

# Liquid phase sintering of W-Ni-Fe composites – Initial melt penetration, agglomerate separation and particle interaction

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## Abstract

The initial stage of liquid phase sintering, involving liquid penetration, agglomerate separation, particle spreading and growth has been investigated in experiments using tungsten heavy alloys. The particle composites used were produced by hot isostatic pressing (HIP) of pure powder mixtures of W-Ni-Fe-(Co). By using different HIP temperatures, volume fractions of tungsten, alloying elements like Cobalt and Sulphur or excluding Iron from the matrix, liquid penetration, agglomerate separation and particle growth conditions were affected. The investigations were performed mainly under microgravity (sounding rockets or parabolic trajectories by airplanes) but at short sintering times or at infiltration of solid tungsten, they were done at normal gravity.

The liquid penetration of the tungsten agglomerates is explained by initial wetting under non-equilibrium conditions, due to the reaction between the liquid matrix and the particles, and a decrease of interfacial energy. The dissolving of tungsten gives a pressure drop in the penetrating liquid and a driving force for the liquid movement by a suggested parabolic penetration model. For cold worked tungsten, a penetration theory was proposed, where an internal stress release in the penetrated tungsten grains creates space for the advancing liquid.

The spreading of the tungsten agglomerates is explained by an interagglomerate melt swelling due to a Kirkendall effect. The liquid matrix undergoes a volume increase since the diffusion rates of Ni-Fe are higher than for W and initial concentration gradients of W and Ni, Fe exists. The suggested model by Kirkendall is also used for an analysis of the interaction behaviour between solid particles and a solidification front and inclusion behaviour in iron base alloys during teeming and deoxidation.

The average tungsten particles size decrease initially since part of the tungsten particles is dissolved when the non-equilibrium matrix phase is melting. When equilibrium is reached, the tungsten particles grow in accordance with the Ostwald ripening process by an approximately  $1/3$  power law. Larger particle fraction of particles showed a higher growth rate, due to shorter diffusion distances between the particles. Cobalt, sulphur and absence of iron in the matrix were found to increase the growth rate of the tungsten particles due to a higher surface tension between the solid tungsten particles and the matrix melt.

**Keywords:** Liquid phase sintering, heavy metal, particle composites, tungsten, penetration, agglomerate separation, particle interaction, parabolic flight, sounding rockets, microgravity, Kirkendall effect.

**The thesis comprises an introduction and the following papers, referred to by roman numerals:**

- I. Liquid Phase Sintering of Tungsten Composites in Space: Results of Tests Performed in Texas.  
L.B. Ekbom and A. Eliasson.  
Adv. Space Res., vol 8, no 12, pp 315-319, (1988).
- II. Liquid Phase Sintering under Microgravity in Space.  
L.B. Ekbom and A. Eliasson.  
Mod. Dev. Powder Met., MPIF, vol 19, pp 63-73, (1988).
- III. Liquid-phase Sintering of Tungsten Composites in Space. Agglomerate Separation and Particle Growth.  
L.B. Ekbom, A. Eliasson and H. Fredriksson.  
High Temp. - High Press., vol 21, pp 507-514, (1989).
- IV. Microgravity Applications Furnace Facility, MAFF, for Parabolic Flights.  
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Proc. VIIIth Europ. Symp. Mat. and Fluid Sci. in Microg., Brussels, April 1992. ESA SP-333, vol 1, pp 383-386, (1992).
- V. Liquid Phase Sintering of Tungsten Composites under Microgravity. Effect of Matrix Composition. Particle Growth.  
L.B. Ekbom and A. Eliasson.  
Proc. Tungsten & Tungsten Alloys, Washington DC, pp 97-110, (1992).
- VI. Liquid Phase Sintering of Tungsten Composites under Microgravity. Effect of Matrix Composition.  
L.B. Ekbom and A. Eliasson.  
Microgravity Q., vol 2, no 4, pp 227-232, (1992).
- VII. Liquid Phase Sintering of Tungsten Composites.  
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Int. J. Refr. Metals & Hard Materials, vol 13, pp 173-179, (1995).

- IX. Liquid Ni-Fe penetration and recrystallisation in tungsten.  
T. Antonsson, L. Ekbom, A. Eliasson and H. Fredriksson.  
Int. J. Refr. Metals & Hard Materials, vol 21, pp 159-170, (2003).
- X. Liquid Penetration and Particle Separation during the Initial Stage of Liquid Phase Sintering.  
A. Eliasson, L. Ekbom, H. Fredriksson.  
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- XI. Interaction behaviour between solid inclusions and solidification front and inclusion behaviour in iron base alloys during teeming and at deoxidation by the Kirkendall Effect.  
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## 1 Introduction and background of thesis

A system frequently used for the study of liquid phase sintering (LPS) is tungsten heavy metal. The tungsten heavy metal is a particle composite of tungsten single crystals in a solid solution matrix of Ni-Fe-W. Ekbom<sup>1</sup> has reviewed the fabrication and properties of tungsten heavy metals and several other authors<sup>2-6</sup> has studied particle growth, particle shape accommodation and pore formation in this system.

These heavy alloys are ideal for studies of the initial processes in liquid phase sintering since the liquid matrix shows good wettability of the solid particles and the solid tungsten phase has a high solubility in the liquid matrix. The matrix elements, Ni and Fe, on the other hand, have a very low solubility in the solid tungsten particles, as shown by Lodding<sup>7</sup>. At sintering, the equilibrium dihedral angle (the liquid penetration angle) is small, around 25-30 deg.<sup>8</sup>, and the surface energy differences, the wetting is favourable both which makes the alloy system suitable for the study of sintering and densification. A schematic representation of the initial stages of the liquid phase sintering process is found in Fig. 1.

