Numerical Simulation of Long-Term Precipitate Evolution in Austenitic Heat-Resistant Steels

Jae-Hyeok Shim\textsuperscript{1}, Ernst Kozeschnik\textsuperscript{2}, Woo-Sang Jung\textsuperscript{1}, Young Whan Cho\textsuperscript{1}

\textsuperscript{1}Materials Science and Technology Research Division, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea
\textsuperscript{2}Institute of Materials Science and Technology, Vienna University of Technology, A-1040 Vienna, Austria

ABSTRACT

Numerical simulation of the long-term precipitate evolution in five different austenitic heat-resistant steels, NF709, Super304H, Sanicro25, CFC8-PLUS and HTUPS has been carried out. MX and M\textsubscript{23}C\textsubscript{6} are predicted to remain as major precipitates during long-term aging in these steels, which agrees with experimental observations. While the average size of MX is maintained below several tens of nanometers during the aging, that of M\textsubscript{23}C\textsubscript{6} exceeds 100 nm after 100,000 hours of aging at 700 °C. The addition of 3 wt\% Cu produces very fine Cu-rich precipitates during aging in Super304H and Sanicro25. It is found that the amount of Z phase start to increase remarkably between 1,000 and 10,000 hours of aging at the expense of MX precipitates in the steels containing a high nitrogen content. However, the growth rate of Z phase is relatively slow and its average size reaches at most a few tens of nanometers after 100,000 hours of aging at 700 °C, compared with 9-12 % Cr ferritic heat-resistant steels.

1. Introduction

There is urgent need to improve the thermal efficiency of fossil fuel power plants by raising the operation temperature and pressure in order to reduce CO\textsubscript{2} emission as well as the cost of fuel. Plant operation at higher temperatures inevitably requires the development of heat-resistant alloys with higher creep strength at an acceptable level of creep ductility [1]. 9-12 % Cr ferritic heat-resistant steels have so far been widely used
in fossil fuel power plants, owing to their high thermal conductivity, low thermal expansion coefficient and low susceptibility to thermal fatigue. Nevertheless, there has recently been increasing interest in applying austenitic heat-resistant steel to fossil fuel power plants in order to raise their operation temperature, because austenitic heat-resistant steels have higher creep strength than ferritic ones. It is generally accepted that ferritic and austenitic steels are useful up to about 620 and 675 °C, respectively, purely from the creep strength point of view at a steam pressure of 35 MPa [1].

The important role of precipitation in the achievement of good creep properties of heat-resistant steels has long been recognized [2]. One of the most effective ways for improving the creep properties is to uniformly distribute fine precipitates with a good long-term stability at elevated temperatures. Austenitic heat-resistant steels are known to exhibit quite complicated precipitation behavior together with various precipitates such as carbides, nitrides and intermetallic phases, as Sourmail [3] reviewed in detail. However, the investigation of the precipitate evolution behavior in austenitic heat-resistant steels has seldom been performed, although it is important in understanding the creep properties.

The purpose of this study is to simulate the long-term precipitate evolution in various austenitic heat-resistant steels using a numerical model based on classical nucleation theory and multi-component evolution equations derived from the thermodynamic extremum principle of maximum entropy production [4]. The simulation results such as the precipitation sequence and the precipitate size will be compared with experimental observations in the literature.

2. Materials and simulation method

Five different austenitic heat-resistant steels, NF709, Super304H, Sanicro25, CFC8-PLUS and HTUPS have been chosen for the simulation of the precipitate evolution. The chemical compositions of these steels are given in Table 1. These steels contain 14-22 wt% Cr, which is higher than the content of Cr in conventional ferritic heat-resistant steels. The content of Ni as an austenite stabilizer is also quite high (9-25 wt%) to maintain the austenite matrix with a high content of the strong ferrite stabilizer Cr in these steels. The content of Mn that plays a similar role to Ni is relatively high in CFC8-PLUS, which contributes to the reduction of the Ni content. Just like ferritic heat-resistant steels, Mo or W is added to improve the creep strength, except for Super304H. All the steels contain a small amount of Nb, which is expected to form fine MX
precipitates. Super304H and Sanicro25 contain 3 wt% Cu, which is known to induce Cu-rich precipitates during aging (service).

Table 1. Chemical compositions of the austenitic heat-resistant steels (wt%).

