Creep modelling of particle strengthened steels

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Licentiate Thesis

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Creep modelling of particle strengthened steels
Akademisk avhandling som med tillstånd av Kungliga Tekniska Högskolan i Stockholm framlägges till offentlig granskning för avläggande av teknisk licentiatexamen onsdagen den 13 juni 2007 10.00 i konferensrummet, Brinellvägen 23, 4 tr, Kungliga Tekniska Högskolan, Stockholm.

ISBN: 978-91-7178-720-0
ISRN: KTH/MSE--07/44--SE+MAT/AVH

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This thesis is available in electronic version at: http://media.lib.kth.se
Printed by Universitetsservice US AB, Stockholm
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Abstract

Materials to be used in thermal power plants have to resist creep deformation for time periods up to 30 years. The role of alloying elements for creep strength of 9-12% Cr steels is analysed. The creep strength in these steels relies on minor additions of alloying elements. Precipitates give rise to the main strengthening and remaining elements produce solid solution hardening. Nucleation, growth and coarsening of particles are predicted by thermodynamic modelling. Phase fractions and size distributions of M_{23}C_{6} carbides, MX carbonitrides and Laves phase are presented. The size distributions are needed in order to determine the particle hardening during creep. At elevated temperatures the climb mobility is so high that the dislocations can climb across particles instead of passing by making Orowan loops.

By solving Fick's second law the concentration profile around a moving dislocation can be determined. The results show an accumulation of solutes around the dislocation that slows down dislocation movement. When Laves phase grows a decrease in creep strength is observed due to a larger loss in solid solution hardening than strength increase by particle hardening. Solid solution hardening also gives an explanation of the low dislocation climb mobility in 9-12% Cr steels.

Three different dislocation types are distinguished, free dislocations, immobile dislocation and immobile boundary dislocations. This distinction between types of dislocations is essential in understanding the decreasing creep with strain during primary creep. The empirical relation with subgrain size inversely proportional to stress has been possible to predict. The total creep strength can be predicted by adding the contribution from individual mechanisms.
List of papers in the thesis

**Paper I - Dislocation climb of particles at creep conditions in 9-12% Cr steels**
Hans Magnusson and Rolf Sandström
Submitted to Metallurgical and Materials Transactions A

**Paper II - Creep strain modelling of 9-12% Cr steels based on microstructure evolution**
Hans Magnusson and Rolf Sandström
Submitted to Metallurgical and Materials Transactions A

**Paper III - Modelling of the influence of Laves phase on the creep properties in 9% Cr steels**
Hans Magnusson and Rolf Sandström
ASME Pressure Vessels and Piping/CREEP8 Conference, San Antonio, Texas, USA, Jul 22-26, 2007
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1 Introduction

Steam power plants produce an important part of the electricity around the world. Hot gasses from fossil fired combustion or waste heat source from gas turbines convert water into superheated steam. By increasing the working steam temperature and pressure the efficiency of the unit increases, which lowers the fuel consumptions and the environmental impact [1]. According to Hald [2] the increase in steam parameters from 18 MPa/530-540 °C to 30 MPa/600 °C has lead to an approximate 30% decrease in CO₂ emissions.

The high temperature strength is strongly related to the creep deformation in components. Creep is the plastic deformation that a material undergoes when subjected to a constant stress. Power plant materials have to resist stresses and temperatures during long-term conditions in order to avoid creep failure. The life-time of a power plant unit can be as long as 30 years. In order to estimate the long-term creep strength basic understanding of the involved mechanisms is essential.

With the correct mechanisms considered the possible failure mechanisms can be predicted and avoided. The great number of existing creep models illustrates the uncertainty in creep modelling. Many models can reproduce creep data of the situation studied, but when moving outside the data range they might fail. A fundamental model for creep must be based on parameters with a physical basis. It is only then possible to predict the creep strength in a more general manner.

The aim of this thesis is to model the processes determining the creep life of a component. The modelled mechanisms are used to predict the creep strength of particle strengthened 9-12% Cr steels. An introduction to this type of material is given and to different approaches to model creep of these materials.

2 Martensitic 9-12% Cr steels

2.1 Development of 9-12% Cr steels

9-12% Cr steels are cost efficient materials that meet the demands in power plant applications. These steels have been improved during the later part of the last century by carefully selecting the alloy additions. The oxidation resistance requires a 9-12% addition of Cr but much of the mechanical strength relies on minor additions of other elements. A schematic comparison between the material cost of 9-12% Cr steel, other
creep resistant steels, and Ni-based superalloys relative plain carbon steel at identical
conditions is shown in Figure 1.

![Figure 1](image1.png)

**Figure 1.** The approximate cost of different steels related to the temperature needed to cause rupture at identical rupture stress and time [3].

The commercial 9% Cr steels T9 developed in 1936 [4] starts the history of 9-
12% Cr steels. During the 1950s the 12% Cr steel was invented by Mannesmann in
Germany, allowing construction of supercritical coal fired power plants [5]. Newer
9% Cr steels have mainly been developed in the USA and Japan, notably P91, P92
and P122. During the 1990s the European steel E911 was developed within the COST
501 program. Figure 2 presents the development in alloying by showing the stress
needed for rupture after $10^5$ h of creep at 600 °C. The important minor alloying
elements contributing to the strength are Nb, V, Mo and W in combination with C and
N.

