both powder using, and spray metal approaches, critical surfaces often have
to be finished by machining. With the freedom of geometry limited to the patterns’ surface,
these approaches do not appear to have the same development potential as the true SFF metal
applications.

CONCLUSIONS
A fundamental question in all technical research should be, “What is the potential impact?”
This implies that research efforts should be aimed for the highest possible impact, and by
doing so limit the scope to where this effect could be achieved. It has previously been
concluded that metallic applications of SFF technology is an area of enormous potential, in a
near perspective especially for the manufacturing of tools, but on a longer term also for a
multitude of other possible applications. Furthermore, in respect to the current situation in the
developing SFF world, it appears that while several systems for the manufacturing of tools for
prototype and short run purposes exists, the technology applications are still hampered by
constraints in materials and processes. To have full benefit of SFF technology for
manufacturing in metallic materials, the gap must be bridged between the material properties
offered by existing processes, and the needs these are expected to fulfil. Otherwise, new
processes, which are less coupled to materials used, must be developed. With both of these
issues the question is not really if they will be fulfilled but when, how, and by whom. The
answer may very well determine the future of the entire manufacturing industry.

It is a principal challenge facing the industry as well as academia, to overcome these
limitations. The highest potential impact of research in metallic applications of SFF
technology apparently is where the results from research not only could enhance SFF based
tooling, but also open opportunities for many other new applications for a critical number of
potential users and thereby expanding the demand for further development. This implies that
the highest impact in a near perspective will be achieved by improving the capacity of a SFF
technology that is well established on the market. However, for long-term development and in
respect of the inherent limiting factors, this development potential will eventually be
constrained in the contemporary SFF metal applications. The full potential of the additive
manufacturing approach to metallic, ceramic materials, pure and combined, will most likely
not be reached within the current available systems. To reach that ultimate goal, new
processes, which have a more uncoupled relationship to materials used, must be developed.
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Paper B
A Vacuum Furnace Process for DTM’s RapidSteel 2.0 Material

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Abstract

The work described in this paper investigates the possibility to use a vacuum furnace in DTM’s RapidTool LR process. This alternative process route is brought about to allow the usage of a more common type of furnace than the one recommended by DTM.

Based on the specified, well-established H₂/N₂ furnace processing, a similar procedure, adapted to conventional cold wall vacuum furnaces has been developed and tested. The testing is described in detail, and the results so far are promising enough to justify the practical usage of this process, and more of in-depth analysis of all the various aspects of the procedure.

Introduction

The field of Rapid Prototyping (RP), or Solid Free Form Fabrication (SFF), has gone through quite a rapid development on its own during the last decade. From crude concept models made of brittle polymer material to more and more production like objects from a variety of materials including ceramics and metals. A major challenge has been to extend the application of RP-technology into the field of RT, -Rapid Tooling, thus a wide array of RT processes has been developed, all with their own limits and benefits. Among the most widely used of those is the Rapid Tool LR process from DTM Corp. Austin, TX.

The Rapid Tool LR process is an indirect SLS based process, where a powder material, RapidSteel 2.0, is processed in the Sinterstation system, followed by two subsequent furnace cycles. During the SLS stage a scanning laser melts the polymeric binder in each powder layer, thus gluing the metal powder together forming a fragile, but solid mass called the “green” part. The green part is placed in a crucible and sintered, at 1120°C in a 30/70 H₂/N₂ furnace atmosphere, forming a rigid but porous object called the “brown” part. A second furnace cycle at 1050°C in the same atmosphere infiltrates the part with bronze giving a final, ideally, fully dense part.

The specified furnace atmosphere with 30% H₂ requires a specialized furnace that in many cases has little other use. Vacuum furnaces, on the other hand, are often used in various heat treatments and brazing operations, and could in many cases, be available to use as an alternative. This paper describes the adaptation of the Rapid Tool LR process for processing in vacuum furnaces.
Our Approach

Vacuum furnaces are used in conventional powder metallurgy to "maintain a clean reproducible, and controlled non-reactive atmosphere" [4], especially for "corrosion resistant materials (stainless steels), vacuum is the most reliable atmosphere" [4]. The RapidSteel 2.0 powder metal is stainless steel, and our hypothesis was that it would process well in a vacuum furnace.

Most sintering practices in the powder metallurgy industry are set by trial and error techniques, but since there is a designated process at hand in this case, it is reasonable that a similar process could be deduced from the effect given by the H₂/N₂ atmosphere during the process and comparing that to the likely effect of vacuum.

Atmosphere: According to [1], the "hydrogen reduces any oxides in the surface of the iron powder and aids in infiltrating the bronze into the part". The nitrogen is simply inert, (and to a small extent dissolves into the metal, thus adding a hardening effect). Apart from chemical activity, the atmosphere gas is also an important medium for heat distribution by means of convection. That is obviously not the case with vacuum, and this difference should be accounted for in the settlement of times for the different process steps.

Temperatures: DTM has settled suitable temperatures for sintering (1120°C) and infiltration (1050°C). Ramp rates are mainly set by the equipment’s (crucible and alumina plate) sensitivity to thermal shock, and a maximum ramp is given to 180°C/h. These values are determined by material properties and there are no reasons to make any changes at this stage.

Chemical activity: In DTM’s standard furnace atmosphere, hydrogen reduces metal oxides, and the better reduction, the better sintering and infiltration. A similar effect can be obtained in a vacuum furnace too; by lowering the partial pressure of oxygen in the equilibrium: MeO $\leftrightarrow$ Me + O.

Thus, the higher vacuum, the better reduction, and the better sintering and infiltration. But high vacuum at high temperatures would not only evaporate the binder, but also risks to evaporate some alloying elements in the metal powder. In relation to that, it can
be justified to assume that the organic binder would evaporate at a far lower temperature and pressure than the alloy components. In the H2/N2 atmosphere, burnout temperatures are between 450-650°C. Therefore, for the most likely success; find the highest vacuum that, with reasonable security, does not evaporate the alloying elements.

The activity of any chemical reaction that takes place in the crucible is dependent of temperature and chemical composition. Since the proportions of the alloying elements are given within rather wide ranges, all calculations will be coarse and all resulting values must include large safety margins. The alloying component with the highest gas pressure at process temperatures gives the lowest possible gas pressure in the vacuum furnace, i.e. the highest vacuum acceptable.

Calculation

The Rapidsteel 2.0 powder is an iron based steel powder. According to [2] the alloying elements are:

**Chromium:** 12 - 30%

**Molybdenum:** 0 - 7%

**Nickel:** 0 - 35%

**Manganese:** 1 - 4%

Given that

\[ p: \text{gas pressure; atm} \]
\[ \Delta H_{\text{m}}: \text{enthalpy for the phase transformation (s) \rightarrow (g); cal} \]
\[ T: \text{temperature; K} \]
\[ R: \text{constant} = 1.987 \text{ cal deg}^{-1}\text{mol}^{-1} \]

\[ \frac{dlnP}{dT} = \frac{\Delta H_{\text{m}}}{RT^2} \Rightarrow dlnP = \Delta H_{\text{m}}/R \cdot dT/T^2 \Rightarrow \int dlnP = \Delta H_{\text{m}}/R \cdot \int T^2 \cdot dT \Rightarrow \]
\[ lnP_1 - lnP_2 = -\Delta H_{\text{m}}/R \cdot (T_1 - T_2), \]

where index (1) is referring to the triple point equilibrium, and index (2) is referring to the process conditions.

For an ideal gas solution, partial pressure of a component = \( p_2 \cdot \text{ (fraction of element)} = p_p \)

For Cr, in the sintering stage, (fractions according to worst case scenario):

\[ p_1 = 1 \text{ atm} \Rightarrow ln p_1 = 0 \]
\[ \Delta H_{\text{m}} = 81.7 \text{ kcal/mol} \]
\[ T_1 = 2893 \text{ K} \]
\[ T_2 = 1393 \text{ K} \]

\[ -lnp_2 = -81.7 \cdot 10^3/1.987 \cdot (2893^{-1} - 1393^{-1}) = -15.3 \Rightarrow p_2 = 2.26 \cdot 10^{-7} \text{ atm} \]

fraction of Cr: \( X_{\text{Cr}} = 0.32 \) \Rightarrow \( p_{\text{Cr}} = 2.26 \cdot 10^{-7} \cdot 0.32 = 7.3 \cdot 10^{-8} \text{ atm} \)

In a similar manner (fractions picked according to worst case scenario):

\[ p_{p\text{Mn}} = 3.98 \cdot 10^{-4} \cdot 0.019 = 7.57 \cdot 10^{-6} \text{ atm} \]
\[ p_{p\text{Mo}} = 1.37 \cdot 10^{-4} \cdot 0.0234 = 3.2 \cdot 10^{-6} \text{ atm} \]
\[ p_{p\text{Ni}} = 1.8 \cdot 10^{-8} \cdot 0.1632 = 2.89 \cdot 10^{-9} \text{ atm} \]

With a calculated partial gas pressure of \( 7.57 \cdot 10^{-6} \text{ atm} \), manganese is the critical component.

A reasonable safety margin gives \( \Rightarrow \) set point value \( 49.3 \cdot 10^{-9} \text{ atm} \), or in a common scale among vacuum furnaces: \( 50 \cdot 10^{-3} \text{ mbar} \).
Experimental

The experimental furnace cycles were run in a conventional cold wall vacuum furnace at Järdfälla Härdverksstads AB, Järdfälla, Sweden. Green bodies were manufactured following recommendations according to DTM’s “Guide to Materials: The Rapid Tool LR Process Using RapidSteel 2.0”[1] and “RapidSteel 2.0 Mold Inserts for Plastic Injection Molding”[3]. Crucible setup was likewise according to recommendations from the same sources, but with one small exception: for increased safety during transportation, the fine grain alumina powder (240 grit) was used for both the infiltration and sintering cycles.

Sample 1. Sintering: The standard setup, ramp rate (180°C/h) and sintering temperature (1120°C) according to [1] was used. Since no other mechanism of heat transfer than radiation is active in vacuum, the dwell time at sintering temperature was prolonged from 3 hrs [1] to 3.5 hrs. For practical reason the furnace allowed to cool down in its own pace from 500°C. Furnace temperature and pressure was monitored during the whole cycle.

The sintering result was quite satisfactory regarding strength, shape accuracy and sharpness of edges. However due to the fact that the equipment (crucible, bricks etc.) had not previously been subjected to a vacuum furnace cycle, some unaccounted gas was released during the furnace cycle, and it was not possible to draw any conclusions from the furnace atmosphere pressure.

Sample 1. Infiltration: The standard setup for solid bar bronze was used. The temperature (1050°C) and ramp rate (180°C/h) was set according to [1]. For reasons mentioned earlier the dwell time at 1050°C was prolonged from 2 hrs [1] to 2.5 hrs.

The infiltration could be termed "half successful", meaning that only half the bronze was infiltrated. Two infiltration plates had at some time lost contact with the sample and no infiltration was possible from those plates.

Sample 1. Conclusion: The sintering cycle seemed good enough, so no further modifications were necessary at this stage. Instead securing the contact between the sample and the plates was the primary aim for the next sample.

Sample 2. Sintering: The setup, ramp rate, sintering temperature and dwell time was identical to sample 1. To secure the best possible contact between infiltration plates and sample, they were sintered in direct contact with each other. Identical, still quite satisfactory results as for the previous sample 1. The plates had bonded to the sample thus forming one large object with the plates stuck like wings to the sides.

Sample 2. Infiltration: Standard setup, and the same procedure as previous sample. All infiltrant bars were infiltrated, but still the result could only be termed a partial success. Each bar left a "foam" of nickel rich residue on the plates.

The sample was measured and scaling factors were calculated in the standard data sheet provided with the RapidSteel powder from DTM. See table 1.

Sample 2. Conclusion: Connection between plates and sample secured infiltration, however since the brown specimen could not be weighed separately infiltration success could not be calculated. Still the nickel rich foam suggests that a modification of the infiltration
procedure would be necessary to achieve a completely successful infiltration. It is also possible that the prolonged sintering time in combination with the extremely low gas pressure in the furnace has allowed the sample to sinter, and shrink a little bit more than expected.

Sample 3. Sintering: The sintering of sample 3 followed the same standard set up as previous samples and the result is also as good as previous samples. From the Time/Temperature/Vacuum-diagram (Fig.2) we find that the Time/Temperature relationship follows the expected program with almost perfect precision. The vacuum likewise behaves as might be expected: after it had reached the set point, it stayed fairly constant with a sharp dip during the binder’s evaporation (burnout).

**Sintering Sample 3.**

**Fig.2. Sintering of sample 3. Temperatures in Celsius. "serie1" gives the temperature set point, "serie2" gives the actual temperature and although no scale values are given in the figure "serie3" indicates the vacuum. Notice the dip in the vacuum between 443 °C and 586 °C. Apparently, that is the interval where the binder evaporates under these circumstances. The fact that there no other dip is indicated verifies that no alloying elements are being evaporated.**

Sample 3. Infiltration: To avoid the same problems as were experienced with the previous samples, some modifications of the procedure was necessary. The joints between the infiltration plates and the sample were powdered with some loose powder. If any vibration would separate the plates from the sample, the void would still be filled with RapidSteel powder thus ensuring free flow of the infiltrant. Since this powder was not weighed together with the plates and sample when the mass of infiltrant was calculated, and in order to assure that there would be enough bronze, 50g extra bronze was added to the calculated amount. To ensure that the nickel rich phases would melt and infiltrate with the rest of the infiltrant, a recommendation from [3] was followed and the temperature was ramped up at a rate of 120°C/h. The furnace was kept at infiltration temperature (1050°C) for 3hrs and lowered, as the previous samples, at a rate of 180°C/h.
This time infiltration was quite satisfactory apart from the fact that the color of the sample was not completely even, and that there still was small amounts of infiltrant remaining on the plates. Still, according to the calculation of the infiltration in [1] and [3], the amount of bronze infiltrated should equal 85% of the mass of the brown part. Since the mass of this brown part was 1360g, ⇒ 1360 \times 85\% = 1156g, and, 1360 + 1156 = 2516g. Hence 2516g is the theoretical mass of the full density object. The actual mass of the infiltrated sample 3 is 2513g, that gives an infiltration success of 99.8%, which we consider satisfactory. Similar to the previous sample, the offset and scaling factors were calculated. See table 1. The Time/Temperature/Vacuum-diagram (Fig 3.) shows a stable behavior, where the temperature follows time according to program, and vacuum keeps around the set point.

Fig.3. Infiltration of sample 3. Temperatures in Celsius, ”serie1” gives the temperature set point, ”serie2” gives the actual temperature and ”serie3” gives the vacuum all identical to Fig.2. The decreased ramp rate has given a longer warm up time. The vacuum stays at the set point during the whole cycle, which verifies that there is no evaporation of any alloying components (or anything else).