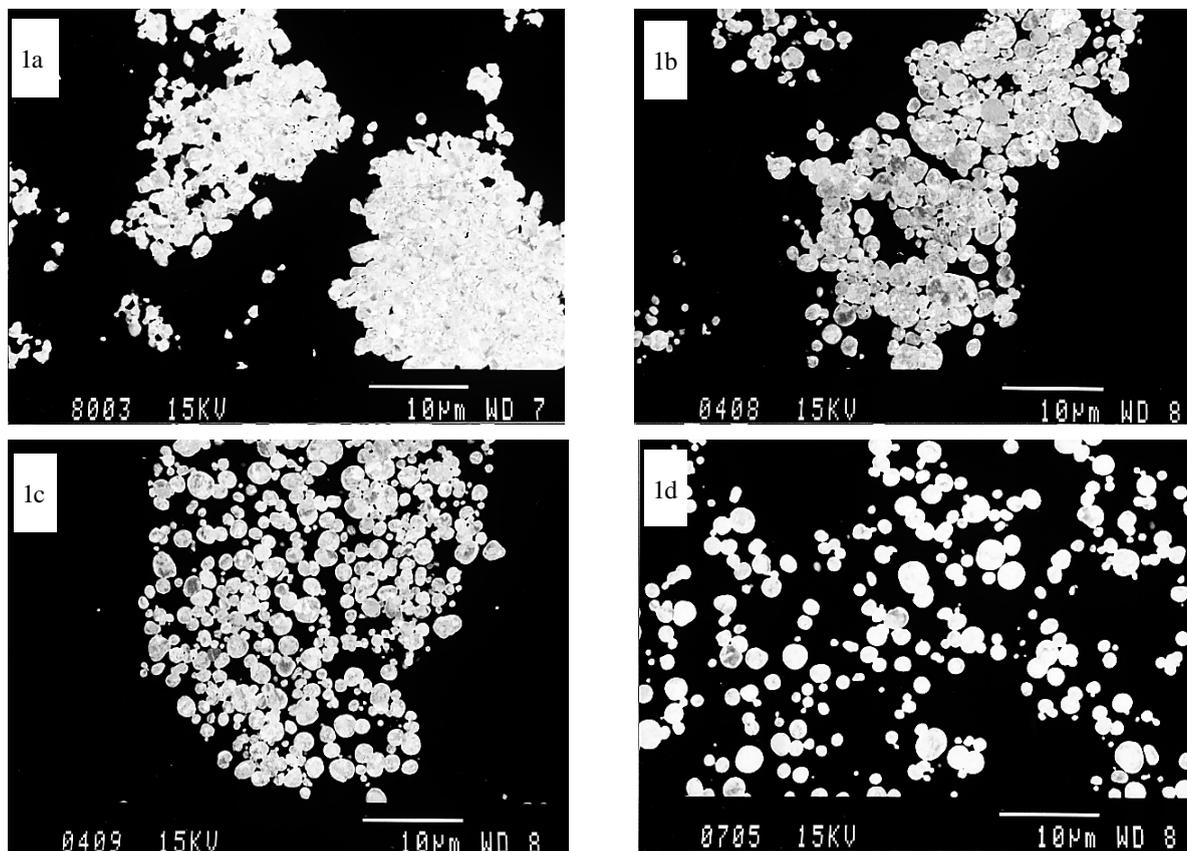


Figure 1. The initial stage of LPS under microgravity conditions in a 50W-30Ni-20Fe-alloy, from an investigation by Antonsson<sup>9</sup>. HIP sample preheated to 1350°C (1a). Sample LPS 1470°C: ~1 sec (1b), ~2 sec (1c), 8 sec (1d). Dark: Ni-Fe-W-matrix. White: Tungsten particles.

The metal matrix composites used were produced by hot isostatic pressing (HIP) of pure powder mixtures of W-Ni-Fe-(Co). The fabrication process is briefly described by Ekbom<sup>10</sup>. At the HIP temperatures used, 950°C and 1150°C, solid-state diffusion takes place and pure Ni and Fe particles form a matrix in which tungsten is successively dissolved. The alloys HIP-ed at the lower sintering temperature of 950°C

gets a lower tungsten content in the solid matrix compared to the ones HIP-ed at the higher temperature of 1150°C, as the tungsten solubility of the matrix increase by temperature. A phase diagram of this ternary W-Ni-Fe-system is presented by Fernández<sup>11</sup>. By using different volume fractions of tungsten particles, between 4-50 vol%, and by adding alloying elements like Cobalt and Sulphur or by excluding Iron from the matrix the liquid penetration and the particle growth conditions were changed.

At liquid phase processing, during heating to the sintering temperature some further dissolving of tungsten particles occurs until a local equilibrium in the solid matrix is reached. When the matrix melts at around 1455°C, it starts penetrating the solid tungsten grain structure by a combination of dissolution reaction and capillary forces. The penetration rate is linked to the gain in free energy of the wetted surfaces, as described by Huppmann<sup>12</sup>, to the reaction that takes place when tungsten is solved in the penetrating liquid matrix, as described by Aksay<sup>13</sup> and to a reduction of the number of lattice defects in the solid, as described by Shatt<sup>14</sup> and Mitkov<sup>15</sup>.

As the penetration of the tungsten agglomerates proceeds and free tungsten particles are formed, a fraction of each tungsten particle is dissolved until total equilibrium between the liquid matrix and the solid particles is reached. During this stage, the mean size of the tungsten particles decrease below the original one for the metal powders used. The liquid penetration and agglomerate separation is strongly affected by the HIP matrix composition and the deviation from equilibrium at the sintering temperature. This behaviour, which is first described by Antonsson<sup>9</sup>, is in this thesis explained by an interagglomerate melt swelling due to a Kirkendall effect<sup>16,17</sup>.