![Figure 2](image2.png)

**Figure 2.** The stress needed for rupture after $10^5$ h at 600 °C [6].

In Table 1 the compositions of some 9-12% Cr steels is shown.
### Table 1. Compositions of some 9-12% Cr steels [5].

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Cr</th>
<th>Mn</th>
<th>Mo</th>
<th>N</th>
<th>Nb</th>
<th>Ni</th>
<th>V</th>
<th>W</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>P91</td>
<td>0.1</td>
<td>8.3</td>
<td>0.4</td>
<td>1.0</td>
<td>0.05</td>
<td>0.07</td>
<td>0.2</td>
<td>0.2</td>
<td>0</td>
<td>bal</td>
</tr>
<tr>
<td>P92</td>
<td>0.1</td>
<td>8.8</td>
<td>0.5</td>
<td>0.5</td>
<td>0.05</td>
<td>0.07</td>
<td>0.2</td>
<td>0.2</td>
<td>1.9</td>
<td>bal</td>
</tr>
<tr>
<td>E911</td>
<td>0.1</td>
<td>8.6</td>
<td>0.5</td>
<td>0.9</td>
<td>0.07</td>
<td>0.09</td>
<td>0.2</td>
<td>0.2</td>
<td>1.0</td>
<td>bal</td>
</tr>
<tr>
<td>X20</td>
<td>0.2</td>
<td>12.1</td>
<td>0.5</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0.6</td>
<td>0.3</td>
<td>0</td>
<td>bal</td>
</tr>
<tr>
<td>P122</td>
<td>0.1</td>
<td>11.0</td>
<td>0.6</td>
<td>0.4</td>
<td>0.05</td>
<td>0.05</td>
<td>0.3</td>
<td>0.2</td>
<td>1.9</td>
<td>bal</td>
</tr>
</tbody>
</table>

#### 2.2 Metallurgy

After a normalising heat treatment in the austenite regime around 1050 ºC a martensitic lath structure is formed during the following air-cooling. Normalising is followed by a tempering heat treatment at about 700 ºC. At this treatment the martensitic structure recovers into a dislocation network that constitutes the subgrains. Normalising and tempering initialise the creep resistant microstructure giving both a high dislocation density and a large number of nucleation sites for precipitates. The dense dislocation and particle structure are the characteristics of 9-12% Cr steels giving the major part of the creep strength.

Possible particle precipitates are divided into groups of $M_aX_b$, where $M$ is metal atoms and $X$ is carbon or nitrogen. The number of atoms, $a$ and $b$, varies depending on the stoichiometry of the compound. Particles of essential importance for 9-12% Cr steels are $MX$, $M_{23}C_6$, Laves phase and the Z phase. Laves phase is an intermetallic compound that does not contain any carbon or nitrogen and takes the form $Fe_2M$. The Z-phase has been found after long-term creep exposure [7] and is formed at the expense of MX particles. A minor part of the MX precipitates does not dissolve during normalisation and stabilise the grain structure. The $M_{23}C_6$ carbide and the major part of the MX are precipitated at tempering. Both Laves phase and Z-phase nucleate and grow during creep. Laves growth is relative rapid and is typically finished before 10 000 h at 600 ºC, depending on composition, see paper III. The Z-phase growth is slower and is of importance during long-term creep, especially for high Cr steels [7].

Figure 3 presents the cumulative size distribution of particles present in a P92 material after 10 000 h of exposure at 600 ºC [8]. The lines represent their fitted size distributions [9]. It is shown that the MX carbonitrides are the smallest particles with a mean radius of about 25 nm. $M_{23}C_6$ are about twice that size and close to 50 nm.
Laves particles are typically quite large compared to the others although the size depends on the nucleation parameters.

Figure 3. Fraction of particles larger than a given radius. Experiments are the observed particle sizes after 10 000 h at 600 °C [8].

Figure 4 presents the fraction of phases that are thermodynamically stable as a function of temperature for a P92 composition. Other precipitates that might exist during heat treatments but are metastable are M_{6}X, M_{3}X, M_{2}X, and M_{7}X_{3}. The values are evaluated using the Thermo-Calc software with the TCFE3 database [10]. The MX phase fraction is the smallest but due to the small size of MX a high density of particles is produced. Their distribution is also more homogeneous compared to M_{23}C_{6} and Laves that are mostly found at subgrain and grain boundaries.

Equilibrium compositions of MX, M_{23}C_{6}, Laves and matrix phase at 600 °C are presented in Table 2. Carbon is mostly located in the stoichiometric M_{23}C_{6} carbide and some minor amount in the NbC phase. The metal elements in M_{23}C_{6} carbide are
Cr, Fe and some additions of Mo and W. The W containing P92 compositions produce the intermetallic Laves phase, which consists mostly of Fe, W, Cr and Mo. A large amount of the added W is found in this phase.