<table>
<thead>
<tr>
<th>Steel</th>
<th>Fe</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>Si</th>
<th>Mo</th>
<th>W</th>
<th>Nb</th>
<th>Ti</th>
<th>V</th>
<th>Cu</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF709</td>
<td>bal.</td>
<td>0.15</td>
<td>20.0</td>
<td>25.0</td>
<td>1.0</td>
<td>0.5</td>
<td>1.5</td>
<td>-</td>
<td>0.2</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>0.167</td>
</tr>
<tr>
<td>Super304H</td>
<td>bal.</td>
<td>0.1</td>
<td>18.0</td>
<td>9.0</td>
<td>0.8</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>3.0</td>
<td>0.1</td>
</tr>
<tr>
<td>Sanicro25</td>
<td>bal.</td>
<td>0.08</td>
<td>22.0</td>
<td>25.0</td>
<td>1.0</td>
<td>0.1</td>
<td>3.5</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.0</td>
<td>0.2</td>
</tr>
<tr>
<td>CFC8-PLUS</td>
<td>bal.</td>
<td>0.07</td>
<td>19.0</td>
<td>12.5</td>
<td>4.0</td>
<td>0.5</td>
<td>0.3</td>
<td>-</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.25</td>
</tr>
<tr>
<td>HTUPS</td>
<td>bal.</td>
<td>0.08</td>
<td>14.0</td>
<td>16.0</td>
<td>2.0</td>
<td>0.15</td>
<td>2.5</td>
<td>-</td>
<td>0.15</td>
<td>0.3</td>
<td>0.5</td>
<td>-</td>
<td>0.021</td>
</tr>
</tbody>
</table>

The simulation of the precipitate evolution in the steels has been performed using the thermo-kinetic software package MatCalc (version 5.30) developed by Kozeschnik et al. [5], which deals with the kinetics of microstructural processes based on the classical nucleation theory and the thermodynamic extremum principle. During the simulation, the thermodynamic and kinetic data were calculated from the MatCalc steel database (version 1.18) and the MatCalc demonstration mobility database (version 1.03), respectively [6].

The matrix phase defined in the simulation is austenite. The partial transformation of the matrix into ferrite at low temperatures was not considered. The grain size of austenite was assumed to be 50 μm, which is in the range obtained after conventional thermomechanical treatments of austenitic steels. The dislocation density of the austenite matrix was assumed to be 10^{12} m^{-2}, conforming to the value observed in a 304 stainless steel [7]. The subgrain size was set to be 25 μm, assuming that the austenite grain has one twin on average.

MX, M_{5}C_{2}, M_{6}C, M_{7}C_{3}, M_{23}C_{6}, Laves phase, Z phase, σ phase and Cu were included in the simulation as possible precipitates. For the crystal structure and chemical composition of these precipitates, see Sourmail’s review [3]. The nucleation sites of MX, M_{23}C_{6}, Laves phase, Z phase, σ phase and Cu were set to be dislocations, grain boundaries and subgrain boundaries, according to Sourmail’s review [3]. It was assumed that M_{5}C_{2}, M_{6}C and M_{7}C_{3} nucleate at grain and subgrain boundaries, as no sufficient information on their nucleation sites is revealed in the literature. The interfacial energy of the precipitates is an important factor determining their nucleation and growth rate. In MatCalc, interfacial energy is calculated from thermodynamic data,
based on a generalized nearest-neighbor broken bond analysis [8]. In this study, the interface energy values of coherent and semi-coherent precipitates were assumed to be 50 and 75% of the calculated values of a planar, sharp interface, respectively, due to size effects of the small precipitates [9] and entropic effects from diffuse interfaces. Cu was regarded as a coherent precipitate, according to the recent transmission electron microscopy (TEM) observation [10]. Since it is known that MX, M23C6, M7C3, Laves phase, Z phase and σ phase have an orientation relationship with austenite [3], they were regarded as semi-coherent ones. For simplicity of analysis, the shape of the precipitates was assumed to be spherical, although some of them have characteristic shapes. During the simulation, precipitates are considered as belonging to a number of size classes of precipitates with the same size and composition. Individual size classes are created, rearranged and deleted during simulation, allowing to model the evolution of precipitate size distributions. In this study, 300 size classes were adopted in order to obtain sufficient precision of the precipitate size distribution.

The simulated heat treatment of the steels is plotted in Fig. 1. The heat treatment started with the solution treatment at 1200 °C for one hour. It was initially assumed that all elements were homogeneously distributed in the matrix and no precipitates existed. After the solution treatment, the steels were cooled linearly down to room temperature within one hour and then heated up to 700 °C, which corresponds to aging (service) temperature, for 30 minutes. The aging was simulated at 700 °C for 100,000 hours.