Sample 3. Conclusion: The process used for sample 3 gives satisfactory results for DTM’s RapidSteel 2.0 material and could be useful to manufacture functional molds.
Table 1.

<table>
<thead>
<tr>
<th></th>
<th>X Offset</th>
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<th>Y Scale</th>
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</tr>
<tr>
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<td>0.0070</td>
<td>1.0130</td>
</tr>
<tr>
<td>H2/N2*</td>
<td>0.1825</td>
<td>1.0072</td>
<td>0.1603</td>
<td>1.0001</td>
</tr>
</tbody>
</table>

* Scaling and offset values for the conventional H2/N2 furnaces have been supplied by courtesy from DTM GmbH, Germany. All individual machines have different scale and offset values, especially between Sinterstation 2000 and 2500(+) there are big differences. In addition to that, comes the difference between individual furnaces. In this case however, all objects, Swedish and German, have been SLS processed on Sinterstation 2000s, and even with the individual differences accounted for, there still remains a significant difference in scaling factors. This must be referred to the difference in furnace processing. Apparently the shrinkage is larger with the used vacuum procedure. Among other things this means that the value of infiltration success in reality is higher than the calculated value of 99.8%.

Conclusion and Further Study

This investigation has showed that it is possible to process DTM’s RapidSteel 2.0 material to satisfactory objects in a vacuum furnace process. Little experience of this process has been accumulated so far, and more work is required to fine tune every aspect of a large number of variables. For example: it is likely that the prolonged dwell time at sintering temperature introduced in the sintering cycle for sample 1, in combination with low the gas pressure in the pores, (vacuum) could have led to higher shrinkage, higher sintering density and more closed pores which could not be infiltrated, which in turn led to the unevenness in color and the comparably large scaling factors in the infiltrated sample 3.

This effect could possible be turned into something very positive. By making use of the enhanced sintering of liquid phase sintering it could be possible to sinter full density objects in a single furnace cycle. During sintering the "liquid phase provides a high diffusivity pathway for atomic motion, and a strong capillary force that induces particle compression at point contacts" [4]. This phenomena continues until the connections between the pores are closed and the remaining pores are filled with furnace atmosphere, which is exerting a gas pressure and thus locking further pore closure. Since vacuum furnace atmosphere means virtually no atmosphere, nothing would fill the pores and nothing could lock the pore closure, thus it would be possible to reach full density.

Acknowledgments

We would like to thank Mr. Berndt Holmer, Mr. Gunnar Palm, and Ms Lena Thorsson, all from IVF, Stockholm, for their interest and good advice during the research and the work with this paper.
References
Paper C
SLS Application of the Fe-Cu-C System for Liquid Phase Sintering

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Abstract
The present work suggests the possibility to exploit the phenomena of copper swelling, and the controlling effect of carbon during liquid phase sintering, to be used in SLS technology to achieve temperable tooling materials in a single furnace cycle. As a basic investigation of this possibility, four powder samples of different copper and carbon content were tried and evaluated in respect to SLS and furnace behavior. The possibility to form green bodies was verified and the different sintering behaviors were studied. It was concluded that this material system holds several interesting phenomena that, if properly managed and if sufficient fractional packing density could be reached, could open distinct possibilities to achieve high quality material for SLS tooling purposes.

1. Introduction
Over the last decade, the field of Solid Free form Fabrication (SFF) has seen the development of several new tooling techniques. Among the more widely used are the SLS-based systems: the Sinterstation from DTM-Corp, Austin TX, and the EOSINT-M from EOS GmbH, Munich, FRG. Both systems have the capacity to build in iron-base metal, but where the Sinterstation is a multi-material system with an indirect approach to metals, the EOSINT-M is specialized on metals with a direct approach. The indirect approach means that the material has to go through further processing to achieve satisfactory properties, for example: DTM’s RapidSteel 2.0 material requires, apart from SLS processing, two subsequent furnace cycles for the sintering and infiltration to full density. This is time consuming, and the infiltration by a second component limits the achievable material properties. The direct approach of EOS means that the metal material is actually sintered by the laser, but by doing so, the material is subjected to pointwise heating and cooling, with the stress that follows. This approach limits the choice of suitable material systems, and thus also limits the achievable material properties. Both approaches give a surface equivalent to the fineness of the powder, and none of the commercially available material systems is hardenable.

This implies that there could be use for a material system with more production-tool-like properties. Due to the inherent stress, the direct SLS approach is less suitable for the processing of a hardenable material. In the indirect approach, on the other hand, such a material system is more feasible, but would require that a satisfactory density could be achieved without infiltration, preferably in a single furnace cycle.
2. Hypothesis and theoretical background

It is the hypothesis of this paper that there is a distinct possibility to exploit the characteristics of liquid phase sintering within the Fe-Cu-C system to achieve a material that allows the SLS based manufacturing of satisfactory tools, with the capacity for heat-treatment to further control material properties.

2.1 Liquid Phase Sintering

Liquid phase sintering is one of the most popular methods to enhance the sintering behavior of a powder material. During liquid phase sintering, a liquid phase coexists with a particulate solid at sintering temperature [1]. If the liquid’s wetting properties of the solid particulate are good and the material of the solid is soluble in the liquid phase, there will be an enhanced sintering over all wetted surfaces. This enhanced sintering implies growth along the wetted grain boundaries. Grains situated at a free surface will thus expand in all lateral directions, whereas the un-wetted free surface is depleted of material. This can lead to a smoothing effect on the material surface [2]. For the most part, in conventional powder metallurgy, liquid phase sintering exhibits sufficient internal force through liquid capillary action on the particulate solid that external forces are not required for the compaction during sintering [1].

2.2 The Fe-Cu-C system

Copper as an alloying substance has unique properties in the field of sintered steels. Copper in small amounts does not only improve strength and rust resistance, it also melts at a lower temperature, has a rapid surface diffusion over solid iron, and a liquid phase where iron easily diffuses [3]. This has made copper a popular choice as the liquid phase, in liquid phase sintering of iron base alloys. However, copper is rapidly dissolved into the steel particles (up to approximately 8.5%), forming a substitutional solid solution. Since copper atoms have a larger diameter compared to iron atoms, this causes a distortion in the crystal structure and thus resulting in a swelling effect, that is larger than the original copper volume [3][1].

Furthermore, the addition of carbon lowers the liquid temperature of the Cu-Fe melt, and delays the dissolution of copper into the steel thus allowing a prolonged time with liquid phase sintering. Fortunately, the suitable copper and carbon levels fall within the span of improved strength and toughness, as well as temperable properties [3] of the steel. These phenomena are well known in conventional powder metallurgy, and by the correct composition within this material system it has been possible to manufacture powder grades with zero dimensional change during sintering to full density.

2.3 SLS Aspects

Apart from having excellent sintering and densification properties during the furnace cycle, a practical powder blend for indirect SLS application is required to process well in the SLS equipment to yield satisfactory green bodies. This means that there must be an efficient binder system, and, in the interest of high precision and high density, it is desirable to use a powder blend with the highest possible fractional packing density.

The fractional packing density of a free flowing powder is primarily dependent on grain size distribution, the proportions, and the mixing of the powder. The density of SLS
manufactured objects would be especially dependent of the arrangement (i.e. the mixing) of particles with different sizes in each new layer. This has been investigated in [5], where a substantial increase was achieved for a two-component system using a Doctor’s blade [5] and in [8], where the counter-rotating roller, such as used in the Sinterstation system, was associated with frictional shear in the underlying layers, [8]. However the roller’s transport of the powder, in a wavlike motion, is very similar to the cascading motion that, in a horizontal rotary blender, generally is associated with optimum blending conditions [6]. Assuming that the powder mass is well mixed in the powder containers, it could probably be assumed that a well designed, multi-component powder blend would yield a substantially higher fractional packing density when applied into a SLS system.

The addition of binder could either be in the form of powder mixed with the metal powder, or as coated on the particulate [7]. Coating is associated with higher green strength but, since the binder is removed during the furnace cycle, is more sensitive to the thickness of the binder layer. For experimental use, it is however easier to add the binder in the shape of a powder.

3. Experimental

The experiments are intended to investigate a) how a Fe-Cu-C commercially available powder system would process under “normal” SLS conditions, and b) how the sintering behavior is influenced by the presence of copper and carbon in the powder blend.

3.1 The powders

For this purpose, two different powder grades from Höganäs AB were selected; Distaloy Acu, with 10% Cu added, and Distaloy DH-1 with 2% Cu added. To ensure even copper distribution, this family of powder grades, has the copper diffusion bonded to the surface of the steel grains. The materials in both these grades are temperable.

![Fig. 1. Powder grains; Distaloy Acu](image1)

![Fig. 2. Powder grains; Distaloy DH-1](image2)

The powders were sifted to a maximum grain size of 63 μm. Given the uncontrolled grain size distribution and the coarse structure of the individual grains (Fig. 1 & 2), these powder samples had very low apparent densities; Distaloy Acu: 3.97 g/cm³ ⇒ 49.9% of theoretical density and Distaloy DH-1: 3.66 g/cm³ ⇒ 46.4% of theoretical density. This will be inherited as a low fractional packing density in the green bodies, but will facilitate the
observation of changes in the powder structure during sintering. However it also means that we despite substantial shrinkage hardly can expect to achieve full density at this stage.

For the binder system, a 5% addition of Hexamethylene Tetramine Phenol was used. Being a phenol based binder it could be expected to function under similar conditions as the binder system in RapidSteel 2.0. As mentioned previously, for this experimental case, the addition of binder by the mixing of powder was found more practical. Two samples of each powder grade, ACu and DH-1, were mixed with binder, and as a source of carbon, 1% graphite powder was added to one sample of each grade, samples ACu+C and DH-1+C.

3.2 SLS processing

The four sample blends were SLS processed with identical build files under conditions similar to the standard settings for RapidSteel 2.0.

3.3 Furnace processing

The samples were sintered together in a graphite crucible, in a vacuum furnace, according to the following cycle: 20 – 600 °C, (the binder burnout stage), raise 150 °C/h. At 600°C, raise temperature in a single step to 1120 °C, (the sintering stage), and remain for two hours. Then let the furnace cool at its own pace.

4. Results and discussion

The selected powder fractions of both grades spread and leveled well as layers in the Sinterstation. The laser scanning was accompanied by some spectacular sparking and smoking, but green bodies were formed, however weak and with a very low fractional powder packing as was predicted, but still quite possible to handle. Powder packing in the green bodies as well as grain shapes can be seen in Fig. 3, 4, 5, & 6.
4.1 Shrinkage

After furnace processing the samples have sintered and show a substantial shrinkage, Fig. 7, 8 and 9, 10. Since the green bodies, and apparently also the sintered products have a considerable porosity, an absolute quantitative study of the shrinkage would not only be inconclusive, but also possibly misleading. A qualitative comparison, on the other hand, could give an indication of the influence of copper as well as carbon. Shrinkage factors can be seen in Table 1.

![Fig. 7. Green body and sintered sample: ACu.](image1)

![Fig.8. Green body and sintered sample: ACu+Cu.](image2)

![Fig.9. Green body and sintered sample: DH-1.](image3)

![Fig.10. Green body and sintered sample: DH-1+Cu.](image4)

Table 1.

<table>
<thead>
<tr>
<th>Shrinkage</th>
<th>ACu</th>
<th>ACu+Cu</th>
<th>DH-1</th>
<th>DH-1+Cu</th>
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<tr>
<td>X</td>
<td>6.70%</td>
<td>4.97%</td>
<td>3.99%</td>
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<tr>
<td>Y</td>
<td>6.41%</td>
<td>4.97%</td>
<td>3.84%</td>
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<tr>
<td>Z</td>
<td>3.22%</td>
<td>3.17%</td>
<td>1.59%</td>
<td>1.61%</td>
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</tbody>
</table>

Table 1. The shrinkage in different directions during sintering of green bodies of the chosen powder grades and blends.
In general we find that the copper rich ACu powders show a larger shrinkage in all directions, compared to the DH-1 powders. This may seem to contradict the thesis on copper swelling, however there are two points to consider: First, the calculated shrinkage factors do not take any account to the porosity, thus there is no information of possible swelling in the base material. Second, liquid phase sintering continues as long as there is a liquid phase present. In the DH-1 powder samples, all the copper (2%) is dissolved into the steel, whereas the copper content of the ACu powders (10%) is higher than copper's solubility at sintering temperatures (approx. 8.5%), thereby the liquid phase sintering, and the related shrinkage, of ACu powder samples continues until the temperature drops below the melting point of copper.

The shrinkage of the carbon-enriched samples is considerably smaller than the carbon free samples. This may also seem like a contradiction of the thesis of prolonged liquid phase sintering, but again, no conclusions can be drawn until porosity has been taken into account. Some differences in shrinkage between x-, y- and z –directions could possibly be accounted for by machine and process variables, it is however notable that the shrinkage in z-direction is almost half the shrinkage in x- or y-direction. This could indicate that the powder in each layer may have been closer packed in z-direction.

Apart from these points, the shrinkage seems almost surprisingly linear considering the low packing density in the green bodies. The magnitude of this shrinkage demonstrates the power of the densifying effect of liquid phase sintering in the Fe-Cu-C system.

4.2 Copper-swelling

The effect of the copper-swelling phenomenon can be estimated by the comparison between the macro magnifications of the ACu samples and DH-1 samples, Fig. 11, 12 and 13, 14. In the DH-1 samples, the shrinkage and rearrangement has been so severe that gigantic pores have formed in a crack like manner. In the ACu samples there are no such “super-pores”, apparently the copper-swelling effect has compensated for the most dramatic changes.

The effect of carbon presence can be illustrated by comparison between the different DH-1 samples Fig. 13 and Fig. 14. Sample DH-1+C has obviously experienced the longer period with liquid phase sintering, resulting in fewer, but larger pores, coarser sponge-like structure and smaller grain surface area compared to sample DH-1.
A similar comparison between the ACu samples reveals a more complex situation, **Fig. 11 and Fig. 12**. In this case the carbon added sample has the finer structure. This could however be explained by the fact that ACu powder carries an excess of copper and thus all copper cannot be dissolved into the steel, which, in turn, means that liquid phase sintering continues in both samples as long as the temperature allows it. However this does not explain why the structure in sample ACu+C is finer than sample DH-1+C, and apparently has been less affected by liquid phase sintering. This indicates even more complex and dynamic phenomena, but could possibly be explained by the following hypothesis: The higher the concentration of carbon in a Fe-Cu-C melt the steeper the wetting angle, and thus the poorer wetting properties on an iron based alloy. Poorer wetting properties mean smaller amount of copper in direct contact with base material and thus delayed penetration of copper along the grain boundaries. This accounts for the prolonged presence of a liquid copper phase, whereas the decreased wetting properties explain why the ACu sample had sintered further than the ACu+C sample. Since the carbon present dissolves into the liquid phase and ACu powders carry 10% copper, whereas DH-1 powders carry only 2%, there will be a much lower concentration of carbon in the liquid phase of the ACu+C sample. That makes the copper more inclined to dissolve the base material thus causing a swelling, which of course also expands the grains’ surfaces. The carbon concentrated liquid phase of the DH-1+C sample is less inclined to release copper, and thus the liquid phase sintering will continue to decrease the free grain surfaces, thereby concentrating the liquid phase over a smaller area, which in turn increases the effect of liquid phase sintering. On the other hand, when the copper dissolution in sample ACu+C has concentrated the carbon present in the liquid phase to the same level as in sample DH-1+C, the liquid phase with its decreased wetting capacity, has been spread over a much larger area and thus diminished the effect of liquid phase sintering.