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Cr</th>
<th>Mn</th>
<th>Mo</th>
<th>N</th>
<th>Nb</th>
<th>Ni</th>
<th>V</th>
<th>W</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>1·10⁻⁴</td>
<td>8.4</td>
<td>0.5</td>
<td>0.07</td>
<td>6·10⁻⁶</td>
<td>6·10⁻⁴</td>
<td>0.06</td>
<td>0.03</td>
<td>0.2</td>
<td>91</td>
</tr>
<tr>
<td>MX</td>
<td>1.1</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>46</td>
<td>9.2</td>
<td>-</td>
<td>43.4</td>
<td>-</td>
<td>0.01</td>
</tr>
<tr>
<td>M₂₃C₆</td>
<td>21</td>
<td>61</td>
<td>0.3</td>
<td>6.9</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
<td>-</td>
<td>1.2</td>
<td>10</td>
</tr>
<tr>
<td>Laves</td>
<td>-</td>
<td>11</td>
<td>0.2</td>
<td>3.3</td>
<td>-</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
<td>29.8</td>
<td>55</td>
</tr>
</tbody>
</table>

* Concentrations are given in mole percent.
** Particle phases without description according to TCFE3 database or element concentration below 10⁻⁴ are entered with - sign.

According to Table 2, much of the alloying elements have been precipitated but some minor amounts are still in solid solution. The precipitated elements give rise to particle hardening while those elements dissolved in matrix can contribute to the creep strength by solid solution hardening. The magnitude of the strengthening mechanisms will be discussed later in this thesis.

3 Creep strength

3.1 Crystalline defects

The mechanical strength of materials is related to the type and the amount of defects in the crystalline structure. The type of defects can be classified from their dimensionality in lattice, starting with the zero-dimensional point-defects, one-dimensional line defects, two-dimensional planar defects and three-dimensional volume defects. The dislocation line defect controls the mechanical strength of many crystalline materials like metals. Dislocations allow local glide of a row of atoms rather than shearing of a whole plane. This possibility of dislocation assisted plastic deformation decreases the strength by a factor of 1000 compared to the theoretical strength. The actual decrease in strength depends on the mobility of the dislocations. Those mechanisms that lower the mobility are denoted as strengthening mechanisms.

At elevated temperatures the thermal vacancies influence the creep strength. These point defects allow the dislocations to climb out of their glide plane [11]. With this kind of movement the dislocations can avoid obstacles during glide and the mobility of the dislocations increases. Planar defects like grain boundaries influence
the component in some different ways. The grain boundaries act as a highway for diffusion and increase the rate of diffusion controlled mechanisms. Plastic deformation can occur by grain boundary sliding. But both mechanisms are reduced by the large grain size of creep resistant materials. The contributing minor amount of grain boundary sliding is believed to initiate creep damage in the form of voids. These defects strongly influence the ductility of creep resistant materials.

3.2 The creep curve

The typical shape of a creep curve can be divided into three regions, primary creep, secondary creep and tertiary creep. The primary creep represents the stage with a continuously decreasing creep rate. As the creep rate approaches the minimum creep rate the secondary stage has begun. The secondary stage is in time the longest stage that ends up at tertiary creep with an increasing creep rate until rupture. The three stages can accurately be represented by the $\Phi$ model for primary creep and $\Omega$ model for tertiary creep [12], giving the total creep rate as:

$$\dot{\varepsilon} = \Phi_1 e^{-\Phi_2} + \Omega_3 \exp(\varepsilon \Omega_4)$$

(1)

$\Phi_1$, $\Phi_2$, $\Omega_3$ and $\Omega_4$ are constants that are fitted to the creep curve. In this case the secondary creep rate or minimum creep rate is given as the minimum when summarising the two models. A fitted creep curve is given in Figure 5a, and Figure 5b shows the corresponding creep rate as function of strain. Experimental data is for a P92 material at 650 °C and 100 MPa [13].

Figure 5. a) Creep curve fitted with $\Phi$ and $\Omega$ model. b) Corresponding creep rate versus creep strain. Creep at 650 °C and 100 MPa, from [13].

3.3 Models for creep strength

Many models have been proposed to explain the creep strength. In creep experiments a constant load is applied and the straining as function of time is
measured. The minimum creep rate is often chosen as a characteristic parameter representing the evaluated material. One reason is that the minimum creep rate often represents in time the major part of the creep life. Another argument is that the minimum creep rate can be related to the rupture time by using the well proven Monkman-Grant relation [14], giving an estimate of the creep strength:

\[ t_R \dot{\varepsilon}_{\text{min}} = \text{const} \]  

(2)

\( t_R \) is the time to rupture and \( \dot{\varepsilon}_{\text{min}} \) the minimum creep rate. Creep can be divided into subgroups where the deformation mechanism of creep differs. Different deformation mechanisms are vacancy directed material flow, dislocation based creep, and grain boundary sliding. Although the creep mechanisms might vary all these models can be generalised into the following expression for creep:

\[ \dot{\varepsilon} = A \frac{D G b}{kT} \left( \frac{b}{d} \right)^{n} \left( \frac{\sigma_{\text{app}}}{G} \right)^{p} \]  

(3)

\( A \) is a constant, \( D \) the self diffusion coefficient, \( G \) the shear modulus, \( b \) Burgers vector, \( T \) the absolute temperature, \( k \) Bolzmanns constant, \( d \) the grain size, \( \sigma_{\text{app}} \) the applied stress, and \( n \) and \( p \) are the exponents of stress and grain size respectively. The different creep mechanisms are represented with their values of the exponents, constant and diffusion coefficient. By evaluating the temperature, stress or grain size dependence on creep the active mechanism can be distinguished.

