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Numerical Simulation of grain boundary carbides evolution in 316H stainless steel

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Abstract

In the present work, a numerical model based on the coupling of Kampmann and Wagner Numerical (KWN) framework and thermodynamic software ThermoCalc has been developed to predict grain boundary precipitate evolution in 316H stainless steel during thermal aging. The model is calibrated and validated against precipitate size distributions obtained by accelerated isothermal heat treatment and analysed using scanning electron microscopy (SEM). Elemental distribution was also investigated using electron microprobe analysis (EPMA). The predicted average particle size, particle size distribution and precipitate number density predicted by the model were found to be in good agreement with the experimental results. The model was then applied to predict the particle size distribution after several years exposure at service temperature. It is demonstrated that these predictions are consistent with measurements from a service-exposed part. The sensitivity of the precipitate size distribution to temperature is emphasised, and it is demonstrated that the model has potential as a useful tool for predicting evolution of the precipitate size distribution during service, providing reliable thermal data are available for the whole service life.

Keywords

316 stainless steel; Carbides; Thermal ageing; Numerical simulation

1. Introduction

AISI 316 austenitic stainless steels are widely used reactor materials in conventional nuclear power plants because of their outstanding mechanical formability, good high temperature strength and corrosion resistance [1]. However, these materials are subjected to degradation due to thermal aging and other external factors (irradiation, stress, temperature, coolant media, etc.), which could affect the reliability of components [2, 3]. Carbides are important precipitates in these austenitic stainless steels. However, these carbides are not always stable; they evolve under thermal aging or welding processes, which have an important influence on material performance. The dominant carbide phase in 316H is $M_{23}C_6$ and it precipitates on the grain boundaries, twin boundaries and dislocations [2, 4-9]. The precipitation of this phase at grain boundaries depletes the local chromium content to an extent which is an important reason for the occurrence of intergranular stress corrosion cracking in stainless steels in high temperature water environment and also results in degradation of strength, toughness and creep ductility properties [10-13]. Many variables such as alloy compositions, exposure temperature and duration, and processing history affect the stability of $M_{23}C_6$ in multicomponent materials such as AISI 316SS.

Several investigations have reported the precipitation behaviour of $M_{23}C_6$ during isothermal heat treatment in 316SS. The evolution of $M_{23}C_6$ has been studied by a range of experimental techniques, but clearly there are practical limits to the duration of such experiments [2, 13-15]. To be able to extrapolate these results to longer timeframes (40–60 years or beyond) requires a reliable method for predicting $M_{23}C_6$ evolution. A physical rather than empirical model potentially provides the most reliable extrapolation as well as helping to understand the mechanisms contributing to the microstructural change in this type of stainless steels. However, the model must have some specific features; it has to have ability to capture the complexity of the multicomponent system and account for the simultaneous occurrence of nucleation, growth and coarsening of the precipitates.

The Kampmann and Wagner Numerical (KWN) method is one of the most appealing approaches to provide a framework to predict precipitate evolution [16-18]. This method uses thermodynamic and kinetic (e.g. mobility) data to predict the essential

processes that occur during precipitate evolution, namely nucleation, growth and coarsening. It has also been widely applied to a number of alloy systems (including stainless steel 316) with the advantage of naturally predicting the evolution of precipitates from nucleation to growth and coarsening without imposed constraints [16, 17, 19-22]. The KWN model requires knowledge of the thermodynamic properties of the precipitate and matrix phase (to calculate interfacial compositions) and the diffusion coefficient of the rate controlling element(s). These inputs can be derived by thermodynamic calculation and from literature. The precipitate/matrix interfacial energy is another critical parameter in the KWN model, and strongly influences both nucleation and growth behaviour. Interfacial energy is usually a calibration parameter in the KWN method, and is determined by fitting the model predictions to experimental results for a limited number of temperatures before validating the model across a wider temperature range.

