Precipitate Stability in Creep Resistant Ferritic Steels—Experimental Investigations and Modelling

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Predictions of long-term microstructure stability of creep resistant ferritic 9–12 % Cr steels up to 200 000–300 000 h at temperatures up to 600–650°C are highly interesting for safe power plant operation. At techni-
cally interesting creep conditions the microstructure stability is mainly controlled by the stability of precipi-
tate particles. Predictions of precipitate stability have to rely on i) Microstructure characterisation methods
to measure volume fractions and mean particle sizes of individual precipitate types, and ii) Microstructure
models to predict the evolution of precipitate volume fractions and mean sizes as functions of temperature,
time and applied stress. Characterisation methods, which allow on-line particle type discrimination in 9–
12 % Cr steels include energy filtered transmission electron microscopy (EFTEM) and scanning electron mi-
croscopy (SEM) with atomic number contrast. Modelling of precipitate stability based on thermodynamic
equilibrium calculations and multicomponent diffusion databases is demonstrated. A multi-component
coarsening model gives accurate predictions of coarsening rates for MX and Laves phase precipitates in
steel P92 with fit values for the interfacial energy in the expected range. For M23C6 carbides in steel P92 the
model results in unexpectedly low apparent values for the interfacial energy. Modelling of published data for
steel P91 indicate much higher coarsening rates for M23C6 carbides, and the fit value for the interfacial en-
gy is as expected. A possible explanation for the low apparent value of the interfacial energy for M23C6 car-
bides in steel P92 is the content of boron in the steel.

KEY WORDS: 9–12 % Cr creep resistant steels; microstructure stability; precipitate characterisation; coars-
ening modelling; MX carbonitrides; M23C6 carbides; Laves phase.

1. Introduction

Alloy development of 9–12 % Cr ferritic creep resistant steels for steam power plant applications like thick section
boiler components, steam lines, turbine rotors and turbine casings, has led to a doubling of the 105 h creep rupture
strength at 600°C over the last 25 years. This has been
achieved through apparently minor compositional changes
to well established steels like the 9Cr1Mo and 12CrMoV.
New alloys, like the modified 9Cr1Mo steel P91 and the
tungsten alloyed 9Cr and 11Cr steels P92 and P122, have
recently been used in full scale in new power plants in
Japan and Europe, and this has resulted in advanced steam
conditions up to 30 MPa/600°C. The decision to introduce
the new alloys in power plant has mainly been based on re-
sults from long-term creep rupture tests lasting up to ap-
proximately 60 000 h. However, power plants are expected
to operate for up to 200 000–300 000 h. Thus, considera-
tions about long-term creep stability of the new alloys are
necessary to ascertain safe plant operation. Considerations
about long-term creep stability can only rely on studies of
microstructure stability and relations between microstruc-
ture and creep strength. The present paper describes recent
advances in the understanding of microstructure stability
based on new developments in techniques to characterise
precipitates and new models of precipitate stability in 9-
12 % Cr steels.

2. Microstructure and Creep Strength of 9–12 % Cr
Steels

2.1. Microstructure

Chemical composition, heat treatment and creep rupture
strength of a number of 9–12 % Cr steels are given in Table
1. The microstructure of the 9–12 % Cr steels is tempered
martensite formed during a final normalising and tempering
heat treatment, Fig. 1. After normalising at approximately
1050°C air hardening will lead to martensitic transforma-
tion in sections up to approximately 100-mm thickness be-
cause of the high chromium content. Tempering in the tem-
perature range 680–780°C leads to recovery of ductility by
annihilation of dislocations and formation of ferrite sub-
grains. The exact choice of tempering temperature depends
on the application. Tempering tempera-
tures in the high end of the range are used for pressurised components like steam pipes, where high toughness is necessary. Another important effect of tempering is the precipitation reactions taking place in the steels. During tempering carbide and nitride particles precipitate on prior austenite grain boundaries, ferrite subgrain boundaries and on dislocations inside subgrains. When the steels are put into service in power plant at temperatures below the final tempering temperature, further particles may precipitate, which are thermodynamically unstable at the tempering temperature, like e.g. the intermetallic Laves phase. In Table 2 the most common precipitates in selected 9–12% Cr steels are listed. 