**Fig. 15.** Sintered micro-structure of sample ACu. Large, but comparably smooth pores, with a higher fraction metal compared to sample DH-1.

**Fig. 16.** Sintered micro-structure of sample ACu+C. Smaller, but comparably coarse pores, with a higher fraction metal compared to sample DH-1+C.

**Fig. 17.** Sintered micro-structure of sample DH-1. Higher porosity and smaller, much coarser pores compared to sample ACu.

**Fig. 18.** Sintered micro-structure of sample DH-1+C. Higher porosity but larger, smoother pores compared to sample ACu+C.

Figures 15, 16 and 17, 18 further illustrate the above-mentioned phenomena. However comparison between the shape of different sponge structures and the powder shape and distribution in the green bodies, **Fig. 3, 4 and 5, 6**, demonstrates that the surfaces of the solid indeed have become smoother, even if the smoothness is on a very small scale in these porous samples.
5. Conclusions and further work

It has been established that the Fe-Cu-C system can be processed in SLS equipment, forming green bodies, with the capacity for furnace processing. It has also been found that the Fe-Cu-C system contains several interesting and complex phenomena that if properly managed could be useful in SLS application. Among those are: liquid phase sintering with enhanced sintering behavior, densification, some smoothing effect on free surfaces, and copper swelling that could compensate for some shrinkage. The liquid phase was found to interact with the concentrations of copper and carbon, thus the rate of sintering and sintering behavior can be further controlled. But the possibility to exploit these properties for SLS purposes is dependent on whether green bodies of sufficient fractional packing density can be manufactured, which in turn is dependent on the composition of the free flowing powder and the achievable density during the spreading of each new powder layer. This is obviously an area where considerably more work must be applied.

References

Paper D
Limits of Loose Metal Powder Density in the Sinterstation

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Abstract
The possibility to increase the density of applied metal powder in the Sinterstation has been investigated by successive addition of smaller sized particle fractions to a base powder. The optimal composition for each blend was determined experimentally, and their apparent densities were compared to the densities after Sinterstation application. The principal limiting factors for the density of metal powder in the Sinterstation were found to be the interparticle friction and the small sized particles’ tendency to form a suspension in the air. Finally, based on the evaluation of the different powder compositions’ behavior, a practical upper limit of loose metal powder density was estimated to 86%, when applied by a Sinterstation. The highest applied powder density in this investigation was a binary blend with 68.60% relative density.

1. Introduction
Some of the major challenges facing the SFF technology today are concerned with the manufacturing of tools and other objects in metal. Several technologies have been developed, but despite rapid progress there are still many more challenges to meet and properties to be improved. The commercial direct tooling and metal applications of SFF technology are dominated by different powder based techniques, such as DTM’s SLS, EOS’ DMLS and ProMetal. In all these approaches, the materialization of objects starts by the spreading of loose powder layers over a processing area. The particles are then either fused by a melting fraction of the compound with the laser, and thus densify by pointwise liquid phase sintering (EOS), or glued together for sintering and infiltration in a separate furnace (DTM, ProMetal). Both strategies does somewhat limit the possible material systems and no manufacturer has yet marketed a hardenable tool steel material. However, a combined approach, using liquid phase sintering of the whole object during a separate furnace cycle, could probably be used to overcome this gap [1], [2].

In all these approaches a crucial point is the density in the applied powder layers. For the furnacing requiring approaches, 50% density is a minimum to avoid distortion during processing [3]. An increased loose powder density would, apart from improving green strength, also have a positive impact on precision and surface quality as well as decrease the need for liquid phase or infiltrant in order to reach the desirable density. It is the purpose of this present work to investigate the practical possibility to increase the density and improve the quality of the loose powder mass applied by a Sinterstation, by the addition of finer powder grades. Thereby indicate what the main limiting factors are, and whether there is an upper practical limit, for the loose metal powder density in the current Sinterstation system.
2. Background

The packing of particles is a field of importance not only within the area of metals SFF, but in a vast range of areas. Needless to say, it has, in different forms been the subject of research several times before. In a fundamental work Mc Geary [4] investigated the basic scientific laws for the packing of spherical particles, and an arrangement with 95.1% of theoretical density was reported. To achieve this, a four component packing composition was used, where each finer grade was vibrated into the voids of a matrix formed by the larger sized grains. Powder densities of that magnitude are usually found only in compressed green bodies prior to sintering. Even though such reports are encouraging, the set up was idealized, and the results could probably not be duplicated on a practical SLS system.

In the field of SFF, Karapatis et. al. [5] used an idealized experimental set up to investigate the effect of relative size ratio on the density of a single applied layer of a binary powder blend, and thereby achieved binary layers with 63% relative density. However the size range used for the particles (up to 150 µm) was but a bit outside what could be used in a practical SFF system with acceptable precision. Furthermore, only single layers were used which gave a large influence to wall effects, which may not be as important in a real powder spreading process. In particular as the spreading procedure used was not similar to the counter-moving roller used in the Sinterstation.

This work takes a practical approach to powder application. The powders were experimentally applied in a Sinterstation, and powder grades were primarily selected in respect to:

1. Size range; for optimal packing of a loose powder mass, it is necessary that the finer powder grains are filling the voids between the larger grains. From a theoretical analysis it has been found that suitable proportions would be 1:7:49:343...[6]. The largest grain size is determined by maximum acceptable layer thickness, which, in respect to precision, is 0.1 mm. The smaller grain sizes are limited by availability in the suitable size range.

2. Shape; smooth spherical shape is superior in respect to internal friction and packing properties [6],[4].

3. Availability; all powders used should be available as commercial grades.
4. Handling; since the current Sinterstation systems requires manual powder handling, it should be possible to handle the powders without damaging the equipment or the health of the operator.

These aspects taken in respect, suitable iron base alloyed powders were selected, Due to limited availability in the smaller size ranges, the number of components in the powder blends are limited to three. If the wall effects are a dominant limiting factor also in reality, then the applied powder density should in all cases be smaller compared to apparent density. To investigate this, each powder compound was prepared with an experimentally determined composition, and the apparent density prior to Sinterstation application was measured to be compared to the density of the applied powder mass.
3. Experimental

3.1 Experimental procedure

A Sinterstation 2000 was used in these experiments. The apparent density of each powder prior to Sinterstation application was measured by a simple procedure with a graduated cylinder and a precision scale. A generic build file was used to apply a sufficient amount of powder in the Sinterstation’s part cylinder. After termination of the build, the powder in the build chamber was removed in level with the chamber floor, and the position of the part piston was noted \( (h_1) \). The powder in the part cylinder was removed by subsequently raising the piston 0.5 mm, and scraping off each layer with a straight edge blade. This was repeated until all the applied powder was collected in a container, and the second position of the part piston was noted \( (h_2) \). The powder mass in the container \( (m) \) was weighed on a precision scale and the density of the applied powder \( (\rho_{app}) \) as well as relative density \( (\rho_{rel}) \) was calculated by relation with part cylinder volume \( (V) \) and theoretical density of the massive material \( (\rho_n) \).

\[
\rho_{rel} = \frac{\rho_{app}}{\rho_n}; \quad \text{where} \quad \rho_{app} = \frac{m}{\left[\frac{d_{col}}{2}\right]^2 \pi [h_1 - h_2]}
\quad \text{Eq. 1. & 2.}
\]

Each powder went through several experimental cycles in order to establish the powder mass’ behavior in the Sinterstation under varying powder application conditions, such as feed rate and roller speed. Following this procedure the behavior of powders, consisting of one, two and three components were examined in respect to general powder behavior and applied powder density. To ensure comparability between the different powders, each composition was made by adding a smaller grained fraction to the previous powder compound.

3.2 One Component

3.2.1 The Powder

Large sized grains: For bulk material, a highly alloyed, gas atomized tool steel powder, Anval 60, from Dynamet Anval, was selected, see Fig. 1. The chemical composition and size range of this powder can be found in Tables 1 & 2.

<table>
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<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>O</th>
<th>N</th>
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Table 1. The chemical composition of Anval 60.

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<td>76</td>
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<td>8</td>
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</table>

Table 2. The sieve analysis (ASTM-E111) of Anval 60.
3.2.2 In the Sinterstation

The powder was cycled twice through the experimental procedure, no visible differences in powder behavior was observed. The powder had excellent free flowing behavior. The applied powder densities found was $\rho_{\text{rel}} = 60.82\%$, and $\rho_{\text{rel}} = 60.09\%$.

3.2.3 Conclusion

The apparent density of this powder may seem rather low, but considering the size range interval, it is reasonable to find a lower density compared to more narrow size intervals. Still, the considerably higher relative density when applied by the Sinterstation indicates that the powder grains are being distributed in a favorable manner, and that the wall effects are not a significant limiting factor in the Sinterstation applied powder mass.

3.3 Two Components

3.3.1 The Powder

Intermediate sized grains: To fit into the voids between the larger particles, the powder of intermediate particle size should not be larger than 1/7th of that grain size. Since a particle size interval for both coarse and fine powders seems unavoidable, a fine powder where the larger part of the grains could fit into the voids of the larger part of the coarser grain mass was selected, in this case Carbonyl Iron CL from BASF, see Fig. 2. The chemical composition and size range of this powder can be seen in Tables 3 & 4.

<table>
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Table 3. The chemical composition of BASF Carbonyl Iron Powder CL.

<table>
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<th>Size Distr.</th>
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<th>D50</th>
<th>D90</th>
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<td>Limit</td>
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Table 4. The particle size distribution (Microtrac X100) of BASF Carbonyl Iron Powder CL.
Optimal composition in terms of weight fraction large particles \( X^* \) can, according to [5] be calculated by: \( X^* = f_1/f^* \), Eq. 3., where \( f_1 \) is the fractional packing of large particles. \( f^* \) is the packing density at optimal composition, given as \( f^* = f_1 + f_s (1 - f_1) \), Eq. 4., where \( f_s \) is the fractional packing of small particles. \( f_1 \) has been determined experimentally to 0.60, and the tap density interval was used to find \( f_s \). Tap density: \( \rho_{t1} = 3.8 - 4.5 \text{ g/cm}^3 \); \( \rho_{t2} = 7.86 \text{ g/cm}^3 \) \( \Rightarrow \rho_{	ext{st}} = 48.35\% - 57.25\% \), thus, \( f_s = 0.4835 - 5725 \). Eq. 3. & Eq. 4. \( \Rightarrow X^* = 0.7245 - 0.7569 \). Compensated for the difference in specific mass this gives that the optimal composition would include 25.30 - 28.65 weight % Carbonyl Iron Powder CL. Such a compound could give a theoretical maximum packing density, \( f^* \), of 79.39 - 82.94% of the solid material. Several compositions with weight fraction Carbonyl Iron CL varying from 21.8% to 32.24% was mixed in a horizontally rotary type-blender, and the densities were measured. With higher fraction fine particles, the free flowing properties decreased, as the interparticle friction and the tendency to form agglomerates in the powder blend increased. This made the measurement of apparent censities more uncertain. The variation of the achieved densities can be seen in Fig. 3.

![Relative Density, Two Components](image)

**Fig. 3.** Relative densities of the binary blend of Anval60 and BASF Carbonyl Iron Powder CL.
With compensation for some divergent values the trend is obvious in Fig. 4.

Fig. 4. Corrected relative densities of the binary blend with trend inserted.

In conclusion of these experiments, a powder compound was composed by blending 26% Carbonyl Iron CL into a base of Anval 60. This binary blend has a relative apparent density experimentally found to be 63.88%. The solid density is calculated to 8.1 g/cm³.

3.3.2 In the Sinterstation

The powder properties were examined according to the experimental procedure. The powder body’s consistency was similar to moist sand, and apart from a tendency to form agglomerates and a general decreased free flowing behavior, the powder showed a disposition to raise dust in the air during handling. Still, the powder spread well and showed no visible signs of powder segregation during the application of layers in the part cylinder. Obtained densities related to roller speed and feed rate can be seen in Fig. 5. & 6.

Fig. 5. Powder densities obtained by variation of feed rate. At feed rate 0.20 the amount of powder was insufficient to fill the layer of the part cylinder. Roller speed is set to 100.

Fig. 6. Powder densities obtained by variation of roller speed. The two extra runs at roller speed 100, was made to find out whether the lower densities in this test series was caused by powder segregation. Left/right feed rate is set to 0.21.
Since the second test series concerning roller speed gave a considerable lower density at conditions identical to the most favorable, it was suspected that a segregation in the powder mass had occurred. However, after recycling the powder in the mixer, a smaller sample of powder obtained an even lower density, and the full amount of powder showed only a slight increase. Evidently segregation was not the problem.

3.3.3 Conclusion

The addition of a second, smaller sized powder gave a distinct increase in powder density. The densities obtained were however, not in the range of the theoretically achievable. Increased roller speed had, if any, a small, and possibly negative effect on the powder packing. Feed rates above the necessary to complete the new powder layer showed a distinct negative effect on the obtainable powder densities. The apparently increased interparticle friction in the powder compound could explain this. A free flowing powder forms a rolling wave in front of the roller during the spreading of each new layer. With the interparticle friction, the free flowing behavior is reduced and the powder partially forms a “wedge” of agglomerates that is being pushed along by the roller. An increase in mass of such a wedge would induce a higher pressure, and thus higher frictional shear in the applied powder bed below, causing cracks and poor packing in the applied layer. The counter rotation of the roller does lift and transport some powder, but only grains in direct contact with the rollers moving surface. There is only a limited rolling motion in this powder blend during the application of new layers.

Densities above the measured apparent density of this powder composition were obtained in the Sinterstation. This could be explained by the strong effect friction has on the used method for the measurement of apparent density, but in the Sinterstation does the powder motion probably also have an influence. The counter rotating motion of the roller is likely to have a vibratory effect on the upper surface of the applied layer, as well as exerting slight downward pressure on the last thin “edge” as the powder is being moved ahead. These conditions are not entirely unlike those idealized conditions used in McGeevy’s experiments, [4], mechanically inducing percolation of fine powder in each layer. These results confirm that the influence of the powders’ interparticle friction dominates over the influence of wall effects on the density of Sinterstation applied powders.