The traditional KWN model was developed to model homogeneous precipitation in a supersaturated matrix. In this work, the KWN method is adapted to simulate the evolution of grain boundary precipitation, specifically the carbides, in 316H stainless steels. The interfacial energy in this alloy was calibrated and optimized using experimental data obtained from specimens exposed at different temperatures for different durations as described in detail later. ThermoCalc with the TCFE9 steels database predicting the phase stability and equilibrium compositions is used as input for the KWN precipitation kinetics model [23]. Once calibrated, the KWN model was applied to predict the likely precipitate evolution in the nuclear power plant materials over long-term service (many years). Such a microstructure model is a key step in producing a physical based ability to predict remnant service life.

2 Material details and experimental method

2.1 Materials

Type 316H stainless steel obtained from the body of a 64 mm wall thickness steam header of an advanced gas-cooled reactor (AGR) component provided by EDF Energy is used in this work. The as-received material block from EDF had been in service for 91,595 hours at 460~540 °C. The chemical composition of this material is shown in Table 1. The chemical composition of the 316H stainless steel from the

NIMS Material Database is listed in Table 1 as well [24], hereafter it is referred to as 316NIMS. The 316NIMS experimental data is used in later sections for comparison and validation of our results and models.

Table1. Compositions (wt%) of selected 316 alloys

Alloy	C	Mn	Si	P	S	Cr	Ni	Mo	Cu	Fe
316H	0.07	0.98	0.42	0.021	0.014	17.17	11.83	2.19	0.15	Bal.
316NIMS	0.07	1.65	0.61	0.025	0.007	16.6	13.6	2.33	0.26	Bal.

Note: chemical compositions of 316H and 316NIMS [24]

2.2 Experimental method

The as-received material was separated into small pieces (10mm×10mm×5mm) and these small pieces were solution-treated at 1100 °C for 1 hour to dissolve the carbides precipitated during service ageing, and were then water quenched to avoid precipitation during cooling. These as-quenched specimens were then isothermally aged at 700 °C and 800 °C for 1 h, 10 h and 100 h, respectively. The themally aged specimens were mounted in conductive resin, and prepared using standard metallographic methods, finishing with a polish using Oxide Polishing Suspension (OPS).

A Quanta 650 scanning electron microscope (SEM) was used for precipitate observation. Compositional contrast backscattered electron (BSE) imaging was used to image the precipitates, and the accelerating voltage used during imaging was 15 kV. It should be noted that, to determine the measured precipitate size distributions, ImageJ software [25] was applied to calculate the areas of the particles in BSE images and then the particle areas were converted to equivalent circle radii to compare with the model predictions. In addition, due to the limitation of resolution, only particles with equivalent radii larger than 25nm were measured.

A challenge in using SEM to quantify particle size distributions is to determine the maximum depth from which the back-scattered signal is emitted, and thus the effective volume of material being sampled. In the present work, the Monte-Carlo electron-sample interaction simulation software Casino [26] was used to determine the equal interaction volumes of the material with the beam for the imaging conditions used (10,000 electrons at 15 kV accelerating voltage with an assumed beam diameter of 10 nm, the density of the steel with 7.79 g/cm³). This simulation

suggested a maximum penetration depth of approximately 350nm, and it may be assumed that back-scattered electrons that penetrate up to half this depth will be emitted and thus contribute to the detected signal. Therefore, an approximate conversion between number/area measured from the SEM image and volume fraction can be made, assuming the sampling depth to be half the maximum penetration depth:

$$N_v = \frac{N_A L}{2} \quad (1)$$

where N_v is the volumetric number density, N_A is the measured number density from the SEM image (per unit area of the image) and L is the total interaction depth (350nm in this case). Since (as shown later) the sampling depth is typically much greater than the measured particle size (radius), it is reasonable to assume that in most cases the whole particle is captured inside the sampled volume, and thus truncation effects were ignored.

The chemical composition of the precipitated carbides and other intermetallic phases (η and σ) were investigated using a JEOL JXA-8530F FEG-EPMA. The analyses were run at 9 kV, 43 nA at a magnification of 6500 $\times$ and 50 ms dwell time on each point.