2.2. Dislocation and Subgrain Microstructures

In the stress and temperature ranges of technical interest for 9–12% Cr steels dislocation creep is the dominant deformation mechanism. Microstructural sources of creep deformation are then the migration of dislocations and subgrain boundaries. It is important to note that as a result of the martensitic transformation in 9–12% Cr steels a high dislocation density and a relatively small subgrain size exist in the steels prior to creep exposure. Consequently, the dislocation density will decrease and the subgrains will grow during creep of 9–12% Cr steels in the interesting stress and temperature ranges. It has been found experimentally that the development in dislocation density and subgrain size can be described mainly as a function of creep strain:

\[
\log x = \log x_0 + \log(x_0 / x) \exp\left(\frac{\epsilon}{k_{\log x}}\right) \quad (1)
\]

\[x\] is either subgrain size \(w\) or the spacing between free dislocations inside the subgrains \(\rho_f^{0.5}\) (\(\rho_f\) is the density of free dislocations). \(x_0\) is the initial value of \(x\) before creep exposure. With increasing strain \(\epsilon\), the subgrain size and the dislocation spacing approach steady state values, depending on the applied stress, given by:

\[
w = 10 \frac{Gb}{\sigma} \quad (2)
\]

\[\rho_f^{0.5} = 3.9 \frac{Gb}{\sigma} \quad (3)
\]

\(G\) is the shear modulus; \(b\) is the Burgers vector and \(\sigma\) is the applied stress. For subgrain development the rate constant \(k_{\log x}\) takes a value close to 0.12. Equation (1) has been found to be valid with the same rate constant for a wide range of 9–12% Cr steels. These include the traditional 12CrMoV steel (X22) and the much more creep resistant new pipe steels P91 and P92 and turbine rotor steels E and B2 from the European COST 522 project.

2.3. Strengthening Mechanisms

Subgrain boundaries consist of dislocation networks, which compared with the subgrain interiors are hard regions in the microstructure of ferritic steels. A small subgrain size is equivalent to a high volume fraction of hard regions in the microstructure, and could thus be expected to be equivalent to high creep strength. However, initial dislocation densities and subgrain sizes of different 9–12% Cr steels in the normalised and tempered condition do not show systematic variation with creep strength of the alloys. Instead, it is the ability of a steel to maintain a small subgrain size and a high dislocation density for long time at stress and temperature, which is significant to high creep strength. This indicates that microstructural mechanisms for the improved creep strength of the new 9–12% Cr steels should be found in mechanisms which retard the migration of dislocations and subgrain boundaries, and thus delay the accumulation of creep strain in time. Such mechanisms include i) solid solution hardening by formation of clouds of solute atoms around dislocations, and ii) interactions with precipitate particles. Solid solution strengthening is often referred to in discussions of the effect of molybdenum and tungsten on creep strength of 9–12% Cr steels, but experimental evidence to demonstrate and quantify the mechanism is sparse. Recent reviews of solid solution strengthening models indicate that the effect is insignificant to creep strength of 9–12% Cr steels. Precipitation hardening by pinning of dislocations and subgrain boundaries should then be regarded as the most significant strengthening mechanism.

| Steel | Precipitate | Formula | Remark |
|-------|-------------|---------|--------|
| X22   | M_2C       | (Cr,Fe)Mo(C,M)  | Precipitate during tempering |
|       | MX         | (Fe,Mo)C   | Undissolved during austenitisation |
|       | Laves phase| (Cr,Fe)Cr(C,N) | Precipitate during creep (750°C) |
| P91   | M_2C       | (Cr,Fe)Mo(C,M)  | Precipitate during tempering |
|       | MX         | (Fe,Mo)C   | Undissolved during austenitisation |
|       | Laves phase| (Cr,Fe)Cr(C,N) | Precipitate during creep (750°C) |
| P92   | M_2C       | (Cr,Fe)Mo(C,M)  | Precipitate during tempering |
|       | MX         | (Fe,Mo)C   | Undissolved during austenitisation |
|       | Laves phase| (Cr,Fe)Cr(C,N) | Precipitate during creep (750°C) |
mechanism in 9–12% Cr steels, and microstructure stability of 9–12% Cr steels under creep load is then equivalent to precipitate stability. This is consistent with the findings that the compositional changes, which have improved the creep strength of the 9–12% Cr steels, have also resulted in clear changes in the precipitate population, see Table 2.

