Strengthening and degradation mechanisms in austenitic stainless steels at elevated temperature

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ABSTRACT

With rapid economic developments and rising living standards, the demand for electricity all over the world is greatly increased. Due to high fuel costs, the steam boilers with higher steam temperature and pressure are needed to decrease the cost of power generation throughout the world extensively. In recent years, human awareness of the gradual strengthening of environmental protection increases, therefore to reduce the CO₂ emissions the power generation efficiency needs to be improved. The development of high temperature materials with improved creep rupture strength and oxidation resistance is critically needed. Materials for these demanding conditions are austenitic stainless steels such as 310, 310NbN and Sanicro 25.

Fundamental models have been developed for the precipitation of coarse particles during long time ageing of austenitic stainless steels and the influence of the particles on the mechanical properties. The models have been verified by ageing experiments. The austenitic stainless steel 310 was aged for up to 5000 h at 800 ºC. The precipitation models could satisfactorily describe the influence of ageing time on the radii and the volume fractions of particles. Models for the influence of the coarse precipitates on the tensile properties and the toughness were developed and reproduce the measured mechanical properties without the use of any fitting parameters. These developed models were utilised to investigate the influence of bands on ductility and toughness at room temperature. Up to 10 % σ-phase was observed to precipitate, which has a pronounced influence of the mechanical properties. Thermodynamic analysis demonstrated that the amount of precipitates due to ageing can significantly be reduced if the nitrogen or the carbon content is increased.

Microstructure investigations of austenitic stainless steel 310NbN and Sanicro 25 were carried out by light microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS). The austenitic stainless steel 310NbN was aged for up to 10000 h at 650 and 750 ºC. The austenitic stainless steel Sanicro 25 was also aged for up to 10000 h at 650 and 700 ºC. Phase fractions and mean radii evolution of precipitates were calculated and compared to the experimental results. Size distributions of the precipitates in these steels were determined. Models for the different contributions to the creep strength have been applied: i) a recovery creep model for the dislocation hardening; ii) a climb controlled model for the precipitation hardening; iii) solid solution hardening from Cottrell clouds of solutes around the dislocations, and iv) A modified Dobes model for the effective stress. The total contributions can describe the experimental creep strength satisfactorily without the use of adjustable parameters.
Keywords: Austenitic stainless steel, microstructure evolution, modelling, mechanical properties, solid solution hardening, precipitation hardening, dislocation climb
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LIST OF APPENDED PAPERS AND AUTHOR CONTRIBUTION IN EACH PAPER

Paper A

Precipitation during long time ageing in the austenitic stainless steel 310
Muhammad Farooq, Rolf Sandström and Mats Lundberg
Materials at High Temperatures, Volume 29, Number 1, 2012, pp. 8-16.

Paper B

Influence of particle formation during long time ageing on mechanical properties in the austenitic stainless steel 310
Rolf Sandström, Muhammad Farooq and Bo Ivarsson

Paper C

Influence of long time ageing on ductility and toughness in the stainless steel 310 in the presence of banded microstructure
Muhammad Farooq and Rolf Sandström
La Metallurgia Italiana-n. 11-12/2012, pp. 33-38.

Paper D

Basic creep models for a 25Cr20NiNbNaustenitic stainless steels
Rolf Sandström, Muhammad Farooq and Joanna Zurek
Accepted in Materials Research Innovations, 2013.

Paper E

Numerical modelling and validation of precipitation kinetics in advanced creep resistant austenitic steel
Stojan Vujic, Muhammad Farooq, Bernhard Sonderegger, Rolf Sandström and Christof Sommitsch

Paper F

Precipitation hardening and other contributions to the creep strength of an 23Cr25NiWCuCo austenitic stainless steel
Muhammad Farooq, Rolf Sandström and Oriana Tassa
To be submitted
Paper A
The author of this thesis made the experiments, measurements, evaluated the results and wrote the manuscript together with Sandström.

Paper B
The author of this thesis made the experiments, measurements, evaluated the results and wrote the manuscript together with Sandström. Modelling part of the work was done by Sandström.

Paper C
The author of this thesis made the experiments, measurements, evaluated the results and wrote the manuscript together with Sandström.

Paper D
The author of this thesis made the experiments, measurements, evaluated the results supervised by Sandström.

Paper E
The author of this thesis made the experiments, measurements, evaluated the results. Modelling part of the work was done by Stojan Vujic.

Paper F
The author of this thesis made the experiments, measurements, made some of the modelling, evaluated the results and wrote the manuscript together with Sandström.
## CONTENTS

1 INTRODUCTION .............................................................................................................. 1
   1.1 The need of creep resistant materials ................................................................. 1
   1.2 Aim of the work ..................................................................................................... 3

2 AUSTENITIC STAINLESS STEEL ................................................................................. 5
   2.1 Precipitates in austenitic stainless steel .............................................................. 8

3 CREEP ............................................................................................................................. 11
   3.1 Grain boundary sliding ......................................................................................... 11
   3.2 Diffusion creep ..................................................................................................... 12
   3.3 Dislocation creep ................................................................................................. 12

4 HARDENING MECHANISMS ....................................................................................... 14
   4.1 Work hardening .................................................................................................... 14
   4.2 Grain boundary hardening .................................................................................... 14
   4.3 Solid solution hardening ....................................................................................... 16
       4.3.1 Solid solution hardening during creep .......................................................... 18
   4.4 Precipitation hardening ....................................................................................... 21
       4.4.1 Precipitation hardening during creep ............................................................ 28

5 EXPERIMENTAL DETAILS AND METHODOLOGY ............................................... 33
   5.1 Materials and heat treatments ............................................................................. 33
   5.2 Optical microscopy ............................................................................................... 33
   5.3 Scanning electron microscopy (SEM) ................................................................. 34
   5.4 Wavelength dispersive spectroscopy (WDS) ....................................................... 35
   5.5 Transmission electron microscopy (TEM) .......................................................... 36
       5.5.1 Procedure for preparation of sample for TEM investigations ....................... 37
       5.5.2 Procedure for preparation of replica for TEM investigations ....................... 37
   5.6 Particle size distributions ..................................................................................... 38

6 SUMMARY OF APPENDED PAPERS .......................................................................... 43
   6.1 Paper A ................................................................................................................. 43
1 INTRODUCTION

1.1 The need of creep resistant materials

In the 21st century, the world faces the critical challenge of providing plentiful and economical electricity to fulfil the requirements of a growing global population while maintaining and improving the environment. Most studies on this matter conclude that new generation technologies and fuels should be developed to ensure that the world will have enough electricity in future. The most important driving force for the future in materials technology is the need to discover materials that allow the introduction of new sustainable technologies for energy production. Although specific requirements vary depending on the application (for example, combustion/gasification of biomass/biofuels, increased efficiency in fossil fire power plants, future generations of nuclear power plants, fuel cells, etc), a common factor in these applications is the need to improve the high temperature mechanical properties of the materials. The conditions in these applications give a new challenge to materials science, because the long-term service life requires a complete understanding of the complex time-dependent chemical and mechanical degradation mechanisms. Advanced models must be developed that take into account the complex interactive chemical, mechanical and thermal degradation mechanisms and connecting these to the microstructural characteristics and the formation of protective layer.

The demand of energy is increasing rapidly throughout the world. It is estimated that world energy consumption will be doubled in 2050 as compared to year 2000. Unless specific measures are taken, CO₂ emissions have doubled from 1990 to 2030 [1]. During the same period, the proportion of CO₂ emissions from electricity production will increase from 35 to 45% [2].

The use of coal for energy production has a distinctive set of challenges. On one side, coal is abundant and cheap in much of the world like Pakistan, India, China and US. Countries with large coal reserves will want to develop coal-fired power plants to meet their needs of electricity. On the other side coal-fired power plants emits pollutants and CO₂ at high levels in comparison to other options. Keeping the coal as a generation option in the 21st century will need methods which can deal with environmental issues. Nowadays 39% of global power generation is based on coal; the same figure is expected for the next few decades [3]. The fossil fired power plants are one of the main sources of carbon dioxide emission. This carbon dioxide emission gives and green house effect leading to global warming. One way of reducing the environmental impacts of electricity generation is to increase the thermal efficiency of the power plants, which results to less fuel consumption and as a result less carbon dioxide emissions. The efficiency of coal-fired power plants has been increased from 39% in 1980 and 42% in 1990 to 48% today in the modern units [4]. The overall average efficiency of coal-fired plants is 28% presently. For each percent
increase in efficiency of power plant, there is a 2-3% decrease in CO₂ emission. Therefore, more than 40% reduction in CO₂ emission can be obtained by replacing all units with fully modern ones. By increasing the efficiency from 37% to 47%, $12.4 million annually in fuel cost or $248 million over a 20-years plant life for an 800MW unit operating at 60% capacity, can be saved. The CO₂ and other fuel-related emissions will be decreased from 0.85 to 0.67 tonnes/MWh, i.e. a reduction of almost 22% [5].

The efficiency of conventional boiler-steam turbine fossil power plants depends upon different factors like auxiliary power needs, coal quality, condenser pressure and discharge temperature, flue gas exit temperature, steam turbine design and steam temperature and steam pressure. By increasing the maximum steam temperature and steam pressure, the efficiency of the power plant can be increased [6],[7]. The increase in efficiency from 42 to 48% was obtained by moving from supercritical to ultrasupercritical (USC) steam conditions. The steam temperature has been increased from 540 to 600 ºC and pressure from 200 to 305 bar. This development was made possible with the introduction of new ferritic/martensitic steels such as P91 and P92 for high pressures and temperatures in USC boiler. The austenitic stainless steels like 347H and Super304H were selected in the superheaters, because they have high temperature corrosion resistance and the required creep strength.

Future generations of coal-fired power plants will have even higher steam temperatures of 650 and 700 ºC to further improve the efficiency of the unit and reduce CO₂ and other fuel-related emissions. For such purpose, new materials should be developed. The materials used at 600 ºC do not have enough oxidation resistance and creep resistance. Ferritic steels cannot be developed so far that they can be used above 600 ºC. Austenitic stainless steels and nickel-based alloys should be applied for temperature at 650 and 700 ºC.

Dramatic increases for energy demands world-wide is expected in 21st century. Nuclear energy is a good option to meet the future energy demands while maintaining and improving environmental values. Large amount of energy can be generated by nuclear reactors without the negative effects on the environment that come with the use of coal or petroleum products. The need to develop materials which can perform in the severe operating environments expected in Generation- IV reactors gives a significant challenge in material science. Improved economic performance is a main goal of the Generation-IV designs. The proposed next-generation reactors include of Gas-cooled Fast Reactor, Lead-cooled Fast Reactor, Molten Salt Reactor, Sodium-cooled Fast Reactor, Supercritical-Water Reactor, and Very-High-Temperature Reactor. Consequently most of the designs require operating temperatures significantly higher than the current generation of reactors for higher thermal efficiency. Reactor materials of the Gen IV will be operated at very high temperatures (up to 900-1000 ºC in Very High Temperature Reactor-VHTR). They will also be exposed to intense neutron radiation and corrosive environments [8]. To produce hydrogen economically, a reactor must be operated at very high temperatures. Therefore VHTR can be selected for future hydrogen production plants. There is a huge and fast-
A growing demand for hydrogen. A limiting factor for these reactors will be the materials used in their operation.