3. Precipitation kinetics simulation

The carbide of interest, $M_{23}C_6$, can precipitate both on grain boundaries and in the grain interior. Grain boundaries are known to be potent nucleation sites for this phase, and it is grain boundary nucleated $M_{23}C_6$ that forms first during the early ageing stages [2, 27]. It is the grain boundary $M_{23}C_6$ that has the most important effect on the long term performance of the alloy, particularly resistance to stress-corrosion cracking, due to its effect on local chromium depletion as already discussed. Therefore, in the present work, the model is focussed on predicting grain boundary $M_{23}C_6$ evolution.

The KWN method is applied to predict precipitation kinetics. A full description of the KWN method is given elsewhere [22]. The model describes the nucleation, growth, and coarsening of particles in the system occurring simultaneously and calculates the particle size distribution evolution during discrete time steps. The growth of particles

is assumed to be governed by the diffusion rate of solute to or from the particle/matrix interface. The particle size distribution and the volume fraction of the precipitate particles are updated at each time step and used to recalculate the matrix composition. Matrix compositions are then determined by a mean-field approach. Coarsening arises naturally in the model. Using this method, the transition from nucleation and growth to a coarsening-dominated regime is naturally predicted as the precipitate volume fraction increases. In the present work, the KWN method has been applied to grain boundary precipitation by application of an appropriate grain boundary growth law and fitting of the nucleation law to grain boundary precipitation.

3.1. Nucleation

In a multicomponent system, the classic nucleation theory developed for binary alloys is not strictly valid. In such cases, a common approximation is to assume nucleation is controlled by the slowest diffusing element in the precipitate phase, which is chromium for $M_{23}C_6$ in 316H. As the most fraction of $M_{23}C_6$ is composed by chromium and carbon in Fig.4, the chromium is considered to control the diffusion process in this case. This simplifies the nucleation to a binary problem where the classic nucleation theory gives the following equation for grain boundary nucleation rate at the steady state [19, 28]:

$$I = N_{GB} \omega \exp \left[- \frac{G^* S(q) + Q^*}{kT} \right] \quad (2)$$

where N_{GB} is the site density for grain boundary nucleation, assuming that every atom within the effective thickness of the grain boundary could act as a nucleation site, and given by [28]

$$N_{GB} = N_v \delta_B / L_B \quad (3)$$

where δ_B is the effective thickness of grain boundary, which was assumed to be a thickness of two or three atom diameters for the grain boundary [29], L_B is the grain size (the measured average size for the present material was 120 μm) and N_v is the number of atoms per unit volume in grain boundary region (which is assumed to be the same as in the bulk) [29]. The nucleation attempt frequency factor, ω , was

assumed to be given by kT/h , where k is the Boltzmann constant, h is the Planck constant and T the temperature, following classical nucleation theory [29].

G^* is the activation energy barrier for homogeneous formation of a critically sized cluster in the matrix, which can be calculated from the critical radius r^* and the interfacial energy for the cluster γ_n .

$$G^* = \frac{4\pi r^{*2} \gamma_n}{3} \quad (4)$$

In the case of heterogeneous grain boundary nucleation, this energy barrier is reduced due to the energy released by destroying part of the grain boundary, and this reduction is given by a scaling parameter, known as the shape factor, which relates to the angle at which the cluster wets the grain boundary (θ) and is given by

$$S(q) = \frac{(2 + \cos q)(1 - \cos q)^2}{2} \quad (5)$$

Where θ is a function of the grain boundary energy and nucleus/matrix interfacial energy [30]:

$$\cos \theta = \frac{\sigma}{2\gamma_n} \quad (6)$$

where σ is the grain boundary energy [30]

Q^* is the activation energy for transfer of atoms across the nucleus/precipitate interface which is given by Smith [31] with the value of 195 kJ/mol.

The critical radius for cluster stability was be calculated using a widely used approximation [32].

$$r^* = \frac{2\gamma_n V_a}{kT \ln \frac{c}{c_\infty^\alpha}} \quad (7)$$

where V_a is the volume per atom in the matrix; c is the concentration (atomic fraction) of Cr solute in the matrix (evolving with time) and c_∞^α is the equilibrium concentration of solute in the matrix at a planar interface with the precipitate, which was calculated by ThermoCalc.

