Anomalous Segregation Kinetics of Phosphorus and Carbon Governed by Carbide Reactions in 2.25Cr-1.5W Heat-resistant Steel

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In a 2.25Cr-1.5W heat-resistant steel containing V and Nb, the formation sequence of carbides are detailed. Such carbide reactions determine directly the anomalous segregation kinetics of phosphorus and carbon at the grain boundary/carbide interface. The anomalous segregation kinetics of phosphorus consists of two maximum segregation peaks and one minimum peak corresponding to the high segregation concentration of carbon. The roles of the carbide reactions on the anomalous segregation kinetics of the solutes are fully understood from the viewpoint of the dissolution of unstable carbides into the matrix for forming the stable carbides, the active segregation of the dissolved carbon into the newly formed carbide interface for the growth and the resultant repulsive segregation between carbon and phosphorus.

KEY WORDS: segregation kinetics; AES; carbides; interface energy; heat-resistant steel.

1. Introduction

The driving force for segregation of a solute to interfaces of an alloy system is composed of two components: the elastic strain energy arising from the atomic size difference between the solvent and the solute and the decrease in interface energy which results from the segregation of the solute.1,2) The equilibrium segregation concentration increases with decreasing temperature due to the increase in elastic strain energy and with increasing bulk content of the solute.2,3) In case of no precipitation reactions related to the segregant, the segregation kinetics is greatly influenced by the precipitation reaction.4,5)

Meanwhile, it was suggested in CrMoV heat-resistant steels containing several hundred ppm of phosphorus that the decrease in grain boundary segregation concentration of phosphorus after a maximum concentration during long-term aging in the temperature range of 480–530°C is related to intermetallic quasi-crystals containing phosphorus which are formed at grain boundaries and the surface of pre-formed M23C6 carbides,6–10) or that it is due to the formation at the grain boundaries of M6C carbides containing molybdenum, iron and phosphorus.11) Recently, it was also proposed that the anomalous segregation behavior of solutes (especially, P, C and Cr) were deeply related to the dissolution of pre-formed carbides into the matrix without any clear evidence.12)

Irrespective of the explanations mentioned above, the anomalous segregation behavior of the solutes observed in heat-resistant steels is not still clearly understood. In this study, the carbide reactions occurring in a heat-resistant steel are detailed and they are correlated to the anomalous segregation behaviors of the solutes.

2. Experimental Procedure

A 2.25Cr-1.5W steel ingot was prepared using a vacuum induction melting. The chemical composition of the steel is shown in Table 1. The ingot was homogenized at 1 150°C for 7.2 ks and subsequently hot-rolled to 12 mm thick plates. Un-notched and cylindrical specimens for stress rupture tests, which have a gage length of 15 mm and a gauge diameter of 6 mm, were machined from the plates in the hot-rolling direction. In order to investigate the carbide reactions and the segregation behavior of solutes (especially, C and P) from the initial stage of the rupture test, the specimens were austenitized at 1 050°C for 3.6 ks and water-quenched. A full martensitic structure was obtained after water-quenching. The stress rupture test was performed at 700°C in the tensile stress range of 75 to 300 MPa, using conventional creep testers (ATS Ltd., USA). Table 2 shows the rupture time for each case of tensile stresses at 700°C. The rupture test specimens to which an N-type thermocouple was attached were heated from room temperature to the test temperature at a heating rate of 1 200°C/h. The rupture test was carried out without

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soaking at the test temperature. Kinds of carbides at each stage and their composition and morphology were investigated, using a carbon extraction replica method and an energy-dispersive spectroscope (EDS) attached to a field emission transmission electron microscope (JEM-2100F, Japan Electronic Optics Ltd., Tokyo, Japan). The interfacial segregation of solutes was investigated, using an Auger electron spectroscope (AES, PHI 700, Japan). The AES specimens machined from the ruptured specimens in the tensile stress direction were chilled in the AES with liquid nitrogen for 3.6 ks and in-situ fractured in an ultra-high vacuum of $9 \times 10^{-8}$ Pa or better. Typical parameters were the primary electron beam energy of 3 keV and an electron beam size of about 200 nm. In investigating the segregation behaviors of solutes, the AES results of the present study have been obtained from the grain boundary surface side among the prior austenite grain boundary/carbide interface of intergranular-fractured AES specimens in which the carbides are absent. The interfaces of about 10 points were chosen for the AES analysis of each specimen. The AES peaks used were Fe$_{703}$, P$_{120}$ and C$_{271}$, and the peak-height-ratios (I/I$_{Fe}$) obtained from the differential AES spectra were averaged.