The lower densities obtained by the repetition of early experimental runs was a mystery with separation ruled out as an explanation. However by re-weighing the powder mass it was found that a significant amount of powder had been lost during handling. There are no obvious leaks, except for the powder’s tendency to raise dust in the air. Given a moderate estimation, that 75% of thereby lost powder is fine sized Carbonyl Iron CL, that would leave a blend with only 23.75% Carbonyl Iron CL. Such a composition had a relative apparent density of approximately 63% (Fig. 4). In that case, the densities obtained in the last experimental runs follow the pattern of the earlier in respect to the obtained densities. Therefore this assumption is being made for the continued experiments.
3.4 Three Components

3.4.1 The Powder

Smallest sized grains: The third size range is supposed to fit into the voids between the grains in the binary powder blend. As both previous components show a size range interval, the prediction of the actual sizes of these voids is hardly possible. However, by selecting the smallest available powder, with an average particle size, within the range to fit into the matrix of the intermediate sized powder, it was estimated that this addition would give an increase in loose powder density. The selected powder was Carbonyl Iron Powder HQ from BASF, see Fig. 7. The chemical composition and grain size distribution can be seen in Tables 5 & 6.

Fig. 7. Carbonyl Iron HQ. Almost pure iron, with the spherical shape typical of carbonyl metal powder. In this size range, the friction is associated with Van der Waals and electrostatic forces, and is thus increasingly independent of particle shape. Nevertheless, the spherical shape still is the best possible considering the achievable packing properties. As in all commercial powders a size range interval is hardly avoidable, and with smaller particle size, the relative size interval increases. Top density, is given by the manufacturer, to 3.0 – 3.5 g/cm³, ASTM B527 (analog). The chemical composition suggests that it is reasonable to estimate the density of the solid material to be the same as pure iron: 7.86 g/cm³.

<table>
<thead>
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<th>C</th>
<th>N</th>
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Table 5. The chemical composition of BASF Carbonyl Iron Powder HQ.

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<tbody>
<tr>
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<td>g/100g</td>
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<td>0.7-1.0</td>
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Table 5. The chemical composition of BASF Carbonyl Iron Powder HQ.

<table>
<thead>
<tr>
<th>Size Distr.</th>
<th>D10</th>
<th>D50</th>
<th>D90</th>
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<td>4.0</td>
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</table>

Table 6. The particle size distribution of BASF Carbonyl Iron Powder HQ.

To find a suitable composition for the ternary powder an experimental approach was used. Different blends with varying composition was mixed and the apparent density was measured. The variation of the achieved densities for respective composition can be seen in Fig. 8.

Considering that the increased interparticle friction in the ternary blends, made the difficulties of apparent density measurement increase with the fraction Carbonyl Iron HQ, and that a different measuring cylinder was used for blends 12 and 13 the difference in density are in general small among these compositions. Nevertheless in conclusion of this experimental series, a powder compound was composed by with 73.35% Anval 60, 14.10% Carbonyl Iron CL, and 12.55% Carbonyl Iron HQ. This ternary blend has a measured relative apparent density of 68.40%. The solid density is calculated to 8.1 g/cm³.
Fig. 8. Compositions and relative densities of the ternary blends.

3.4.2 In the Sinterstation

The powder was examined in the Sinterstation according to the experimental procedure. With a body consistency quite similar to wet sand, the powder showed much interparticle friction and was also difficult to handle without raising smoke-like dust. The compound hardly had anything like free flowing behavior and was more likely to form agglomerates than not. Since the powder tended to stick to the roller, scrapers were installed. Several cycles were performed to investigate the powder compound’s spreading behavior and find suitable process conditions. The obtained densities can be seen in Fig. 9. In difference from the powder in the part cylinder, the powder distributed around the building area settled to a stable and apparently very dense surface, whereas the powder mass in the part cylinder, remained unstable and shifted with every pass of the roller.
3.4.3 Conclusion

The addition of a third component did increase the apparent density of the powder mass, but in difference to the binary blend that increase could not be observed in the Sinterstation. The obtained densities were on the contrary significantly lower than those obtained with the binary blend. Despite variation in both roller speed and feed rate, a stable behavior in the applied powder mass could not be found. This is explained by the strong disposition to form agglomerates and is in analogy with the explanation of the behavior of the binary powder. A higher interparticle friction in the powder mass causes a stronger frictional shear in the underlying layers. When the shear is too big the powder mass starts to shift. The frictional shear depends on both the inner friction in the powder mass and the pressure applied by the mass of transported powder during spreading.

These phenomena in combination with the general problems of handling extremely fine powder, makes metal powder compositions containing grain sizes in the range of one micron or smaller, unlikely as practical SLS materials.

4. Conclusions

It has been established that the addition of particles of a smaller size range can increase the relative density of a powder mass applied in the Sinterstation. It is furthermore concluded that the principal limiting factors for such an approach to densification of the powder mass are: the availability of suitable powder grades, the inner friction of the powders with smaller particle sizes, and the dusting of fine sized powder grades.

1. Availability: Each additional smaller sized powder component should be of a narrow size interval, and maximum 1/7th of the diameter of the larger particles to increase the density of a powder mass. It is obvious that there are limits to how fine powders and how narrow grain size ranges can be obtained at a reasonable cost.

2. Inner friction of fine powders: As particle sizes reach the range of 1-2 microns or smaller, the pure powder shows a dominant tendency to agglomerate, which counteracts the densification as well as separation. This effect could possibly be reduced by addition of
some sort of lubricant to the powder. However this lubrication would in itself reduce the powder density, and it is most uncertain how such an addition would influence the behavior during the further processing.

3. Dusting of fine powders: A suspension of metal particles is not an ideal atmosphere for electronic equipment, which must include SFF equipment. Even less so considered that suspensions are deemed highly flammable and hazardous to the human health. Iron, for example, is probably harmless to ingest, but ill-advised to inhale. Even if the previous limits could be overcome, the dusting of fine powders is hardly possible to address without an entirely new powder handling system.

These points taken in consideration, size range compositions beyond binary are unlikely to become of practical use. The highest theoretical density that thus could be expected to come of use is 86%. Still considering the practical difficulties, any density in a stable powder mass above 70% should be considered an achievement. In this work, the highest achieved applied powder density was 68.60%.

These limits of applied loose powder density, makes further densification a necessity to build full density objects. This, in turn, will have a limiting effect on the material choice, achievable green strength, and also influence the process precision. It is unlikely that these issues could be fully addressed successfully to their full extent without designing an entirely new machine.

References
Paper E
INVESTIGATION OF SIZE RANGE COMPOSED POWDER FOR SLS BASED LIQUID PHASE SINTERED TOOLING

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Department of Production Engineering
The Royal Institute of Technology
Stockholm
Sweden

ABSTRACT
The present work investigates the possibility to develop a homogenous, heat treatable, tool steel material for SLS based Rapid Tooling application. The work addresses general powder mixing and sintering problems as well as the possibility to form stable metallic bonded green bodies prior to sintering. Two different iron based powders have been mixed with copper coated iron powder and milled together until no further densification occurred. Behaviour and densities acquired in the Sinterstation was monitored, for the pure powders, as well as after the addition of each different powder blend component. Finally green bodies were formed, with and without binder, and sintered in a vacuum furnace cycle. It was concluded that the addition of a coarse small sized powder with the following milling, and further additional powder components had increased the inter particle friction with a significant negative effect on the powder packing properties. This, in turn, led to fragile green bodies and failure to sinter to full density. However, the possibility to form stable, metallic bonded green bodies has been proven, thus suggesting the opportunity not only to omit binder systems altogether, but also to increase the robustness of future materials systems.

KEYWORDS: Rapid Tooling, Selective Laser Sintering, Liquid Phase Sintering, particle size range, interparticle friction, composition, relative powder density, binder system, binderless green bodies, sintering

INTRODUCTION
Rapid Tooling (RT) technologies are gaining momentum in the manufacturing industry worldwide. More and more companies recognize the advantage of integrating RT as a natural part of their product development process. Among the most widely used systems for direct approach RT, are the different metallic applications of laser sintering, Direct Metal Laser Sintering (DMLS) by EOS Gmbh, and SLS of the metallic material by DTM Corp. These processes have that in common that they use inhomogenous composite metal materials with different and limited properties compared to conventional tool steels. Since most of the potential users of RT technologies have tool steel as their point of reference, the RT materials are evaluated by the performance compared to tool steel. Homogenous, steel based RT materials, with the capacity for heat treatments would therefore not only improve the performance of RT tools, but also bring the technology closer to the customers’ point of reference and thereby make the technology appear less alien to the potential user.
One fundamental process difference between EOS and DTM is that when EOS actually pointwise sinters the metal to full density with their laser, DTM’s laser melts a binder to form a green body, and the actual consolidation to full density objects, takes place in a separate furnace. If a RT material is supposed to be homogenous and have heat treatment capacity, it is hardly suitable to subject the metal to pointwise heating and chilling. Therefore the DTM approach seems more promising for the development of such a material. However, since the powder mass consists of approximately 40% porosity, there is need for a substantial densification during sintering. In their commercial process, DTM has solved this by integration of bronze infiltration as a step in the process cycle, but to receive a homogenous material, sintering to full density during the furnace cycle would be required. As one way to achieve this, Rockwell Science Center has developed Liquid Phase Sintering (LPS) material systems, under the name of “Direct Metal Fabrication” (DMF) [1]. However in this process approach, is the debinding procedure as well as a substantial shrinkage during sintering critical issues. To ensure densification with minimal shrinkage to a solid, homogenous material, it is necessary to have the highest possible fraction of solids in the powder mass. That can be achieved without compression, if a composition of selected particle sizes is being used, where each smaller sized fraction fills the voids between the larger particles. This solution could also offer the opportunity to bypass the critical issue of debinding the green bodies. Since the reactivity of powder particles’ surfaces increases with smaller particle sizes, there is a distinct possibility that the smallest powder particles, could be made to work as a metallic binder by diffusion bonding. This present study has therefore two principal objects; to investigate size range composed powders, aiming at the RT manufacturing of homogenous tool steel material, and to find out if metallic bonded green bodies, can be formed using SLS with a moderate laser power.

**BACKGROUND**

This investigation addresses the development of size range composed powders for SLS based liquid phase sintering (LPS) tool steels. According to a rule of thumb for size ratio compositions of conventional powder metallurgy [2], size ratios of 1:7:49:343… should be suitable for increased powder packing densities of even spherical particles. Moreover, in a renowned work, McGearry [3] managed to compose powder blends with four size ranges and particle packing densities up to 96%, but since the practical size range of particles for SLS based rapid tooling is limited, such high densities cannot be expected in this application. The upper practical limit of particle size range in the indirect SLS metal approach is determined by the demand for process precision and maximum acceptable layer thickness. The precision of each layer, X-Y direction, is limited by the largest particle size, and in precision in Z direction is limited by layer thickness. To minimize the need for post processing, the layer thickness should preferably be smaller than 0.1 mm, and therefore an upper particle size range limit of 80 μm has been determined for base material. Previous work [4] has addressed the issue of the practical limit of density in a size range composed powder mass in a Sinterstation. It was found that the principal limiting factors for densification by size range composition are interparticle friction, caused by Van der Waals and electrostatic forces, around the smallest size particles. Another difficult issue is the metal powder dust that is raised in the air during handling, which could make an unhealthy atmosphere for human operators and electronic equipment. It was further concluded that particle sizes in the range 1 - 2μm are too small
to be practically handled. The highest applied metal powder density achieved during these experiments, was 68.60% in a two-component blend. Therefore, this investigation has been limited to evaluate two size range components powder blends.

If the finer sized particles are to increase the powder packing density, it is necessary that no segregation occur is the powder mass during the application of each new layer. In conventional powder metallurgy, this is a familiar problem, which may be accentuated if the smaller sized particles have a higher specific mass. However, this tendency seems to decrease with smaller powder particle sizes, where interparticle friction is more influential on the powder mass behaviour [2]. This behaviour will however be monitored.

The melting phase in a LPS material system should have the best possible wetting and diffusion properties, as well as sufficient solubility for the base material system. For iron base materials, copper has excellent wetting and diffusion properties, as well as solubility up to approximately 8% at sintering temperatures. Further more there is an option to control the rate of diffusion by the addition of carbon to the liquid phase. A basic investigation of this material system for SLS, has been the subject of a previous work. Despite some promising results, it was found that a most important limiting factor was the powder packing density [5], this present study combines the two previous investigations by investigation of the iron-copper-carbon material system with particle size range composition.

The formation of green bodies is a crucial step for Rapid Tooling application in the Sinterstation. In the conventional process a polymer binder is used to glue the particles together, in this particular case a different approach could also be considered. Binders could either be added to the metal powder as thin coating on the particle surface, or as another powder in the blend [6]. For monosized powders the first alternative has showed to result in a higher green strength [6]. Still with the coating on the surface, each particle will have an increased diameter and thus the fractional packing of actual metal powder particles will be decreased. In the case of size range composed powder the size ratio between the different powder fractions is of crucial importance and the addition of a binder coating would disrupt this ratio. A mixed powdered binder in the blend would on the other hand surely decrease the powder density, but on the other hand when that binder is melted by the laser it could be possible for the metal particles to reorient and fill the in the voids previously occupied by the binder. Thus a mixed powder binder approach was used in this investigation.

However since the presence of very small sized particles in the powder blend opens the possibility form diffusion bonds with the smallest sized particles and thus form binderless green bodies. Apart from not needing a binder and thereby avoiding the decrease in powder density, such green bodies might not require any supporting powder material during the furnace process, which would be advantageous for a LPS material system

**EXPERIMENTAL**

Two different iron based powders were selected for the investigation. Each was blended with a small sized, but uneven and agglomerated, copper carrying iron powder in proportions according to previous experimental work [4] and literature studies [2][3]. The powder blends were milled for deagglomeration in a cemented carbide mill until the
densification of the powder mass reached a steady state. By applying the powder blends several times in a Sinterstation 2000, the relative densities of the applied powder mass, and general powder behaviour was monitored, with particular interest to segregation of the different powder components. Graphite powder was added to one of the powder blends, resulting in slightly changed powder mass behaviour. The investigation was completed by the formation and sintering of green bodies, with, and without, the use of an added powder binder material.

**Powder selection**

For this investigation two different iron base powders, mesh 325, were selected. The iron base materials were selected to exemplify low-alloyed tool steel and stainless steel. The tool steel example is based on an iron powder, which combined with carbon and copper, would yield a hardenable material. This powder, Fe 110, mesh 325, is 99.9%, pure hydrogen reduced iron, see **Fig. 1.** Since this powder is of low relative apparent density (36-37%), and the particles are of uneven shape, the achievable relative density in the powder mass and thereby also green bodies, is probably not so high, still 50% relative density is a must to reach full density after sintering. [6] The stainless steel powder is Anval 420, mesh 325, a gas-atomised powder with an excellent free flowing behaviour, and packing properties see **Fig. 2.** The spherical grains and the high apparent density (60%), indicates good prospects for densification by the addition of small particle powder.