The rate of nucleation is highly sensitive to the matrix/nucleus interfacial energy, γ_n , a value that is difficult to determine empirically. There is no directly measured value for γ_n available for $M_{23}C_6$. The determination of interfacial energies will be discussed in Section 4.3.

In the KWN method, the nucleation rate and therefore number of new particles is calculated for each short time interval. These particles are added into the particle size distribution at a size that is 10% larger than the critical radius for stability (r^*) to ensure their growth in the next time interval. The values of the input parameters to the model are presented in Table 3.

3.2. Growth

In the KWN model, the $M_{23}C_6$ precipitates are assumed to have a spherical morphology. Previous studies have shown that although this is a poor approximation in many cases, the particle shape has a relatively minor effect on the results [17]. The growth rate is limited by the rate at which Cr can diffuse to the particles. For grain boundary precipitates, the effect of fast diffusion along grain boundaries must be accounted for. This fast diffusion allows grain boundaries to act as collector plates, drawing in solute from a wider region and enabling faster precipitate growth than if they were not there. An established collector plate model was used to calculate the growth rate in each time interval and for each size class [16, 33]

$$\frac{dr}{dt} = \frac{4D_{Cr-GB}\sqrt{D_{Cr-matrix}t} (c_i - c_r^\alpha)}{3r^2\sqrt{\pi} (c^\beta - c_r^\alpha)} \quad (8)$$

Where D_{Cr-GB} is the grain boundary diffusion coefficient of Cr, $D_{Cr-matrix}$ is the volume diffusion coefficient for the Cr in the matrix, r is the mean radius for a given size class, c_r^α is the concentration of solute in the matrix at the interface (which depends on the particle radius due to the effect of capillarity), c^β is the concentration of solute in precipitates and c_i is the instantaneous concentration of Cr in the matrix. c_r^α is calculated using the Gibbs–Thomson equation from the planar interfacial composition (which is itself calculated using Thermocalc):

$$c_r^\alpha = c_\infty^\alpha \exp\left(\frac{2\gamma_n V_m}{RT} \frac{1}{r}\right) \quad (9)$$

where γ_n is the interfacial energy of the growing (or shrinking) particle; c_∞^α is the equilibrium concentration of solute in the matrix for a planar interface; V_m is the molar volume of the precipitate phase.

The mean solute concentration of the components in the matrix, c_i , is updated after each time step:

$$c_i = c_0 - (c^\beta - c_\infty^\alpha) \int_0^\infty \frac{4}{3} \pi r^3 \phi dr \quad (10)$$

where ϕ is the size distribution function. The newly obtained matrix composition is employed as an input for the thermodynamic computations in the next time step. The values of c_0 , c^β and c_∞^α can be obtained from thermodynamic calculations which depend on the chemical compositions and temperatures. The values at each temperature in this work are calculated by ThermoCalc, and are shown in Table 2 in Section 4.2. The diffusion coefficient $D_{\text{Cr_GB}}$ and $D_{\text{Cr_matrix}}$ which refers to D in Eq.(11) can be calculated using the general form:

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \quad (11)$$

The D_0 refers to lattice volume pre exponential coefficient D_{0v} and grain boundary pre exponential coefficient of chromium D_{0b} in 316 stainless steel are cited from [31] which is shown in Table 3.

3.3. Precipitate coarsening

Coarsening occurs when large precipitates grow at the expense of small ones, without a change in the overall volume fraction. As the fraction of solute in the matrix decreases during precipitation, the driving force for nucleation and growth of the precipitate particles decreases and the critical particle radius increases. The growth rates of all the particle size classes were calculated at the edges (i.e. upper and lower bounds) of each class. For particles with radii smaller than the critical radius, r^* , the growth rate will become negative, according to Eq.(8). Particles with radii larger than r^* will retain a positive growth rate and increase in size. When the size of a group of shrinking particles reaches zero they are removed from the size distribution.