![Figure 1. Simulated heat treatment of the steels.](image)

### 3. Results and discussion

Fig. 2(a) shows the variation of the simulated phase fraction of precipitates during
the heat treatment in NF709. Three kinds of precipitate, MX, M23C6 and Z phase appear during the heat treatment. The precipitation of MX starts as soon as the solution treatment starts and is almost complete in a very short time. M23C6 starts to precipitate during the cooling after the solution treatment. The amount of Z phase starts to increase significantly after 10,000 hours of aging and continues to increase until the service terminates, which is in contrast with MX and M23C6 exhibiting the saturation of precipitation in a short time. As the amount of Z phase increases, that of MX starts to decrease slowly. It has been well known that Z phase grows at the expense of MX in 9-12 % Cr ferritic heat-resistant steels containing Nb or V and a high content of nitrogen in a long-term service [11]. This growth behavior of Z phase seems to be common in both ferritic and austenitic heat-resistant steels. Sourmail and Bhadeshia [12] investigated the precipitation behavior of NF709 during long-term aging for up to 10,000 hours at 750 °C using TEM and X-ray diffraction (XRD) analyses. The XRD measurements of extracted residues of NF709 revealed that M23C6 remains as a major precipitate together with MX type precipitates such as TiN, NbN and (Ti,Nb)C through the long-term aging, which is in good agreement with the simulated results. Z phase started to precipitate after 200 hours of aging and its fraction consistently increased up to 10,000 hours at the expense mainly of NbN. Although the consistent increase in the fraction of Z phase with increasing aging time agrees with the present simulation, Z phase started to form quite earlier than the simulation. This difference might result from the difference in aging temperature. Since they performed aging at higher temperature than the present simulation by 50 °C, the transformation from MX to Z phase was probably accelerated. They also observed Cr3Ni2SiN after 2,500 hours of aging. However, Cr3Ni2SiN was unfortunately not included in the present simulation due to the lack of the thermodynamic data.

Figure 2 Variation of the simulated (a) phase fraction and (b) average size of precipitates during heat treatment in NF709.
The variation of the simulated average precipitate size during the heat treatment in NF709 is given in Fig. 2(b). The size of $\text{M}_{23}\text{C}_6$ precipitates is generally in the order of hundred nanometers. The size of MX stays around 10 nm during the aging. On the other hand, Z phase continually grows up to about 60 nm during the aging. Sourmail and Bhadeshia [12] summarized the precipitate size after 200 hours of aging at 750 °C in NF709 using TEM. The observed size ranges of $\text{M}_{23}\text{C}_6$ and Z phase were 200 to 500 nm and 20 to 50 nm, respectively, which is similar to the simulated values in order of magnitude. Nevertheless, there is a significant difference in MX size between the experimental observation and the present simulation. The observed size range of MX was 1 to 5 $\mu$m, a few hundred times larger than the simulated one. As Sourmail and Bhadeshia [12] mentioned, these very coarse MX particles were likely to form during solidification and remain undissolved during solution treatment. This simulation considered only the precipitation of MX in austenite, assuming that all the precipitates were not present before the solution treatment. Unfortunately, they did not mention the presence of fine MX precipitates, which form in austenite after the solution treatment.

Fig. 3(a) shows the variation of the simulated phase fraction of precipitates during the heat treatment in Super304H. Cu develops as a major precipitate during the service in addition to $\text{M}_{23}\text{C}_6$ and MX. The fraction of $\text{M}_{23}\text{C}_6$ slowly increases until about 1,000 hours of aging, after the considerable amount of $\text{M}_{23}\text{C}_6$ forms instantaneously at the initial stage of the aging. Compared with NF709, the precipitation of $\text{M}_{23}\text{C}_6$ tends to be quite slowly saturated. This might be attributed to a lower driving force for the precipitation of $\text{M}_{23}\text{C}_6$ in Super304H due to a lower content of Cr and C than in NF709. It is found that the precipitation of Cu is saturated in about 100 hours of aging. Although Z phase starts to form after about 10 hours of aging, its fraction remarkably increases after about 1,000 hours of aging. The fraction of MX slowly decreases with increasing Z phase fraction after about 1,000 hours of aging. $\text{M}_7\text{C}_3$ exists for a short time at the initial stage of the aging. Wu [10] investigated the precipitation behavior in Super304H aged at 700 °C for up to 10,000 hours using TEM analysis. He confirmed the presence of MX, $\text{M}_{23}\text{C}_6$ and Cu-rich precipitates, as predicted by the present simulation. However, he did not mention the presence of Z phase, although NbCrN type precipitates were observed without confirming their crystal structure. The variation of the simulated average precipitate size during the heat treatment in Super304H is presented in Fig. 3(b). The size of $\text{M}_{23}\text{C}_6$ stays around 100 nm until 10,000 hours of aging and it grows relatively fast after 10,000 hours of aging. The size of Cu precipitates stays around 30 nm and grows to about 60 nm after 100,000 hours. While MX maintains its size at about 50 nm
through the aging, Z phase continually grows up to about 20 nm. The size of M$_{23}$C$_6$ observed by Wu [10] ranged from 100 to 300 nm, which agrees with the simulation. Wu [10] also measured the average size of Cu-rich precipitates after 100, 1,000 and 3,000 hours of aging. The measured size is compared with the simulated one in Fig. 3(b). The comparison exhibits the accordance in the order of magnitude, although the growth rate of Cu-rich precipitates observed by TEM is faster.