Austenitic stainless steels are frequently used for high temperature applications, since they can survive in the hot and corrosive environment and maintain their mechanical properties better at higher temperatures than ferritic steels. Both types of steels are used in large quantities in various parts of a modern, GenII light water reactors. The outlet temperatures in GenII reactor or even GenIII/III+ are in the range of 300 °C. GenIV concepts will drive as much as 1000 °C. Austenitic alloys have better creep resistance at high temperatures than ferritic steels, but they also suffer void swelling under neutron bombardment which can compromise their mechanical strength.

Four classes of candidate materials (austenitic steels, Ni based alloys, ferritic/martensitic steels and Zr alloys) were studied in U.S. for potential use in different components of supercritical water cooled reactor (SCWR). They found that austenitic stainless steels show better corrosion resistance than ferritic/martensitic steels [9]. Austenitic stainless steel SS316 and its modifications are generally used for the fast reactor structural components [10]. Austenitic stainless steel PNC1520, developed by Japan Atomic Energy Agency (JAEA), was selected for possible use in supercritical water systems as a nuclear fuel cladding material for Na-cooled fast breeder reactor due to their good corrosion resistance and radiation resistance [11].

Due to high temperatures envisioned in the designs of Generation-IV reactors, austenitic stainless steels are potential candidate materials for the reactors of Generation-IV.

The development of high temperature materials with improved creep rupture strength and oxidation resistance is required. The high temperature strength is related to the creep deformation in the components. Power plant components have to resist temperature and stresses for long times to prevent creep failure. The life time of a future power plant can be as long as 80 years. Due to these reasons, new cost effective materials with good oxidation resistance, superior creep strength, good fabricability and good weldability are required. Austenitic stainless steels are potential candidate materials because of low cost and high ability of operations at the designed steam temperature and steam pressure conditions of the ultra-supercritical power plants [7], [12]. So, it is important to maximize the creep strength of the materials, which is a critical property of the material when used for higher steam temperature-pressure applications.

1.2 Aim of the work

The purpose of the first part of the work is to perform long term aging of the austenitic stainless steel AISI 310, characterise the precipitates, and model the nucleation and growth of particles and to determine the influence of the particles on strength, ductility and toughness properties. After long time aging the precipitates form bands in the microstructure. The influence of these bands on ductility and toughness is determined.

The aim of the second part is to establish quantitative models for predicting the contribution of precipitation hardening, solid solution hardening and dislocation hardening to the creep strength.
Such models have been applied to the austenitic stainless steel 310NbN and Sanicro 25. The precipitation in the microstructure of these steels has been characterised.


2 AUSTENITIC STAINLESS STEEL

Austenitic stainless steels with a Fe-Cr-Ni base system are frequently used for high temperature applications. Nickel is added to stabilize austenite which highly increases the general resistance to corrosive environments. High chromium content gives excellent corrosion resistance to stainless steel. Since chromium is a ferrite stabilizer, it should be balanced by austenite stabilizing elements for an austenitic structure to be stable. The ferrite-stabilizing elements are chromium, molybdenum, silicon and niobium, while the austenite-stabilizing elements are nickel, manganese, carbon and nitrogen. Chromium and nickel equivalents are calculated on the basis of the various strengths of the elements stabilizing austenite or ferrite such as [13]

\[
\begin{align*}
Ni_{eq} &= [Ni] + [Co] + 0.5[Mn] + 30[C] + 0.3[Cu] + 25[N] (\text{wt\%}) \\
Cr_{eq} &= [Cr] + 2.0[Si] + 1.5[Mo] + 5.5[Al] + 1.75[Nb] + 1.5[Ti] + 0.75[W] (\text{wt\%})
\end{align*}
\]

Corrosion resistance can be improved further by increasing the weight percentage of chromium and nickel up to about 25% respectively. Type 310 and 309 are the examples of such steel. But they do not have good creep rupture strength at high temperatures.

Good creep resistance can be achieved by dispersion of secondary phases like nitrides and carbides through precipitation hardening. So the addition of strong carbide/nitride formers such as Ti, Nb, V, Zr in the austenitic stainless steel is more general. These nitrides and carbides impede dislocation movement at higher temperatures and thereby increase the strength of steel. On the other hand, carbide formation can cause intergranular corrosion by depleting the adjacent of elements like Cr and Mo that increase the corrosion resistance. This event can be prevented by the addition of Nb and Ti because they bind the carbon and prevent the formation of chromium carbides.

The creep strength of the existing and potential stainless steels for USC applications is given in Table 2.1. Austenitic steels of 18Cr-8Ni type have good corrosion resistance and excellent high temperature properties. Steels that are used in corrosive environments must have low carbon content typically below 0.03% to prevent intercrystalline corrosion. In the steel description, it is denoted with an L. High temperature application steels have a carbon content of about 0.08% that slightly increases the creep strength. These steels are denoted with an H. The role of nitrogen is very important for the steels creep strength. With increasing amount of nitrogen in steel, a significant increase in rupture life can be obtained [19]. The effect of nitrogen is represented in Fig. 1. The effect of Nb and Ti can be increased if their amounts are balanced to that of carbon. An atomic ratio of (Nb+Ti)/C= 0.3 has given an increase in creep strength of 20 MPa at 650 °C [20]. This result has been the basis for the development of Tempaloy A-1 steel.
### Table 2.1. Approximate 100000 h creep rupture strength (MPa)

<table>
<thead>
<tr>
<th>Steel Name</th>
<th>Composition</th>
<th>600°C</th>
<th>650°C</th>
<th>700°C</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP304H</td>
<td>18Cr-8Ni</td>
<td>89</td>
<td>52</td>
<td>28</td>
<td>[14]</td>
</tr>
<tr>
<td>TP316H</td>
<td>16Cr-12NiMo</td>
<td>120</td>
<td>43-78</td>
<td>20-50</td>
<td>[15]</td>
</tr>
<tr>
<td>TP321H</td>
<td>18Cr-10NiTi</td>
<td>100</td>
<td>62</td>
<td>35</td>
<td>[14]</td>
</tr>
<tr>
<td>TP347H</td>
<td>18Cr-10NiNb</td>
<td>85-181</td>
<td>53-109</td>
<td>38-60</td>
<td>[15]</td>
</tr>
<tr>
<td>Tempaloy A-1</td>
<td>18Cr-10NiNbTi</td>
<td>139</td>
<td>93</td>
<td>58</td>
<td>[15]</td>
</tr>
<tr>
<td>Super304H</td>
<td>18Cr-9NiCuNbN</td>
<td>185</td>
<td>125</td>
<td>70</td>
<td>[15]</td>
</tr>
<tr>
<td>Tempaloy AA-1</td>
<td>18Cr-10NiCuTiNb</td>
<td>189</td>
<td>126</td>
<td>77</td>
<td>[17]</td>
</tr>
<tr>
<td>TP310</td>
<td>25Cr-20Ni</td>
<td></td>
<td></td>
<td></td>
<td>[16]</td>
</tr>
<tr>
<td>HR3C</td>
<td>25Cr-20NiNbN</td>
<td>192</td>
<td>125</td>
<td>67</td>
<td>[15]</td>
</tr>
<tr>
<td>Alloy 800H</td>
<td>21Cr-32NiTiAl</td>
<td>160</td>
<td></td>
<td>53</td>
<td>[15]</td>
</tr>
<tr>
<td>NF709</td>
<td>20Cr-25NiMoNbTi</td>
<td>170</td>
<td>130</td>
<td>85</td>
<td>[15]</td>
</tr>
<tr>
<td>SAVE25</td>
<td>22.5Cr-18.5NiWCuNbN</td>
<td>150</td>
<td></td>
<td>89</td>
<td>[15]</td>
</tr>
<tr>
<td>Sanicro25</td>
<td>22Cr-25NiWCuNbN</td>
<td>285</td>
<td>178</td>
<td>97</td>
<td>[18]</td>
</tr>
<tr>
<td>CR30A</td>
<td>30Cr-50NiMoTiZr</td>
<td>170</td>
<td>130</td>
<td>90</td>
<td>[15]</td>
</tr>
<tr>
<td>HR6W</td>
<td>23Cr-43NiWNBi</td>
<td></td>
<td></td>
<td>93</td>
<td>[15]</td>
</tr>
</tbody>
</table>

**Fig. 1.** Influence of nitrogen on rupture life for 316LN at 650°C for four creep stresses. Data from [19]
The most efficient way to increase the creep strength is to introduce fine precipitates. Addition of copper can give a significant strengthening effect. This is shown in Fig. 2.

**Fig. 2.** Influence of Cu additions on the rupture time of 18Cr–9NiNbN steel (Super 304H) at 700 and 750 °C. Data from[21]

Austenitic stainless steels 310 and Alloy 800H have chromium contents in the range of 20 to 25%. Both steels have low creep strength at 700 °C. 310 is generally used at much high temperatures due to its excellent corrosion resistance, in spite of modest creep strength. The creep strength of 310 is improved by developing the HR3C steel (25Cr-20NiNbN).

NF709, SAVE25, Sanicro25, CR30A, and HR6W are five steels listed in Table 2.1 that have rupture strengths at 700 °C between 85 and 100 MPa. During service precipitation strengthening occurs due to carbonitrides and fine intermetallic phases such as laves and carbides. Solid solution strengthening achieved by alloying of dissolved atoms is one of the important strengthening mechanisms in austenitic stainless steel. There are two types of solid solution strengthening mechanisms i.e. substitutional solid solution and interstitial solid solution. Substitutional solid solution involves the solute atoms which are replacing the atoms in the crystalline lattice of the base metal. Solute atoms and solvent atoms must have the same crystal structure. Interstitial solid solution involves the solute atoms which are smaller than the solvent atoms and end up in spaces between the atoms in the lattice.

A combination of precipitation hardening and solid solution strengthening can give high strengthening in austenitic stainless steel. Precipitation hardening by carbonitrides is one of the most common strengthening mechanisms for austenitic stainless. When the material is exposed at high temperature for long times, theses particles coarsen, which enables dislocations to bypass them during deformation, then strength starts to decline.
2.1 Precipitates in austenitic stainless steel

Austenitic stainless steels are the most widely used stainless steels for high temperature applications. Due to excellent corrosion resistance and mechanical properties at high temperatures, they are used for power plant tubes and aero engines. The role of precipitation for the achievement of good creep properties is very important. Different types of precipitates are found in the austenitic stainless.

σ phase is a well known intermetallic phase which may occur in stainless steel. The precipitation of σ phase reduces the ductility, toughness and corrosion resistance of steel. Padilha [13] studied precipitation in AISI 316L(N) during creep tests at 550 and 600 °C up to 10 years. σ phase, laves phase and M23C6 were detected and found that volume fraction of precipitated σ phase was significantly higher than laves phase and carbides. Minami [22] found that σ phase precipitation occurred after 1000h at 700 °C in austenitic stainless steels 347 and 321. In 304H, 316H and Tempaloy A1, a significant amount of σ phase was found after 10000 h as shown in Fig. 3.