In the KWN method, it is necessary to assume that dissolution is simply the reverse of growth, controlled by the same growth law but with the concentration gradient driving solute flux away from rather than towards the dissolving precipitate. In the present case, this means that the collector plate law operating in reverse controls dissolution. The true situation is expected to be more complex than this, and this approximation introduces a source of error into the ability of the model to predict coarsening behaviour. The significance of this error is expected to be small.

The precipitate size distribution is updated at each time step using a third order Runge–Kutta scheme [19] with an adaptive time step to ensure numerical accuracy. The time step was adjusted to ensure that the error in the change in radius was less than 0.1 nm between steps and the error in the prediction of number density was less than 0.01 particle/ μm^3 . In the early stages of precipitation, the time step is very small to ensure these criteria are met when nucleation and growth rates are most rapid. In the later stages of precipitation and during coarsening, the time step expands, where changes occur more slowly, allowing more efficient calculation.

4. Results and discussion

4.1 Experimental results

4.1.1 Carbides precipitation during ageing

Clusters of precipitate particles were observed in all specimens after thermal aging at 700 °C and 800 °C for different durations, representative images showing the precipitates are shown in Fig. 1. The morphology of carbides growing on the grain boundaries varies considerably. The size varies from small to large and the density varies from widely-spaced to almost continuous sheets.

Fig.1 BSE images of carbides precipitated in specimens aged for (a) 1h at 800 °C; (b) 10h at 800 °C (c) and (d) 100h at 800 °C

4.1.2 Composition Analysis

Fig. 2 presents the EPMA elements distribution maps of the precipitates and the grains. These maps show that the precipitates precipitated along the grain boundaries and within the grains are all rich in chromium, molybdenum. Precipitation of these chromium-rich phases (presumed to be primarily $M_{23}C_6$ carbides) decreases the carbon content of the bulk austenite and appreciably alters the local chemical content of Cr, Ni, Mo, Fe at the grain boundaries (Fig.2). Consequently, a chromium, molybdenum and carbon depleted, precipitate-free zone formed adjacent to the grain boundaries as shown in the EPMA maps (Fig. 2).

Fig.2. Series of elemental maps showing the distribution of key elements in a 316H stainless steel. The coloured scale bar at the right shows relative concentration.

4.2 Thermodynamic calculations

ThermoCalc [23] employing the TCFE9 thermodynamic database was used to calculate phase stabilities and compositions in 316 stainless steel.

The validation of thermodynamic predictions was achieved by comparing the experimental data obtained from the steel studied in the present work (316H) and the data for 316NIMS from the literature [24]. The compositions of these two stainless steels are very similar. The calculated equilibrium phases and their mole fractions in both alloys are shown in Fig. 3. The solid symbols denote the matrix phase (FCC_A1). The open symbols in Fig. 3 denote the precipitate phases formed in 316H stainless steels. The phases precipitated in the alloys are $M_{23}C_6$, Sigma and Laves phases, and they have been routinely observed in austenitic steels including 316H. The calculated results suggest the equilibrium phases in 316NIMS from high to low temperature are $M_{23}C_6 + \chi$, $M_{23}C_6 + \chi + \eta$, $M_{23}C_6 + \chi + \eta + \sigma$, and $M_{23}C_6 + \eta + \sigma$ in sequence. This is in good agreement with the phases observed in the experimental Time–Temperature–Precipitation diagram of 316NIMS from the literature [24]. The calculated plot of phase fraction vs temperature of 316H in Fig. 3 is similar to that of 316NIMS [34].

The predicted compositions of $M_{23}C_6$ precipitates are shown in Fig.4. Each element in $M_{23}C_6$ is within 20% of the measured values in [24], suggesting that ThermoCalc can give a reasonable prediction of the composition of the precipitates. The deviations in predicted composition are greatest at lower temperatures, and above 650°C agreement is excellent.

The predicted concentration of Cr in the precipitates and the equilibrium concentration of Cr in the matrix from the ThermoCalc calculation are input to the precipitation model. The equilibrium concentration in the matrix is used to calculate the composition in the matrix at the precipitate/matrix interface, accounting for interfacial curvature, as discussed later. These concentrations corresponding to the temperatures simulated in this work are listed in Table 2.