In a later stage, a growth of larger particles occurs at the same time, as smaller particles are dissolved. The driving force for this reaction is not only the reduction of surface energy but also the differences in free energy between the original unalloyed and the growing alloyed equilibrium tungsten particles, as described by Ekbohm<sup>18</sup>. When equilibrium is reached, the tungsten particles will grow in accordance with the Ostwald ripening process. During this stage, the mean particle size is found to be increasing by time by an approximately 1/3 power law.

Several of the LPS investigations were performed under microgravity either with sounding rockets or by parabolic trajectories by airplanes, as a matrix melting under microgravity conditions minimise the sedimentation of the heavier tungsten particles. At high tungsten particle fractions or very short sintering times, the investigations were performed at normal gravity.

The aim of this thesis is to evaluate the initial liquid phase sintering process, by study of the liquid penetration and spreading of the tungsten agglomerates and the initial growth of the tungsten particles in tungsten heavy metals.

## **2 Liquid phase sintering**

Sintering is the process when powders bond together when heated to above approximately half of their melting temperature. The main driving force for sintering is the reduction of total surface energy by the formation of interparticle bonds, as particle surface energies are larger in magnitude than grain boundary energies.

At liquid phase sintering, a liquid phase coexists with a solid at the sintering temperature. It is a common production process for the fabrication of near net-shape products like hard metals (cemented carbides) and for dense tungsten based heavy metals. A mixture of different metal or ceramic powders is heated to the melting temperature of one constituent. At melting, the liquid phase, the matrix, wet and infiltrate the solid grain structure by a combination of reaction and capillary forces, followed by a dissolving and growth of the solid particles by coalescence and Ostwald-ripening. The driving force for liquid phase sintering is not only the reduction of surface energy by capillary forces but also the reduction of chemical potential by dissolving of original and growth of equilibrium solid phase.

A major advantage of liquid phase sintering is the enhanced liquid atomic diffusion and mass transport, which results in rapid sintering of the components. The wetting by capillary attraction also provides a smooth rearrangement of the solid particles and a densification without the need of external pressure. The disadvantages is related to the parameters that control the sintering process, the solubility, diffusivity and the surface energies of the phases present, which coupled with the rapid rates of sintering give less predictability of structure and properties for the components produced.

## 2.1 Liquid penetration of a solid grain structure

The penetration of a liquid into a solid grain structure has been evaluated by Pejovnik<sup>19</sup> and Zagar<sup>20</sup>. For a system without a vapour phase, wetting is defined by the dihedral angle, which describes the equilibrium between the solid and liquid phases, Fig 2. The dihedral angle is characterised by the energy ratio between the solid-solid grain boundary and the solid-liquid surfaces. Wetting or penetration is often associated with a chemical reaction at the interface and the dihedral angle is then affected by:

- Solubility of solid in the liquid (alloy system)
- Melting time, i.e. chemistry change in the liquid (equilibrium conditions)
- Interdiffusion into the solid (alloy system)
- Crystallographic orientation of the solid grains (misorientation)

A solubility of the solid in the liquid or vice versa decreases the solid-liquid interfacial energy, which promotes wetting and melt penetration. As described by Aksay<sup>13</sup>, the initial dissolution of solid during liquid penetration decrease interfacial energy below the equilibrium value and this quasi-equilibrium condition will promote liquid penetration, Fig 3. When the solid is dissolved in the penetrating liquid, a transient decrease in the interfacial energy by an amount equal to the free energy of the effective chemical reaction at the interface takes place. Based on the model of Gibbs, the change in free energy due to the change of composition in the surface is found. A simultaneous reduction of the number of lattice defects in the solid gives an extra driving force for this decrease of interfacial energy and promotes melt penetration by some different mechanisms. A by-product of liquid penetration is fragmentation of solid particles or disintegration of solid particle agglomerates.

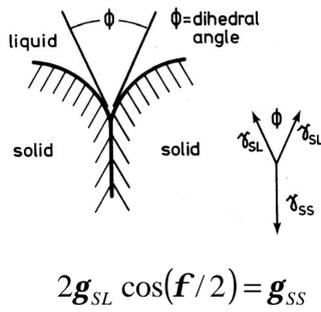


Figure 2. The dihedral angle and the Young equation. The dihedral angle expression for a planar case<sup>13</sup>.

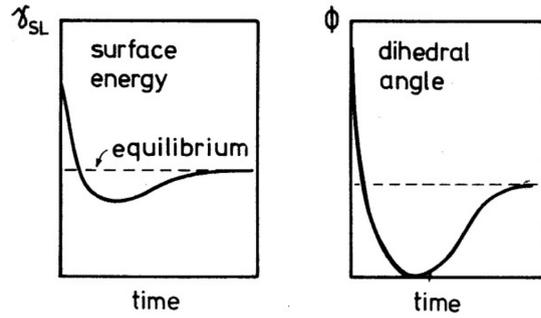


Figure 3. The variation in solid-liquid surface energy and dihedral angle with time<sup>13</sup>.

## 2.2 Liquid solution and solid reprecipitation

After the initial liquid penetration and solid solution stage, the particles start to grow by some solution-reprecipitation processes<sup>12,21</sup>. The mean particle size will increase (normally by a 1/3 power law), the number of grains will decrease and the mean distance between grains will increase, with sintering time. Greenwood<sup>22</sup>, suggested a solution for a dilute solid concentration, eq. (1).

$$\bar{R}^3 = \bar{R}_0^3 + 4Kt/9 \quad K = 2DC\Omega g / (kT) \quad (1)$$

Where  $K$  is a rate (kinetic) constant,  $D$  is the solid diffusivity in liquid,  $C$  is the equilibrium concentration of solid in the liquid,  $\Omega$  is the atomic volume of the solid,  $\gamma$  is the liquid-solid interface energy,  $k$  is the Boltzmann constant and  $T$  is the absolute temperature. This growth rate relation has been experimentally verified by many authors<sup>3,23</sup>.