The interaction between precipitate particles and sub-grain boundaries or dislocations under creep conditions can be complicated, and a detailed discussion of interaction mechanisms and back stress formulations will not be attempted here. However, equations to describe the contribution of precipitate particles to creep strength have similarities to the Orowan stress:

\[
\sigma_{\text{Orowan}} = 3.32 G b \sqrt{\frac{f_p}{d_p}} \quad \text{(4)}
\]

\( G \) is the shear modulus, \( b \) is the burgers vector, \( f_p \) is the precipitate volume fraction and \( d_p \) is the mean precipitate diameter. This formula demonstrates that the basic information needed to describe the effect of precipitate particles on creep strength is their volume fraction and their mean size.

Predictions of long-term stability of precipitate particles and their influence on creep stability of 9–12% Cr steels has to rely on measurements of volume fractions and mean particle sizes at certain points in time and on models describing the evolution of these parameters as functions of temperature, time and stress.

3. Precipitate Characterisation

As mentioned the new 9–12% Cr steels contain several precipitate types, which form either during the final normalising and tempering heat treatment or during subsequent creep exposure of the steels, see Table 2. For the modelling of long-term precipitate stability it is necessary to know volume fractions and mean particle sizes of the individual precipitate types. As seen in Table 2 the various precipitates in 9–12% Cr steels have distinct chemical compositions, which means that it is possible to discriminate between them by measurements of their chemical composition. With traditional EDS methods in transmission electron microscopes statistically sound particle size measurements of individual precipitate types is very time consuming. However, with the newly developed Energy Filtered Transmission Electron Microscope (EFTEM) high-resolution element mapping can be achieved based on information from electron energy loss spectra (EELS). With this technique it is now possible to make accurate measurements of particle sizes down to a few nm, and on-line discrimination between the individual precipitate types, see Fig. 2.

Due to technical constraints there is a lower limit to the usable magnification in EFTEM microscopes, which means that statistically sound size determination for a population of particles with mean diameters larger than approximately 200 nm become unpractical with the EFTEM method. However, in recent years the introduction of new high intensity electron sources in the Scanning Electron Microscope (SEM) has improved the resolution power of this instrument. This means that mean particle sizes down to approximately 100-nm diameter can be measured with SEM. Particle discrimination in the SEM can be obtained from the atomic number contrast in backscattered electron images. The authors have recently demonstrated this technique for tungsten containing Laves phase particles in steel P92), see Fig. 3.

4. Modelling of Precipitate Stability

Modelling of long-term precipitate stability should include predictions of phase stability, nucleation rates, growth rates and coarsening rates as functions of chemical composition, temperature and stress.

4.1. Phase Stability

Recent developments of databases and software, like e.g. the Thermocalc, to calculate thermodynamic equilibria in multicomponent systems allow predictions of phase stability for 9–12% Cr steels based on chemical composition. The accuracy of the predictions depends critically on the available phase descriptions in the thermodynamic databases. A few critical gaps and inaccuracies in these descriptions have been identified, e.g. the predictions of Laves phase stability in 9–12% Cr steels alloyed with molybdenum but no tungsten has been proven wrong by experiments. In such cases revised thermodynamic phase descrip-
4.2. Nucleation