Figure 3. Variation of the simulated (a) phase fraction and (b) average size of precipitates during heat treatment in Super304H.

As shown in Fig. 4(a), the simulated precipitate evolution in Sanicro25 is similar to that in Super304H, except that M$_7$C$_3$ does not form and the precipitation of M$_{23}$C$_6$ and Cu exhibits faster saturation behavior. Rautio and Bruce [13] performed microstructural examination of Sanicro25 aged at 700 °C for up to 3,000 hours using scanning electron microscopy (SEM) and TEM. They observed M$_{23}$C$_6$ and Nb-rich precipitates that were enriched with Cr. The observed Nb-rich precipitates can be Z phase and/or MX enriched with Cr, since Cr continues to be enriched in MX during the aging (Fig. 5). The enrichment of Cr in MX during aging is common in the simulated austenitic heat-resistant steels. However, they did not mention whether Cu precipitates existed or not in aged samples. The simulated average size of MX and Z phase in Sanicro25 is very similar to that in Super304H, as shown in Fig. 4(b). On the other hand, the size of M$_{23}$C$_6$ in Sanicro25 is quite larger than that in Super304H and the size of Cu in Sanicro25 exceeds that in Super304H after about 3,000 hours of aging.

The simulated precipitation evolution in CFC8-PLUS is also similar to that in Super304H, except that Cu precipitates do not form and the fraction of MX is larger (Fig. 6(a)). Actually, CFC8-PLUS exhibits the largest amount of MX among the simulated steels, which might be attributed to the largest content of Nb in CFC8-PLUS. Shingledecker et al. [14] observed M$_{23}$C$_6$ and MX precipitates consisting mainly of
NbC in CFC8-PLUS aged at 850 °C for 24,100 hours. They did not mention the presence of other precipitates, although it is predicted that a small fraction of M7C3 appears and disappears at the initial stage of aging and the fraction of Z phase starts to increase remarkably after about 3,000 hours at the expense of MX. The variation of the simulated average precipitate size during the heat treatment in CFC8-PLUS is presented in Fig. 6(b). The simulated average precipitate size of MX and Z phase in CFC8-PLUS is very similar to that in Super304H and Sanicro 25. The size of M23C6 shows a tendency to increase continually during aging and exceeds that of MX after about 1,000 hours. The size of MX precipitates Shingledecker et al. [14] observed using TEM at 850 °C is less than 50 nm. For comparison, we have performed the same simulation at an aging temperature of 850 °C. The simulated average size of MX after 24,000 hours aging is about 56 nm, which is consistent with experimental observations.

Figure 4. Variation of the simulated (a) phase fraction and (b) average size of precipitates during heat treatment in Sanicro25.

Figure 5. Variation of the content of Nb and Cr in MX during heat treatment in Sanicro25.

HTUPS is quite different from the previous austenitic steels in that it has a relatively
low nitrogen content (0.021 wt%) [15]. Only two kinds of precipitate MX and M_{23}C_{6} are observed in HTUPS through the simulation, as shown in Fig. 7(a). While MX remains stable as a major precipitate during the aging, the amount of M_{23}C_{6} decreases very slowly after it reaches the maximum in about 3 hours of aging. There is no formation of Z phase due to the low nitrogen content in this steel. Maziasz [16] reported the precipitation behavior of HTUPS during aging at 700 and 800 °C using TEM. He found that fine MX and coarse M_{23}C_{6} precipitate form during the aging. He also mentioned the presence of fine FeTiP precipitates, which was not included in the simulation due to the lack of its thermodynamic data. Interestingly, he observed that Laves phase (Fe_2Mo) precipitates form occasionally adjacent to the austenite grain boundary, which is not predicted in the simulation. Actually, Laves phase was not experimentally observed in the previous austenitic steels. The reason for the formation of Laves phase adjacent to the grain boundary is presumably because HTUPS has a relatively high content of Mo (2.5 wt%) and Mo tends to segregate to austenite grain boundaries so that the local concentration of Mo can be enough to form Laves phase [17]. The average size of MX precipitates is maintained at about 60 nm during the aging in the simulation and the average size of M_{23}C_{6} precipitates continues to increase and exceeds that of MX precipitates after about 1,000 hours of aging (Fig. 7(b)).