![Graph showing precipitation of σ in different grades of austenitic stainless steel at 700 °C](image)

**Fig. 3.** Precipitation of σ in different grades of austenitic stainless steel at 700 °C [14]

The term M23C6 is a common notation for Cr23C6, where M denotes the metal atom of the carbide, which might contain iron and molybdenum with chromium. Intergranular corrosion in high chromium austenitic stainless steel is caused by the depletion of chromium in the vicinity of the boundaries due to chromium carbide formation [23]. High concentration of chromium in M23C6 particles decreases the chromium contents of the matrix locally below 12% which is required for stainless steel to prevent from corrosion and oxidation. M23C6 precipitation takes place on grain boundaries, non-coherent and coherent twin boundaries and on dislocations. Trillo
and Murr [24] investigated the M$_{23}$C$_6$ carbide precipitation behaviour on varying grain boundary misorientations in 304 stainless steels and observed that predominant growth of carbide occurred at grain boundaries. M$_{23}$C$_6$ precipitation was found in type 316 austenitic stainless steel resulting from long term high temperature service [25]-[26]. Other carbides such as M$_7$C$_3$ and M$_6$C are also reported in literature.

M$_{23}$C$_6$ precipitations degrade the intergranular corrosion resistance and reduce the tensile properties, particularly toughness and ductility. Gan [27] studied the effects of creep on the mechanical properties of stainless steel type 316 and found that intergranular carbides caused a moderate reduction in tensile ductility and fracture energy.

Z phase is a complex chromium niobium nitride which is found in niobium stabilized austenitic stainless steels. It forms on grain boundaries, twin boundaries and within grains. Since it forms a fine dispersion of particles, it is an interesting phase when good creep properties are required. The Z phase was found during the investigation of precipitates in a high-nitrogen stainless steel 20Cr-9Ni containing 0.38 N and 0.27Nb (wt%) [28]. Sourmail [29] studied precipitation in the creep resistant austenitic stainless steel NF709, 20Cr-25Ni (wt%) and observed Z phases.

MX carbonitrides are observed in austenitic stainless steel when elements such as Ti, V, Zr, Ta Nb are added [30]. MX has a NaCl face centered cubic structure. These elements are added to the alloy to increase intergranular corrosion resistance and to improve creep resistance of the material. Dispersion strengthening is a good choice for obtaining high creep strength in metals and alloys. A fine dispersion of alloying elements in metal matrix can result in high strength of the materials. Ti and Nb are the most commonly used stabilising addition to stainless steel. They form stable nitrides in the presence of N and carbides in the presence of C.

The dispersoids can proficiently block dislocation moment at higher temperature and prevent the materials from plastic deformation [31] and increase the strength of steel. Now a days nitrogen-rich Nb-based precipitates are of great interest for practical applications. These dispersoids have been used in the most advanced commercial austenitic alloys developed recently such as HR3C and Sanicro 25 [32], [33]. The creep strength is generally based on solid solution hardening and particle strengthening. One of the most common hardening mechanisms for austenitic stainless steel with higher creep strength is precipitation-strengthening. Continuous efforts to improve heat-resistant austenitic stainless steel will lead to the development of a new generation of austenitic stainless with higher creep strength for the application in steam boiler of ultra-supercritical power plants with higher steam temperature and pressure.

The positive effect of MX type particles on creep strength of ferritic steel is well known [34]. The precipitation hardening by fine MX type particles can be tremendously efficient.

Laves phase is an intermetallic phase that forms in various grades of austenitic stainless steel. It precipitates normally intragranularly but it is occasionally found on grain boundaries [35]. The addition of W in the austenitic stainless steel increases the strength of steel through solid solution
hardening. The addition of W gives rise to precipitation of Laves phase in austenitic stainless steel HR6W (23Cr45Ni7WNbB) and increases solid solution hardening [36], [37].
3 CREEP

Creep is plastic deformation that takes place at constant load when the material is exposed at high temperatures for longer times, even if the stresses are less than the yield strength. Creep also occurs in materials that are used for high temperature applications and is of great technical significance. Boiler, gas turbine engines and furnace components are the examples of systems where creep frequently occurs. The creep rate is increased by an increase in temperature or applied stress. A typical creep curve is shown in Fig. 4. In the primary region, deformation hardening dominates. The creep rate is decreased in this region due to the increase in dislocation density. In the secondary region, the number of dislocation has increased leading to an increased annihilation. The secondary region is characterised by a constant creep rate, which is the result of a balance between deformation hardening and dislocation annihilation. In the tertiary region, accumulation of creep damage increases the creep rate. The material is approaching fracture in this region.

![Creep strain versus time graph](image)

**Fig. 4.** Creep strain versus time graph

There are three basic mechanisms that can contribute to creep in metals, namely:

### 3.1 Grain boundary sliding

Grain boundary sliding is one of important deformation mechanisms during creep. Grain boundaries play an important role in the creep of polycrystals at high temperatures as they slide past each other or create vacancies. At higher temperatures, grain boundaries of ductile metals become soft and grains start to slide against each other. Grain boundary sliding increases with
increase in temperature and total grain boundary area, i.e. with decreasing grain size. At temperatures above 0.5 $T_m$ (Melting temperature), the viscosity of the grain boundaries becomes so small it allows them to slide against each other. But at low temperatures, grain boundaries behave like a very viscous liquid separating the neighbouring grains and provide effective hindrance to dislocation motion. The grain boundaries ease the deformation process by sliding at high temperatures but at low temperatures, grain boundaries increase the yield strength by impeding the dislocations. Therefore small grains are not used when creep resistance is needed, because they increase the grain boundary area [38].

### 3.2 Diffusion creep

Diffusion creep occurs due to the flow of vacancies and interstitials through a crystal under the influence of applied stress which leads to grain deformation. When temperature increases, the diffusivity of the material increases which leads to more deformation in the material. There are two types of diffusion creep [39]. If the diffusion of vacancies occurs predominantly along the grain boundaries, the creep process is called Coble creep which is favoured at lower temperatures. If the migration of vacancies occurs through the grains themselves, the creep process is called Nabarro-Herring creep, which occurs at higher temperatures. This process is shown in Fig. 5 where it is obvious that vacancy flow linked with the idealized square grain can take place through the crystalline matrix in Nabarro-Herring creep process or along the grain boundaries in Coble diffusion creep. Diffusion creep is more common in small size crystals at low stresses and high temperatures.

![Fig. 5. The principle of diffusion creep showing vacancy flow through the grains (Nabarro-Herring creep) or along the grain boundaries (Coble creep) [40](image)](image)

### 3.3 Dislocation creep

Dislocation creep mechanism involves the motion of dislocations. In general, the dominating creep mechanism is dislocation creep. Dislocations can move by glide in a slip plane in the
crystal lattice or by climb. For decreasing the creep rate, there should be some obstacles against dislocation movement. These obstacles may be other dislocations, solute atoms, grain boundaries and precipitates. Therefore the creep strength of the metal can be increased by introducing obstacles. These strengthening mechanism are grain boundary strengthening, solid solution strengthening and precipitation hardening.

An important characteristic of high temperature creep is the steady state creep rate, $\dot{\varepsilon}$, which changes with the applied stress and temperature and the grain size of the material. Fig. 6 illustrates the creep behaviour in a typical metal. Creep behaviour in terms of steady state creep rates may be divided into three regions. First region covers very low stress levels. This region is generally credited to diffusion creep and/or grain boundary sliding. The second region covers intermediate stresses. This region is connected to dislocation creep in which creep strains occurs due to the movement of dislocations by glide and climb process. Third region is a deviation from linearity at very high stresses and is referred to as power–law breakdown (PLB).

![Schematic figure of the variation in a logarithmic plot of the steady-state creep rate, $\dot{\varepsilon}$, with the applied stress, $\sigma$, for a typical polycrystalline metal: The plot reveals an extensive region with constant creep rate (power-law creep) at intermediate stresses. PLB (Power-law breakdown) occurs at very high stresses and a transition to a region having a lower slope at low stresses due to the occurrence of diffusion creep or grain boundary sliding [40]](image)

**Fig. 6.** Schematic figure of the variation in a logarithmic plot of the steady-state creep rate, $\dot{\varepsilon}$, with the applied stress, $\sigma$, for a typical polycrystalline metal: The plot reveals an extensive region with constant creep rate (power-law creep) at intermediate stresses. PLB (Power-law breakdown) occurs at very high stresses and a transition to a region having a lower slope at low stresses due to the occurrence of diffusion creep or grain boundary sliding [40]
Plastic deformation occurs due to the direct result of dislocation movement which results into macroscopic deformation. In other words, the ability of a material to deform plastically depends on ease of dislocation motion. Any obstruction of this movement will act as a hardening mechanism by improving mechanical properties like yield and tensile strength. There are different mechanism to obstruct the motion of dislocations including work hardening, grain boundary hardening, solid solution hardening and precipitation hardening.

4.1 Work hardening

Work hardening (known as strain hardening) is a strengthening mechanism which takes place due to interaction between dislocations. When a material is plastically deformed, dislocations move and addition dislocations are produced. Due to increasing the dislocation density within a material, the more they will interact and become pinned or scrambled. As a result, by decreasing the mobility of the dislocations, the strength of the material will increase. This process should be occurring at a temperature low enough to prevent the atoms rearranging themselves. This type of strengthening is generally called cold-working. At higher temperatures (hot-working) the dislocations can rearrange themselves and modest strengthening is attained. However this type of strengthening results in a significant reduction in ductility. The increment of stress due to density of dislocations is generally expressed with the Taylor equation:

\[ \sigma_{w.h.} = M\alpha G b \sqrt{\rho_d} \] (3)

where \(\alpha\) is a numerical constant of the order of 0.2, \(G\) is shear modulus, \(b\) is burgers vector and \(\rho_d\) is dislocation density. The value of dislocation density increases with strain. Work hardening is more effective at low temperatures and higher strain rates because of lower annihilation of dislocations.

4.2 Grain boundary hardening

The influence of grain size on the mechanical properties of stainless steel is complex because grain boundaries may either act as a barrier to dislocation motion and contribute to the strengthening of the material or provide a positive contribution to deformation and softening of the material. These two opposite effects depend on the temperature as pointed out by Kutumba Rao et al. [41]. This is illustrated in Fig. 7. The cross-over temperature, \(T_c\) for a given alloy depends on the microstructure and the deformation rate.
Fig. 7. Influence of grain size on the flow stress at 0.2% and 5% strain in manganese stainless steel. The range of temperature is straddling the cross over point [41]

At low temperatures, material becomes harder with decreased grain size. Grain boundary strengthening depends on grain boundary structure and misorientation between individual grains. The smaller the grain size, the higher the yield strength. The relationship between the strength and the grain size is determined by Hall-Petch equation [42].

\[
\sigma_y = \sigma_0 + Kd^{-0.5}
\]

where \(\sigma_0\) is a friction stress and \(k\) is the Hall-Petch coefficient. The Hall-Petch law is only applicable for deformation at low temperature.