Fig.3 Calculated equilibrium phase mole fraction vs temperature for (a) 316H stainless steel and (b) 316NIMS

Fig.4. The calculated phase compositions (solid lines) in 316H for (a) $M_{23}C_6$ which was compared with the experimental data (dots) [24] (b) FCC_A1

Table 2 The Cr concentration calculated by ThermoCalc

T (°C)	c_{∞}^{α}	c_0	c^{β}
460	0.101	0.184	0.647
520	0.117	0.184	0.637
540	0.124	0.184	0.634
700	0.161	0.184	0.616
800	0.175	0.184	0.607

4.3 Model calibration and validation

The calibration procedure of the microstructural model is as follows:

Step 1: the experimental information of particle size distribution, number density and mean radius is summarised and analysed for the model calibration and validation. The experimental $M_{23}C_6$ information at 700 °C and 800 °C with thermal ageing for 1 h, 10 h and 100 h are measured which are represented as red symbols in Fig. 5 - Fig.7. The frequency of $M_{23}C_6$ size distributions, f , is plotted as a function of particle radius in Fig.5. As the measured $M_{23}C_6$ by SEM in this work ranges from 25nm to 250nm and the interaction depth was calculated to be about 350 nm, it can be considered that all the particles were measured up to a depth of 175nm (i.e. half the total path-length). Equation (1) is then used to calculate the number density and the calculated results are

shown in Fig.6. The number density increases first and then is constant before finally decreasing as time increases at both temperatures. The mean radius of $M_{23}C_6$ particles for samples aged at different temperatures is measured as well in Fig.7. Specifically, the average measured mean radius is 31 nm after aging for 1h, while it increased to 50nm and 112 nm after aging for 10h and 100h, respectively at 700 °C. At 800 °C, the measured mean radius is 99 nm, 132 nm and 236 nm after thermal aging for 1h, 10h and 100h, respectively. The size of $M_{23}C_6$ reported in other research is similar, which varies from 20nm to 250 nm [2, 14, 35-38].

Step 2: the unknown physical parameters, i.e. interfacial energy for nucleation and growth, are calibrated in order to fit the predicted results to the experimental data in a limited range of temperatures. In the KWN model, the “interfacial energy” parameter is assumed to be temperature independent. In this modelling approach, this parameter should be considered more as a fitting value, although it does have an association with the true interfacial energy. Implicit in the assumption of a constant interfacial energy is the assumption that the interface type does not change with temperature – for $M_{23}C_6$, this is reasonable. In this case, the true interfacial energy should only be weakly temperature dependent. The results of the KWN model are very sensitive to the precise value chosen for the interfacial energy. The effect of changing interfacial energy on the results of a similar KWN model has been demonstrated elsewhere [39]. Following common practice, the interfacial energy for nucleation is determined by fitting the predictions of the model to the experimental data for a limited range of temperatures. To make this comparison, only particles larger than 25nm are considered. This is reasonable as it is coarsening dominant for higher temperatures (e.g. 700 °C and 800 °C) after 1 h from Fig.6 and Fig.8(c). This means that more and more particles become larger than 25nm. The published interfacial energies for $M_{23}C_6$ precipitation in 304 stainless steel are $0.016 \text{ J/m}^2 < \gamma < 0.265 \text{ J/m}^2$ [40]. As a first approximation, the interfacial energies are calibrated iteratively in the range of values from the literature [40] and then refined to give the best fit to experimental data.

However, in this work, a single interfacial energy cannot predict the experimental data very well for both early and later stages of precipitate evolution. Therefore, two different interfacial energy values were used: one for nucleation and the other for

growth/coarsening process (See Table 3). This is reasonable as the nucleus contains only a small number of atoms, which corresponds to a very small size at the start of transformation. This means the nucleus has considerable freedom to arrange them to minimize the interfacial energy. Conversely, a coarsening particle typically contains hundreds of thousands of atoms. As the particles grow from small nuclei into distinct precipitates, the interfacial energy will increase to the value measured from coarsening rate experiments [41]. Exactly how the interfacial energy varies as a function of particle size between the nucleation and coarsening stages is unclear.