![Fig. 1. Fe-110, coarse uneven irregular shaped particles of pure hydrogen reduced iron. High interparticle friction and low packing densities are expected in this powder material.](image1)

![Fig. 2. Anval 420, smooth spherical particles of gas atomised stainless steel. Low interparticle friction, free flowing behaviour and high relative packing densities is typical of this type of powders.](image2)

The upper limit of the smaller particle size range is determined by the void space between the larger sized particles. For optimal packing purposes the smaller sized particle diameter should be 1/7th –1/13th of the larger diameter. Since mesh 325 means a grain size maximum of approximately 45μm, the smaller sized grains should be in the range 4 –6 μm. In a liquid phase sintering powder material system, the melting phase should be evenly distributed around the base material particles in the powder mass. Since the smaller sized particles ideally should be oriented to the void space between the larger sized particles, it is natural to use the smaller sized grains to carry the melting phase material, in this investigation copper. Since the solubility of copper in iron at sintering temperatures is limited to approximately 8%, whereas the suitable proportions of smaller sized particles is above 20%, was an iron core powder coated with 15 % copper.
(FeCu15), see Fig. 3, selected. That would, with standard composition [2],[4], yield around 4% copper in the final mixture, which is well within the soluble interval. The selected powder has a size range interval, 4-6µm, which is should be perfect for the base material powders. However the size range for the FeCu15 powder was determined by the Fisher Sub Sieve Sizer [], this method does not take uneven particle shapes or agglomerates into account, which may have strong influence on the powder properties.

![Fig. 3. FeCu15 powder. Copper coated iron, coarse uneven, or agglomerated powder. The particle shape of this material is apparently not spherical, and the size range is thus not exactly determined. To achieve increased powder density in a Sinterstation applied powder mass particle size and interparticle friction is crucial. Therefore modification of the powder was necessary. The interparticle friction of small sized powder makes deagglomeration milling of unblended fine powder unpractical, the milling was therefore performed with prepared blends.](image)

**Composition**

Since the FeCu15 powder appeared agglomerated on delivery, and the high friction in the pure powder mass made deagglomeration of unblended FeCu15 unpractical, it was not possible to determine the optimal composition of each powder blend experimentally. From literature [2] and previous work [4], it was concluded that suitable proportions for the smaller sized particles is within the 25% to 27% interval of the total powder mass. Therefore, each base powder was mixed, Anval 420 with 26.88 weight % FeCu15, and Fe-110 with 25.92 weight % FeCu15, and milled together until the increase in powder density reached a steady state. The milling was done with cemented carbide cylindrical milling stones in a cemented carbide mill. This may have contaminated the powder with small carbide chips, but that would not have had any significant effect on powder densities or sintering behaviour.

**Acquired densities**

Since an increase in smaller sized particles means an increase in interparticle friction the milled powder densities had to be measured by a special procedure. A graded cylinder was filled by successive addition of a small amount of powder. Between each addition of material the cylinder was “tapped” in the bottom, vibrating the powder to increased density, hence the term “tap density” for these values. When the cylinder was filled with 100 ml “tapped” powder, it was weighed and the mass was used to determine powder density. The density of a Sinterstation applied powder mass was determined by dividing the mass of the applied powder mass in the part cylinder with the volume, which in turn was calculated from cylinder diameter and completed build height.[4]

**Fe-110.** The apparent density of the unmixed powder was found to be 36% of the massive material. When applied in the Sinterstation the powders reached relative densities of 40%. This result is well aligned with the results from a previous investigation where the densifying effect of the Sinterstation’s powder distribution system was experienced for single, as well as bimodal size range composed powders.
Fe-110 & FeCu15, 25.92 weight%. To achieve any densification in this powder composition, a fairly brutal milling was required. However this did cause plastic deformation of the powder particles, see Fig. 4, resulting in increased interparticle friction. Still, the powder density reached a steady state at 46 – 51% tap density, which is a significant increase compared to unmixed powder. In difference to previous work the powder spreading system in the Sinterstation did not increase the applied powder density, relative densities in the applied powder mass remained around 46%. With the final addition of 1% graphite powder, the relative applied powder density decreased further to 44%. No segregation of particles could be observed in the Sinterstation applied powder masses.

Fig. 4. Milled Fe-110 & FeCu15 powder blend. The larger sponge like Fe-110 particles have been plastically deformed adding to the densification in the powder mass. Still the density is too low for the material to be expected to sinter to full density.

Fig. 5. Milled Anval 420 & FeCu15 powder blend. The spherical Anval 420 particles appear unaffected but the FeCu15 particles appear deformed and somewhat deagglomerated still densities acquired were below the density of the unblended powder.

Anval 420. The smooth spherical particles and excellent free flowing behaviour of this powder facilitates powder packing and thus the apparent density is, 60% a common value for spherical powders. With Sinterstion application relative densities of 65% were reached.

Anval 420 & FeCu15, 26.88 weight%. The base powder’s low interparticle friction made this powder more demanding to mill. To achieve densification low rotational speed and long milling time was required, even then, tap densities barely reached 62% of the solid material see Fig. 5. When applied in the Sinterstation, the powder mass acquired relative densities around 58%. Likewise the previous powder blend, no segregation of particles or materials could be observed in the powder. Since this composition is based on a stainless steel powder, no addition of graphite powder was included in this investigation.

Formation of green bodies
Green bodies were formed with the use of additional binder as well as by the binderless approach. As the additional binder system, 4% Hexamethylene Tetramine Phenol was mixed into the powders. Each powder was applied and processed by the Sinterstation, using process variables and laser power found suitable for this binder system in previous work [5].

Binder added, base powder FE-110. Despite high hopes there was no apparent reorientation or densification of the particles during laser processing. The relative
powder density reached a modest 35%, with a very small green strength. This is too low green density to reach full, homogenous density during sintering in the furnace cycle. The modest green strength makes the bodies brittle and difficult to handle without breaking. See Fig. 6.

Binder added, base powder Anval 420. This powder showed a similar behaviour. The density in the applied and sintered powder mass reached 40%. As in the previous material, this is too low density to expect satisfactory density during sintering. See Fig. 6.

Binderless. With increased laser power and reduced scanning speed it was possible to form green bodies of both the investigated powder mixtures. However, as the laser scanned the layers and bonds were formed, each layer curled upwards. This caused them to move during the spreading the new powder layers and therefore the connection between the layers was somewhat random. Instead of green cylinders, it was formed a series of loosely connected green discs. See Fig. 7. Still, the elasticity of the connections verified that metallic bonds had formed.

Sintering
Binder joined green bodies were packed in a graphite crucible with supporting aluminium oxide powder according to standard DTM procedure. The largest Fe-110 based green body was too weak, and cracked upon placing in the crucible, but the other green bodies, the smaller Fe-110 cylinders as well as all the Anval 420 green bodies were packed unharmed. See Fig. 6. To examine the strength of the metallic bonds in the binderless green bodies, these were placed, without any supporting powder, on the surface of the alumina powder bed. The samples were sintered together in a vacuum furnace according to procedure developed in previous work [7][5].
After sintering the pieces showed some interesting results. See Fig. 8. All binder jointed objects had sintered to some extent, but none had reached full density. The cylindrical Fe-110 based green bodies had gone through a substantial shrinkage and reached a relative density of 60%, (starting at 35%), whereas the corresponding Anval 420 based samples only reached 55% (starting at 40%). This is in analogy with the behaviour observed in previous work, where the addition of carbon has prolonged the presence of liquid copper and thus the liquid phase sintering. The slowed densification in Anval 420 samples indicates that all copper has dissolved into the steel material, finishing LPS, and forming a homogenous alloy.

Despite extremely thin sections, complex shape, and lack of supporting powder, the binderless green bodies have maintained their geometry as far as can be observed. See Fig. 9. This suggests that the metallic bonds formed indeed can be useful in eliminating the need for binder addition in a size range composed LPS material system.

**DISCUSSION AND CONCLUSIONS**

The increase in densities brought about by the size range composition in this investigation was not as high as could have been expected. On the contrary, for the already fairly dense Anval 420 powder, the addition of a finer fraction decreased the density of Sinterstation applied powder beds. Actually, this is not so surprising. The added material required the powder blend to be milled, and even if the base powder emerged undamaged from the mill, the FeCu15 powder seems to have changed particle shape and increased the interparticle friction during the milling process (see Fig. 5). The vibrations used when measuring the tap density may have had a particle arranging effect, but the roller application mechanism apparently had not any such effect with this blend. The sponge like Fe-110 powder had much porosity from the beginning, with rough uneven particles to resist densification. However, the milling apparently deformed the sponge like as well as the FeCu15 particles (see Fig. 4.), which appears to have improved the packing properties for the powder blend. It is an obvious, but hardly ground braking conclusion that interparticle friction is a critical issue in the composition and behaviour of size range composed powder blends.
If high interparticle friction is negative for the blending and spreading of the powder, it also opposes particle segregation in the powder, which on the other hand is a positive effect for LPS application. Obviously there is need for optimisation between blending properties and segregation behaviour in the powder bulk.

Considering the nature of the limitations for powder packing, it is hardly surprising that the additions of graphite and binder had a negative effect on the applied powder densities. It would have been desirable if these components also could have been integrated in the size range composition, however, these kinds of soft powdered materials are being milled by the other particles during blending and handling, and it is not possible to know what size and shape the particles will have at the time of use. Moreover, any not metallic particles added to the powder blend does decrease the potential metal powder density and should therefore be kept as small as possible.

With densities in the powder mass being what they were, the result of the sintering of the binder held green bodies was expected. The massive shrinkage of graphite added samples has been observed in a previous work [5] and is explained by prolonged presence of liquid copper brought about by the dissolved carbons’ slowing of copper diffusion into iron, whereas copper otherwise is swiftly diffused into the iron forming a homogenous alloy. These phenomena could possibly be exploited in a future technical material system. See Table 1, for an overview of acquired relative powder densities.

<table>
<thead>
<tr>
<th>Base material</th>
<th>Pure Apparent</th>
<th>Applied</th>
<th>+FeCu15 milled Tap</th>
<th>Applied</th>
<th>+Graphite Applied</th>
<th>+Binder Applied Sintered</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>FE-110</td>
<td>36%</td>
<td>40%</td>
<td>50%</td>
<td>46%</td>
<td>44%</td>
<td>35% 60%</td>
<td></td>
</tr>
<tr>
<td>Anval 420</td>
<td>60%</td>
<td>65%</td>
<td>62%</td>
<td>58%</td>
<td></td>
<td>40% 55%</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Relative densities acquired for the powders, by different measurement procedure, depending on added components and further processing.

Far more encouraging is the formation of metal bonded green bodies, even with respect to their acquired geometry. The stability of these green bodies during sintering indicates the possibility to build very complex shapes without the need for binder or supportive powder during sintering. If the curling could be controlled and each layer be bonded in position, much is won regarding the capacity for a LPS material system. A possible way to achieve this could be the establishment of a support system that resists the curling of newly sintered layers as well as keep them in position. This could be an obvious object for further work. However many issues for this type of powder material system still remains unsolved, and much more work is required before any certain predictions of the potential success could be done.
ACKNOWLEDGEMENT
The author wishes to express his deep gratitude to Dr Ove Alm and associates at Sandvik Coromant, Stockholm, without whose help, good advice, and generosity with use of equipment the research presented in this paper would not have been possible.

REFERENCES


Investigation of the Liquid Phase Sintering of Size Range Composed Powder for SLS Application

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Abstract
In order to find the constraints and limiting factors for the development of a series of homogenous steel materials has three different aspects of such a material system been investigated in relation to each other; the composition of powders, the formation of green bodies and sintering in a vacuum furnace. It was found that particle size range intervals must be optimised, not only in respect to maximum part precision and powder density but also to interparticle friction and laser penetration. Sintering time and temperatures should be adapted to particles shape and diffusion rates, as well as the possible evaporation of alloy components. Furthermore should the fraction of melting phase be balanced between solubility of liquid agent in base material and the wetting of solid particles as well as being integrated in the smaller sized fraction of the powder composition. While these issues remain undetermined, the possibility for parts of homogenous steel materials by SLS cannot be eliminated.

1. Introduction
Among the most widely used systems for powder based metallic application of SFF technology, are different metallic applications to laser sintering, Direct Metal Laser Sintering, (DMLS) by EOS, and metallic material SLS by 3D Systems. Both systems have several traits in common, however one fundamental difference is that while EOS uses a powerful laser to consolidate the material by point wise liquid phase sintering in the machine, 3D Systems uses a two step approach where the metallic consolidation by solid state sintering and infiltration takes place in a separate furnace. However, as the metallic applications of SFF technology have been gaining momentum for the purpose of prototyping and small series manufacturing over the last few years, there has been a growing interest to expand the capacity into production grade tooling and fully functional metallic parts. Since objects made of various steel alloys traditionally have fulfilled many of these applications, the possibilities for the SFF application of a variety of homogenous steel materials, from traditional tools steels to stainless steels, is an area of obvious interest. Therefore, a material system that would allow the building of objects in homogenous steel materials, would if applied to a process that is well established on the market, greatly expand the possible applications of SFF technology, and thereby make a significant contribution to bridge the gap between conventional practice and SFF technology.

The two-step SLS based process, in combination with Liquid Phase Sintering (LPS), has been suggested as an alternative route to make full density objects. As one way of exploiting this possibility, Rockwell sciences center has developed a set of (LPS) materials, under the name of Direct Metal Fabrication (DMF)[1]. However in this process is the debinding of the green bodies as well as a substantial shrinkage during sintering critical issues. One possibility to minimize the shrinkage while sintering to full density, is to compose the powder of selected particle sizes where each smaller fraction fills the voids between the larger particles, thereby
acquiring the highest possible fraction of solids in the powder mass [2], [3]. Some practical aspects and limitations high-density powder composition in relation to SLS equipment have been investigated in a previous work [4]. However any addition of organic binders to the powder blend would decrease the density of metal particles. But since the reactivity of the powder particles increase with smaller particle size, there is a distinct possibility that the smaller particles could be stimulated to bond to the larger particles and thus act as a metallic binder. However, to reach a homogenous material by LPS, the liquid phase must be completely integrated with the base material after full density has been reached, one possible way to achieve this is to use a liquid phase that slowly dissolves into the other powder components.