At high temperatures, material becomes softer with decreased grain size as shown in Fig. 7. At high temperatures, the secondary creep rate in the majority superalloys is usually a decreasing function of increasing grain size \(d\). The lack of creep resistance for small grain materials is generally due to the grain boundary sliding. Fig. 8 presents the effect of grain size on the minimum creep rate for different alloys containing various \(\gamma\) volume fraction, \(f_\gamma\). At smaller grain sizes the steady state creep rate is proportional to \(d^{-2}\).
4.3 Solid solution hardening

Solid solution is a type of alloying that can be used for the improvement in strength. It involves the addition of elements in the crystalline lattice of the base metal which produces high distortion due to difference of sizes of solute atoms and base atoms. This obstructs the dislocation motion and increase the strength of the material. The stress field in the region of the solute atoms can interact with the dislocations. The added atoms may be located in either interstitial or substitutional sites, depending on their sizes relative to those of base atoms. Solute atoms with radii upto 57% of the base atom may occupy the open spaces in the matrix, while those that are within ±15% of base atom radii substitute the original atoms in the crystal lattice.

Since the solute atoms have different sizes and shear moduli from the base atoms, they produce extra strain fields within the material. These strain fields interact with those of dislocations, impede the dislocation movement, causes the increase in strength of a material.

The efficiency of solid solution hardening depends upon the size mismatch and modulus mismatch between the solute atoms and base atoms. Size mismatch produces misfit strains and the resulting misfit strains are proportional to the change in the lattice parameter per unit
concentration. Similarly modulus mismatch also produces modulus misfit strains. The size misfit
is defined by eqn. (5) and shear misfit by eqn. (6).

\[ \varepsilon_b = \frac{db}{bdc} \]  
\[ \varepsilon_G = \frac{dG}{Gdc} \]

where \( b \) is burgers vector and correspond to the magnitude and direction of the lattice distortion
of dislocation in a crystal lattice, \( c \) is the fraction of elements in solid solution in atomic percent
and \( G \) is the shear modulus. Labusch and Nabarro [44], [45] combined the size misfit parameter
and shear misfit parameter into a single misfit parameter, which is a linear combination of size
and modulus misfit factors.

\[ \varepsilon_L = \left[ (\varepsilon'_G)^2 + (\alpha\varepsilon_b)^2 \right]^{1/2} \]

where \( \varepsilon'_G = \varepsilon_G / \left[ 1 + (0.5)\varepsilon_G \right] \) and \( \alpha \) is equal to ±16 for edge dislocation. The edge
dislocations identify the positive or negative sign of \( \alpha \).

Labusch also determined the interaction force \( f_m \) between a dislocation and the solute atoms and
is defined by the expression:

\[ f_m = \left( \frac{Gb^2}{120} \right) \varepsilon_L \]  

In a later article Nabarro[46] obtained the expression for the critical resolved shear stress for
solid solution strengthening.

\[ \tau_{LN} = \left( \frac{1}{2b} \right) \left( \frac{f_m^4 \varepsilon^2 w}{E} \right)^{1/3} \]

where \( w \) is the range of the maximum interaction force \( f_m \) between a solute atom and a
dislocation, \( c \) is the fraction of solute. Empirical expressions for solid solution hardening at room
temperatures in the form of element contents exist. Examples of such expression are [47].

\[ \Delta R_{p0.2} = 77\sqrt{N} + 20Mn + 7Cr + 33Si + 2.9Ni + (0.24 + 1.1N)d_{grain}^{-0.5} \]  

In the similar way, tensile strength is also decreased due to the loss of solid solution hardening
\[ \Delta R_m = 481N + 9.3Cr + 9.5Mo + 13Si - 6.9Ni + 0.21d_{grain}^{-0.5} \]

\( N, Mn, Cr, Si, Ni, Mo \) are the element contents (wt%), \( d_{grain} \) is the diameter of grain in m, \( \Delta R_{p0.2} \)
is the increase in yield strength and \( \Delta R_m \) is the increase in tensile strength.
### 4.3.1 Solid solution hardening during creep

Sandström and Andersson [48] have determined the solid solution hardening of about 50 ppm phosphorus in copper using Labusch-Nabarro’s model. The solid solution hardening effect on the creep rate was calculated by considering the additional times for dislocations to pass a solute and for the solute to diffuse away from the front of the dislocation.

The interaction energy between a solute atom and an edge dislocation can be calculated as

\[ W = -bE \frac{y}{x^2 + y^2} \]  

(12)

where \((x,y)\) is the position of the solute relative to a dislocation that is climbing in the \(y\)-direction or gliding in the \(x\)-direction. The maximum interaction energy \(E\) between the solute and the dislocation can be determined by the eqn.(13).

\[ E = -\frac{1}{3\pi} \frac{(1+\nu)}{(1-\nu)} G\nu_a \varepsilon_b \]  

(13)

where \(\nu\) is Poisson’s number, \(G\) is the shear modulus, \(\varepsilon_b\) is the lattice mismatch and \(\nu_a\) is the atomic volume.

The drag stress due to the presence of the solutes which retard the dislocation can be expressed as

\[ \sigma_{drag} = \int_{y_L}^{y_R} c_{Pdyn} \left( -\frac{\partial W}{\partial y} \right) dy \]  

(14)

\(c_{Pdyn}\) is the concentration of solute around a moving dislocation and calculated by the following equation.

\[ c_{Pdyn} = \frac{v c_{po}}{D_p} \left( e^{-\frac{W(y)}{KT}} \int_{-\infty}^{-\infty} e^{-\frac{W(y')}{KT}} \frac{dy'}{D_p} \right) \left( e^{-\frac{vy}{D_p}} - e^{-\frac{vy'}{D_p}} \right) \]  

(15)

where \(v\) is the velocity of the dislocation, \(c_{po}\) is the equilibrium concentration of solute, \(D_p\) is the diffusion coefficient for solute in matrix and \(y\) is the coordinate in climb direction.

For a dislocation to move further, it should break away from the solute clouds. An additional stress known as break stress is required. Break stress can be calculated from an energy balance between the work done by the applied stress and the binding energy between a solute and a dislocation. The break stress \(\sigma_{break}\) can be expressed as [48]

\[ \sigma_{break} = \frac{E}{b^2} \left( 1 - \frac{\sigma_{app}}{\sigma_m} \right) \int_{y_L}^{y_R} c_{Pdyn} dy \]  

(16)
where $\sigma_{\text{app}}$ is the applied stress, $\sigma_m$ is the tensile strength. With the help of the model above influence of phosphorus on the creep strength has been calculated. The effect of $\sigma_{\text{break}}$ on the creep rate versus stress curves is shown in Fig. 9 for 180-250 °C. The difference between the marked Glide and Model curves is $\sigma_{\text{break}}$ and it is the influence of phosphorus on the stationary creep stress at a given creep rate. When climb is controlling, then the values of $\sigma_{\text{break}}$ are half of those for glide.

![Creep rate versus stress](image)

**Fig. 9.** Creep rate versus stress. Data at 180, 215 and 250 °C are presented forming three groups in the figure. The left hand curve in each group marked Model for Cu-OF. The curves marked Climb (middle curve) and Glide (right hand curve) represent $\sigma_{\text{break}}$ added to the model values for two deformation mechanism according to Eq. (16).[48]

In Fig. 10 the Climb and Glide curves are compared with the experimental results for Cu-OFP. The creep stress that is needed for a given strain rate is higher for Cu-OFP than Cu-OF. The break stress increases with decreasing temperature and applied stress.
Fig. 10. Creep rate versus stationary stress for Cu-OFP. The curves marked Climb and Glide represent the result when these two mechanisms are controlling. Temperature range 180-250 °C [48].

Magnusson and Sandström [49] used the same model for the solid solution strengthening. Three elements W, Mo and Cr were selected for solid solution analysis. Fig. 11 shows the interaction energies as a function of distance from the dislocation for elements W, Mo and Cr. The differences in interaction energy are due to the difference in size misfit.

Fig. 11. Interaction energy around the dislocations. The length unit is in Burger vectors in climb direction with compression at positive coordinate [49].

The reduction in climb mobility due to solid solution hardening, $k_{sol}$ is a function of temperature and stress. $K_{sol}$ factor is defined as
\[ K_{sol} = \frac{M_{climb}}{M_{climb_{old}}} \]  

(17)

The \( k_{sol} \) parameter is also time dependent due to the depletion of elements with the growth of precipitates. The predicted reduction in climb mobility keeping time and concentration constant at 600 °C is shown in Fig.10a. Fig. 12b represents \( k_{sol} \) as a function of temperature keeping stress and concentration constant. Temperature has greater influence on the \( k_{sol} \) parameter compared to the stress.

![Graph](image)

**Fig. 12 a)** The reduction in climb mobility defined as \( k_{sol} \) shown as function of stress keeping time and concentration constant  

**b)** \( k_{sol} \) parameter as function of temperature with stress and time constant [49]

### 4.4 Precipitation hardening

Precipitation hardening is probably the most potent way of increasing the creep strength of metal alloys including stainless steels. It is based on small uniformly dispersed second phase particles which increase the strength and hardness of a material by impeding the dislocation movement in a crystal lattice. However, some precipitates like \( \sigma \) phase, laves phase and chi phase have an unfavourable effect on the strengthening of a material. These phases often in the form of larger particles provide a suitable place for stress concentration, initiation and propagation of cracks which results in failure of a material. These intermetallic particles also reduce the amount of solute atoms that are contributing in solid solution strengthening and thus decrease the creep strength.

The first hardenable aluminium alloy was discovered by A. Wilm in 1911. This alloy was aluminium-copper alloy named Duralumin [50]. This alloy was discovered accidently, when left over a weekend, and during that time natural aging increased the strength of alloy significantly as shown in Fig.13 [51].
Fig. 13. The first age hardening curve published by Alfred Wilm in 1911, and referring to an aluminium based alloy [50].

Precipitation hardening depends upon different factors like size, shape, structure, strength, spacing between the precipitates and distribution of precipitates [52]. The sizes of hardening precipitates may range around 1 to 100 nm. Fig. 14 illustrates the dislocation-particle interaction mechanism, where $T_L$ is the line tension of the dislocation, $R$ is the radius of the curvature of the dislocation, $\lambda$ is the distance between the obstacles and $\phi$ is the breaking angle and $F$ is the resistance force of the second phase particle. Balance of forces between line tension of dislocation and resistance force of the obstacle gives the relation

$$F = 2T_L \cos(\phi/2)$$

(18)

When breaking angle $\phi = 0$, then particle acts as impenetrable obstacle and for $\phi > 0$, then the particle will be sheared by the dislocation.
Fig. 14. Dislocation held up at array of point obstacles, where $T = T_L$ is the line tension of the dislocation, $\lambda$ is the distance between obstacles, $R$ is the radius of curvature of the dislocation, $F$ is the strength of the obstacles, $\phi$ is the breaking angle \[50\]

There are two concepts to deal with the resistance to dislocation movement within a material because of the presence of precipitates i.e. particle shearing and Orowan bowing. There are different shearing mechanisms that give different contributions to the strength. Precipitate particles can obstruct the motion of dislocations by different mechanisms such as chemical strengthening, stacking-fault strengthening, modulus strengthening, coherency strengthening and order strengthening.