Grain coalescence may appear even early in liquid phase sintering if low angle grain boundaries are formed between connecting grains. Once a particle-particle contact has formed, the driving force for coalescence is lowering of the total system energy by grain boundary elimination. Particle agglomeration and coalescence are also coupled with Brownian motion in the absence of gravitational forces<sup>24</sup>. Coalescence is favoured by a high volume fraction of solid, high diffusivity and high dihedral angle (poor wetting) and is more likely to appear among the very largest grains<sup>25,26</sup>.

## 2.3 Tungsten agglomerate separation

In all the short-time LPS investigations a remarkable rapid separation and spreading of the tungsten particles after only a few seconds of matrix melting is found, see Fig. 1. This behaviour seem to be associated with a composition gradient in the solid matrix, as the effect is less pronounced in samples HIP-ed at higher temperature, where diffusion has evened the composition and the composition gradient is smaller<sup>9</sup>.

When the liquid matrix penetrates the tungsten agglomerate structure, the particles get a radial outward movement, which will contribute, to the initial separation. However, the particle retardation in the liquid matrix is too high to give the spreading effect found in the experiments.

Since the partial molar volume of tungsten is higher in solid than in liquid, any dissolving of solid tungsten gives a net volume decrease. This shrinkage results in a pressure drop and a force acting on the particle. The tungsten particles will thus move outwards, towards matrix areas with lower tungsten content. However, the diffusion rate of tungsten in the liquid matrix is higher than this particle movement, which does not make this kind of movement likely to occur.

If a liquid melt front moves from the matrix in-between and around the tungsten agglomerates towards surrounding areas, the tungsten particles are pushed forward. A high content tungsten matrix actually melts at a lower temperature than a matrix lower in tungsten content<sup>9</sup>. However, if the matrix in-between and around the agglomerates melts and penetrates the particle agglomerates the melt composition is quickly evened out and a front movement like this is not probable.

If the particles are free floating, like under microgravity conditions, the Brownian motion moves the particles. However, the Brownian motion of a tungsten particle around 1  $\mu m$  in diameter is comparatively slow, approximately  $0.5-1 \mu m/s^{24}$ , which makes this explanation of the particle separation unlikely.

A tungsten particle movement can result from a rapid diffusion of Ni-Fe-(Co) from the surrounding low-content tungsten matrix areas to the high-content tungsten matrix areas around the particles, which is a kind of Kirkendall effect<sup>16,17</sup>, in liquid phase. The interagglomerate melt will undergo a volume increase, a swelling, and the tungsten particles will “move” out from the centre of the agglomerate. However, for this to happen the diffusion rate of Ni-Fe-(Co) must be distinctly higher than the diffusion rate of tungsten in the liquid matrix. The diffusion rate of nickel<sup>27</sup> is around 50% faster than the one for tungsten<sup>28</sup>, which makes this a plausible explanation of the tungsten agglomerate separation. A theoretical model of this behaviour is presented in the thesis.

### 3 The Kirkendall effect in liquids

In solid substitutional alloys, diffusion is known to take place by a vacancy mechanism. In liquids, the mechanism of the diffusion process is not that well known. However, a mass flow will take part if the solute elements have different diffusion mobility and a concentration gradient exists.

Let us consider a binary metal alloy consisting of two elements, A and B, by equal molar volume. By assuming that the total concentration of the two elements is constant, the concentration gradients must be equal and opposite, eq. (2). Insoluble markers are introduced at some fixed positions.

$$\left( \frac{\partial x_A}{\partial y} \right) = - \left( \frac{\partial x_B}{\partial y} \right), \quad (2)$$

Where  $x_A$  and  $x_B$  are the atomic fraction of element A and B, and  $y$  is the distance.

The diffusion fluxes across any given plane, eq. (3), are given by Fick's First Law. Note: the fluxes  $J_A$  and  $J_B$  are in opposite direction.

$$\begin{aligned}
J_A &= -D_A \left( \frac{\partial x_A}{\partial y} \right) \\
J_B &= -D_B \left( \frac{\partial x_B}{\partial y} \right) = D_B \left( \frac{\partial x_A}{\partial y} \right)
\end{aligned}
\tag{3}$$

Where  $D_A$  and  $D_B$  are the diffusion coefficients of element A and B.

Any difference in the fluxes for A-, and B-atoms means there is a net flux of mass  $J_M$ , opposite to the net flux of diffusing atoms, eq. (4).

$$J_M = -J_A - J_B = (D_A - D_B) \left( \frac{\partial x_A}{\partial y} \right), D_A > D_B
\tag{4}$$

Since the overall mass should remain constant, mass are then being “created” on one side of an interface plane (or a marker position) and “destroyed” on the other side. Thus, any insoluble marker in an unequal substitutional diffusion field will move from the initial position at a velocity  $v_M$ , in the opposite direction of the faster diffusing element and in the direction of the slower diffusing element<sup>29</sup>, eq. (5).

$$v_M = (D_A - D_B) \frac{\partial x_B}{\partial y}, D_A > D_B
\tag{5}$$

The, eq. (5), is used to analyse the separation of particles as a sort of Kirkendall effect in the thesis. The tungsten particles can in this case be treated as the marker in the Kirkendall experiments. The estimated W-particle displacement in the liquid matrix for different HIP temperatures is in accordance with the experimental observations. Even if there is an uncertainty of the used solid and liquid diffusion constants and the initial and equilibrium concentrations of tungsten in the matrix, it is still in accordance with the W-particle movements found.