Modelling of nucleation rates is challenging because it depends critically on the interfacial energy, which is very difficult to predict or determine experimentally. It is therefore most often necessary to make simplifying assumptions about nucleation. Based on classical nucleation theory it is possible to estimate size ranges of critical nuclei from the formula:

$$r^* = \frac{2\gamma V_m}{-\Delta G_m}$$ ........................................(5)

where $\gamma$ is the interfacial energy, $V_m$ is the molar volume of the precipitate phase and $\Delta G_m$ is the driving force for precipitation. The driving force $\Delta G_m$ can be calculated by thermodynamic equilibrium calculations, and based on the normal ranges for the interfacial energy $\gamma=0.1-1$ J/m$^2$ the critical nucleus radius $r^*$ can be estimated. More ambitious modelling of nucleation has to include strain energy and nucleus shape.\(^{11}\)

4.3. Growth

The author has previously modelled Laves phase growth in steel P92 using an Avrami type equation together with thermodynamic calculations.\(^{12}\) However, recent developments of multicomponent diffusion databases like the DICTRA\(^{13}\) allow more advanced modelling. Based on the assumption of local equilibrium at precipitate/matrix interfaces the problem of particle growth can be reduced to a one dimensional moving boundary problem. This can be solved by solution of multicomponent diffusion equations, which can be handled by DICTRA. In this growth model the contribution from interfacial energy is ignored, but this will in most cases only affect growth rates in the early stages. The model needs experimental input to determine the nucleus density or the final size of fully-grown particles. Predicted growth rates are in good agreement with experimental observations.\(^{14,15}\)

4.4. Coarsening

Particle coarsening is one of the most important degradation processes for creep resistant steels, and the detailed understanding of the influence of chemical composition on coarsening rate is essential to the understanding of long-term microstructure stability. Coarsening can be modelled by DICTRA in a similar way as described above for growth by incorporation of a contribution from the interfacial energy to the Gibbs energy of the particle. This leaves the interfacial energy as the only fit parameter in the coarsening model.\(^{16}\) However, the DICTRA calculations can be time consuming, and a simpler approach, which allow a quicker overview of coarsening rates for different steels, will be attempted here. Particle coarsening is observed to follow the well-known Ostwald ripening equation:

$$r^3 - r_0^3 = K \cdot t$$ ........................................(6)

$r$ is the precipitate radius at time $t$ and $r_0$ is the precipitate radius at time 0. Lifshitz and Slyozov\(^{17}\) and Wagner\(^{18}\) calculated the coarsening rate $K_p$ for binary alloy systems, but only recently extensions to multicomponent systems have been obtained by Umantsev and Olson\(^{19}\) and by Agren et al.\(^{20}\) The latter resulted in the following formula for the coarsening rate constant $K_p$ in a C-component system of $\beta$ precipitate particles in a $\alpha$ matrix:

$$K_p = \frac{8}{9} \gamma \frac{V_p^\beta}{\gamma} \sum_{i=1}^{C} \left( x_i^\beta - x_i^\alpha \right)^2 D_i / RT$$ ........................................(7)

As above $\gamma$ is the interfacial energy and $V_p^\beta$ is the molar volume of the precipitate phase. $D_i$ is the diffusion coefficient of element $i$ in the matrix, $x_i^\beta$ is the mole fraction of element $i$ in the precipitate and $x_i^\alpha \beta$ is the mole fraction of element $i$ at the precipitate/matrix interface. The diffusion coefficients are in general proportional to the diffusion matrix extracted from the DICTRA database, and include effects of chemical composition. Volume diffusion is assumed. The effect of interface curvature on the equilibrium solubilities is relatively small in this case, and the values of $x_i^\beta$ and $x_i^\alpha \beta$ obtained by thermodynamic equilibrium calculations assuming a flat precipitate/matrix interface can be used as a good approximation. $V_p^\beta$ is calculated from lattice parameter data and precipitate composition. The only unknown is then the interfacial energy $\gamma$, which is used as a fit parameter when comparing to experimental observations.