**Chemical strengthening**

Chemical strengthening is the result from the additional interface of energy, $\gamma_{m/p}$ between the precipitate and matrix created by the dislocation when it shears the particle. The chemical strength is calculated by the eqn. (19).

\[
\sigma_{chem} = 1.95M \frac{1}{Gb} \gamma^{3/2}_{m/p} \sqrt{\frac{f}{r}}
\]

(19)

where $M$ is the Taylor factor, for austenite $M = 3.06$, $G$ is the shear modulus, $b$ is the burgers vector, $f$ is the volume fraction of the precipitates and $r$ is the radius of the particle [53].

**Stacking –fault strengthening**

This mechanism occurs due to the difference of the stacking-fault energies of the precipitates and the matrix. The strength due to stacking-fault energies is proportional to $\Delta \gamma_{sf}$ and $\sqrt{fR}$, where $\Delta \gamma_{sf}$ is the difference of stacking fault energies between the matrix and the particle, $f$ is the volume fraction of the particles and $r$ is the radius of the particles.

**Modulus strengthening**

Modulus strengthening occurs due to the difference of shear modulus of the matrix and the precipitate. Melander and Person [54] studied this effect and gave the following model for increment in strength.
\[ \sigma_{\text{mod}} = 0.16M \sqrt{\frac{1}{Gb}} \Delta G^{3/2} \left[ \ln \left( \frac{2r}{\sqrt{fr}} \right) \right]^{-3/2} \]

(20)

where \( M \) is the Taylor factor, \( \Delta G \) is the difference of shear modulus between the matrix and precipitate, \( f \) is the volume fraction of the precipitates and \( r \) is the radius of the particles.

**Coherency strengthening**

Coherency strengthening produced from the elastic coherency strains around a particle where the lattice does not fit the matrix exactly. The strengthening of alloys by misfitting coherent particles takes place due to the interaction of stress fields of the dislocation and the precipitates. The increase in strength due to this mechanism is expressed by the following equation.

\[ \sigma_{\text{coh}} = \frac{3M G}{\sqrt{b}} \varepsilon_{m/p}^{3/2} \sqrt{fr} \]

(21)

where \( G \) is the shear modulus, \( \varepsilon_{m/p} \) is the coherency strain, \( r \) is the average radius and \( f \) is the volume fraction of precipitates [55].

**Order strengthening**

Strengthening by ordered precipitates takes place, when a dislocation shears an ordered precipitate and produces an antiphase boundary (APB), a region where the order is disturbed. The APB energy per unit area, \( \gamma_{APB} \) gives the force per unit length opposing the dislocation motion when it passes through the particle. The strength due to this mechanism is given by the following expression.

\[ \sigma_{APB} = 1.95M \sqrt{\frac{1}{Gb}} \gamma_{APB}^{3/2} \sqrt{fr} \]

(22)

where \( \gamma_{APB} \) is the energy required to create an antiphase boundary (APB) [53].

Different shearing mechanisms including chemical strengthening, coherency strengthening and modulus strengthening are illustrated in Fig. 15 for changing the size of the particles and keeping the volume fraction of particles as 0.5% in each case. For austenite, shear modulus \( G \) is \( 8 \times 10^{10} \) Pa, burgers vector \( b \) is \( 2.52 \times 10^{-10} \) m [56]. For chemical strengthening eqn.(19), the particle/matrix interfacial energy \( \gamma_{m/p} \) is \( 1.5 \) J/m\(^2\) [57]. The shear modulus of the particle, \( G_{copper} \) is \( 4.8 \times 10^{10} \) Pa. So \( \Delta G \) for the modulus strengthening eqn. (20) is \( 3.2 \times 10^{10} \) Pa. The coherency strengthening depends on the misfit strain between the matrix and the precipitates. The value of \( \varepsilon_{m/p} \) is 0.0057 for Cu in Fe base alloys [58].

All mechanisms contribute to the strength in the similar way except chemical strengthening. With the exception of chemical strengthening all other mechanisms can be modelled approximately as [59].
\[ \sigma_{\text{cut}} = c_1 M \frac{1}{\sqrt{T_L}} \Delta^{3/2} \sqrt{f r} \]  \hspace{1cm} (23)

where \( c_1 \) is constant, \( M \) is Taylor factor, \( T_L \) is line tension of the dislocation normally taken as \( Gb^2/2 \) and \( \Delta \) is the particular interaction term with the dimension of energy.

---

**Fig. 15.** The strengthening as a function of radius of the precipitates for different shearing mechanisms. The fraction of particles \( f \) is 0.5 volume %.

When precipitates grow, the resistance force of the precipitates to dislocation movement \( F \) in Fig. 14 is increased and dislocations can no longer shear the particles. But dislocations will bypass the particles as shown in Fig. 16. Eqn. (18) shows that when \( F \) increases, the breaking angle \( \phi \) decreases and finally becomes zero, and then dislocations will bypass the particles. Now precipitation strengthening depends only on the interparticle spacing, \( \lambda \). Strength is inversely proportional to the \( \lambda \) and this mechanism is called the Orowan mechanism[60].
A basic form of the Orowan equation is given by the following expression.

$$\sigma_{Or} = \frac{MGb}{\lambda}$$

(24)

where $\sigma_{Or}$ is the increase in strength due to Orowan mechanism, $G$ the shear modulus of the matrix, $b$ the burger vector of the dislocation, $M$ Taylor factor and $\lambda$ is the distance between the particles. Assuming that $\lambda$ is determined from a square network of particles, the Orowan stress can be expressed as

$$\sigma_{Or} = M \sqrt{\left(\frac{3}{2\pi}\right) \frac{Gb}{r} \sqrt{f}}$$

(25)

According to the Orowan-Ashby model of precipitation strengthening where the interaction between the two parts of the dislocation surrounding a particles are taken into account, the increase in strength can be represented as [61]

$$\sigma_{Or} = \left(10.8\sqrt{f / D}\right)\ln(1630D)$$

(26)

where $\sigma_{Or}$ represents the precipitation strengthening increment in MPa, $f$ is the precipitate volume fraction and $D$ is the mean particle diameter in micrometers. The Friedel estimate of the interparticle distance is also used. Eq. (26) often gives a slightly lower value than (25). Myhr et al [62] calculated the strength with the following equation

$$\sigma_{Or} = \frac{M}{b} \sqrt{\left(\frac{3}{2\pi}\right) (2\beta Gb^2) \frac{f}{r}}$$

(27)

where $\beta$ is a statistical factor accounting for the variations in particle spacing in the plane and equal to 0.36 according to Myhr. Eq. (27) gives a value of 0.72 of the value from Eq. (25).
For very fine particles, shearing of particles by the dislocations normally gives a lower stress than bowing around the particles. With the increase of particle size, shearing becomes more difficult which results in increase of strength due to particles. Above a critical particle size, bowing dominates. For a given volume fraction of particles, bowing of dislocations becomes easier with increasing of particle size, which results in decreasing the strength. Therefore the particle size for the maximum strengthening is found at the transition from shearing mechanism to bowing mechanism. This is illustrated in Fig. 17. The critical size of the particle, where the shearing mechanism goes to bypassing mechanism, depends upon the strength of the particles and volume fraction of the precipitates. Schuller and Wawner[64] determined the critical size of σ-phase is 1.35nm and the critical size for Mg_2Si particle was calculated to 5nm [65]. Since particles in creep resistant stainless steel are typically larger than 10 nm, the shearing stress is much larger than the Orowan stress and consequently the particles will be bypassed according to the Orowan mechanism (or climbed as will be discussed below).

Fig. 17. Representation of relationship between strength and particle size for particles shearing (using eq. (23)) and particles bypassing (using eq. (25)). The fraction of particles \( f \), are 2 volume %

On the precipitation strengthening curve, a transition region takes place where neither particle shearing nor Orowan bypassing dominate the strengthening process. This is for the reason that a given microstructure has a distribution of both types of particles .i.e. shearable particles and the particles looped by the dislocations. Especially at the peak strength condition, both particle shearing and particle looping occurs. In artificially aged hardened alloy, a greater number of precipitates will be looped and a smaller number will be sheared. Fragomani [66] determined the simultaneous effect of both strengthening mechanisms on precipitation hardening and gave the model such as.
\[ \sigma_{\text{Particle}} = \frac{\sum_{i=1}^{m} F_{\text{ishear}} + \sum_{i=m}^{n} F_{\text{iloop}}}{A_{\text{particle}}} \]  

where \( F_{\text{ishear}} \) is the total force to shear all the shearable particles and \( F_{\text{iloop}} \) is the total force required to bypass all non-shearable particles, \( n \) is the total number of particles in the distribution, \( m \) is the total number of shearable precipitates, \( n-m \) is the total number of precipitates that are looped by dislocation and \( A \) is the total area of the particles.

### 4.4.1 Precipitation hardening during creep

Eliasson et al. [67] developed a kinetic model for particle strengthening during creep and this model can describe the exponential decrease in strength with increasing temperature. At lower temperatures, the dislocations either cut the particles when they are extremely small or form the Orowan loops around them. At higher temperatures, the dislocations have the possibility to climb or cross slip over the particles. Orowan strength is inversely proportional to the interparticle spacing. The contribution from the Orowan mechanism can be calculated from the following equation.

\[ \sigma_o = \frac{M G b}{L_{sq}} \]  

where \( M \) is the Taylor factor, \( b \) is burgers vector, \( G \) is shear modulus and \( L_{sq} \) is the mean Orowan particle distance and is determined by the following relationship.

\[ L_{sq} = r \sqrt{\frac{2\pi}{3f}} \]  

At higher temperatures, the dislocation can climb over the particles. The effectiveness of climb depends on different factors. The strength contribution related to Orowan strength is decreased by considering the climb factor.