## 4 Survey of papers

The appended papers are summarised below together with a presentation of the main objectives, results and conclusions. The original papers are found in the Supplements part of the thesis.

### 4.1 Supplement I-III

These three papers deal with results and conclusions from the very first liquid phase sintering (LPS) experiments performed under microgravity conditions at the ESA sounding rocket campaigns Texas 10, 16 and 19.

The objective of these primary experiments was to study the different phenomenon involved at the LPS of these metal matrix particle composites and especially the influence of different parameters like surface energy and crystallographic anisotropy on the separation and growth of the tungsten particles. A secondary task was to study the dependence of tungsten particle fraction on the mechanical properties. Due to the large difference in density between the tungsten particles (heavy) and the molten matrix (light), a matrix melting under microgravity conditions would minimise the sedimentation of the heavier tungsten particles.

At the Texus 10 campaign, two alloys with a nominal amount of 25 and 50 vol% tungsten particles were processed at short times (< 1 min), in a specially designed tetragonal parabolic mirror furnace<sup>30</sup>. At the Texus 16 campaign, the experimental material was destroyed due to a not functional payload parachute. However, at the substituting Texus 19 campaign, two other alloys with a nominal amount of 10 and 20 vol% tungsten particles were processed at somewhat longer times (~5 min), this time in a high temperature furnace from ERNO, TEM 01. The alloys used were produced by hot isostatic pressing (HIP) of powder compounds<sup>10</sup>. In the former case at Texus 10, by HIP of a mixture of pure tungsten and pre-alloyed matrix powders (W-Ni-Fe-Co) and in the latter case at Texus 19, by HIP of a mixture of pure tungsten, nickel and iron powders. Comparative reference tests under normal gravity were also performed for times between 1/2 to 4 minutes on small pieces of the four different alloys.

The results for the Texus 10 experiments showed that the tungsten particles after LPS were rather evenly distributed despite the very uneven distribution of tungsten in the specimens after HIP. The tungsten particles growth rate and especially the tungsten agglomerate separation were rather fast, despite the short LPS times for the two alloys. Since neither sedimentation nor segregation of the tungsten particles was found, microgravity by sounding rockets was proved suitable for liquid phase sintering experiments of heavy metals.

The results of the Texus 19 were the same as for the earlier Texus 10 experiments when it came to the particle distribution and observed rather fast growth rate of tungsten particles after LPS. The rapid separation of the tungsten particles for the short liquid-phase sintering time at Texus 10 was surprisingly not followed by an even further separation at the longer sintering times at Texus 19. An explanation of this behaviour could be that the initial matrix melt was not in equilibrium with the solid tungsten particles and the wetting and particle separation initially is more effective. By time, equilibrium is reached and coalescence will start to reduce the number of particles in the agglomerates. A balance between the increase and decrease in the number of particles in the agglomerates will thus be achieved.

Concluding remarks for both ground reference materials and microgravity-processed samples were:

- That the size of the particles increased, and the numbers decreased with increased sintering time, as expected while this LPS process likely is a classical solution-reprecipitation and coalescence growth process.
- The growth rate of the tungsten particles increased with increasing particle fractions, as expected while higher particle densities facilitate diffusion and particle coalescence. However, the overall particle growth rate was found to be somewhat lower than the earlier reported<sup>3</sup> cubic law ( $t \sim D^3$ ) relationship for this kind of alloys.
- The very rapid separation of the tungsten agglomerates of the Texus 10 experiments is associated with the non-equilibrium conditions at the initial matrix melting.

- Neither sedimentation nor segregation of the tungsten particles was found in the microgravity LPS samples, which proved microgravity in sounding rockets to be a suitable environment for this kind of LPS experiments.

## 4.2 Supplement IV

This paper describes the experimental equipment used for microgravity experiments at the parabolic flights to follow. The Microgravity Applications Furnace Facility, MAFF, developed by Swedish Space Corporation (SSC) and KTH/Casting of Metals in cooperation was the principal equipment used for many Parabolic Campaigns to follow. Short durations of microgravity can be achieved with an airplane flown in a parabolic trajectory. During a flight, the airplane repeats the parabolic pattern 20-40 times which results in the same amount of microgravity periods each lasting approximately 20 seconds.

The objective was to get a facility designed for high temperature microgravity processing of metals, alloys and composites, with a controlled heating, melting and solidification of a large number of samples during the short period of microgravity at a parabolic trajectory. The MAFF, which is a semi-automatic furnace facility, is equipped with six IR-heated furnaces, a PC for control and data storage, a gas cooling system, accelerometers, electronics and a power supply, all mounted in a 19" rack, which is mounted on the floor of the airplane. The facility operator, which also is subjected to microgravity, monitors the experiments via a computer screen and controls it directly via the computer keyboard. The experimental sequence for each furnace is individually pre-programmed but can also be controlled during the flight via the PC keyboard. The six furnaces are placed in a drawer to simplify the change of samples; which makes it possible to process a large amount of samples per flight. The gas cooling system enables active cooling of the samples and all experimental data inclusive accelerometers data of microgravity levels is collected by the data storage system at the PC.

A Mirror Furnace (MF), consists of two halogen lamps (36 V, 680 W totals) placed in gold plated ellipsoidal mirrors with a common focus where the sample is positioned. The furnace is capable of producing a maximum sample temperature around 1600 °C. The sample has a typical diameter of around 3 mm and a length of 6 mm and temperature control is conducted by a thermocouple placed in the sample. The dimensions of the sample are optimized according to desired heating, melting and cooling conditions.

A typical experiment sequence has the following pattern. During the pre-microgravity period, the sample is preheated to a temperature below the melting point of the sample material and held at this temperature until the microgravity period starts. At the start of the microgravity period, the sample is heated, melted and held at the processing temperature for a pre-defined time. Slightly before the end of the microgravity period, the heating is switched off and the active cooling system is turned on, to get cooling and solidification before the entrance of the enhanced gravity period. The recorded parameters as sample temperature, g-levels etc can be plotted after each flight for direct analysis.