It is the purpose of this present work to investigate this approach to the development of a family of steel materials for SLS application. The basic principle is to use blend of small sized powders, consisting of a melting phase material with the capacity to dissolve into iron-based alloys, in this case copper, and an iron powder as filler material. This blend can be combined with a choice of base material steel powder to achieve a variety of steel materials. During sintering, the copper melts, providing the liquid phase for sintering, and a diffusion route for the homogenization of alloy components, while slowly dissolving into the steel material. Since the outcome of approach is dependent on every part of this multi-step process, this investigation takes an over-all approach to finding the limiting factors and monitoring the behavior, from the composition of the powder blends, over the powder application and the formation of green bodies in the Sinterstation, to the final metallic consolidation during the furnace process.

2. Background

2.1 Powder Composition

The density of powder beds been addressed in previous research, both in general, [2], [3], and for SLS technology, by experimental setup [5], and by this author, in a more practical approach by application in a Sinterstation [4]. It was found that given a maximum particle size, the number of additional powder size fractions is limited by the increasing interparticle friction that accompanies the addition of smaller sized particles. When the particle sizes are as small as 1-2 \( \mu \text{m} \), the powder mass is too "sticky" to form acceptable powder layers. Since the size relationship between larger and smaller particles ideally is at least 7:1, [2], [3], it was concluded that powder compositions with more than two size fractions hardly are feasible for Sinterstation application. Furthermore, it was found that the powder spreading system in the Sinterstation has a positive densifying effect on the applied layer, unless the interparticle friction in the powder mass dominates over the free flowing behavior, then the effect is opposite.

Since copper is well established as a liquid phase, in conventional powder metallurgy [2], [10], with the capacity to dissolve into iron base alloys and with positive effects on for example strength and corrosion resistance, copper is the choice of melting phase in this investigation. An even distribution of the liquid phase is important for LPS purposes therefore should the copper particles be intermixed among the smaller sized particles. An early investigation into the SLS aspects of the Fe-Cu-C LPS system [11], concluded the importance of loose powder density, and also registered some effects of the copper amounts and presence carbon on the sintering behavior. Following up, a primary investigation much similar to this [6], took these aspects in consideration while composing powder blends by combination of iron-based powders with a small sized copper covered iron powder. However since the smaller
particle size had been determined by an approximation of the powder material surface assuming spherical shape, the particle size was different from powder specification. This resulted in a much lower powder density than expected, which made sintering to full density impossible. Nevertheless, metallic bonded green bodies were formed. This present investigation, while taking these experiences in respect, looks further into the behavior of the materials during the formation of green bodies and furnace processing.

2.2 Formation of Green Bodies

In the previously mentioned primary investigation [6] metallic bonded green bodies were formed in a Sinterstation, using a moderate laser power and low scanning speeds. Much research along the same lines for the iron copper material system has been performed at the Katholieke Universiteit, Leuven, [7], [8], [9], however mostly in the aspect of the powder spreading mechanism [7] and laser interaction with powder material [8]. Apparently aiming at LPS by laser exposure, these efforts have not been directed towards maximizing powder mass density. Aiming at homogenous steel material by furnace consolidation is the applied powder density and the arrangement of particles in the green body is of critical importance in this present work. However improving the strength of green bodies, pointwise melting and solidification causes thermal tensions and distortions in each layer. Therefore is the melting of copper and LPS at laser exposure not necessarily desirable for this approach, however it may turn out to be unavoidable.

2.3 Sintering

The Fe-Cu system for LPS is well known in conventional powder metallurgy and has consequently also been the subject for research with the aspect of combination with SLS [6], [9], [11]. However none of these investigations has taken the diffusion of copper into the base material into real consideration. Copper dissolves into iron base alloys by substitution, which is a slow process and thereby allowing prolonged LPS. This could possibly offer the opportunity to control the sintering behavior by the combination of particle sizes with the amount of copper and sintering temperature to achieve a homogenous material within reasonable sintering times. Another critical limiting factor for the sintering behavior is the oxidation of the powder. In order to reduce the inevitable oxides, and provide a reliable atmosphere [2], is a vacuum furnace atmosphere suitable for the sintering operation. However, certain essential alloying elements, for example Cr can evaporate during vacuum processing at high temperatures [12], which put a serious constraint to the process temperatures in this approach. This will be taken into consideration while determining the process parameters.
The time and temperatures for the furnace procedure in order to achieve a homogenous material are controlled by some important boundary conditions. The temperature must be high enough, and process time must be long enough to allow the complete dissolving of copper into the base material, as well as the homogenization of all other alloying components. However, vacuum furnace processing temperatures are limited by the risk of evaporation alloying components from the material, thus placing an upper limit on the temperatures, while the times are limited primarily by the competitiveness of the process. The time to dissolve the copper into the base material is controlled by the fractional saturation of copper in the base material particles. Darken & Gurry [13] gives us the relationship:

For diffusion into spherical shape: \( \frac{DT}{L^2} = -0.05043 - 0.2333 \log(1 - F) \), [Eq. 1]

Diffusion constant, \( D = D_{eff}^{Cu} = 1.8 \exp\left(\frac{-295kJmol^{-1}}{RT}\right) \text{cm}^2/\text{s} \), [Eq. 2]

Fractional saturation, \( F = \frac{C_n - C_o}{C_i - C_o} \), [Eq. 3], and \( L \) is the diffusion distance, here the radius of the base material particles which in the case of 44\,\mu m powder is 0.00225 cm. For saturation this gives [Eq. 1] \( \frac{DT}{L^2} = 0.9 \). At 1120 °C is \( D_{eff}^{Cu} = 1.56 \times 10^{-11} \Rightarrow 81.13 \text{ h} \), which is too long.

In a similar manner are the times to saturation at 1200 °C \( \Rightarrow 19.89 \text{ h} \), at 1250 °C \( \Rightarrow 9.23 \text{ h} \), and at 1300 °C \( \Rightarrow 4.3 \text{ h} \). However, the upper temperature limit is determined by the evaporation of critical alloying components during vacuum processing. Since stainless steel is one material of particular importance in this investigation, the evaporation of chromium is of critical importance during the sintering operation [12]. Gas pressure equilibrium can be calculated from the known relationship \( \ln p_1 - \ln p_2 = \frac{\Delta H_m}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \) [Eq. 4], [12], where index “1”, is referring to the triple point equilibrium, and index “2” to process conditions. This gives: \( p_1 = \text{latm} \Rightarrow \ln p_1 = 0 \), for chromium: \( T_1 = 2620 + 273 = 2893 \text{K} \), \( \Delta H_m = 8.17 \times 10^7 \text{cal} \cdot \text{mol}^{-1} \), and \( R = 1.987 \text{calK}^{-1}\text{mol}^{-1} \). Assuming standard vacuum furnace settings \( \rho = 4.94 \times 10^7 \text{ atm} \) and ideal gas behavior, chromium gas pressure of the selected stainless steel alloy (22.4% Cr, \( \Rightarrow X_{Cr} = 0.2357 \)), will be \( p_2 = 2.096 \times 10^{-6} \text{ atm} \), inserted in [Eq. 4] this gives the gas pressure equilibrium temperature for this alloy in a vacuum furnace \( T_2 = 1506.78 \text{K} \Rightarrow 1233.6 \text{ °C} \).

Therefore should the process temperature not be much higher than 1200 °C, though sintering times of close to 20 h at 1200 °C would lead to unreasonable process times. However a slight reduction in copper content, from equilibrium at approx. 9% to 8%, would change the fractional saturation value, [Eq. 3] to 0.888, which in turn gives [Eq. 1] \( \frac{DT}{L^2} = 0.17 \) which would give a process time of 3.85 h, a much more reasonable value.
4. Experimental

4.1 Powder Composition

Since the powder mass is going to be densified by addition of smaller sized particles, and the experiments are aiming at achieving homogeneity after completed sintering, the alloy of the base material will be diluted. In order to maintain some of the desirable properties, it is suitable that the base materials powder is slightly over-alloyed. For the purpose of this experiment was two different base powders selected, one tool steel, Anval 9044, see Fig. 1. & Tab.1, and one stainless steel, Anval 2205, see Fig. 2. & Tab.2. Both base material powder were cf ~44 μm particle size.

![Image of tool steel powder](image1)

**Fig.1.** Anval9044. An alloyed tool steel material, with the characteristic spherical shape of gas atomized metal powder. The spherical shape is known to have the lowest interparticle friction and thus the best possible flowing behavior and packing. Size analysis: ASTM-E11 sieve, 88 %<~45μm.

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
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</thead>
<tbody>
<tr>
<td>1.31</td>
<td>0.65</td>
<td>0.41</td>
<td>0.018</td>
<td>0.02</td>
<td>4.2</td>
<td>0.13</td>
<td>5.1</td>
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<table>
<thead>
<tr>
<th>Nb</th>
<th>Cu</th>
<th>Co</th>
<th>V</th>
<th>Sn</th>
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<th>O</th>
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<tbody>
<tr>
<td>0.01</td>
<td>0.08</td>
<td>0.1</td>
<td>3.10</td>
<td>0.01</td>
<td>6.65</td>
<td>0.06</td>
<td>70</td>
</tr>
</tbody>
</table>

*Table 1. The chemical composition of the tool steel base material, Anval 9044.*

![Image of stainless steel powder](image2)

**Fig.2.** Anval2205. A stainless steel material, with the characteristic spherical shape of gas atomized metal powder. This alloy has been selected in order to maintain some desirable properties, should it reach full density after sintering. Size analysis: ASTM-E11 sieve, 91 %<~45μm.

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.017</td>
<td>0.68</td>
<td>1.11</td>
<td>0.017</td>
<td>0.001</td>
<td>22.4</td>
<td>5.19</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Mo</th>
<th>Nb</th>
<th>Cu</th>
<th>Co</th>
<th>V</th>
<th>W</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.00</td>
<td>0.01</td>
<td>0.14</td>
<td>0.03</td>
<td>0.07</td>
<td>0.02</td>
<td>0.18</td>
<td>110</td>
</tr>
</tbody>
</table>

*Table 2. The chemical composition of the stainless steel base material, Anval 2205, O in ppm.*
As the melting copper phase, a fine sized copper powder from Micron Metals, “Cu-110, 99.9%, spherical 1-5 micron” was selected, see Fig. 3, however, both the particle size and shape had apparently been evaluated by approximative method. The particles were considerable larger, thus out of the suitable size range for densification, and also of sponge like constitution. This will most likely have a less than positive effect on the densification of the powder mass when added to the base powder.

The filler material, particles to fit into the voids between the base material particles and melting phase particles, were a carbonyl iron powder, “Carbonyl SM” see Fig. 4. & Tab.3. This powder, of very small sized particles, has very high inner friction due to van der Waal’s and electrostatic forces, which will have a significant influence on the powder behavior.

**Table 3.** The chemical composition of the filler material, Carbonyl SM.
The composition of the different powders for optimization of particle density was determined by the same experimental procedure as described in [4]. However, since the amount of copper has been settled at 8%, the variation in composition concerned base and filler materials. The sampled tap densities of different powder compositions showed little variation, which suggests that the internal friction, (and probably also the less than perfect shape of the copper particles) has a significant influence on the behavior of powder composed of these powders. Still, a composition of 75% base material, 17% Carbonyl SM and 8% copper was found to have a modest maximum of tap density for both base materials, 63.3% for Anval 2205, and 66.3% for Anval 9044. However, after a few trials in the Sinterstation, the internal powder friction, was found to be to high, and the composition was modified to consist of 77% Anval 2205, 15% Carbonyl SM and 8% copper. Assuming that the present oxygen is in the shape of metal oxides and to ensure the deoxidizing of the material during vacuum processing, was a small addition of graphite made to the powder compound. Thus, the investigated powder compositions were:

<table>
<thead>
<tr>
<th>Anval 2205 I</th>
<th>Anval 2205 II</th>
<th>Anval 9044</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anval 2205</td>
<td>Anval 2205</td>
<td>Anval 2205</td>
</tr>
<tr>
<td>Carbonyl SM</td>
<td>Carbonyl SM</td>
<td>Carbonyl SM</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu</td>
<td>Cu</td>
</tr>
<tr>
<td>Graphite</td>
<td>Graphite</td>
<td>Graphite</td>
</tr>
<tr>
<td>74.91%</td>
<td>76.99%</td>
<td>74.92%</td>
</tr>
<tr>
<td>16.98%</td>
<td>15.00%</td>
<td>16.98%</td>
</tr>
<tr>
<td>7.99%</td>
<td>8.00%</td>
<td>7.99%</td>
</tr>
<tr>
<td>0.107%</td>
<td>0.097%</td>
<td>0.106%</td>
</tr>
</tbody>
</table>

4.2 Formation of Green Bodies

Build file: The software used in this experiment was slightly manipulated versions of standard material files for this equipment. Since this investigation required the option to vary a number of variables, such as laser powers and scanning speeds, a material file for DTM’s Duraf orm material was used, although this limits the powder layer thickness not to be smaller than 0.08 mm, which probably is thicker than optimal for this application. Since the metallic bonded green bodies in previous work has been known to curl in each layer, [6], [8], was one of the parts integrated in the build file a 10 mm thick mesh structure in which the other parts were partially embedded. This piece, while curling slightly, anchored the parts in the surrounding powder and thus acted as a support, until the formed green body was rigid enough to resist the curling effect, see Fig. 5.

*Fig. 5. Support mesh and parts in position. The powder is spread in this picture’s left-right direction.*

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Investigation of the Liquid Phase Sintering of Size Range Composed Powder for SLS Application

Powder application: Initial trials were used to investigate the spreading behavior and to determine the suitable powder deposition variables, following the same procedure as in [4]. It was found that, while tap densities for the Anval 2205 I and Anval 9044 blends had been well above 63%, the applied densities of these blends barely reached 61%. Since the applied powder layers, especially for Anval 2205, also had a small tendency to crack at the surface, a behavior typical for powders with too high inter particle friction, it was concluded that the combination of these powders, despite only two size range components and altogether smooth and spherical particle shapes, still involves too much interparticle friction to arrange in a favorable manner in the Sinterstation.

Test 1. Anval 2205 I: Fine but very brittle metallic bonded green bodies were formed using fill laser powers 25–35 W, fill scan speeds 450–500 mm/s, outline laser power 25 W, outline scan speed 600 mm/s, and layer thickness 0.08 mm, see Fig. 6. Monitoring the powder bed’s behavior during scanning, it was noted that some rearrangement of powder apparently took place, and that the green body, apart from some curling, occurring from layer 2 until approximately 5 mm build height, tended to rise slightly from the surrounding powder mass.

Test 2. Anval 2205 II: More curling and slightly stronger green bodies were formed using the new powder composition, fill- and outline laser powers 30-35 W, and fill- and outline scanning speeds 400-450 mm/s. Similar powder orientation behavior as in the previous test was noted, see Fig. 7. However, the applied powder density was raised to 64.6%.