![Figure 6. Variation of the simulated (a) phase fraction and (b) average size of precipitates during heat treatment in in CFC8-PLUS.](image)

In order to check the long term stability of the precipitates with respect to temperature, we have simulated the long-term precipitate evolution between 600 and 800 °C with an interval of 50 °C in Sanicro25, which exhibits various precipitate population. Fig. 8(a) shows the variation of the precipitate fraction after 100,000 hours of aging with temperature. While the fraction of M_{23}C_{6} remains almost constant, that of Cu, MX and Laves phase decreases with increasing temperature. MX and Z phase show...
the opposite correlation. The fraction of Z phase increases as much as that of MX decreases and exceeds that of MX at 750 °C. The formation of Laves phase is predicted only at 600 and 650 °C. On the other hand, the formation of Laves phase is not predicted even below 650 °C in the other steels. The corresponding variation of the average precipitate size is plotted in Fig. 8(b). As expected, the size of all the precipitates increases with increasing temperature. Especially, the growth tendency of $M_{23}C_6$ is very large. On the other hand, the size of MX does not vary much with respect to temperature. The size of Z phase becomes similar to that of MX at 800 °C.

Figure 7. Variation of the simulated (a) phase fraction and (b) average size of precipitates during heat treatment in in HTUPS.

The formation of Z phase has been regarded as a main cause of a drastic loss of the creep strength in 9-12 % Cr ferritic heat-resistant steels, because Z phase dissolve fine MX precipitates that are major contributors to creep strength over long periods of time [11]. However, it has not been well known if the formation of Z phase is also detrimental to the creep strength in austenitic heat-resistant steels. In 9-12 % Cr ferritic heat-resistant steels, the amount of Z phase tends to increase remarkably at the expense of MX precipitates after 10,000-30,000 hours of aging and it grows very fast up to several hundred nanometers [11]. On the other hand, our simulation results show that Z phase grows relatively slowly and its average size reaches at most a few tens of nanometers after 100,000 hours of aging in austenitic heat-resistant steels, although the amount of Z phase starts to increase significantly between 1,000 and 10,000 hours of aging, which is quite early compared with 9-12 % Cr ferritic heat-resistant steels. Therefore, it seems that the formation of Z phase is not so detrimental to the creep strength in austenitic heat-resistant steels as 9-12 % Cr ferritic heat-resistant steels, although it is difficult to judge if the formation of Z phase is rather beneficial.
4. Conclusions

Simulation of the long-term precipitate evolution in five different austenitic heat-resistant steels, NF709, Super304H, Sanicro25, CFC8-PLUS and HTUPS has been performed using a numerical model based on the classical nucleation theory and the thermodynamic extremum principle. It is predicted that MX and M23C6 remain as major precipitates during aging in all the steels, which is consistent with experimental observations. The average size of MX does not vary much and is maintained below several tens of nanometers during aging. On the other hand, the size of M23C6 exceeds 100 nm at 100,000 hours of aging. The appearance of a small amount of M7C3 is predicted only at the initial stage of aging in Super304H and CFC8-PLUS. In Super304H and Sanicro25 containing 3 wt% Cu, Cu starts to precipitate during aging and the precipitation of Cu is saturated before 100 hours of aging. Although the size of Cu precipitates is very fine like MX precipitates, they tend to grow continually during aging. The formation of Z phase is predicted in all the steels except HTUPS, which has a relatively low nitrogen content. The fraction of Z phase starts to increase remarkably between 1,000 and 10,000 hours of aging at the expense of MX precipitates, which is similar to the case in 9-12 % Cr ferritic heat-resistant steels. However, it is predicted that Z phase grows relatively slowly and its average size reaches at most a few tens of nanometers after 100,000 hours of aging, compared with 9-12 % Cr ferritic heat-resistant steels. The formation of Laves phase is predicted during aging below 650 °C only in Sanicro25, although Laves phase is experimentally observed adjacent to the grain boundary in HTUPS.

Figure 8. Variation of the simulated (a) phase fraction and (b) average size of precipitates after 100,000 hours of aging with aging temperature in Sanicro25.
References