3. Results and Discussion

3.1. Anomalous Segregation Kinetics of Solutes Occurring during Rupture Test and Various Kinds of Carbide Reactions

As shown in Fig. 1, the intergranular fracture surface is generally composed of carbide-free grain boundaries and grain boundary/carbide interfaces that carbides resided. The elevated temperature intergranular cracking occurs initially at the grain boundary/carbide interfaces showing the segregation concentration of phosphorus higher than that of the carbide-free grain boundaries. The decohesion at the carbide-free grain boundaries follows finally the initial cracking. Figure 2 shows the anomalous segregation kinetics of phosphorus and carbon at grain boundary/carbide interfaces. This was obtained through the correction of the experimental errors made in a previous research. That is, the previous research showed that the segregation concentration of phosphorus increased with further increasing time after the minimum peak and it was saturated to a high concentration. Unlike the equilibrium segregation kinetics, the profile of phosphorus segregation concentration in Fig. 2 shows two maximum peaks and one minimum peak in a time to failure versus segregation concentration plot. Two maximum peaks of phosphorus correspond to the very low segregation concentration of carbon. In addition, the minimum peak of phosphorus corresponds to the strong carbon peak, which is named as the repulsive segregation between carbon and phosphorus. In order to investigate the correlation between the anomalous segregation kinetics of the solutes and the carbide reactions, the equilibrium phase fractions in the present steel were calculated, and carbides existing in specimens ruptured at stages of a, b, c, d and e of Fig. 2 were analyzed.

Figure 3 shows the equilibrium phase fractions which were calculated by Thermo-Calc software using the TCFE6 database. According to the calculation and the related Table 3, carbides of M$_6$C (M=W, Fe), M$_2$C$_6$ (M=Cr, W, Fe), M$_7$C$_3$ (M=Cr, Fe) and MC (M=V, Nb) can be formed during heating to 700°C for the rupture test. Based on the calculation, the additional formation of M$_3$P (M=Fe, Cr) phosphides is

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>V</th>
<th>Nb</th>
<th>Ti</th>
<th>W</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.13</td>
<td>0.35</td>
<td>0.5</td>
<td>0.060</td>
<td>0.002</td>
<td>2.28</td>
<td>0.24</td>
<td>0.047</td>
<td>0.006</td>
<td>1.48</td>
<td>0.009 Balance</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. The rupture time of specimens for each of tensile stresses at 700°C.12)

<table>
<thead>
<tr>
<th>Tensile stress (MPa)</th>
<th>300</th>
<th>275</th>
<th>250</th>
<th>225</th>
<th>200</th>
<th>150</th>
<th>125</th>
<th>100</th>
<th>75</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time to rupture (s)</td>
<td>300</td>
<td>600</td>
<td>1320</td>
<td>2160</td>
<td>3780</td>
<td>13800</td>
<td>22920</td>
<td>51960</td>
<td>179160</td>
</tr>
</tbody>
</table>

Fig. 1. Fracture surface of AES specimen which is composed of carbide-free grain boundaries (○) and grain boundary/carbide interfaces (◇) that the carbides resided. The specimen corresponds to the condition of 200 MPa in Table 2.

Fig. 2. The anomalous segregation kinetics of phosphorus and carbon at grain boundary/carbide interfaces that carbides resided.
also expected, but the phases were not observed in the present study. **Figure 4** shows bright field images obtained from the phases at the stage \( a \) of Fig. 2, the electron diffraction patterns and the EDS analysis results. Phases are mainly composed of Cr-rich \( \text{M}_7\text{C}_3 \) carbides with a trace of unexpected Fe-rich \( \text{M}_3\text{C} \) carbides, both of which are the non-equilibrium phases at 700°C. Both of the \( \text{M}_3\text{C} \) and \( \text{M}_7\text{C}_3 \) carbides show an orthorhombic crystal structure, based on the electron diffraction patterns of Fig. 4. It has been suggested that various types of carbides such as \( -\text{carbide}, \text{M}_7\text{C}_3, \text{M}_6\text{C}, \text{M}_2\text{C}_3, \text{M}_2\text{C}_6 \) and \( \text{M}_3\text{C} \) are in turn formed during tempering in Cr-added steels\(^{16-23} \) and that the carbides are formed through either the independent nucleation in the matrix or the \textit{in-situ} transformation from the pre-existing carbides. Experimentally, it takes about 3.6 ks in heating the creep specimen to the test temperature of 700°C. Because the \( \text{M}_7\text{C}_3 \) carbide nucleated from a \( \text{M}_3\text{C} \) carbide was not observed at the stage \( a \), the formation of the \( \text{M}_7\text{C}_3 \) carbides in the present study is attributed to not the \textit{in-situ} transformation from the \( \text{M}_3\text{C} \) carbides. Therefore, the \( \text{M}_7\text{C}_3 \) carbides are directly formed from the supersaturated matrix of solutes in the temperature range of 450–650°C during heating to 700°C or through the dissolution of the pre-formed \( \text{M}_3\text{C} \) carbides into matrix and the subsequent nucleation reaction.