The average speed of the dislocation is determined by

\[ v_p = \frac{\dot{\varepsilon} M}{\rho_m b} \]  

where \( \rho_m \) is the mobile dislocation density. The dislocation climb speed is given by:

\[ v_{\text{climb}} = M_s b \sigma \]  

where \( M_s \) is the mobility of dislocation. If the glide time between the particles neglected, then climb yields an effective average dislocation speed and is given by:

\[ v_{\text{eff}} = v_{\text{climb}} \frac{L_{sq}}{2r} \]
when $v_{\text{eff}} > v_p$, the contribution of climb becomes important. If the particles are very small then they will be crossed by climb and they do not contribute to Orowan strength. The critical radius at which climb starts to be of importance is calculated by:

$$r_{\text{crit}} = r_{\text{part}0} \frac{v_{\text{climb}}}{v_p} \sqrt{\frac{\pi}{6f_0}}$$  \hspace{1cm} (34)

where $r_{\text{part}0}$ is the average particle size, $f_0$ is the volume fraction of particles. The threshold stress at intermediate stresses is given by:

$$\sigma_{\text{crit}} = \frac{\sigma_0 r_{\text{part}0}}{r_{\text{crit}}} e^{(-0.5\beta(r_{\text{crit}} - r_{\text{res}}))}$$  \hspace{1cm} (35)

where $r_{\text{res}}$ is the smallest particle size recorded due to the instrumental resolution limit and $\beta$ is a constant, which is approximately equal to $1/r_{\text{part}0}$. It can be seen from Fig. 18 at 650 °C that the creep strength is reduced with time but still the Orowan mechanism is dominating the strength contribution from the particles. In Fig. 19 at 800 °C, there is a large reduction in creep strength at longer times. In this case the dislocations at some extent climb over the particles.

![Fig. 18-19. Creep stress vs. rupture time at 650 °C and 800 °C, experimental and calculated data for material 15Cr15Ni0.1C0.4Ti [67]](image)

Magnusson and Sandström [68] studied the role of dislocation climb across particles at creep conditions in 9 to 12 % Cr steels. The strength of the particle-hardened materials during creep depends upon the amount and size of the particles. The particle size distribution for 9% Cr steel can be represented by an exponential function as shown in Fig. 20. The cumulative size distribution i.e. the area fraction of particles $f_j(r)$ that are larger than a given particle size $r$, can be written as

$$f_j(r) = F_j \exp\left(-\beta_j \left(r - r_{0,j}\right)\right)$$  \hspace{1cm} (36)

where $F_j$ is the total area fraction of particle kind $j$ in subgrain interiors, $r_{0,j}$ is the smallest accurately recorded particle size and $\beta_j$ is a constant.
Fig. 20. Fraction of particles larger than a given radius. Experimental data for M$_2$C$_6$ and MX at 600 °C and 10,000 h for P92 steel [68]

With the help of the model [80], the influence of particle size distribution, particle area fraction, temperature and stress on the creep rate can be explained. By using the critical radius, which is the maximum particle size for that time for dislocation to climb over the particles is enough or the smallest particle size contributing to Orowan strength.

The total particle hardening at climb conditions can be calculated by using Pythagorean addition of the contribution from different particles. The creep strength can be predicted by using the modified Norton equation.

\[
\dot{\varepsilon} = A_n \exp\left(-\frac{Q_c}{RT}\right)\left(\sigma_{\text{app}} - \sigma_{\text{back}}\right)^n
\]

(37)

where $A_n$ a constant, $Q_c$ the activation energy of creep, $n$ the Norton exponent, $\sigma_{\text{app}}$ the applied stress and $\sigma_{\text{back}}$ the back stress. The back stress is the obstructing stress of the microstructure to the dislocation movement. The particle strengthening decreases with decreasing creep rate as shown in Fig. 21. Fig. 21(a) represents the total particle strength when dislocation climb around particles is to be considered. In Fig. 21(b) dislocation climb is not taken into consideration. With decreasing creep rate, the time available for dislocations to climb over the particles increases and then dislocation will climb across the particles instead of Orowan looping, resulting in a decrease in particle strength. Dislocation climb has a more significant effect on particle strength at high temperatures as shown in Fig. 21(a).
Fig. 21—(a) Particle strength according to dislocation climb model. (b) Particle strength if climb is not taken into account [68]

Particle hardening also decreases with increasing temperature as shown in Fig. 22. One part of this decrease is related to the particle coarsening and a major part is due to the increase in dislocation mobility with increasing temperature. The contribution of larger $\text{M}_2\text{C}_6$ to particle strength at lower temperature is smaller and nearly constant than MX. But the contribution of smaller MX to particle strength decreases as the temperature increases because at higher temperatures MX particles are more easily climbed.

Fig. 22 Particle strength as a function of temperature at minimum creep rate of $10^{-9} \text{ s}^{-1}$ [68]

In the section above models for different contributions to the creep strength has been summarised. By combining these contributions the total creep strength can be predicted. This is illustrated with the following example. The applied stress required to create a minimum creep rate of $10^{-9} \text{ s}^{-1}$ as function of temperature is shown in Fig. 23. Particle hardening is determined by considering the dislocation climb across particles. Subgrain boundaries represents the back stress contribution from the dislocation rich subgrain walls. The dislocation hardening is due to the
static dislocations in subgrain interiors. The chemical composition of P92 is 0.11C, 0.3Si, 0.6Mn, 0.017P, 0.004S, 0.2Ni, 0.5Mo, 1.9W and 9.5Cr (wt.%) [69].

![Fig. 23](image)

**Fig. 23.** The applied stress needed to produce a creep rate of $10^{-9}$ s$^{-1}$, as function of temperature and compared to experimental data [49]

As can be seen from Fig. 13, the different contributions approximately add up to a value close to the applied stress, which is the measured value. The contributions from subgrains in stainless steels has not been possible to discuss since only very limited information can be found in the literature.
5 EXPERIMENTAL DETAILS AND METHODOLOGY

5.1 Materials and heat treatments

In the present work, three austenitic stainless steels 310S, 310NbN and Sanicro 25 were investigated. The chemical compositions of the investigated austenitic stainless steels are listed in Table 5.1. More details can be found in papers A, E and F. Samples of 310S were solution annealed at 1150 °C for 10 min or at 950 °C for 60 °C. Then they were aged at 800 °C for 500, 2000 and 5000 h, respectively. Samples of 310NbN were solution annealed at 1200 °C and quenched after annealing. Some of them were aged at 750 °C for 1000, 3000, or 10000 h and others were aged at 650 °C for 1000, 3000 and 10000 h respectively. Specimens of Sanicro 25 were also solution annealed at 1200 °C. They were aged at 650 and 700 °C for 1000, 3000 and 10000 h, respectively.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Cr</th>
<th>Ni</th>
<th>N</th>
<th>C</th>
<th>Nb</th>
<th>Mo</th>
<th>Cu</th>
<th>W</th>
<th>Mn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>310S-0.4N</td>
<td>24.71</td>
<td>19.94</td>
<td>0.036</td>
<td>0.046</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>0.013</td>
<td>-</td>
<td>1.02</td>
<td>Bal.</td>
</tr>
<tr>
<td>310S-0.12N</td>
<td>24.68</td>
<td>19.91</td>
<td>0.12</td>
<td>0.053</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>0.011</td>
<td>-</td>
<td>0.96</td>
<td>Bal.</td>
</tr>
<tr>
<td>310NbN</td>
<td>24.7</td>
<td>20.6</td>
<td>0.182</td>
<td>0.062</td>
<td>0.44</td>
<td>-</td>
<td>-</td>
<td>2.9</td>
<td>3.7</td>
<td>0.5</td>
</tr>
<tr>
<td>Sanicro25</td>
<td>22.6</td>
<td>25.4</td>
<td>0.2317</td>
<td>0.0646</td>
<td>0.48</td>
<td>-</td>
<td>2.9</td>
<td>3.7</td>
<td>0.5</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

5.2 Optical microscopy

The optical microscope is a fundamental tool for microstructure characterisation. It is used for the determination of surface morphology, shape and size of the grains, shape, size and distribution of the particles of the specimen at micrometer scale.

The specimens of 310S austenitic stainless steel were cut both radial and axial within the gauge length and then mounted, ground, polished and etched to determine the size and shape of grains and size distribution of the particles. The particle distributions have been calculated by manual point counting from light optical micrographs.

Austenitic stainless steel 310NbN specimens were prepared by a melting, casting and hot rolling. Then these specimens were prepared according to a standard method including mechanical grinding, polishing and electrolytic etching. Electrolytic etching in a 10% solution of oxalic acid in distilled water at 3 volt for 10 to 60 s was used. Fig. 24 represents the optical micrograph of
310NbN steel aged 1000 h at 750 °C. Coarser $\sigma$-phase can be observed at the grain boundaries. Finer 23-carbides are also seen at the grain boundaries.

**Fig. 24.** Light optical micrograph of 310NbN aged 1000h at 750 °C

5.3 **Scanning electron microscopy (SEM)**

Scanning electron microscopy is a versatile technique which gives very useful information about surface morphology, size and shape of the grains, size, shape, chemical composition and distribution of the particles of the sample at nanometer scale.

All SEM samples of 310NbN were prepared by mechanical grinding, polishing and electrolytic etching. For the electrolytic etching a 10% solution of oxalic acid in distilled water at 3 volt for 10 to 60 s was used. When the size distribution of the precipitates was determined by SEM, the specimens were prepared by mechanical grinding and polishing only without etching.

The particle structure of Sanicro 25 aged for 10000 h at 700 °C taken from SEM is shown in Fig. 25. The big gray particles are Z phase. Small white particles are laves phase and small black particles are $\text{Cr}_2\text{N}$. Size distribution of these particles were calculated automatically using SEM JEOL 7000F at KIMAB and by manual point counting.
5.4 **Wavelength dispersive spectroscopy (WDS)**

Wavelength dispersive spectroscopy is a precise technique which is used for quantitative analysis of spots as small as a few micrometers and for elements from atomic number 5 and higher. It gives fundamental quantitative compositional information of solid materials. WDS is a complementary to energy-dispersive spectroscopy (EDS) but WDS spectrometers have significantly higher spectral resolution. EDS is normally used for quick elemental analysis of the material and WDS is used to get precise element analysis of the selected phase.

Fig. 26 represents the WDS image of austenitic stainless steel 310 with 0.12%N annealed at 1150 °C for 10 min and aged for 2000 h at 800 °C. A streak of particles can be seen in this Fig. For the identification of these particles, their chemical composition has been detected with the help of wavelength dispersive spectroscopy (WDS). The particle marked 1 has the chemical composition 58%Cr, 0.6%C, 9%Ni and 25%Fe. This particle is $M_{23}C_6$ carbides. The streak may also consist of $\sigma$-phase.
Fig. 26. WDS image of stainless steel 310, high N cast (0.12%N), coarse grained (solution treated at 1150 °C for 10 min) and aged for 2000 h at 800 °C

5.5 Transmission electron microscopy (TEM)

Transmission electron microscopy is an imaging technique widely used for the characterization of specimen’s morphology including the size, shape and distribution of the particles of the sample in the nanometer range. It also gives crystallographic information like the arrangement of atoms in the sample and their degree of order.

Fig. 27 shows a TEM image of the specimen of austenitic stainless steel 310NbN aged for 10000 h at 650 °C taken from a carbon replica sample. The chemical composition of precipitate 1 is 87Cr-0.8C-4Fe. This particle is M23C6 carbide and its size is 594 nm. Precipitate 2 has a chemical composition of 91Cr-3N-4Fe. This precipitate is Cr nitride and its size is 377 nm. The chemical composition of precipitate 3 is 93Nb-0.5Cr-0.6C. Precipitate 3 is a Nb carbide with 262 nm size.