Test 3. Anval 9044: The further increase of laser powers: fill- 35-40 W, outline laser power 30-37 W, and decrease in scanning speeds: fill- 350-400 mm/s, and outline scanning speed 300-370 mm/s, relative to the previous tests, has further increased orientation and curling. However, the green bodies were strong enough to be handled and cleaned without breakage despite thin sections, see Fig. 8. It is also noted that the bonds in each layer is considerably stronger than the bonds between layers. Meanwhile, the surface quality along the outlines decreases with increased exposure to laser energy.
Test 4. Anval 9044: At these levels laser power, fill- 35-40 W, outline- 30-37 W and scanning speeds fill- 300-350 mm/s, outline- 250-320 mm/s, is the curling severe, and the green bodies so strong that the first layers, up until approximately 6 mm, shifts and moves with the passing of the roller. While the green bodies were strong, the surface quality along the outline was rather poor, see Fig. 9.

SEM micrographs of the green bodies’ surfaces reveal further information about the powders’ behavior during the SLS processing see Fig. 10, 11, & 12. The powder has not been arranged in any favorable manner, which confirms the negative influence of interparticle friction. Apparently, a fraction of the powder has melted, and since copper is the powder blend component with the lowest melting temperature, it is reasonable to assume that the melted part is copper. Furthermore, it appears, as the smallest particles are arranged closer together, opening wider pores as the green bodies had been exposed to more laser energy (Fig. 10, & 12.). This implies that there has been some sort of rearrangement among the smaller particles, which has been dependent on heat exposure.
4.3 Sintering

Furnace procedure: The green bodies were sintered in a conventional vacuum furnace in accordance with calculations and the principles described in [12]. The temperature was raised to 1200 °C at a rate of 200 °C/h, held at this temperature for 4 h, when the temperature was lowered at the same rate. The parts were placed on an alumina powder bed, in a graphite crucible, with no surrounding powder for support.

Result: Some sintering and thus shrinkage took place, see Fig. 13, 14, 15 & 16, however not to full density and significant porosity remained in all parts, see Fig. 17, 18 & 19. Green bodies that had been subjected to a higher laser energy were more rigid and maintained their shape better, including overhangs, during sintering, whereas the weaker bonded green bodies tended to sag under their own weight. The porosity is mainly oriented along the layers and laser scanning paths, and appears to be more severe if the green bodies were formed with a higher laser power, Fig. 17 & 18. This could be an effect of the particle orientation observed in the green bodies.
5. Discussion and Conclusions

Despite being composed by powder within the size range interval determined in [4], it appears that the interparticle friction is too high to reach any higher powder packing densities, though the achievable powder densities was further limited by the copper particles’ deviation from the expected size and shape. Nevertheless, interparticle friction is dependent on the particle size of all particles in the powder blend, and it is likely that improved powder performance could be achieved by using larger particles for the base material, both in respect to interparticle friction and the less than perfect copper particles. However, this solution would prolong the sintering times to dissolve all the liquid material and could also make thicker layers necessary, and thus obstruct the laser heat penetration and bonding to the underlying layer.

The green bodies were joined by metallic bonds. Partially by of surface diffusion, but as it appears, mostly by the melting of copper particles, not at all unlike brazing. If so, it can also be concluded that the principal cause for the curling of the layers is the shrinking of copper curing solidification. With the copper melted, it is further reasonable to assume that some liquid phase sintering is in progress at this stage, which would account for the increased green strength and curling of the green bodies at increased laser powers and slower scanning speeds. Furthermore, this could explain a part of the rearrangement of particles noted. Rearrangement is caused by surface diffusion, and occurs normally at the initial stage of sintering [2], and normally leads to densification. However, in this case the powder particles are arranged with local areas of higher density while there are other areas of lower density. Since the liquid copper only seems to wet a fraction of the particles, this causes uneven LPS, for a brief period of time. Meanwhile, the surface diffusion strives to straighten the points of contact between particles, which will cause a movement among the small sized particles, which has been known to widen large pores in areas of already low density [14]. This effect is also known to increase with smaller particle sizes and could have affected the behavior during the furnace process.
Investigation of the Liquid Phase Sintering of Size Range Composed Powder for SLS Application

This effect could have been further enhanced by the laser formation of metallic bonded green bodies. Since the exposed areas have been subjected to a higher thermal impact, the melted material has been concentrated to these areas, likewise braze in a brazing operation. Areas that have not directly been exposed to the laser have thus only sintered and bonded by heat conduction. The new layers have been applied to surfaces with oriented particles, and the points of contact with the previous layer have not been directly exposed to the laser and therefore have weaker bonding. When the green bodies are processed in the furnace the sintering has been directed by the particle orientation, and there has not been enough liquid phase to wet all surfaces simultaneously to compensate for this and allow complete pore closure.

This investigation was aimed at finding the principal limiting factors, to form solid parts from a variety of homogenous steel materials by LPS of SLS shaped green bodies using size range composed powder. While this possibility cannot be eliminated at this stage, here are some difficulties to come to terms with.

1. Powder composition: The particle size ranges of the different powders should fulfill certain criteria to allow the application with high density in a Sinterstation. Apart from particle shape and size proportions there are smallest acceptable sizes for base material (larger particles) as well as fill material and melting phase, (smaller size range). The adverse effect of interparticle friction caused by small sized particles is well known. However, the size of the larger particles is a principal limiting factor for the layer thickness, which is important not only for part precision but also for laser energy penetration and therefore also a determining factor for the green strength. This is obviously a matter for optimization.

2. Sintering time and temperatures: To achieve homogeneity in the material, the sintering time must be long enough and temperatures must be high enough to permit the homogenization by diffusion of all materials. One critical variable for this is the largest particles’ size. Diffusion rates increase with increased temperatures, however dependent on the base material there are upper practical limits for the sintering temperatures. For most traditional tool steels, these are determined mainly particle coarsening and melting temperatures. In the present tool steel this would probably allow processing at somewhat higher temperature than used in this investigation. Stainless steels are due to evaporation of important alloying components, more sensitive to high temperatures during vacuum furnace processing, and would require a different strategy to reach full density.

3. The fraction of melting phase: Despite no apparent segregation of copper in the applied powder material and long sintering time, there has been a concentration of liquid copper to certain areas during the laser- and subsequent furnace treatment. The liquid phase during the furnace sintering has not been sufficient, by amount and/or distribution to wet all surfaces and stimulate pore closure in the whole green body. But if homogeneity is to be achieved, copper levels are limited by the solubility in the base material during sintering. Therefore, one likely way for further investigation of this possibility would be to identify another suitable liquid phase material with the capacity to dissolve into the base material. But even so, will that material have to be successfully integrated in the powder, particularly in regard to powder density and spreading characteristics as well as interaction with the laser.
References
A GENERIC SYSTEM FOR HOMOGENEOUS SLS STEEL MATERIALS

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Sweden

Abstract
A generic approach to a variety of different steel materials for SLS based application has been examined. This approach is based on a base steel alloy powder mixed with a powder blend of much smaller particles. The powder blend is designed to both provide the highest possible density in the powder mass and melting material components for liquid phase sintering to full density. Furthermore, the liquid phase components in the powder blend are composed to both serve as a metallic binder for the green bodies and maintain the possibility to completely dissolve into the base material, forming a homogenous alloy. A powder blend with stainless steel base material was composed and tested and taken through the different process steps. While the formation of green bodies had limited success, to a large extent due to limitations in the process equipment, the sintering and diffusion behaviour showed promising results, both in respect to acquired densities, and homogeneity of the material.

1. Introduction
While conventional polymer based SFF has established a position as an important strategic tool for the manufacturing of prototypes, and is gaining momentum as a competitive direct manufacturing process for parts with complex or unique shapes, a similar development for the metallic applications still seems distant. The most important reasons for this may be found in the combination of the inherent constrains within the different approaches to metallic SFF processes, and the limitations in the selections of materials, available for SFF applications [1]. Therefore, developments in these areas could significantly improve the capacity for new applications of SFF technology. Since steel materials are established for a very wide set of applications, with a long tradition as the engineering materials of choice, most potential users are likely to have steel materials as a major point of reference. Homogenous, SFF applicable steel materials, with similar properties as conventional steels, would therefore not only improve the capacity for SFF manufactured parts, they would also bring the technology closer to the users’ point of reference and thereby make it appear less alien to the potential user.

However, for such a material development to have any significant impact, it should preferably be applicable to a SFF system with a wide distribution on the market. This is possible with a procedure beginning with the formation of porous steel powder green bodies by the use of SLS, followed by metallic consolidation and homogenisation by liquid phase sintering in a subsequent furnace process. A generic approach to this procedure, where most variables can be kept constant, except for those characteristic for the desired outcome, would not only offer SFF products of a homogenous steel material to a wider market, it would also facilitate the development of a much larger number of steel materials for a wide set of applications. (The term "homogeneous" is in this text referring to solid non-porous steel alloy, with phase structure corresponding to as-cast material of the specific alloy composition, with respect to heat
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treatments. This term is used to mark the difference from the composite or highly segregated materials used in some commercial application of metals SFF.)

The whole procedure, from powder composition, application and processing in the SLS equipment, to the sintering and consolidation during the furnace treatment, is a vast area with a large number of variables, which could be used in many possible different combinations. Considering the endless possible variations, it is hardly possible to scientifically prove that such a material system and procedure is impossible. However, since this hypothesis is concerning technical matters, any successful attempt on any part of the procedure, would indicate that the whole procedure is possible, which is the principal object of this research. Another object is to find which variables are critical to control, and how they affect the outcome of the process. In respect of this, the style of this work will be investigative and argumentative.

2. Background

The formation of parts made of homogenous steel alloy, from SLS, with a subsequent furnace procedure, is a very complex project where a number of variables may be of significant importance. This has been the subject for a series of investigations in the past [2], [3], [4], and [5]. This present work is based on conclusions and acquired knowledge from the preceding investigations as well as the application of established knowledge in conventional powder metallurgy. The approach can be separated into three distinct steps: powder composition, formation of green bodies, and the furnace process, were the limitations and results of each step, affects the conditions for the others.

2.1. Powder composition

If one step should be singled out as being the most critical, it should be the powder composition. Obviously, the powder composition determines the alloy composition of the finished material, but it is also fundamental for every part of each process step, from spreading and application of powder in thin layers, to the sintering into full density and homogenisation of the finished product.

The principal idea of the present process approach, is to combine a base material powder, which’s alloy composition will dominate the finished material, with lower melting temperature components, that will serve as a liquid phase during sintering and ideally completely dissolve into the base material, forming the desired homogenous steel alloy. As a most demanding example, a stainless steel, Anval 2205, has been selected as base material for this present investigation, however the principle as such, is generic and could be applied to a vast number of different steel materials.

For liquid phase, previous work has exclusively used copper, [2], [4] and [5], partly for being established in conventional powder metallurgy, as a liquid phase with good sintering properties for iron based alloys, but also because it does improve some desirable properties, such as corrosion resistance, strength and toughness, [6].

However, the amount of copper that can dissolve into the base material is limited, and for successful liquid phase sintering into full density, with a limited amount of liquid phase, it is important to have the powder mass as dense as possible. This has been experienced and
addressed in the past [2], [4] and [5]. It was found that using a suitable combination of size ranges and particle shapes in the correct proportions, will improve the density of the powder layers applied in the SLS equipment, [3]. Since the base material is expected to remain stable, and maintain the geometrical shape of the part during the furnace process, the base material should obviously be the largest fraction and also largest sized particles in the powder blend. Additional components, such as the melting material, should, if possible be kept at particle sizes that will fit into the voids between the larger particles.

This approach has been tried with -44µm Anval 2205 powder, copper powder of the smallest particle size available, and with an additional amount of small particle size carbonyl iron powder for further densification, [5]. However the high inner friction, and the unexpected unfavourable size range relation between base powder and copper in the powder mass gave the powder blend poor particle packing properties. This, in combination with the low fraction of melting material for the liquid phase sintering (8%), made it impossible to achieve full density in the material. Therefore has this present investigation changed the size range for the base material to 44µm - 75µm, and added a second melting material: ferrophosphorus. Fig.1, & Tab.1, Fig.2, Fig.3, & Tab.2, Fig.4, & Tab.3.

**Table 1.** The chemical composition of the stainless steel base material, Anval 2205. O in ppm.

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<td>0.02</td>
<td>0.19</td>
<td>165</td>
</tr>
</tbody>
</table>

**Fig.1.** Anval2205. A stainless steel material, with the characteristic smooth shape of gas atomised metal powder. This alloy has been selected as a challenging material with interesting properties. Size analysis: ASTM-E11 sieves, 99% < 75µm, 9% < 45µm.

**Fig.2.** Copper powder, 99.9% Cu. According to vendor 1-5 µm spherical shape, which in reality obviously is not the case. This discrepancy is however most likely due to the method of measuring and calculating size. In many cases are such small sized particle’s size estimated by a measured value for particle surface that is recalculated to volume and diameter assuming spherical shape. For a sponge like powder such as this, this method would indicate a much smaller particles size than really is the case. For this investigation this defect will not disturb the size range composition, however, it will limit the density improvement.
Phosphorus, P, is a well-known additive to powder compositions to improve sintering properties by liquid phase sintering, though other positive side effects, such as improved tensile strength, elongation and hardness, with small additions of P, has been reported from conventional powder metallurgy, [7]. The best results were acquired with additions of 0.75 % - 0.80% P, and the added amount of ferrophosphorus will therefore be adjusted to yield this content of P to the finished material.

2.2. Formation of green bodies
This process is expected to be capable to deliver hollow parts and geometries with deep cavities, and since the part in all cases will be subjected to a significant shrinkage during liquid phase sintering, a supportive powder during the furnace process is not desirable. Therefore, organic binders, requiring a supportive powder during the binder burn out and the early stages of sintering, should be avoided. This issue has been addressed in previous work, [4] and [5], and it has been found that despite the low absorbance of energy from a carbon dioxide laser, copper can be melted during SLS processing and thus work as a metallic binder. The green bodies formed are however quite brittle, with especially weak bonds between the layers. On the other hand, in this present investigation, there is possibility that the second melting phase, ferrophosphorus, also could melt at process conditions and improve this situation.
Since copper has such low absorbance for energy transmitted by carbon dioxide lasers [8], it is more likely that it is secondary heating that melts the copper. The laser energy is absorbed by the iron-based particles, which in turn heats the adjoining copper particles until melting and bonding occurs. If so, the increased particle size will require more energy to raise the temperature of the base material particles to the melting point of copper (1084.5 °C) and even more for ferrophosphorus, (melting point 1168.0 °C), if the same heating mechanism is active as in copper. Since the equipment available for this investigation is a rather old Sinterstation 2000, 50 W CO2 laser, with a measured maximum output of 41.5 W, this may be a crucial limiting factor for the formation of green bodies. However, the formation of perfect green bodies is not the primary object of this investigation, but the establishment of a generic principle for a series of homogenous steel materials that could be achieved from a procedure consisting of SLS and a subsequent furnace process. For this object, sintering and homogenisation behaviour is more vita, and it is sufficient to show that green bodies can be formed by SLS, while quality is of less importance at this stage.