### 4.3 Supplement V-VII

These three papers present results and conclusions from LPS microgravity experiments made at the earlier sounding rocket campaigns Texas 10 and 19, the later Texas 26 and 27 and a final Parabolic Flight campaign. The previous studies are here combined with the more recent ones to sum up results and conclusions for particle growth and agglomerates separation, for sintering times from a few seconds up to several minutes. A model for the dissolution and growth of particles and a mathematical evaluation of surface tensions is presented. Note; At the later papers some corrections of the particle fractions of the older alloy systems are introduced (new 4 vol% is the same as old 10 vol%, 18 vol% is the same as old 20 vol%, 20 vol% is the same as old 25 vol%).

The objective of these microgravity experiments was to study the initial stage processes in liquid phase sintering and especially the influence of interfacial energy and alloy composition on particle growth and melt penetration of the agglomerates. The samples were prepared from pure powders of tungsten, nickel and iron. Additions of sulphur or cobalt to the alloys were used to decrease while an absence of iron in the matrix was used to increase the interfacial energy between the liquid and the tungsten particles ( $\gamma_{S/L}$ ). An increase of solid/liquid interfacial energy should increase the particle growth rate but lower the liquid penetration rate and vice versa.

At the Texas 26 and 27 sounding rocket campaigns, samples of four alloys with different particle fractions respectively solid/liquid interfacial energies were liquid phase sintered for longer times, 1-5 minutes, under microgravity conditions. The two alloys used at Texas 26 had the same nominal amount of 4 vol% tungsten particles but one contained cobalt. The two alloys used at Texas 27 were more different in composition; the first one had a nominal amount of 18 vol% tungsten particles and contained sulphur (FeS) while the other one had a nominal amount of 9 vol% tungsten particles and contained no iron, but only tungsten and nickel in the matrix. The equipment used at the flights was the high temperature furnace from ERNO, TEM 01, earlier used at the Texas 19 flight.

At the Parabolic Flight campaign, samples of seven alloys with different particle fractions respectively different liquid/solid interface energies were liquid phase sintered for shorter times, 8 and 13 seconds, under microgravity conditions. The alloys used were the ones produced for the earlier microgravity campaigns except the one containing sulphur and with addition of an alloy containing tungsten-nickel-cobalt with 9 vol% tungsten particles. The equipment used at the three flights during the campaign, was the earlier described Microgravity Applications Furnace Facility, MAFF.

The experiments on the Texas 26 were successful and those on Texas 27 were not so successful. The two alloys processed at Texas 26 were both low tungsten particle fraction alloys (4 vol% tungsten particles), one with the addition of cobalt. Cobalt was added in order to decrease the surface tension between the tungsten particles and the molten matrix, thereby increase the agglomerate penetration and lower the particle growth rate. Both samples were successfully LPS and the numbers of large agglomerates were not so frequent in the cobalt-containing alloy, which is consistent

with the predicted behaviour. However, the particle growth rate was higher for the same alloy, which is not consistent with the previous observation.

Of the two alloys processed at Texus 27, the one that contained sulphur (FeS, NiS) unfortunately was subjected to gas evolution. The tungsten particles in this sample had anyhow separated extremely well and grown to a very large particle size. The second sample of Texus 27 had due to gas evolution from the first sample received a severely disturbed positioning and only been partial molten on the surface. The region between the molten and unmolten part of the sample was clearly visibly and illustrates well the change in particle shape and agglomerate separation when the matrix melts. However, any reliable evaluation of the experimental data from these two samples could not be made.

Of the Parabolic Flight experiments, 48 out of 50 tests were successfully processed. The time interval for melting, molten state and solidification were evaluated and found to be very accurate to the pre-defined times of 8 and 13 seconds of molten state. The short time LPS at the parabolic flights illustrated very well the initial liquid penetration of the solid agglomerate structure. The particles have partially been dissolved in the matrix and become spherical. The relations between surface tension, agglomerate separation and particle growth were similar to that of the earlier Texus flights.

Concluding remarks, for the eight investigated alloys processed at microgravity experiments at the sounding rocket campaigns, the Parabolic Flight campaign and at the ground reference experiments, will be:

- In general, the calculations of the growth curves for alloys with a larger particle fraction showed a higher growth rate, due to shorter diffusion distances between the particles at higher particle fractions.
- The average tungsten particles size is decreasing during the first seconds of liquid phase sintering because part of the tungsten particles is dissolved when the solid non-equilibrium matrix phase is melting. To take care of this change in the  $R_0$  value a new term has been introduced in the cubic growth law.
- Cobalt was found to increase the growth rate of the tungsten particles and simultaneously to improve the separation of tungsten particles in the agglomerates. Those two effects are in contradiction with each other but a possibly explanation could be that in the non-equilibrium state of initial melting and disintegration of the tungsten particle agglomerates, cobalt will initially increase the wettability by lowering the surface tension between the liquid matrix and the solid particles. When equilibrium is established, the surface tension and thus the driving force for the growth process of the tungsten particles will increase.
- For tungsten alloys without iron in the matrix, the similar growth rate and agglomerate separation behaviour was found as for the cobalt containing alloys but even more pronounced. The growth rate was found to be about twice that of the iron containing alloys, due to a high surface tension between the solid tungsten particles and the matrix melt. A possible explanation to this separation behaviour might be that the original tungsten particles were larger in the non-iron alloys due to coalescence and a higher solid diffusion rate of tungsten in the absence of iron.

The larger original tungsten particles will then lead to a more rapid separation of the tungsten particles in the agglomerates during the liquid formation.