Grain boundary related mechanisms are vacancy creep and grain boundary sliding. It has been proposed that grain boundary sliding occurs by the movement of dislocation in grain boundaries [15]. The rate controlling step at grain boundary sliding is the deformation resistance within grains due to the requirement of plastic compatibility. The temperature dependence is given from the climb mobility that is related to the self diffusion coefficient. Grain boundary sliding can be detected when observing the macroscopic deformation of a marked surface. Diffusion creep was first suggested by Nabarro and Herring [16, 17]. The flow of vacancies takes place within the grains where grain boundaries or external surfaces act as sources and sinks of vacancies. The applied stress will direct this material flow and the material creeps. If the vacancy transport takes place at grain boundaries the creep mechanism is denoted Coble creep [18] with temperature dependence from grain boundary diffusion.

Dislocation based creep models are based on glide and climb of dislocations that give the creep rate. Dislocation motion starts with the generation of dislocations, for

13
instance a Frank-Read source. The dislocation travels a distance until it is annihilated by a dislocation of the opposite kind. The many dislocation based models have their version of the time controlling step during the dislocation life time. One example is the model by Weertman [19], where dislocation climb is the time controlling step. In the model by Weertman dislocation climb gives the creep rate but plastic strain is still generated as the dislocations glide between the obstacles.

Other dislocation based theories are derived from the dislocation glide mobility. Solute atoms might accumulate at the dislocation giving a local increase in element concentration, a Cottrell atmosphere [20]. During motion this atmosphere has to be dragged and the creep rate is lowered. The effect of alloying elements in solid solution on creep strength divides metallic materials into two classes [21]. Class I alloys which are glide controlled behave like pure metals when solute elements are added with the stress dependence as pure metals and the temperature dependence is related to the diffusion coefficient of the alloy. Some examples of Class I alloys are Al-Mg, Au-Ni, Pb-Sn. Class II alloys that are climbed represents most commercial creep resistant materials like Fe or Ni based alloys. The effect of alloying elements is not given by the change in diffusion coefficient of the alloy compound, and some strengthening of solutes exists [21]. Class II metals exhibit a distinct primary creep, in contrary to Class I materials. Due to primary creep and the generation of dislocations through work hardening these materials are subgrain forming materials.

Harper and Dorn evaluated creep data at those conditions where vacancy directed creep is typically found [22]. The stress dependence was correct but the creep rate was about 1400 times greater than what is suggested by Nabarro-Herring and Coble creep. The conclusion by Harper and Dorn was that this represented a new type of creep, which shows the same stress dependence but is independent of grain size. 50 years since the study of Harper and Dorn was presented there is still discussions about the existance of Harper-Dorn creep, see [23]. Other mechanisms of dislocation motion has been proposed like the non-conservative motion of jogged screw dislocations by Barrett and Nix [24], and dislocation climb of Bardeen-Herring sources by Nabarro [25]. Table 3 presents a summary of the mentioned models by showing the diffusion coefficient and exponents to grain size and stress used in Eq. (3).
Table 3. Parameters to some of the creep models, according to Eq. (3).

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>$p$</th>
<th>$n$</th>
<th>$D$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain boundary sliding</td>
<td>1</td>
<td>3</td>
<td>$D_s$</td>
<td>[15]</td>
</tr>
<tr>
<td>Nabarro-Herring</td>
<td>2</td>
<td>1</td>
<td>$D_s$</td>
<td>[16]</td>
</tr>
<tr>
<td>Coble</td>
<td>3</td>
<td>1</td>
<td>$D_{gb}$</td>
<td>[18]</td>
</tr>
<tr>
<td>Harper-Dorn</td>
<td>0</td>
<td>1</td>
<td>$D_s$ or $D_p$</td>
<td>[22]</td>
</tr>
<tr>
<td>Weertman</td>
<td>0</td>
<td>4.5</td>
<td>$D_s$</td>
<td>[19]</td>
</tr>
<tr>
<td>Barrett-Nix</td>
<td>0</td>
<td>3</td>
<td>$D_s$</td>
<td>[24]</td>
</tr>
<tr>
<td>Nabarro</td>
<td>0</td>
<td>3</td>
<td>$D_s$</td>
<td>[25]</td>
</tr>
</tbody>
</table>

* $D_s$, $D_p$ and $D_{gb}$ are self diffusion coefficients in lattice, pipe (dislocation) and grain boundaries.

3.4 Experimental observations of creep strength

The temperature dependence of creep in pure metals is normally represented by an Arrhenius expression with activation energies given by the dominant diffusion mechanisms according to Table 3 and Eq. (3). It has been found that the activation energy of creep of pure metals is often close to the activation energy of self diffusion, which is illustrated in Figure 6 for pure metals.

![Figure 6](image_url) Evaluated activation energy for creep compared to activation energy of self diffusion in lattice. All data points are from Sherby and Weertman [26].

The stress dependence of creep is more difficult to represent in a general manner. The dislocation based creep laws given in Table 3 are not directly related to the grain size and Eq. (3) transforms into Norton's law:

$$
\dot{\varepsilon} = A_n \sigma^n \exp\left(-\frac{Q_C}{RT}\right)
$$

(4)
\(A_N\) is a constant, \(n\) the Norton exponent, \(Q_C\) the activation energy of creep, and \(R\) the gas constant. For some cases the stress exponent increases with creep rate and an exponential relation is a more appropriate choice. Then the creep rate takes the form [27]:

\[
\dot{\varepsilon} = A \exp\left(\frac{V^* \sigma_{\text{app}}}{MkT}\right) \exp\left(-\frac{Q_C}{RT}\right) \tag{5}
\]

\(M\) is the Taylor factor, \(V^*\) an activation volume of about 100 b 3 m 3. This relation is useful when describing the power-law breakdown that occurs at lower temperatures. Figure 7 presents the normalised minimum creep rate of pure metals as a function of normalised stress. Figure 7a shows BCC materials and Figure 7b FCC materials. The slope gives directly the Norton coefficients, which are in the range 3-6.