2.3. Furnace process conditions

The feasibility, as well as process time and temperatures for the furnace procedure, in order to achieve a homogenous, liquid phase sintered steel material, are determined by some important boundary conditions. First of all, the process parameters must allow the liquid components (here: copper and ferrophosphorus) in the powder composition to melt and sinter the material to full density. Second, the process time and temperature must be sufficient for the liquid material to completely dissolve into the base material, as well as allowing the alloy components from the base steel to homogeneously be distributed within whole part, both by means of diffusion. Third, since the risk of evaporation of alloy components from the material during the vacuum process is controlled by the combined effect of temperature and pressure, there is an upper limit on the acceptable temperatures, or a lower limit for pressures, at process conditions. Meanwhile the pressure in the process chamber must be kept low enough to allow deoxidation of the material during the process. Fourth, the processing time must be as short as possible, partly to avoid unnecessary grain growth, but also to keep the process times at a competitive level.

However, this complex situation can be simplified by applying standard settings for vacuum pressure, and thus leave time and temperatures as the process controlling variables. Further simplifications can be made by application of conclusions from previous work. It has been found that at standard vacuum settings, temperatures above 1200 °C will cause evaporation of chromium from stainless steel powder, (1233.6 °C for 22.4% Cr) [5]. Therefore 1200 °C can be considered a maximum process temperature, which, in combination with vacuum, will allow the deoxidation reaction between carbon present in the powder blend, and oxide on the particles’ surfaces. This leaves process time as the critical variable to control.

Since the copper’s only means for dissolving into the steel material under these process conditions is by self-diffusion, and the longest predictable diffusion distance for any material under these circumstances is from the surface to the centre of the largest particles, the diffusion of copper through the base material will be the determining factor of the process times. This simplification may overlook the closure of large pores, but the occurrence of those, as well as their size and distribution, is not entirely predictable, and must be experienced experimentally.
The previously mentioned investigation, [5], also found that 4 h would be sufficient process time for 8% copper to completely dissolve into -44μm base material steel powder. However, in this present investigation the size range for the base material has been changed to 44μm - 75μm, and ferrophosphorus has been added as a second melting material. The increased particle diameter gives an increased maximum diffusion distance, which, reasonably, would increase the required process times beyond practical and competitive limits. However, that investigation and the following estimation of process time are based on the assumption of the atomic configuration of γ-iron, which would normally be the phase present for most steels at process temperatures, especially since the added copper is γ-stabilising. But, in this case, ferrophosphorus is added as a second melting material, and this could vitally change the conditions for the diffusion of copper and other alloying components.

Phosphorus is known to have a powerful stabilising effect for α-phase and, compared to for example copper, a rapid diffusion behaviour in both α- and γ-phase. Therefore, the hypothesis is, that the phosphorus will diffuse into the base material of γ-phase configuration, ahead of copper and other significant alloying components, and thus cause a phase transformation to α-phase. Since the atomic configuration of α-phase steel allows higher rates of diffusion for copper than γ-phase, this would probably make it possible to achieve homogeneous distribution of alloying- and former liquid components in the finished steel material within reasonable process times. This, in combination with the additional amount of liquid phase and increased powder packing densities could make it possible to achieve a homogenous steel material with no, or very low porosity, by SLS and a subsequent furnace processing.

2.4. Calculations

The time to dissolve the copper into the base material is controlled by the fractional saturation of copper in the base material particles. Darken & Gurry [9] gives us the relationship:

For diffusion into spherical shape: \[ \frac{Dt}{L^2} = -0.05043 - 0.2333 \log(1 - F) \] [Eq. 1]

Diffusion constant, \[ D = D_T \frac{F}{C_0} = 1.8 \exp \left[ \frac{-295 \text{kJ} \text{mol}^{-1}}{RT} \right] \frac{\text{cm}^2}{\text{s}} \] [Eq. 2], [10].

Fractional saturation, \[ F = \frac{C_a - C_0}{C_s - C_0} \] [Eq. 3], and \( L \) is the diffusion distance, here the radius of the base material particles. From previous work [5], we know that at 1200 °C, 8% copper can theoretically be completely dissolved in spherical -44μm steel powder, in 3.85 hours. For reasons previously mentioned, a particle size range of 44μm - 75μm has been used for this present investigation. With 75μm powder particles, the diffusion distance is 0.00375 cm. Added copper, \( C_a = 8\% \), at 1200 °C saturation of copper is \( C_s = 9\% \), which gives \( F = 0.889 \). Applied to [Eq. 1], \[ \frac{Dt}{L^2} = 0.17 \]. At 1200 °C is \( D_T \frac{F}{C_0} = 6.21 \times 10^{-11} \Rightarrow t = 369.42 \) h, which is too long. However, with phosphorus induced phase transformation, diffusion is expected to take place in α-phase where,

\[ D = D_{\alpha} \frac{F}{C_0} = 8.6 \exp \left[ \frac{-250 \text{kJ} \text{mol}^{-1}}{RT} \right] \frac{\text{cm}^2}{\text{s}} \] [Eq. 4], [10]. Under these conditions \( D_{\alpha} \frac{F}{C_0} = 1.17 \times 10^{-8} \Rightarrow t = 204.32 \) s (!), which is much more reasonable.
However, these ideal conditions cannot be fully expected under real process conditions. For example, if the material has sintered to full density, the particles will not be spherical during the whole dissolving process. Complete homogeneity concerning pore size and orientation, or particle distribution within the green body can neither be expected. Furthermore, the liquid phase will be a solution melted copper and ferrophosphorus, which means that the concentration of the different elements will vary during the process, and during the diffusion of copper, the balance between α-, and γ-phase in the outer perimeter of each particle is difficult to predict, and therefore also the real diffusion rate. Considerable longer process times will therefore be used for this investigation, however the calculations above demonstrates that complete dissolving and diffusion to homogeneity is not unreasonable to expect with this material composition and process conditions.

3. Experimental

The experimental part of this investigation follows the principles outlined in the background section. The powder blend is composed to yield maximum applied powder density using the selected powders. Green bodies are formed using SLS equipment, and processed to full density in a vacuum furnace. Samples examined regarding porosity and have been further analysed regarding alloy composition and distribution using SEM equipment at the Department of Materials and Engineering, KTH.

3.1. Powder composition

The different selected powder materials have to be combined in the correct proportions to yield the expected results. The amounts of the different liquid components is determined by their respective solubility in the base material, and possible desirable effects on the material properties of the final alloy. Copper has a good solubility in iron-based alloys up to around 8 %, at process conditions, which settles the share of copper. Phosphorus has been reported to have most positive effect on material properties at 0.8 % P. The added ferrophosphorus contains 15.6 % P, which makes an addition of 5.12 % yield the desirable amount of P in the final material. This combination would give a liquid share of 13.12 %, which is slightly less than conventional, [11]. However if the experiment should indicate that the liquid share is too small for pore closure, it is possible to increase the addition of ferrophosphorus.

Besides getting the right amount of liquid phase, it is also important have the highest density possible in the powder mass. Since the amount of small sized particles for the liquid phase has been determined by other boundary conditions, the remaining means to control this issue is the combination of large particle base material, Anval 2205, and a fill material powder with much smaller particle size, in this case Carbonyl Iron SM.

The suitable proportions was found experimentally using the procedure described in [3], with the amounts of copper and ferrophosphorus kept constant at 8 % respective 5.12 %. The final powder composition can be seen in Tab.4, Fig.5, showing the powder blend gives an impression of particle size proportions and packing behaviour. The density of the applied powder layers in the SLS equipment was measured by the procedure described in [3], and was found to range between 65.8 % and 67.4 %, which seems promising for the following process steps.
Table 4. The composition of the powder blend.

Fig. 5. The powder composition after mixing.

3.2. Formation of green bodies
The determined powder composition was exposed to SLS processing for several attempts with successively increased laser power and decreased scanning speeds before any usable green bodies could be formed. This occurred at the very limit of machine capacity. Apparently, the assumption concerning the need for increased energy due to the increase in base material particle size was correct. Still, green bodies were formed, however of poor strength, with very weak bonds and high porosity between the layers, and with a strong tendency for curling of the layers. It is a likely assumption that only copper melted to serve as a binder, and that this situation could improve, in terms of improving green strength by melting the of ferrophosphorus, with the use of a more powerful laser, such as the 100 W laser common in more modern versions of SLS equipment from DTM/3Dsystems, or the even stronger lasers used by EOS.

3.3. Furnace processing
Samples were sintered in a conventional vacuum furnace, in accordance with conditions described in the calculations section, and the principles described in [12]. The parts were placed on an alumina bed, in a graphite crucible, with no supportive powder and loaded into the furnace. The temperature was raised to 1200 °C at a rate of 200 °C/h, held at that temperature for 4 h, when the temperature was lowered at the same rate.

4. Results and analysis
The samples had sintered to solid objects and undergone some shrinkage, **Fig. 6**, notable is the fact that the samples with less successful layer adhesion have had less shrinkage in X–Y direction, instead, the more separated layers have had a predominant shrinkage in Z–direction, whereas the samples with more successful adhesion between the layers have shrunk more equally in all three dimensions. Furthermore, some sagging of large overhangs can be noted. Looking deeper into the material we find that there are some remaining pores, predominantly oriented in between powder layers, **Fig. 7**. However none of these imperfections are unexpected, and could probably be traced to the less than perfect conditions during the formation of green bodies.
More interesting, still, is the analysis of material alloy and distribution of alloy elements in the material. It shows that complete homogeneity has not been reached, which is quite reasonable, complete homogeneity hardly exist even in conventional steels. Certain elements naturally concentrate into certain phases, and nothing else could be expected under these circumstances. But the distribution analysis as shown in Fig.8 and Fig.9, displays encouraging tendencies.
From an overall view, all elements are fairly even distributed over both areas analysed. There are however some points were certain elements (for example Cu & Si) are especially concentrated, and other elements, for example iron, is sparse. This could probably be traced back to the liquid phase during sintering. Silicon is highly soluble in both liquid copper and iron (such as in ferrophosphorus), and since phosphorus has the higher diffusion rate, iron will leave the liquid phase ahead of copper, thus the dissolved silicon will concentrate to the liquid copper. As pores are closing during the sintering process, remaining liquid material, in this case copper, will concentrate to the remaining larger pores. With the larger amounts of copper amassed in a small region, it is hardly surprising that all copper will not dissolve into the surrounding material within the limited process time.

Fig.9. The second distribution analysis of important elements covering an area of 51.0 x 42.3 μm. The tendencies from previous analysis appear to be confirmed. There are some areas where Cu and Si have been enriched, while P and Mo have been concentrated to certain phases.
5. Discussion and conclusions

The primary aim for this investigation was to explore a possible generic principle to build parts of homogenous steel, using SLS equipment in combination with a subsequent furnace procedure. Despite the obvious shortcomings of the parts manufactured, it is not unreasonable to say that this possibility has been confirmed. Solid pieces of steel were formed from green parts made in the SLS machine, and the analysis of the distribution of the principal alloy elements shows, with some exceptions, a reasonable even dispersion.

However the material selected for this investigation was a stainless steel, and apart from the most general material properties, such as tensile strength, hardness, and others, the corrosion resistance of the new alloy still has to be determined. This could be problematic, however, since there still are some areas with significant porosity or with excess concentration of, for example, copper. How much this would influence the corrosion resistance by crevice- or galvanic corrosion is unclear, but any measurements on the available pieces would not be conclusive either. As mentioned earlier, the areas with excess copper concentration probably originates in large pores, and since the porosity is primarily oriented between the applied powder layers, these could thus in many cases be deduced to poor adhesion of powder layers. Small pores could be addressed by increasing the fraction of liquid phase in the powder blend, but the large pores, which could end up filled with remaining copper, are more difficult and the best would be if they could be avoided altogether. One likely way to at least decrease their frequency could be to improve the adhesion between the layers.

The most obvious method to improve layer adhesion would be to increase the laser power. A more powerful laser, such as those installed in more modern SLS machines on the market by DTM/3D Systems and EOS would penetrate deeper into the powder layer and thereby increase the melting of material in between the layers. Furthermore, the higher laser effect would enable the melting of the ferrophosphorus during SLS, thus increasing the metal bonding and thereby further improve the quality of the green bodies. On the other hand more extensive metallic bonding will also increase the temperature induced tensions in the green bodies, though these tensions will be relieved during the furnace process. If needed for complete pore closure, the fraction of liquid phase (here the ferrophosphorus) could be increased. However, a less desirable effect, of increased fraction liquid phase would most likely be an increase of the small sagging observed on the sintered parts, and thus loss of part geometry. On the other hand this behaviour could probably be moderated by stronger metallic bonds in the green bodies that comes with an increase in laser power.

The full process of making solid homogenous steel objects from an SLS approach could not be verified by this investigation. However, the acquired results concerning sintering and diffusion are encouraging, and while the observations of the SLS behaviour are challenging, they do not contradict this possibility.
References

Appendix 1

Appendix 1: Analysis Results By SEMQuant

SEMQuant results. Listed at 16:54:41 PM on 15/09/2003
Operator: Hans Bergqvist
Client: none
Job Code 030582
Spectrum label: kurttings smitt mitt
System resolution = 71 eV
Quantitative method: ZAF 3 iterations.
Analysed all elements and normalised results.
1 peak possibly omitted: 0.00 keV

Standards :

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* = < 2 Sigma

SEMQuant results. Listed at 16:54:41 PM on 15/09/2003
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Client: none
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System resolution = 62 eV
Quantitative method: ZAF 3 iterations.
Analysed all elements and normalised results.
1 peak possibly omitted: 0.00 keV

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* = < 2 Sigma

SEMQuant results. Listed at 16:54:41 PM on 15/09/2003
Operator: Hans Bergqvist
Client: none
Job Code 030582
Spectrum label: kurttings smitt atm transm aver area
System resolution = 62 eV
Quantitative method: ZAF 3 iterations.
Analysed all elements and normalised results.
1 peak possibly omitted: 0.00 keV

Standards :

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Appendix

SEM Quant results, listed at 13:34:06 PM on 16/09/2003
Operator: Hanne Bergsøe
Client: none
Job: Boivie 030427
Spectrum label: Rutnat snitt parallelt med ytan
System resolution = 62 keV
Quantitative method: ZAF (3 iterations).
Analysed all elements and normalised results.
1 peak possibly omitted: 0.00 keV

Standards:
- O K 21/08/2003
- Al K Al203 08/07/93
- Si K 21/08/2003
- P K Gap 07/07/93
- Ti K Wide 06/07/93
- Cr K Ca 06/07/93
- Fe K Fe 06/07/93
- Ni K Si 06/07/93
- Cu K Cu 07/07/93
- Mo L Mo 06/07/93

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