5. Comparison between Model and Experiment

5.1. Calculated Coarsening Rate Constants

In order to investigate the influence of diffusivities and
solubilities on particle coarsening, rate constants $K_p$ were calculated for MX carbonitride-, $M_23C_6$ carbide- and Laves phase particles in steel P92 using a fixed value of 1 J/m$^2$ for the interfacial energy in Eq. (7). See Fig. 4. The calculations show that only the substitutional elements, which segregate to the particles, have significant influence on the coarsening rates. Interstitial elements have too high diffusion rates to have any significant influence. Results of the calculations indicate clearly higher stability of MX carbonitrdes compared with Laves phase, which are again more stable than $M_23C_6$ carbides. It is often assumed that diffusivities have a large influence on coarsening rates, but the calculations indicate that the influence of solubilities in precipitate and matrix are much more important. The diffusion rates in ferrite at 600°C of tungsten ($1.5 \times 10^{-20}$ m$^2$/s) and vanadium ($1.8 \times 10^{-20}$ m$^2$/s) are similar, but the calculated coarsening rates for MX is 20 times smaller than for Laves phase due to the solubilities. Calculations based on equilibrium solubilities at the final tempering temperature generally show higher coarsening rates than calculations based on equilibrium solubilities at the exposure temperature. This effect is especially strong for the $M_23C_6$ carbides, which indicates that Laves phase precipitation—which removes Mo and W from solid solution in ferrite—has a beneficial effect on the stability of the $M_23C_6$ carbides, see Table 3.

The effect of steel composition on calculated coarsening rates is shown in Fig. 4. It is seen that the difference in calculated particle stability is biggest for the $M_23C_6$ carbides, where the coarsening rate of carbides in steel P92 is up to a factor of eight smaller than in steel P91. For the MX carbonitride and Laves phase particles the variations between the steels are smaller.

5.2. Particle Size Measurements

Experimental data was mainly obtained by EFTEM at Chalmers University using thin foil samples from isothermally annealed specimens or creep specimens of steel P92 exposed at 600°C or 650°C. Details on the measurements are published elsewhere.6) The authors made EFTEM measurements at Chalmers University on one creep sample of steel P92 tested to rupture at 600°C/125 MPa/59 000 h. Laves phase particle sizes were measured by the authors using SEM.7)

5.2.1. MX Carbonitrdes

EFTEM measurements included particles with a high content of vanadium, i.e. vanadium carbonitrides V(N,C). The number fraction of V(N,C) was found to be much bigger than the number fraction of MX particles rich in niobium, Nb(C,N). The measurements show that the MX (V(N,C)) particles are highly stable against coarsening. At 600°C the MX particles coarsen from approximately 18-nm radius to approximately 20-nm radius during 59 000 h of exposure. At 650°C the MX particles coarsen from approximately 18-nm to approximately 22-nm radius during 26 000 h of exposure. The uncertainty in the measurements was estimated to be $\pm 5$ nm.

5.2.2. $M_23C_6$ Carbides

EFTEM measurements included particles with a high content of Chromium. The $M_23C_6$ carbides were found to coarsen slowly from approximately 45-nm to approximately 50-nm radius during 59 000 h at 600°C. At 650°C the $M_23C_6$ carbides coarsen from approximately 45-nm to 75-nm radius during 26 000 h of exposure. The uncertainty in the measurements was estimated to be $\pm 10$ nm.

5.2.3. Laves Phase

Laves phase particles were found to precipitate and grow in the steels during exposure at 600°C and 650°C. As mentioned, the EFTEM method has a lower limitation to the us-
able magnification, and the results from EFTEM measurements were only regarded to be accurate for mean particle sizes smaller than 100-nm radius. For larger particle sizes SEM measurements were used. Laves phases were found to grow to a radius of approximately 107 nm during 10 000 h at 600°C. From 10 000 to 59 000 h the particles coarsen from approximately 107- to 125-nm radius. At 650°C the Laves phase particles were found to grow to a radius of approximately 207 nm during 10 000 h. From 10 000 to 26 000 h the particles coarsen from 207- to 215-nm radius. The uncertainty in the measurements was estimated to be ±10 nm for specimens exposed at 600°C and ±15 nm for specimens exposed at 650°C.