In the present work, firstly, the interfacial energy is optimised to fit the experimental carbide size distribution and mean radius after long ageing times at 700 °C and 800 °C. This value corresponds to the interfacial energy for growth and coarsening. Then the interfacial energy for nucleation is optimised to fit the carbide size distribution and mean radius. Compared with the experimental information at 700 °C and 800 °C, the interfacial energies are slightly refined to give the best fit to experimental data both at 700 °C and 800 °C. After several iterations, the optimised interfacial energy used for nucleation is 0.024 J/m² while the value used for growth and coarsening is 0.07 J/m². The comparison between the predicted results and experimental data is shown from Fig.5 to Fig.7. In Fig.5, the experimental M₂₃C₆ size distribution has a considerably lower peak than predicted values. This may be explained that the measured M₂₃C₆ size scatters. In general, they are in good agreement in the particle size distribution, number density and mean radius. As it was found that the predictions were not very sensitive to the exact value used for the size at the end of the transition, or the form (e.g. linear or logarithmic) of the function used to vary the interfacial energy, this approximation was adequate to allow good reproduction of the experimental measurements [16].

Table 3 Parameters used in this work

Parameter	value	Reference
N_v		Calculated in this work
a	1.06e-9 m	[42]
γ_n	0.024 J/m ² for nucleation and 0.07 J/m ² for growth	Fitted in this work
Q^*	195 KJ/mol	[31]

D_{0b}	$2.50 \times 10^{-6} \text{ m}^2/\text{s}$	[31]
Q_b	195 KJ/mol	[31]
D_{0v}	$6.30 \times 10^{-7} \text{ m}^2/\text{s}$	[31]
Q_v	240 KJ/mol	[31]
V_m	$6.53 \times 10^{-6} \text{ m}^3/\text{mol}$	Calculated by Thermo-Calc
V_a	$1.17 \times 10^{-29} \text{ m}^3$	[43]
k	$1.38 \times 10^{-23} \text{ m}^2 \cdot \text{kg}/(\text{s}^2 \cdot \text{K})$	[29]
R	8.314 J/(mol $\cdot$ K)	[29]
h	$6.63 \times 10^{-34} \text{ m}^2 \cdot \text{kg}/\text{s}$	[29]
$\cos\theta$	0.707	[44]

Fig. 5. Predicted and measured carbide size distribution for specimens aged for: (a) 10h at 700 °C; and (b) 100h at 700 °C; (c) 10h at 800 °C; and (d) 100h at 800 °C

Fig. 6. Predicted and measured evolution of number density of carbide sizes larger than 25nm (a) at 700 °C (b) at 800 °C

Fig. 7. Mean radius evolution of $M_{23}C_6$ in 316H (a) at 700 °C (b) at 800 °C.

4.4 Model application

After proving the accuracy, the model developed above is used to predict the long term thermal ageing effects in 316H. The original specimens from EDF had entered into service at 460 °C~540 °C for 91,597 hours with an average temperature of 520 °C (see Table 4), and their microstructure was analysed by SEM as well to compare with predictions. A difficulty for the prediction of the as-received material is that the precise service temperature was not known for the full component lifetime. To consider the effect of temperature changes within the known service range, predictions were made for both the upper and lower temperature bounds and the average temperature.

The predicted $M_{23}C_6$ particle size distributions at 460 °C, 520 °C and 540 °C after thermal ageing for 91597h are shown in Fig. 8(a) - Fig. 8(c) respectively. The measured $M_{23}C_6$ particle size distribution is shown in Fig.8 for comparison as well. It is clearly observed in Fig.8 that the predicted particle size distribution, mean radius

and volume fraction of $M_{23}C_6$ after long term thermal ageing vary greatly with the assumed service temperature: 460 °C, 520 °C and 540 °C. The predicted results at 520 °C agree well with the experimental values, but changes in the effective service temperature have a very strong effect on the precipitate parameters. This emphasizes the importance of capturing accurate and complete service temperature histories if such models are to be used efficiently in a predictive model. In addition, the model currently ignores the influence of other phase that form during very long thermal exposure (e.g. σ -phase) and may compete for solute.