**Table 3.** The mass fraction of alloying elements in equilibrium precipitates calculated by Thermo-Calc software using the TCFE6 database.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>Cr</th>
<th>Nb</th>
<th>Ti</th>
<th>V</th>
<th>W</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{M}_6\text{C} )</td>
<td>0.240</td>
<td>0.017</td>
<td>–</td>
<td>–</td>
<td>0.001</td>
<td>0.001</td>
<td>–</td>
<td>0.016</td>
<td>0.725</td>
<td>–</td>
</tr>
<tr>
<td>( \text{M}_2\text{C}_6 )</td>
<td>0.140</td>
<td>0.048</td>
<td>0.009</td>
<td>–</td>
<td>0.567</td>
<td>–</td>
<td>–</td>
<td>0.035</td>
<td>0.201</td>
<td>–</td>
</tr>
<tr>
<td>( \text{M}_7\text{C}_3 )</td>
<td>0.173</td>
<td>0.088</td>
<td>0.002</td>
<td>–</td>
<td>0.680</td>
<td>–</td>
<td>–</td>
<td>0.044</td>
<td>0.013</td>
<td>–</td>
</tr>
<tr>
<td>( \text{V} \text{C} )</td>
<td>0.047</td>
<td>0.153</td>
<td>–</td>
<td>–</td>
<td>0.009</td>
<td>0.005</td>
<td>–</td>
<td>0.720</td>
<td>0.060</td>
<td>0.006</td>
</tr>
<tr>
<td>( \text{Nb} \text{C} )</td>
<td>–</td>
<td>0.120</td>
<td>–</td>
<td>–</td>
<td>0.057</td>
<td>0.777</td>
<td>0.0378</td>
<td>0.008</td>
<td>–</td>
<td>0.0002</td>
</tr>
<tr>
<td>( \text{M}_3\text{P} )</td>
<td>0.467</td>
<td>–</td>
<td>–</td>
<td>0.160</td>
<td>0.373</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

**Fig. 3.** The equilibrium phase fractions which were calculated by Thermo-Calc software using the TCFE6 database.

**Fig. 4.** Bright field images obtained from precipitates of the stage \( a \) of Fig. 1, the electron diffraction patterns and the EDS analysis results.
Figure 5 shows the bright field image obtained from a precipitate of the stage b and the electron diffraction pattern. Without any trace of the M₃C carbides, all the carbides are composed of the Cr-rich M₇C₃ non-equilibrium carbides formed during heating to 700°C. Figure 6 shows bright field images obtained from precipitates of the stage c and the electron diffraction patterns. The Cr-rich equilibrium M₂₃C₆ carbides begin to be observed, while the Cr-rich M₇C₃ carbides still remain at the stage c. Because the M₂₃C₆ carbides formed on the M₇C₃ carbide surface are not observed, the transformation from M₇C₃ to M₂₃C₆ also results from the dissolution of the M₇C₃ carbides into the matrix and the subsequent nucleation of the new equilibrium M₂₃C₆ carbides. Figure 7 shows bright field images obtained from precipitates of the stage d, the electron diffraction patterns and the EDS analysis results. Additional equilibrium M₆C carbides, which contain tungsten more than the M₂₃C₆ carbides, are observed together with the pre-existing M₂₃C₆ and M₇C₃ carbides. The EDS result for the M₆C carbides shows a strong Cr peak, which is not consistent with the calculation result of Table 3. Unlike the calculation, the Cr peak from the M₆C carbides was also noticeable even at the stage d, although it became weaker than the W peak. Figure 8 shows bright field images obtained from precipitates of the stage e, the electron diffraction patterns and the EDS analysis results. Equilibrium V- or Nb-rich MC carbides are observed in the matrix as well as on the M₂₃C₆ carbide surfaces, while the non-equilibrium M₇C₃ carbides disappear completely. Based on Fig. 8(b), the weak Cr peak obtained from the Nb-rich MC carbide surface of Fig. 8(a) is due to the interference effect of the M₂₃C₆ carbides just near the MC carbides. The mass fraction of alloying elements in the carbides of Table 3 is roughly consistent with the experimental results of Figs. 4, 7 and 8.