![Figure 7](image_url)

**Figure 7.** The normalised minimum creep rate versus normalised stress for pure metals. a) BCC metals and b) FCC metals. All data points are from [28].

Figure 7 indicate that for many pure metals the activation energy of creep is close to the activation energy of self diffusion in lattice. Figure 6 shows that the stress dependence is in the range of 3-6. These two facts indicate that creep is most often dislocation based, and Norton's law can be used to represent the creep rate.

4  Modelling of creep curves

4.1 Modelling of transient creep

The temperature and stress dependence are included in Norton's law giving the creep rate. The creep rate is not a constant quantity but varies during time as presented in Figure 5. To simulate the entire creep curve the state the creep rate is calculated from has to be determined at every step in the calculation. Predicting the creep curve would allow a better physical understanding of those mechanisms giving creep
strength. As Blum pointed out [29], it is disadvantageous to simulate the minimum creep rate only since the lifetime is often determined from the primary creep.

Primary creep and the transition to minimum creep rate are physically described by the evolution of the dislocation density. Dislocations are the source of plastic deformation by their movement in lattice, but a high dislocation density also slows down the glide due to work hardening. The shape of primary creep with a continuously decreasing creep rate is then explained as an increase in dislocation density and a lowering in dislocation mobility. The evolution in dislocation density eventually saturates since there is a balance between dislocation generation and annihilation. This steady-state condition is close to the minimum creep rate. The obstructing stress due to work hardening was first suggested by Taylor as:

\[
\sigma_{\text{disl}} = \alpha M G b \sqrt{\rho}
\]

where \(\alpha M\) is a constant of about unity, and \(\rho\) the dislocation density.

It is common to represent the dislocation density with the average spacing between dislocations. For a perfect parallel dislocation arrangement the spacing is simply \(L = 1/\sqrt{\rho}\). The relation between dislocation spacing and applied stress is given in Figure 8 for pure Fe and 9-12% Cr steels. The lines correspond to the Taylor equation when substituting the dislocation density with dislocation spacing. This gives the linear relationship between work hardening and applied stress.

![Figure 8](image)

**Figure 8.** Average distance between dislocations for pure Fe, and 9-12% Cr steels. Experimental data is gathered from [30, 31, 32, 33].

The approach of using one dislocation density describing transition creep cannot be used for martensitic steels. This problem is solved by making a distinction between the different kinds of dislocations, see paper II. Free dislocations contribute to plastic
strain by their movement in the lattice. These dislocations get obstructed during motion by immobile dislocations. The immobile dislocations are located at both subgrain interiors and subgrain boundaries, but are separated since their dislocation processes are quite different. Thus three different types of dislocations are needed to simulate the creep process, free dislocations, immobile dislocations and boundary dislocations. The evolution of free and immobile dislocation densities in subgrain interiors versus creep strain is illustrated in Figure 9 for a X20 alloy crept at 650 ºC and 120 MPa compared to experimental observations using both TEM and XRD techniques. The free dislocation density decreases from a high initial value of $9 \cdot 10^{13}$ m$^{-2}$ [30, 34]. The material is assumed to be relaxed at the start of creep with a low amount of immobile dislocations present. The immobile dislocation density then increases quickly at low creep strains due to a high recovery rate of free dislocations. The dislocation densities approach steady-state conditions at minimum creep rate with lower and constant dislocation generation rates. The experimental observations should be compared to the sum of the free and immobile dislocation densities.

![Figure 9](image.png)

**Figure 9.** Simulated free and immobile dislocation densities in subgrain interiors during creep at of a X20 material at 650 ºC and 120 MPa. Experimental observations were done using both TEM and XRD techniques [30]. The high strain observations are at 0.08.

### 4.2 Creep modelling of subgrain forming materials

Due to heterogeneities in microstructure some dislocations will be more favoured for movement compared to others. This will lead to an inhomogeneous deformation giving rise to lattice rotations [35]. These rotations are relaxed by the boundary dislocations acting like geometrically necessary dislocations constituting the subgrain networks. The subgrain size can be represented in a similar way to the dislocation spacing in Figure 8, with subgrain size at rupture proportional to the inverse of the...
stress. This kind of relation is shown in Figure 10 for pure Fe and for 9-12% Cr steels. The ratio subgrain spacing to dislocation spacing is about a factor of 10 [36], as observed by comparing Figure 8 and Figure 10. The ratio is greater for pure metals compared to alloys. This is typically explained by the particles located at subgrain boundaries of alloys that reduce the subgrain growth [37]. An approach to model subgrain growth is also presented in Figure 10. The simulations are performed for a P92 composition and evaluated at minimum creep rate, see paper II.