In Fig.8(b), the average size of $M_{23}C_6$ particles for samples aged at different temperatures increases rapidly initially. The rate of increase then slows down, finally increases very slowly with aging time, indicating that the $M_{23}C_6$ precipitates are in a regime where growth and coarsening are dominated. The mean radius of $M_{23}C_6$ precipitates at higher temperature grows faster than at lower temperature especially at early times. It can be also observed in Fig.8(b) that the higher temperature used the less time is required to reach the fixed mean radius of $M_{23}C_6$, e.g. 60nm. This means that if we need to study the $M_{23}C_6$ under a lower temperature for a longer period of time which is usually realistic situation in service, we could obtain the precipitate particles under a higher temperature for much shorter times which is less time-consuming.

From Fig.8(c), the predicted volume percentage of $M_{23}C_6$ decreases and the time required to reach the maximum volume percentage of $M_{23}C_6$ decreases as the aged temperature increases which shows the opposite change for the mean radius. At each temperature, the volume fraction of $M_{23}C_6$ increases steeply at initial times and then plateaus. Initially, nucleation dominates and the number of $M_{23}C_6$ precipitates increases steeply. At longer times, growth and coarsening become dominant. This is because the supersaturation of solute in the matrix decreases during precipitation, therefore the driving force for nucleation and growth of $M_{23}C_6$ decreases, and the critical particle radius increases. Particles in the size distribution which have a radius $< r^*$ will have a negative growth rate according to Eq. (8) and will thus start to shrink. Particles with a radius $> r^*$ will retain a positive growth rate and will continue to increase in size. Eventually, this leads to pure coarsening behaviour, where large precipitates grow at the expense of small ones, without a significant change the

overall volume fraction. Both the volume fraction and size of $M_{23}C_6$ needs to be taken into account for the effects on intergranular stress corrosion cracking, strength, toughness and creep ductility properties.

Table 4 Service history of headers

YEA R	Temperature Bands °C								Total
	460- 470	470- 480	480- 490	490- 500	500- 510	510-520	520- 530	530- 540	
1984	220	70	480	530					1300
1985	100		1660	4610					6370
1986	2	2	66	229	405	144			848
1987	7		12	49	235	3923	428	12	4666
1988	15	13	13	22	630	4404	164		5261
1989			6	304	260	2945	1565		5080
1990				61	993	2270	2005	847	6176
1991	9	9	9	38	126	1437	3258	214	5100
1992	20	17	16	29	34	714	5103	962	6895
1993	8	7	7	16	46	132	3574	3938	7728
1994	6	9	11	28	104	1343	4283	863	6647
1995	9	10	11	66	162	6057	17		6332
1996	16	15	14	39	1850	2428	2175	195	6732
1997	10	12	20	26	118	3765	3961	4	7916
1998	9	17	15	27	117	7414	361		7960
1999	18	26	39	62	926	5464	42	9	6586
Total	449	202	2379	6136	6006	42445	26936	7044	91597

Fig.8. Predicted (a) carbide size distribution (b) mean radius (c) volume percentage in 316H after ageing for 91kh at various temperatures, the measured data from the material entered serviced are also included for comparison

5 Conclusions

A model describing the precipitation kinetics of grain boundary $M_{23}C_6$ in 316 stainless steels is developed. The model is based on the Kampmann Wagner numerical framework with grain boundary nucleation and growth laws incorporating capillarity effects. The model is coupled with ThermoCalc thermodynamic databases for obtaining equilibrium condition at $M_{23}C_6$ /matrix interface. The model is capable of capturing the complete precipitation sequence, from nucleation to coarsening, without artificial constants. The size distributions and particle size evolutions, predicted by the model in this study agree well with the experimental data across a wide range of ageing temperatures. The model is able to predict the overlapping nucleation-growth-coarsening kinetics in a natural way and trace the particle size distribution throughout the process. The model is of a general nature, and it can be applied to other precipitate phases present in similar stainless steels and more complicated conditions such as welding process, which is a subject of on-going work.

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