5.3. Fit to Experimental Data

The measured particle sizes were fit to the coarsening model (Eqs. (6) and (7)) by adjustment of the interfacial energy \( \gamma \). Generally a value of \( \gamma \) in the range 0.1–1 J/m² is expected, where the lower values correspond to coherent particle/matrix interfaces and the higher values correspond to incoherent interfaces. The mentioned effect of different solubilities in particle and matrix on coarsening rates is included in the calculations by assuming that equilibrium is reached during tempering. The initial coarsening rate at the beginning of creep or isothermal exposure is therefore based on equilibrium solubilities at the tempering temperature. Precipitation of Laves phase will gradually lower the matrix content of Mo, W and Cr during creep exposure, and at longer exposure times the coarsening rate constant should be calculated based on equilibrium solubilities at the exposure temperature. Growth calculations with DICTRA indicate that the Laves phase growth process in steel P92 has finished after 4 000–6 000 h at 600°C and after 3 000–5 000 h at 650°C.\(^{15}\) In the modelling of MX carbonitrides and \( \text{M}_2\text{C}_6 \) carbides it was therefore decided to use coarsening rates calculated from equilibrium compositions at the tempering temperature to fit data with times less than 5 000 h at 600°C and less than 3 000 h at 650°C. The coarsening rates calculated from equilibrium compositions at the exposure temperatures were used to fit the data with longer times.

5.3.1. MX Carbonitrides

Good agreement with the experimental data was obtained at both 600°C and 650°C with an interfacial energy of 0.5 J/m², Fig. 5. The obtained interfacial energy is in good agreement with results from DICTRA modelling of the same data.\(^{16}\) MX carbonitrides were observed in the microstructure partly as coherent precipitates on dislocations inside ferrite subgrains and partly as incoherent precipitates on ferrite subgrain boundaries. The value of 0.5 J/m² of the interfacial energy is in good agreement with the microstructure observations.

5.3.2. Laves Phases

As mentioned, growth calculations with DICTRA indicate that the growth process has finished after 4 000–6 000 h at 600°C and after 3 000–5 000 h at 650°C.\(^{15}\) The calculated coarsening rates were therefore used only to fit data with times above 10 000 h at both temperatures. Good agreement with the experimental data was obtained with an interfacial energy of 1 J/m², Fig. 6. This value of the interfacial energy is in reasonable agreement with results from DICTRA modelling of the same data, where a value of 0.8 J/m² was determined.\(^{15}\) An interfacial energy in the range 0.8–1 J/m² indicates that the interfaces between Laves phases and ferrite are incoherent. This is consistent with microstructure observations, where the Laves phase particles were found to precipitate on prior austenite grain boundaries and ferrite subgrain boundaries.

5.3.3. \( \text{M}_2\text{C}_6 \) Carbides

Good agreement with experimental data at both temperatures is obtained with an interfacial energy of 0.1 J/m², Fig. 7. This interfacial energy is unexpectedly low, and indicates that the carbide/ferrite interfaces should be coherent even though the \( \text{M}_2\text{C}_6 \) carbides are observed to precipitate on similar locations in the microstructure as the Laves phase particles.

In order to check the apparent inconsistency of the interfacial energy of \( \text{M}_2\text{C}_6 \) carbides the coarsening model was used to fit experimental data from literature. Kimura et.

![Fig. 5. Measured particle sizes and calculated curves for coarsening of MX (VN) precipitates in steel P92. \( \gamma=0.5 \text{ J/m}^2 \).](image)

![Fig. 6. Measured particle sizes and calculated curves for coarsening of Laves phase precipitates in steel P92. \( \gamma=1 \text{ J/m}^2 \).](image)