Fig. 27. TEM image of specimen of austenitic stainless steel 310NbN aged for 10000 h at 650 °C
5.5.1 Procedure for preparation of sample for TEM investigations
Transmission electron microscopy needs the preparation of extremely thin specimens from bulk samples so that the electron beam can penetrate through the specimen. For metals, the thickness of the specimen should be 1000 Å or less. Therefore the preparation and handling of such specimens is a matter of considerable practical difficulty.

The most commonly used techniques for TEM specimen are the preparation of thin foils from bulk material by electropolishing or preparation by focused ion beam (FIB). In this study TEM specimens were prepared by using electropolishing. Preparation of thin metallic foils by electropolishing consisted of the following steps.

1. Cut a thin slice of the metal of about 1 cm × 1 cm area and 1 mm thickness
2. Ground and polished the slice of the metal to a foil of 50 to 100 µm thickness
3. Punched the discs with 3 mm diameter suitable for the TEM specimen holder
4. Electropolished the discs until perforation surrounded by small electron transparent material occurred. Electrolyte used was a mixture of perchloric acid, acetic acid, ethanol and butylglyte.
5. Took the discs on the copper grid and then used for TEM investigations

5.5.2 Procedure for preparation of replica for TEM investigations
The replica technique for the examination of surfaces has been extensively used for studying the structures of polished and etched samples. Replication technique can be divided into surface replication and extraction replication. Surface replicas give an image of the surface topography of the sample and extraction replicas lift particles from the sample. Extraction replica techniques can be used to characterize small particles that are embedded in a matrix like second phase particles, Nb(C,N), M23C6 in austenitic stainless steel Sanicro 25. For TEM investigations, the following procedure for the preparation of extraction carbon replica was used and illustrated in Fig. 28.

1. Prepared the metallographic specimens by embedding in epoxy (ethoxylen) resin that is resistant to chemical etching
2. Chemically etched the metallographic specimens. Sanicro 25 specimens were etched with a solution of 40%HCL and 20% HNO3 in distilled water at 60 ºC for 10s.
3. Deposited a carbon film of about 200-250Å thickness on the surface of the sample by evaporation
4. After the carbon deposition, the carbon on the sample surface was cut into squares by a scalpel or mincing knife
5. Separated the carbon film by immersion the sample into the chemical etchant solution. The chemical solution used was 40%HCL and 20% HNO3 in distilled water at 60 ºC. In this phase the metallographic specimen remained in the solution and carbon film was suspended.
6. Then extracted the carbon film fragments on the copper grid and used for TEM investigations.

![Fig. 28. Extraction of carbon replica for TEM investigations](image)

**5.6 Particle size distributions**

The size of different phases in the specimen of 310NbN aged at 750 and 650 °C is measured by scanning electron microscopy and transmission electron microscopy. Sizes of all precipitate increase with increasing aging time. At higher aging temperature the sizes of precipitates are higher corresponding to the sizes of precipitates at lower aging temperature.

The mean diameter of the different precipitates at 750 °C obtained from scanning electron microscopy is plotted against aging time in Fig. 29. The particle diameter of σ-phase increases rapidly with increasing aging time, while the size of Z-phase increases more slowly. The rate of increase is even lower for M₂₃C₆ and the η-phase.
The cumulative size distribution of $\sigma$-phase in specimen 310NbN aged at 650 and 750 °C are shown in Fig. 30 and Fig. 31. The distributions are fitted to the exponential function

$$F = Ne^{-kd_{\text{part}}}$$

where $N$ is the total number of particles per unit area, $k$ the slope of the distribution, and $d_{\text{part}}$ the equivalent area diameter of the particles. The experimental results for $\sigma$-phase can clearly be represented with an exponential function. In Table 5.2, values of the parameters when fitted to the size distribution equation are listed.
Table 5.2. Evaluated Size Distribution Parameters for the precipitate \( \sigma \)-phase in Fig. 30 and Fig. 31

<table>
<thead>
<tr>
<th>Ageing temperature (^{\circ}\text{C})</th>
<th>Ageing time ((h))</th>
<th>Total number of particles per unit area (N, m^2)</th>
<th>Slope of distribution (k, m^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>10000</td>
<td>3.89\times10^9</td>
<td>6.96\times10^5</td>
</tr>
<tr>
<td>650</td>
<td>3000</td>
<td>3.67\times10^9</td>
<td>9.47\times10^5</td>
</tr>
<tr>
<td>750</td>
<td>10000</td>
<td>6.95\times10^9</td>
<td>6.27\times10^5</td>
</tr>
<tr>
<td>750</td>
<td>3000</td>
<td>6.33\times10^9</td>
<td>6.43\times10^5</td>
</tr>
<tr>
<td>750</td>
<td>1000</td>
<td>6.24\times10^9</td>
<td>6.49\times10^5</td>
</tr>
</tbody>
</table>

With increasing ageing time, the particles grow and to some extent increase in number of particles. The ageing temperature has only a small effect on the distributions.

Fig. 30. Cumulative particle distribution of \( \sigma \)-phase in 310NbN at 650 \(^{\circ}\text{C}\) at different aging times
Fig. 31. Cumulative particle distribution of σ-phase in 310NbN at 750 ºC at different aging times

The other types of particles observed can also be represented with an exponential distribution. This is illustrated in Fig. 32 and Fig. 33 for M23C6 aged for 1000, 3000 and 10000 ºC at 650 and 750 ºC respectively. The sizes and cumulative no of particles increase with the aging time and temperature. Values of the parameters when fitted to the size distribution Eq. (38) are shown in Table 5.3. Due to their small size, M23C6 particles contribute to the precipitation hardening.

Table 5.3. Evaluated Size Distribution Parameters for the precipitate M23C6 in Fig. 32 and Fig. 33

<table>
<thead>
<tr>
<th>Ageing temperature (ºC)</th>
<th>Ageing time (h)</th>
<th>Total number of particles per unit area ( N, m^2 )</th>
<th>Slope of distribution ( k, m^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>10000</td>
<td>( 4.59 \times 10^{10} )</td>
<td>( 3 \times 10^6 )</td>
</tr>
<tr>
<td>650</td>
<td>3000</td>
<td>( 3.97 \times 10^{10} )</td>
<td>( 7.22 \times 10^6 )</td>
</tr>
<tr>
<td>650</td>
<td>1000</td>
<td>( 2.88 \times 10^{10} )</td>
<td>( 9.04 \times 10^6 )</td>
</tr>
<tr>
<td>750</td>
<td>10000</td>
<td>( 5.45 \times 10^{10} )</td>
<td>( 1.88 \times 10^6 )</td>
</tr>
<tr>
<td>750</td>
<td>3000</td>
<td>( 4.63 \times 10^{10} )</td>
<td>( 1.99 \times 10^6 )</td>
</tr>
<tr>
<td>750</td>
<td>1000</td>
<td>( 3.49 \times 10^{10} )</td>
<td>( 2.77 \times 10^6 )</td>
</tr>
</tbody>
</table>
Fig. 32. Cumulative particle distribution of $\text{M}_{23}\text{C}_6$ in 310NbN at 650 °C at different aging times

Fig. 33. Cumulative particle distribution of $\text{M}_{23}\text{C}_6$ in 310NbN at 750 °C at different aging times
6 SUMMARY OF APPENDED PAPERS

6.1 Paper A

During service of high temperature materials, extensive precipitation of coarse particles can occur. This is known to significantly affect the mechanical properties in general in a negative way. In particular, the ductility and the toughness are affected. This is of importance for all high temperature plants, not least for power production.

The purpose of paper A was to predict the precipitation behaviour in the austenitic stainless steel 310 and model the formation of particles that can deteriorate ductility and toughness of the material. Particle formation in the austenitic stainless steel 310 has been worked out. Especially σ-phase and M\(_{23}C_6\)-carbides have been analysed. Samples have been aged up to 5000 h at 800 °C. The precipitation of the two phases has been modelled. The basis of the model is diffusion controlled growth. σ-phase showed a spherical growth and M\(_{23}C_6\) planar growth. The soft impingement of the diffusion zones with respect to both chromium and carbon was taken into account. The sizes and the volume fractions have successfully been predicted.

The results show how the composition of the austenitic stainless can be changed to reduce the amount of precipitates and thereby limit their effect on the mechanical properties. This is of direct use in the design of high temperature materials. For example Fig. 34 represents the effect of increasing N on the amount of precipitates. The amount of σ phase decreases rapidly with increasing nitrogen content. The amount of M\(_{23}C_6\) decreases more slowly.

![Equilibrium mol fractions of phases versus nitrogen content at 800 °C.](image)

**Fig. 34.** Equilibrium mol fractions of phases versus nitrogen content at 800 °C.
6.2 Paper B

The purpose of paper B was to investigate the effect of the changes in the microstructure of AISI 310 during long time aging on mechanical properties. For austenitic stainless steels, solid solution hardening can be expressed as

\[
\Delta R_{p0.2} = 77\sqrt{N} + 20Mn + 7Cr + 33Si + 2.9Ni + (0.24 + 1.1N)d_{grain}^{-0.5}
\]  

(39)

Particle hardening due to presence of fine carbides can be determined by the following equation.

\[
\sigma_p = M\frac{3f}{2\pi} \cdot (2\beta Gb) \cdot \frac{1}{r}
\]  

(40)

Ageing in general first increased the strength due to precipitation of fine M23C6. This effect is gradually reduced due to the growth of the carbides. The strength is also influenced by reduced solid solution hardening due to alloy element depletion. Fig. 35 represents the change in yield strength with increasing aging time for the low N cast in the fine grained condition. The yield strength is initially higher in comparison to the unaged sample due to the formation of M23C6. Then yield strength decreases slowly with increasing aging time due to the growth of the M23C6. The yield strength is also affected by the reduction in solid solution hardening due to the consumption of the allowing elements.

A model has been developed for the influence of ageing on the ductility. The model takes into account how the stress distribution around particles changes the uniform elongation. Chen and Knott’s model for the influence of coarse particles on fracture toughness has been further developed and used successfully. The measured impact toughness values were transferred to fracture toughness with the aid of Samuel et al’s approach. The results are of great value in the assessment of residual life time by being able to estimate how much the mechanical properties have been changed during service.

![Fig. 35. Yield strength versus ageing time for the low N cast in the fine grained condition](image_url)
6.3 Paper C

The purpose of paper C was to investigate the influence of long time aging on ductility and toughness in the stainless steel 310 in the presence of banded microstructure. During service at elevated temperatures extensive formation of particles can occur that can have a dramatic influence on ductility and toughness of the material. Particle formation of $\sigma$-phase and $M_{23}C_6$ have been investigated both experimentally and with thermodynamic modelling for the austenitic stainless steel 310 at 800 °C for up to 5000h. After long time aging these precipitates form bands in the microstructure as shown in Fig. 36. These bands influence the ductility and toughness of the material. The modelling of nucleation and growth of these precipitates has been done successfully in paper A. Models for the influences of these precipitates on ductility and toughness has been derived in paper B. In paper C, these models were used to describe the role of the particles in bands. The coarse $\sigma$-phase particles that were expected to influence the ductility and toughness were found at grain boundaries and in bands. Model values for banded and non-banded microstructures were generated for cast of 310 in fine and coarse grained conditions with 0.04 and 0.12%N. The model values indicated that in the coarse grained condition, no reduction in ductility and toughness was expected in the banded microstructure. In the fine grained condition, a modest reduction was predicted.