- The tungsten alloys produced at a lower solid-state sintering temperature (HIP) have a better separation than alloys produced at a higher one. This behaviour is due to lower tungsten content in the solid matrix after HIP, which increases the reactive liquid penetration and separation of the tungsten agglomerates.

#### 4.4 Supplement VIII-IX

These two papers deal with infiltration and penetration of melts into grain boundaries of solid pure tungsten. The solid tungsten samples have been treated in different ways like cold working, annealing and recrystallisation, before the exposure to a saturated Ni-W-Fe melt. Some new models for the melt penetration mechanism are also proposed.

The objective of these experiments was to get a better understanding of the mechanisms of melt penetration into a solid phase. This is the actual case for the initial stage processes of liquid phase sintering when the molten matrix penetrates the tungsten particle agglomerates of a heavy alloy.

Small cylindrical samples of pure tungsten, of the original cold worked condition, or treated in different ways (annealed, recrystallised, recrystallised and cold worked, and recrystallised, cold worked and annealed), were exposed to tungsten saturated Ni-Fe melts for different periods of time. The IR-heated mirror furnace (MF) unit described in paper V and with samples of the same design as used in the Parabolic Flight were used for the liquid penetration experiments.

The maximum infiltration depth of matrix melt into the samples of in different ways treated pure tungsten was evaluated. The early penetration experiments were performed using original cold worked and recrystallised pure tungsten for times between 5 to 120 seconds while the later ones were performed using original, annealed, recrystallised, recrystallised and cold worked, and recrystallised, cold worked and annealed pure tungsten for times between 10 to 240 seconds.

The initial early penetration experiments showed that the penetration rate was much faster in the cold worked tungsten samples than in the annealed ones. However, it was impossible to evaluate the penetration depth as a function of exposure times for the original, untreated tungsten rods due to the scatter and the very large penetration depths into the rods. An explanation to this penetration behaviour is supposed to be that the deformation energy stored in the material is released when the molten matrix penetrates the tungsten grain boundaries. For the recrystallised material, the penetration depth by time could be described by a parabolic law. A model was derived for the penetration of liquid into three-boundary junctions. In the model, the driving force is the pressure drop,  $DP$ , of the penetrating liquid and the diffusion of tungsten outwards into the melt determines the penetration rate. Compared with experimental data it was found to explain the results very well.

The results for the later penetration experiments showed orders of magnitudes higher penetration rates for the hard-drawn and annealed tungsten materials compared to any of the other recrystallised tungsten materials. The penetration mechanisms in the two

cases are obviously not of the same origin. The much higher penetration rates of the heavily cold worked material cannot be explained by a diffusion-controlled process. A new theory for the penetration in which the internal stress release in the solid and vacancy diffusion creates space for the liquid tip propagation is proposed. The new model show good agreement with the experimental data. A noticeable fact was that the penetrating liquid caused a rapid recovery or recrystallisation of the grain structure in the cold worked samples.

Concluding remarks for Ni-Fe saturated liquid penetration in solid tungsten were that:

- The penetration rate in recrystallised tungsten, with a low dislocation density, was moderate and could be described with a parabolic law. In the model, the driving force for diffusion of tungsten outwards into the melt is due to the pressure drop in the penetrating liquid.
- The penetration rate in cold worked tungsten, with a high dislocation density, was very fast, magnitudes faster compared to recrystallised tungsten. High internal stresses in the solid grain structure enhance penetration and by relaxation, give space for the advancing liquid at the same time as penetrated areas get a rapid tungsten grain recovery. A new penetration model expressed as a power law, shows good agreement with experimental data.

#### **4.5 Supplement X**

This paper deals with the initial stage of liquid phase sintering, involving liquid reaction and agglomerate penetration in tungsten heavy alloys and the following agglomerate separation and spreading of the tungsten particles.

The objective of these experiments were to evaluate further the first part of the liquid phase sintering process, the initial liquid matrix penetration and to get an explanation of the remarkable very rapid separation and spreading of the tungsten particles, as earlier shown in an investigation by Antonsson and Ekbom<sup>9</sup>.

Previously fabricated HIP heavy alloys were used in these experiments. The thermal processing of the samples was done in the ellipsoid mirror furnace described in supplement IV. At the thermal processing of the W-Ni-Fe-(Co) alloys the temperature of 1470 °C was reached and hold in the central part of the samples. Since the samples were longer than the isothermally heated zone, the heating did not melt the whole length of the sample. Instead, as the matrix melting temperature of ~1450 °C was successively reached outside the central zone, melting was spreading towards the outward region of the samples. This gave a successive decrease in melting time and temperature of the matrix along the sample length. The experiments were not performed under microgravity conditions since the very short melting times used limited sedimentation of the tungsten particles.

The results for the experiments by this arrangement was one zone with approximately 8 seconds of melting, the “Molten zone”, one zone with a continuously decreasing melting time, the “Heated zone” and one zone of not further thermally affected HIP structure at the far end of the sample, the “HIP-structure zone”.

Initial melting and penetration was found along the three-grain boundaries of the agglomerates in the “Heated zone”. This links the penetration rate to the gain in free energy (diminution of total surface energy) of the wetted surfaces. A free energy gain between pure tungsten and equilibrium nickel-iron-cobalt alloyed tungsten is another driving force for the penetration. Calculations of a penetration rate constant by a parabolic penetration law fits well with experimental observations.

A rapid separation and spreading of the tungsten particles from the agglomerates was found in the “Border region”, the region between the “Molten zone” and the “Heated zone”, after only a few seconds of matrix melting. A close look at the separation movement gives an impression of an in-flow of molten matrix in-between and a radial movement outward of the separated particles from the agglomerates. Such a particle “movement” can result from a rapid diffusion of Ni-Fe-(Co) from the surrounding low-content tungsten matrix areas to the high-content tungsten matrix areas around the particles, which is a kind of Kirkendall effect in liquid phase. Calculations were done for the W-particle displacement in liquid state by this theory and the results were in accordance with the experimental observations.