3.2. Formation Sequence of Carbides

Finally, the formation sequence of carbides in the present steel is 1) the M₃C carbides appearing in the low temperature range at the expense of the supersaturated carbon during heating to the rupture test temperature, 2) the M₇C₃ carbides...
in the relatively high temperature range, 3) the dissolution of the M₇C₃ carbides into the matrix and the additional formation of the M₃C₃ carbides during the time period of the stages a and b of 700°C, 4) the dissolution of the M₃C₃ carbides into the matrix and the formation of the M₇C₃ and M₆C carbides during the time period between two maximum peaks of phosphorus, and 5) the final formation of the V- or Nb-rich MC carbides in the matrix as well as on the pre-formed M₂₃C₆ carbide surface.

Because the composition of the M₂₃C₆ carbides is, as shown in Table 3 and Fig. 7, more similar to that of the M₇C₃ carbides than the M₆C carbides of a high tungsten content, the formation of the M₂₃C₆ carbides are easier than the formation of the M₆C carbides during the dissolution of the M₇C₃ carbides into the matrix. The V- and the Nb-rich MC carbides are finally formed due to the similarly low diffusivities of vanadium and niobium. Based on Fig. 8, the V- and the Nb-rich MC carbides are mainly formed through some dissolution of the M₂₃C₆ carbides which increases slightly the dissolved carbon content in the matrix.

3.3. Correlation between Carbide Reactions, Interface Energy and Anomalous Segregation Kinetics of Solutes

In order to form the M₂₃C₆ and M₆C equilibrium carbides, the non-equilibrium M₇C₃ carbides after the disappearance of the M₃C carbides should be massively dissolved into the matrix. This causes the abrupt increase in the dissolved carbon content of the matrix. As a result, while the equilibrium M₂₃C₆ and M₆C carbides are formed at the grain boundaries and in the matrix, the dissolved carbon segregates actively into the fresh carbide interface in order to minimize the total interface energy. Considering the minimization in total interface area, it is reasonable that the formation of the MC carbides on the pre-formed carbide surface is, as shown in Fig. 8(a), energetically more favorable than that of the carbides in the matrix of Fig. 8(b). As a result, the abrupt decrease in segregation concentration of phosphorus after the second maximum peak can be attributed to two factors: the partitioning effect in Fig. 9 of the phosphorus pre-segregated on the surface of the M₂₃C₆ carbides preferentially formed at the prior austenite grain boundaries onto the interface of MC carbides newly formed on the carbides and the additional slight increase in segregation concentration of carbon. The correlation between the formation sequence of the carbides in the present steel and its effect on the anomalous segregation kinetics of the solutes is finally summarized in Fig. 10.
4. Summary

The carbides in a 2.25Cr-1.5W heat-resistant steel containing V and Nb are $\text{M}_2\text{C}_3$ and $\text{M}_7\text{C}_3$ formed during heating to 700°C. The $\text{M}_2\text{C}_6$, $\text{M}_6\text{C}$ and MC carbides are in turn formed during rupture test at 700°C. Such carbide reactions result in the anomalous segregation kinetics of carbon and phosphorus at the grain boundary/carbide interface. The anomalous segregation kinetics is composed of two maximum segregation peaks of phosphorus and one minimum peak which corresponds to the maximum segregation peak of carbon. The maximum segregation peak of carbon is due to the active segregation of the dissolved carbon into the interface for forming and growing the equilibrium $\text{M}_2\text{C}_6$ and $\text{M}_6\text{C}$ carbides, which arises from the massive dissolution of the non-equilibrium $\text{M}_7\text{C}_3$ carbides into the matrix. The decrease in phosphorus segregation concentration after the second maximum peak is mainly attributed to the partitioning effect of the phosphorus pre-segregated on the surface of the $\text{M}_2\text{C}_6$ carbides onto the interface of MC carbides newly formed on the carbides and the additional segregation of the dissolved carbon to the interface.

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REFERENCES