![Figure 10. Observations of subgrain sizes [5, 31, 36, 38]. The straight lines represent a numerical relation with different fitting constants. The x-marked line is simulated values, according to paper II.](image)

One approach to include the role of subgrain networks on creep strength is to treat the material as a composite [39, 40]. The subgrain walls are mechanical hard areas while the subgrain interiors are softer. Creep will then proceed under different conditions in the two regions but a requirement is that the two regions deform at an equal rate giving compatibility in plastic deformation. Creep modelling of 9-12% Cr steels using the composite model typically assumes equal strain criteria between the two areas [31, 41, 42]. With equal strains the differences in plastic strains are accomplished by the elastic strains, giving rise to internal stresses in the material.

According to experiments [31] the dislocation density in subgrain boundaries is rather insensitive to the applied stress and in the range of $10^{15}$ to $10^{16}$ m$^{-2}$. If the boundary thickness of subgrains is nearly constant during creep the area fraction of boundaries will decrease due to subgrain coarsening. Coarsening will recover the material by decreasing the amount of boundary dislocations resulting in a loss in creep strength according to the composite model. Particles hindering the subgrain...
coarsening will then be an important strengthening mechanism in materials that show subgrain structure.

4.3 Influence of particles on creep strength

By including the back stress from dislocations in the Norton equation the time dependence of creep of pure metals are explained. Alloying influences the creep properties due to the precipitation of stable particles such as carbides, nitrides or intermetallic phases. The role of particle hardening on creep strength is typically included in analogy with work hardening, as an extra back stress on the moving dislocation. The classic equation of particle hardening by Orowan is the stress to push a dislocation past two impenetrable particles as:

$$\sigma_{\text{Oro}} = \frac{2MT_L}{bL_{\text{part}}}$$ (7)

where $T_L$ is the dislocation line tension, and $L_{\text{part}}$ the interparticle spacing. At higher temperatures particle coarsening will increase the average distance between the particles and thus lowering the particle strength. Particle coarsening increases the average size of particles, as the larger particles will grow at the expense of the smaller ones. Ostwald ripening can be used to describe the coarsening:

$$r_j^3 = r_{0,j}^3 + k_j t$$ (8)

where $r_{0,j}$ is the initial particle size, $k_j$ the coarsening coefficient [43] and $t$ the time.

Particle coarsening is typically a slow process and the Orowan stress is only weakly dependent on temperature. It is obvious that this temperature dependence cannot explain the large decrease in creep strength with temperature, as explained in paper I. At higher temperature, climb allows the dislocations to bulge out of the slip plane and surmount the particle. The temperature dependence of the dislocation climb mobility is given by the self diffusion coefficient [11], and makes dislocation climb across particles an important mechanism.

Climb mechanisms are often divided into local climb and general climb. At local climb only the dislocation segment in contact with the particle climbs [44]. Lagneborg pointed out that local climb would produce unrealistically sharp dislocation bends where the dislocation leaves the glide plane, and climb in a more general manner is more realistic [45]. Another theory of dislocation climb, first introduced by Srolovitz et al. [46], was that the threshold stress arises due to the attractive surface at particle
and matrix interface. Some experimental TEM micrographs confirm this theory showing attached dislocations on the departure side of the particle [47].

Predictions of particle hardening at climb conditions typically end up with an expression of the minimum particle hardening, i.e. the thresholds stress. Depending on the investigated conditions like particle geometry the size of the threshold varies over a wide range, as explained by Blum et al. [48]. The shape of the climbing dislocation is more relaxed at general climb compared to local climb and general climb threshold should represent the true threshold. Suggested values of the ratio of threshold stress $\sigma_{th}$ to Orowan stress are about $0.004<\sigma_{th}/\sigma_{Oro}<0.02$ [48]. Many studies of particle hardening at climb conditions focus on the threshold stress. A more useful scenario in creep modelling would be to estimate the particle hardening when some dislocations climb across particles while other pass by the Orowan mechanisms, thus representing the case when particle hardening $\sigma_{\text{part}}$ is somewhere between the threshold and the Orowan stress, $0.02<\sigma_{\text{part}}/\sigma_{\text{Oro}}<1$. The dislocation climb model by Eliasson et al. [9] compares the dislocation glide kinetics with the climb kinetics. With this approach, the importance of dislocation climb can be determined. A study on 9-12% Cr steels presented in paper I shows that the particle hardening increases approximately linearly to the applied stress with an upper limit at the Orowan stress. One conclusion from these simulations is that a fine distribution of small particles will produce a low interparticle spacing and an important strength contribution according to the Orowan equation. Smaller particles are however more easily climbed and a deviation from the Orowan for small particles is expected at creep.

4.4 Solid solution hardening and creep

Alloying elements still solved in the matrix will not contribute to particle hardening but is believed to lower the dislocation mobility by solid solution hardening. The role of solid solution hardening during creep is debated. For 9-12% Cr steels Hald [49] showed by experiments that the creep strength actually increased with the precipitation of Laves phase and the decreased solid solution elements. Other studies from Sawada et al. [50] have shown that the addition of W slows down the dislocation reaction rates, and thus the creep rate. The dislocation climb mobility as suggested by Hirth and Lothe for pure metals [11] cannot directly be used in creep modelling of 9-12% Cr steels as it will overestimate the dislocation related recovery mechanisms [50].
The stress field around a dislocation will create a hydrostatic pressure. This pressure is relaxed by inserting a solute atom. The size of the reversible work is then directly related to the volume change times the pressure, where the size difference is represented by the differences in atomic volume between solute and matrix [11]. This attractive potential will lead to an accumulation of solutes, forming a Cottrell atmosphere. As the dislocation starts to move the solutes will give rise to solid solution hardening as this solute atmosphere get dragged. The interaction energy of a solute at position \((x, y)\) away from the dislocation core is given by Eq. (9) [11, 51], where the first factor is the volume difference and the second factor the hydrostatic pressure at a distance away from the dislocation core.