![Fig. 7. Measured particle sizes and calculated curves for coarsening of \( \text{M}_2\text{C}_6 \) carbides.](image)
al. recently published particle size measurements for steel P91 obtained on extraction replica samples from creep specimens exposed at 600°C or 650°C. Particle discrimination was obtained by EFTEM. Because of the use of extraction replicas the uncertainty in the measurements is estimated to be ±20 nm. The data indicate much faster coarsening of M\textsubscript{23}C\textsubscript{6} carbides in steel P91 compared with steel P92. Further, the data indicate that the Laves phase precipitation reaction is slower in steel P91 than in steel P92. Consequently, the coarsening rates calculated from equilibrium compositions at the tempering temperature were used to fit data with times less than 10,000 h at 600°C and less than 7,500 h at 650°C. Coarsening rates calculated from equilibrium compositions at the exposure temperatures were used to fit data with longer times. Reasonable fits to the experimental data were obtained in the short term regions using interfacial energies of 1 J/m\textsuperscript{2} at 600°C and 0.8 J/m\textsuperscript{2} at 650°C. These values of the interfacial energy indicate incoherent interfaces between M\textsubscript{23}C\textsubscript{6} carbides and ferrite, which is in good agreement with the observations of subgrain and grain boundary precipitation of the carbides. At both temperatures lower values of the interfacial energy of 0.5 J/m\textsuperscript{2} and 0.3 J/m\textsuperscript{2} are needed to fit to one experimental point at long times. However, there is some uncertainty about the use of the model to predict the two long-term points because of heterogeneous development in the microstructure in grain interiors and near grain boundaries of the prior austenite grains.

A possible explanation for the low apparent value of the interfacial energy of M\textsubscript{23}C\textsubscript{6} carbides in steel P92 is the boron content in the steel. This element is not included in the calculations for the coarsening model, but it has been found to segregate to M\textsubscript{23}C\textsubscript{6} carbides in steel P92. Boron could affect the interfacial energy as indicated by the modelling here, but it could also affect the diffusivities. It is possible that grain boundary diffusion plays an important role in coarsening of the M\textsubscript{23}C\textsubscript{6} carbides, but bulk diffusion is assumed in the present model. The well-known segregation of boron to interfaces and dislocations could be expected to have a strong effect on grain boundary and dislocation pipe diffusion. A lowering of the diffusivities used in Eq. (7) would result in increased fit values for the interfacial energy.

In summary, the presented coarsening model gives a good description of the influence of chemical composition of 9–12% Cr steels on the stability of precipitate particles. In combination with measured particle sizes of individual precipitate types the model allows a more advanced interpretation of the complicated influence of elements like boron on the microstructure stability of 9–12% Cr steels. The obtained coarsening rates and interfacial energies are presented in Table 4.

6. Conclusions

Microstructure stability of ferritic 9–12% Cr steels used in advanced steam power plants was discussed. At technologically interesting creep conditions the microstructure stability is mainly controlled by the stability of precipitate particles in the steels. Predictions of long-term stability of precipitate particles up to 200,000–300,000 h at temperatures up to 600–650°C are highly interesting for safe plant operation.

Predictions of precipitate stability have to rely on i) Microstructure characterisation methods to measure volume fractions and mean particle sizes of individual precipitate types, and ii) Microstructure models to predict the evo-
coarsening rates for M23C6 carbides, and the fit value for the interfacial energy in steel P92 indicate incoherent interfaces as expected.

Characterisation methods, which allow on-line particle type discrimination in 9–12% Cr steels include energy filtered transmission electron microscopy (EFTEM) and scanning electron microscopy (SEM) with atomic number contrast. EFTEM was found to be highly useful for particle size measurements of MX and M23C6 precipitates. For Laves phase with mean particle sizes larger than approximately 200-nm diameter SEM should be used.

Modelling of precipitate stability based on thermodynamic equilibrium calculations and multicomponent diffusion databases was demonstrated. A multi-component coarsening model allows predictions of the influence of chemical composition on coarsening rates. The only fit parameter to the model is the interfacial energy.

The coarsening model gives accurate predictions of coarsening rates for MX and Laves phase precipitates in steel P92 with expected values for the interfacial energy.

For M23C6 carbides the coarsening model results in unexpectedly low apparent values for the interfacial energy for steel P92 indicating coherent precipitate/matrix interfaces. Modelling of published data for steel P91 indicates much higher coarsening rates for M23C6 carbides, and the fit value for the interfacial energy in this steel indicate incoherent interfaces as expected.

A possible explanation for the low apparent value of the interfacial energy for M23C6 carbides in steel P92 is the content of boron in the steel. Boron could be affecting both the interfacial energy and the diffusivities.

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