Concluding remarks for the liquid matrix penetration and the separation and spreading of the tungsten agglomerates were that:

- Wetting under non-equilibrium conditions and the decrease of interfacial energy seem to be the driving force for the liquid penetration of a matrix melt into the solid agglomerate structure, which also is experimentally verified.
- Of the presented hypothesis to explain the remarkable fast separation of the particles after a few seconds of liquid matrix formation and the effect of the composition gradient in the matrix, the suggested theory by interagglomerate melt swelling due to a Kirkendall effect seems to be a plausible explanation.

#### **4.6 Supplement XI**

This paper deals with different interaction phenomena concerning particles in liquid metals. The intention was to analyse how models for diffusion phenomena in solids, i.e. the model by Kirkendall<sup>16,17</sup>, could be used for the analysis of particle motion in liquids.

In solid substitutional alloys, diffusion is known to take place by a vacancy mechanism. In liquids, the mechanism of the diffusion process is not that well known. However, a mass flow will take part if the solute elements have different diffusion mobility and a concentration gradient exists. The objective was to study the interaction between solid particles and a solidification front and inclusions behaviour in iron base alloys during teeming and at the deoxidation process.

The interaction between solid particles and a solidification front was studied by the movement of slag oxide particles of  $\text{Al}_2\text{O}_3$ . They are formed in an Al deoxidised melt before the solidification starts and a critical velocity for the pushing/engulfment transition of these particles at an advancing solid-liquid interface exists. The  $\text{Al}_2\text{O}_3$ -particles movement is analysed as a sort of Kirkendall effect where the particles are treated as the markers in the Kirkendall experiments.

Inclusion behaviour during teeming and at the deoxidation process in iron base alloys is studied by the same movement of slag oxide particles of  $\text{Al}_2\text{O}_3$ . At teeming the oxide inclusions originating from the deoxidation process may be attached to alumina refractory walls and tubes and by time hinder the melt flowability. The refractory walls will leak both Si and O to the melt by a diffusion process and the movement of precipitated insoluble alumina inclusions are analysed as a sort of Kirkendall effect.

Before deoxidation the oxygen content in the steel is controlled by the equilibrium with other elements like Si or Fe. These  $\text{SiO}_2$  or FeO inclusions formed in the melt before deoxidation, react with Al at deoxidation and  $\text{Al}_2\text{O}_3$ -particles are formed ahead of the old particles. The movement and clustering of these precipitated alumina inclusions are analysed as a sort of Kirkendall effect.

Concluding remarks for the analysis of the interaction behaviour between solid particles and a solidification front and inclusion behaviour in iron base alloys during teeming and at deoxidation were that despite the uncertainty of the used liquid diffusion constants and the assumed concentration profiles, the results of the study is in accordance of shown particle movements. Future work is suggested to validate usage of the theory in this field.

## **5 Discussion and summary**

The aim of this thesis was to evaluate the initial liquid phase sintering process, by study of liquid penetration and spreading of tungsten agglomerates and the initial growth of tungsten particles, in tungsten heavy metals.

The initial liquid penetration in tungsten particle composites produced by solid state sintering by HIP seems to be explained by initial wetting under non-equilibrium conditions and a decrease of interfacial energy. The diffusion of tungsten outwards into the melt gives a pressure drop in the penetrating liquid and a driving force for the movement of the liquid tip. The suggested parabolic penetration model show good agreement with experimental data. Three-grain boundaries are penetrated more easily and faster than two-grain boundaries since the gain in energy is more for the previous ones. Any internal or external stress influence the penetration rate greatly and for cold worked tungsten a new penetration theory was proposed, where an internal stress release in the penetrated tungsten grains creates space for the advancing liquid. The new model expressed as a power law show good agreement with experimental data.

The spreading of the penetrated solid tungsten agglomerates seems to be explained by the suggested theory by interagglomerate melt swelling due to a Kirkendall effect. The penetrating and the interagglomerate melt will both undergo a volume increase, a swelling, since the diffusion rate of Ni-Fe-(Co) in the liquid matrix are distinctly higher than the diffusion rate of W. Because of the concentration gradients of W and Ni, Fe, Co, in the matrix liquid, the tungsten particles will move out from the centre of the agglomerates during the levelling process of the matrix melt. This new model give an explanation to why heavy alloys HIP-ed at a lower sintering temperature and a lower tungsten content in the solid matrix will separate faster and more than heavy alloys HIP-ed at a higher temperature and with a higher tungsten content in the solid matrix.

The suggested Kirkendall model were used for an analysis of both the interaction behaviour between solid particles and a solidification front and inclusion behaviour in iron base alloys during teeming and at deoxidation. Future work is suggested to validate the new theory in this field.

The initial growth of tungsten particles takes part after the initial liquid penetration and solid solution stage. The driving force for this reaction is not only the reduction of surface energy but also the differences in free energy between the original unalloyed and the growing alloyed equilibrium tungsten particles. When equilibrium is reached, the tungsten particles will grow in accordance with the Ostwald ripening process by an approximately 1/3 power law. During this stage, the mean particle size is found to be increasing by time. However, it is found that the average tungsten particles size is decreasing during the first seconds of liquid phase sintering because part of the tungsten particles is dissolved when the solid non-equilibrium matrix phase is melting. In general, larger particle fraction of particles showed a higher growth rate, due to shorter diffusion distances between the particles at higher particle fractions. Cobalt, Sulphur and no iron in the matrix was found to increase the growth rate of the tungsten particles due to a higher surface tension between the solid tungsten particles and the matrix melt.

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