![Fig. 36. Line SEM image of high N cast, coarse grained and aged for 2000h at 800 °C](image)

6.4 Paper D

The purpose of paper D was to develop basic models for creep deformation in stainless steels. The austenitic stainless steel 310NbN was used in this investigation. Specimens were aged at 650 and 750 °C for 1000, 3000h and 10000h. Size distributions of the particles were determined by SEM and TEM. The investigations in TEM were made by using carbon replicas. The composition of the particles was determined with EDS analysis.
The main contribution to effective stress was due to the activation energy for the Nb atoms to break away from the dislocations. The particle size distribution plays an important role in calculating precipitation hardening. Exponential particle size distributions were obtained for the austenitic stainless steel 310NbN as shown in Fig. 37. The dislocations gave the largest contribution to the strength. The particle strengthening from Nb(C,N) gave a small but significant contribution to the strength. A good agreement with the assessed experimental results for the creep rupture strength at 600 to 750 °C was obtained.

![Size distributions for Nb(C,N) particles after ageing at 650 and 750 °C](image)

**Fig. 37.** Size distributions for Nb(C,N) particles after ageing at 650 and 750 °C

### 6.5 Paper E

The global energy demands are increasing rapidly. The most efficient way to fulfil the electricity demands is to increase the efficiency of power plants. Steam temperature and pressure should be raised for increasing the efficiency of power plants. Austenitic stainless steel Sanicro 25 is one of the austenitic steels with the highest potential for in superheater tubes in power plants at 700 °C under ultrasupercritical conditions. The microstructural evolution in Sanicro 25 was investigated. Specimens were aged up to 10000 h at 700 °C. The investigations were done by using light optical microscopy, scanning electron microscopy, transmission electron microscopy with carbon replica technique and energy dispersive spectroscopy. Different precipitates found in Sanicro 25 experimentally were primary Nb-rich precipitates, Al-oxides Si-oxides and secondary Nb(C,N), Laves phase, Cr2N and M23C6. The precipitation calculation at 700 °C for 12000 h was made. Fig. 38 shows the calculated results for phase fractions and particle radii and a comparison with the experimental data.
6.6 Paper F

Intensive precipitation can occurs in creep resistance steels during service at high temperatures that affects the mechanical properties of the material. The purpose of paper F was to predict the strength contribution due to solid solution hardening and precipitation hardening in the 23Cr25NiCuWNb austenitic stainless steel Sanicro 25. The specimens were aged at 650 and 700 °C for 1000, 3000 and 10000 h. The investigations were carried with the help of light optical microscopy, scanning microscopy and transmission electron microscopy with carbon replica technique. The chemical composition of the precipitates was determined using energy dispersive spectroscopy. Z phase, chromium carbide, chromium nitride, Laves phase, aluminium oxides, silicon oxides and niobium carbonitrides were found. A comparison to predictions with Thermo-Calc was made. Size distributions of these precipitates were determined. Exponential particle size distributions were obtained for the austenitic stainless steel Sanicro 25. Fig. 39 presents the contributions from solid solution hardening, particle hardening, dislocations and effective stress. The sum of the contributions from dislocation, solid solution hardening and precipitation hardening gives the total applied stress. A good agreement between the total applied stress and the experimental rupture stress data has been achieved.
Fig. 39. Creep stress versus rupture time at 700 °C. The strength contributions from dislocations, particles and solid solution are shown together with the effective stress. The total applied stress is compared to the experimental data.
7 CONCLUSIONS

This thesis includes microstructure investigations and thermodynamic calculations of the austenitic stainless 310, 310NbN and Sanicro 25.

Austenitic stainless steel 310 was aged at 800 °C for up to 5000 h. The purpose was to characterise and model the formation of coarser particles that can reduce ductility and toughness of the material. Two casts with different nitrogen contents were investigated. Both casts were analysed in coarse grained and fine grained conditions.

- In aged specimens coarse precipitates of \( \sigma \)-phase have been observed. The size of the precipitates increases with ageing time. Volume fractions up to 10% have been recorded. The precipitates are mainly formed at the grain boundaries. As a consequence the fine grained conditions have a larger volume fraction of particles.
- \( M_{23}C_6 \) carbides precipitate at grain boundaries, twin boundaries, and slip bands emerging from the grain boundaries. The carbides grow and finally coarsen during ageing.
- Comparing the low and high nitrogen casts, the amount of 23-carbides precipitated are about the same whereas there is more \( \sigma \)-phase in the low N cast. The differences follow what is expected from the amounts of precipitates in thermodynamic equilibrium.
- The particle radii for \( \sigma \)-phase and \( M_{23}C_6 \) are predicted as a function of temperature. The model is based on classical nucleation theory and a modified quasi-stationary model for diffusion controlled growth. In the quasi-stationary model soft impingement is explicitly taken into account. In general an acceptable agreement is observed with the experiments at 800 °C.
- By assuming that the dominating nucleation position is at the grain boundaries in agreement with the observations, the volume fraction of precipitates can be predicted. These predictions are in reasonable agreement with the metallographic observations. In several cases the final amounts of precipitates are close to the thermodynamic equilibrium values.
- By increasing the nitrogen content to 0.20 % or the carbon content to 0.10-0.15 %, significant reductions of the total amount of precipitates can be obtained.
- Ageing reduced or increased the strength depending on the competition between reduced solid solution hardening due to alloy element depletion and precipitation strengthening.
- A model has been developed for the influence of ageing on the ductility. The model takes into account how the stress distribution around particles changes the uniform elongation. A satisfactory agreement with observations was obtained.
- Chen and Knott’s model for the influence of coarse particles on fracture toughness has been used successfully to represent the experimental data. The measured impact toughness values were transferred to fracture toughness with the aid of Samuel’s approach.
Both for ductility and toughness the models values are a bit lower for the banded than for the non-banded microstructure for the fine grained casts considering high volume fraction of $\sigma$. However, for coarse grained casts this is not the case. The model values are in good agreement with the measured mechanical properties.

Long term ageing of the austenitic stainless steel 310NbN at 650 and 750 ºC for up to 10000 h has been performed.

- $\sigma$-phase, $M_{23}C_6$, Z-phase, $Cr_2N$, Nb(C,N) and $\eta$-phases have been observed after ageing both at 650 and 750 ºC. The phases were identified with the help of EDS analysis.

- Four of the phases $\sigma$-phase, $M_{23}C_6$, Z-phase, $Cr_2N$ are given as equilibrium phases in Thermo-Calc. At higher temperatures than those studied Nb(C,N) is also an equilibrium phase. In accordance with previous studies, Nb(C,N) at 650 and 750 ºC is believed to be a transient phase that is gradually transformed to Z.

- $\eta$-phase is not available in most Thermo-Calc databases. It primarily appears after long time ageing so it is likely to be an equilibrium phase as well. $\eta$-phase is not so commonly observed. It is a cubic phase with the composition $M_5SiX$ where M stands for Cr, Ni and Mo (in our case Cr and Ni) and X for C and N (in our case N).

- The observed particle sizes of $\sigma$, $M_{23}C_6$, Z and $\eta$ increased with temperature and ageing time. $\sigma$ mainly form at grain boundaries. $M_{23}C_6$ was initially observed at grain boundaries, but after longer ageing times also at twin boundaries and slip bands. Z-phases was observed on grain boundaries, twin boundaries and within matrix.

- Cumulative size distributions of the precipitate $\sigma$-phase, $M_{23}C_6$, Z-phase, $Cr_2N$, Nb(C,N) and $\eta$-phases have been determined. They can be represented with an exponential function.

- A basic model for the solid solution contribution to the creep strength of austenitic stainless steel 310NbN has been applied. The basic assumption in this model is that atmospheres of solute elements are formed around the dislocations and follow their motion. The contribution of Nb to solid solution hardening is very small and almost negligible.

- The main contribution to effective stress was due to the activation energy for the Nb atoms in 310NbN to break away from the dislocations. The presence of Nb increases the activation energy by 83 KJ/mol, by giving a significant reduction of the creep rate.

- A recovery creep model was used to determine the contribution from the dislocations to the creep strength. The dislocations gave the largest contribution to the strength.

- A model by Dobes was used after modification to calculate the effective stress.

- A climb controlled model for precipitation hardening was applied. With increasing temperature and time, precipitation hardening in 310NbN decreases rapidly by comparing the other strength contributions.

- The creep strength of austenitic stainless steel 310NbN can be predicted in a suitable way without using the adjustable parameters.

Microstructure investigations and thermodynamic calculations of austenitic stainless steel Sanicro 25 at 650 and 700 ºC for up to 10000 h were carried out. The purpose was to establish
quantitative models for predicting the contribution of precipitation hardening, solid solution hardening and dislocation hardening to the creep strength.

- Primary Nb-rich precipitates, Al-oxide and Si-oxide and secondary precipitates Nb(C,N), Laves phase, Cr$_2$N, and M$_{23}$C$_6$ were observed after ageing both at 650 and 750 ºC. The phases were identified with the help of EDS analysis.
- The size of Z phase at 700 ºC increases rapidly with increasing aging time while the size of Laves phase, Cr$_2$N, M$_{23}$C$_6$, Nb(C,N) and Cu rich phase changes only slowly. The general behavior at 650 ºC is similar to that at 700 ºC but precipitates at higher aging temperature are larger than precipitates at lower aging temperature.
- Scheil calculations have been done by thermo-kinetic software Matcalc to analyse the solidification process which represents Nb(C,N), Cr$_2$N and Laves phase in the melt.
- Phase fractions and mean radii growth of precipitates have been calculated and compared to the experimental results. Calculated precipitate growth indicates good agreement with experimental data.
- Cumulative size distributions of precipitates Z phase, Nb(C,N), Laves phase, Cr$_2$N and M$_{23}$C$_6$ have been determined. The cumulative number of particles as a function of radius can be represented with an exponential function.
- A basic model for the solid solution contribution to the creep strength has been applied to the austenitic stainless steel Sanicro 25. In this model, the amount of solid solution hardening is proportional to the amount of solutes at the core of the dislocation and size of the lattice misfit. The largest contribution to solid solution hardening in Sanicro 25 comes from tungsten.
- The main contribution is due to the activation energy E of the elements in solid solution which slow down the dislocations most efficiently. W, Nb and Cu contribute to solid solution hardening for Sanicro 25.
- A recovery creep model has been used to calculate the contribution from the dislocations to the creep strength. This contribution is the largest of the evaluated ones.
- Dobes’ model after modifications was used for the calculation of effective stress.
- A climb controlled model for precipitation hardening was used. The precipitation hardening is decreased more rapidly than the other strength contributions by increasing temperature and time.
- Creep strength of the austenitic stainless steel Sanicro 25 can be predicted in an acceptable way without the use of any adjustable parameters.
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