\[
W_i = \Omega_i \epsilon_{b,i} \frac{Gb}{3\pi} \frac{1 + \nu}{1 - \nu} \frac{x}{x^2 + y^2} \tag{9}
\]

\(x\) is the glide direction, \(y\) the climb direction, \(\nu\) Poisson's ratio, and \(\Omega_i\) the atomic volume. \(\epsilon_{b,i}\) represents the size mismatch defined as \(\epsilon_{b,i} = \frac{db_i}{b_{dc}}\), where \(c_i\) is the concentration of element \(i\). The deviation from equilibrium concentration of solutes due to the interaction energy is given by:

\[
c_i = c_{0,i} \exp\left(-\frac{W_i}{kT}\right) \tag{10}
\]

c\(_{0,i}\) is concentration of solute in matrix. When including the movement of a dislocation the diffusivities of solute atoms will determine the amount of accumulation. A solution to Fick's second law with a moving frame of reference gives the concentration profile around a dislocation at steady-state diffusion conditions and origin at dislocation core [11]:

\[
c_i = \frac{v_{climb}c_{0,i}}{D_i} \exp\left(-\frac{W_i}{kT} - \frac{v_{climb}x}{D_i}\right) \int_{-\infty}^{x} \exp\left(-\frac{W_i}{kT} + \frac{v_{climb}x}{D_i}\right) dx \tag{11}
\]

\(v_{climb}\) is the dislocation climb velocity. For concentrated solutions the concentration profile is modified so that two solutes do not occupy the same position in lattice. This is done by using a Fermi-Dirac expression for each concentration profile. Figure 11a presents the interaction energy of elements W, Mo and Cr, and Figure 11b the resulting concentration profiles using Eq. (11) simulated at creep rate of \(10^{-9} \text{ s}^{-1}\) and 600 °C. Both figures are from paper III. It is shown how the element W that produces the largest misfit also gives the greatest deviation from equilibrium concentration.
Figure 11. Figure a) presents the interaction energy for W, Mo and C at distance in climb direction away from dislocation core. Positive coordinates is on expansion side. Figure b) presents the resulting concentration profile, evaluated at creep rate of $10^{-9}$ s$^{-1}$ and 600 ºC. Simulations are from paper III.

5 Contributing papers

Paper I - Dislocation climb of particles at creep conditions in 9-12% Cr steel

The influence of particles on creep strength is analysed. Particle size distributions are accurately fitted to MX carbonitrides and M$_2$C$_6$ carbides in 9-12% Cr steels using an exponential function. The particle size distributions are used to determine the amount of particles that climb across particles or make Orowan loops. The model is based on parameters such as dislocation climb mobility and creep rate. Phase fractions and coarsening rates are predicted by thermodynamic modelling in order to explain the degradation of microstructure and to reproduce experimental creep data for P92 steel.

Figure 12 presents the simulated applied stress needed to produce a minimum creep rate of $10^{-9}$ s$^{-1}$ as function of temperature. In the figure, particle strength denotes the strengthening of particles with dislocation climb taken into account. Subgrain boundaries is the contribution from the subgrain boundaries, and dislocation hardening the contribution from immobile dislocations in subgrain interiors. All back stresses decrease with temperature making it possible to explain the strong temperature dependence on the creep rate.
Figure 12. Showing the applied stress needed to produce a minimum creep rate of $10^{-9}$ s$^{-1}$ as function of temperature. Particle strength, subgrain boundaries and dislocation hardening are back stresses to dislocation movement. Experimental creep data is from [52].

Paper II - Creep strain modelling of 9-12% Cr steels based on microstructure evolution

In this work a model for creep is presented. Creep is simulated by the Norton equation using parameters typically observed for pure metals. Alloy material, such as 9-12% Cr steels, is modelled by including back stresses from immobile dislocations and precipitates. The dislocations are divided into free dislocations, immobile dislocations and boundary dislocations. With this approach the primary creep can be modelled for a material with an initially high dislocation density. Mechanisms for generation and recovery of dislocations are discussed and compared to experimental data.

To summarise the approach to model creep, the Norton's equation given as Eq. (4) is modified to be used in creep rate predictions of 9-12% Cr steels:

$$\dot{\varepsilon} = A_n \exp\left(-\frac{Q_c}{RT}\right)\left(\sigma_{\text{app}} - \sigma_{\text{back, tot}}(\sigma, T, t, c, \dot{\varepsilon})\right)^n$$

(12)

The back stresses are calculated and summarised according to the composite theory. The shape of the creep curve and the time dependence of creep strain are determined from the microstructure evolution. The microstructure evolution is based on external parameters such as composition and described in terms of temperature and deformation (stress). Particle climb across particles is related to the dislocation kinetics, creep rate, so that Eq. (12) has to be solved in an iterative manner. Estimates of the Norton constant are also given.
Figure 13a presents subgrain growth during creep. The characteristic subgrain growth shape is due to a time dependent growth law, but here presented as function of creep strain. Figure 13b gives the subgrain size at minimum creep rate, which follows frequently used numerical relation with subgrain size inversely proportional to the stress.

![Figure 13a](image1) ![Figure 13b](image2)

**Figure 13.** a) Predicted subgrain evolution during creep at 600 °C and 162 MPa, data from [5]. b) Longterm subgrain size as function of simulation stress. The deformation rate is held constant so that each step in stress corresponds to temperature change, from 700 °C down to 550 °C.

A simulated creep curve compared to experimental data and Ω and Φ model is shown in Figure 14a. Creep rate as function of strain is shown in Figure 14b.

![Figure 14a](image3) ![Figure 14b](image4)

**Figure 14.** a) Simulated creep curve for P92 steel at 104 MPa and 650 °C, compared to experimental creep data [53]. b) Creep rate as a function of strain and compared to the regression model.

**Paper III - Modelling of the influence of Laves phase on the creep properties in 9% Cr steels**

The role of alloying elements on the creep strength is analysed by including the role of solid solution strengthening. Concentration profiles around a climbing dislocation are predicted using a solution to Fick's second law with a moving frame of reference. The obstructing force to the climbing dislocation is then determined.
Nucleation and growth of Laves phase is predicted. The simulated Laves growth using SSOL4 and mob2 databases with DICTRA software [54] is shown in Figure 15. The cell-sizes are approximated as the subgrain sizes at long times.

![Figure 15](image.png)

**Figure 15.** Simulated Laves growth compared to observations [5, 55].

The influence on creep strength is discussed by analysing the contribution from particle hardening and solid solution strengthening. The results show that the growth of Laves phase softens the material. The simulated reduction in climb velocity, denoted $k_{sol}$, is shown in Figure 16. The increase with Laves fraction is due to solid solution depletion of solid solution elements like Mo and W. The observed needed reduction in climb mobility is about a factor of 100. The predicted values cannot fully predict this decrease.

![Figure 16](image.png)

**Figure 16.** The calculated reduction in climb velocity due to solid solution hardening. The increase from the initial values is due to Laves growth.
6 Conclusions

The evolution in particle structure of 9-12% Cr steels is predicted by thermodynamic modelling. Diffusion controlled growth of Laves phase and coarsening behaviours are simulated for a multicomponent system. Particle size distributions are presented and used to discuss the influence of particle size on creep. The phase fraction of MX is relatively small but is compensated by its small size which produces the greatest contribution according to Orowan. At 550 ºC nearly all particles are passed by the Orowan mechanism and the particle hardening equals the Orowan stress. With increasing temperatures the amount of climb increases and particle hardening thus decreases. The MX size distribution has the smallest particles and therefore shows the most severe decrease in particle hardening. At high temperatures the contribution of $M_23C_6$ to particle hardening becomes even greater than that from MX particles. However, a fine particle distribution like MX particles in matrix will produce a low interparticle spacing which influences the climb rate of all particle kinds. The total particle hardening during climb shows approximately a linear relationship to the applied stress with an upper limit in the Orowan stress.

The climb mobility of the dislocation strongly influences the creep strength of the component. The rate of dislocation climb, dislocation recovery and subgrain growth are all related to the climb mobility. The effect of alloying elements on climb mobility is analysed. It shows a decrease in climb mobility a factor of about 100 due to solid solution strengthening mostly due to W but also Mo. The influence of Laves growth on creep strength is discussed by comparing the strengthening of precipitation hardening with the softening due to solid solution depletion. It shows that Laves growth softens the material.

A study of dislocations in 9-12% Cr steels shows that free dislocations, immobile dislocations and boundary dislocations are needed to predict the creep curve. Primary creep can then be calculated for dislocation rich materials using a traditional approach with an increasing work hardening with creep. Subgrain growth shows a good correspondence to experimental observations. The long time size follows an established relation the stress. Subgrain growth decreases the amount of subgrain boundaries and thus the total creep strength according to the composite model.
7 Future work

The contributed papers provide a possible explanation of the transient creep of particle strengthened materials. The important mechanisms that determine creep strength have been identified and fundamentally explained in order to predict creep in a more general manner.

Future work should include tertiary stage for a better representation of the creep curve. The solid solution hardening approach could be refined to reproduce the measured creep data. Long-term creep data should be modelled to better evaluate the practical use of the creep model. Much of the presented work typically have rupture times less than 25 000 h.

The model for creep can still be used for evaluation of creep strength. A possible action within the COST538 program is to study the effect of Al on creep strength. This kind of work can be done with the present model.

8 Acknowledgements

I would like to thank partners from the CROX collaboration for fruitful discussions about creep related topics, as well as colleagues participating in the European COST538 project. The MATOP participation has provided me valuable feedback about my own project and nice presentations about related topics.

I would also like to thank Prof. Rolf Sandström for accepting me as a graduate student and for all the help and guidance during my work.

Past and present colleagues at the department and Fikagänget are thanked for the various discussions and events, especially my room mate Johan for together experiencing all the graduate courses, project meetings, squash games and the weakly competitions in general knowledge.

Finally I would like to thank my parents, brother and sisters for making all this possible, and Alfons and Laban for their good spirit and most of all Mimmi.

*This work was supported by the Swedish foundation for strategic research (SSF) programmes CROX, “Mechanisms of creep and oxidation of high performance alloys” and MATOP, “Development of tools for integrated optimisation of materials”, which is gratefully acknowledged.*
9 References


