Evaluation of Sensitization and Self-Healing in Austenitic Stainless Steels Based on Simulations of Cr-Depleted Zones

Tatsuya TOKUNAGA,¹⁾ Hiroshi OHTANI²⁾ and John ÅGREN³⁾

1) Formerly Department of Applied Science for Integrated System Engineering, Kyushu Institute of Technology. Now at Department of Mechanical Engineering, Kagoshima University, Kagoshima 890-0065, Japan.

2) Department of Materials Science and Engineering, Kyushu Institute of Technology, Kitakyushu 804-8550, Japan.

3) Department of Materials Science and Engineering, The Royal Institute of Technology, Stockholm, S-100 44 Sweden.

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A simulation of the grain boundary precipitation of the Cr-rich carbide, $M_{23}C_6$, in austenitic stainless steels has been carried out using the DICTRA software package employing kinetic and thermodynamic databases. Our calculations reproduced the evolution of the Cr-depleted zone close to $M_{23}C_6$ carbide and the disappearance of the zone after a long annealing time. In addition, the calculated time-temperature-sensitization diagrams were in line with the experimental results of typical corrosion trends with annealing time. According to our results, despite the simple treatment used, a reasonable approximation for the simulations was to set the initial width of the austenite region from which the carbon was drawn as a sixth of the grain size. We also confirmed that the onset of sensitization for a steel with 0.1 mass%C shifted to shorter times and to higher temperatures compared with a steel with 0.06 mass%C.

KEY WORDS: sensitization; self-healing; simulation; Cr-depleted zone; $M_{23}C_6$; austenitic stainless steels.

1. Introduction

Austenitic stainless steels lose their corrosion resistance either if they are cooled slowly in the temperature range 550–800°C or if they are reheated to this temperature range after rapid cooling. This phenomenon, called sensitization, is ascribed to the evolution of a local Cr-depleted zone caused by the precipitation of a Cr-rich carbide, $M_{23}C_6$, at the austenite grain boundaries. The corrosion resistance can be restored after prolonged annealing in the temperature range that initially caused sensitization. This self-healing is a consequence of the removal of the Cr-depleted zone, resulting from the diffusion of Cr into the Cr-depleted zone from the matrix located further away from the grain boundary. The first detailed analysis of the above phenomena was carried out by Stawström and Hillert¹⁾; and since then, various attempts to model the intergranular precipitation have been made.^{2–9)} Among these, only Arai and Takeda,⁴⁾ Ohtani and Ågren⁶⁾ and Sourmail *et al.*⁹⁾ have considered the effect of nickel on the Fe–Cr–C ternary system, which influences the precipitation behavior; other authors have not taken into account the effect of a fourth element on the ternary system.

Figure 1 shows a schematic Fe–Cr–C ternary phase diagram at the temperature at which sensitization occurs. At the beginning of the precipitation of the carbide, only carbon diffusion occurs, and this removes all the carbon potential gradients near the interface, because carbon can diffuse very much faster than chromium and iron can. In this case, the austenite/carbide interface conditions can be characterized

Fig. 1. A schematic Fe–Cr–C ternary phase diagram showing the variation of the equilibrium during $M_{23}C_6$ carbide precipitation.

by the isoactivity line for C that passes through the super-saturated austenite, *i.e.*, the original composition of the steel. Under this local equilibrium condition, the austenite composition of the operative tie-line (austenite + $M_{23}C_6$) is represented by point x^γ in Fig. 1, which is given by the point of intersection of the carbon isoactivity line in austenite and the solubility line for $M_{23}C_6$ in austenite. This extremely low Cr content in austenite at the interface may cause sensitization, resulting in intergranular corrosion. As the precipitation of $M_{23}C_6$ carbide progresses, the activity of C decreases, and the Cr content in austenite at the interface changes gradually, indicated by the arrow in Fig. 1. During continuous precipitation, self-healing occurs when a critical

Cr content is reached (approx. 12 mass%Cr); finally, the situation is represented by the global equilibrium tie-line that passes through the composition of the steel. Although assumptions were made in a previous work,¹⁾ the calculations reproduced the sensitization and self-healing phenomena well, and the predicted annealing time for self-healing was in reasonable agreement with the experimental data.

In this study, based on preliminary work by two of the authors,⁶⁾ simulations of the grain boundary precipitation of $M_{23}C_6$ carbide in austenitic stainless steels were carried out using the DICTRA software package,¹⁰⁾ in which most of the simplifying assumptions made in a previous study¹⁾ were removed, and the calculated results were compared with the available experimental data.

2. Calculation Procedures

In this study, the simulations were restricted to the Fe–Cr–Ni–C quaternary system because the growth of $M_{23}C_6$ is controlled mainly by the diffusion of Cr, Fe, and Ni. The two compositions shown in **Table 1** were chosen based on the results from previous experimental works.^{1,11)} The simulations were performed using the DICTRA code,¹⁰⁾ which is a software package used for the simulation of diffusion-controlled transformations in multicomponent alloy systems having a simple geometry. The simulations were based on a numerical solution of multicomponent diffusion equations using kinetic and thermodynamic databases, assuming a local equilibrium existed at the moving phase interface. Details of DICTRA simulations have been described elsewhere.¹²⁾

In the simulations, the thermodynamic and kinetic data used were taken from the Scientific Group Thermodata Europe (SGTE) solution database¹³⁾ and the MOB2 database,¹⁴⁾ respectively. The thermodynamic calculations were carried out using the Thermo-Calc software package.¹⁵⁾ We assumed that $M_{23}C_6$ carbide grew in the planar austenite/carbide interface, reducing the problem to one dimension, with diffusion occurring perpendicular to the grain boundary. In setting up the DICTRA simulations, $M_{23}C_6$ carbide with a width of $0.1 \mu\text{m}$ and an austenite matrix were placed side by side to form a planar austenite/carbide interface, as shown in **Fig. 2**. The significance of the initial width of the austenite (d_a) used in the simulations has been discussed

Table 1. Chemical composition of steels used (mass%).

Type	C	Cr	Ni
18–8 steel with 0.06C	0.06	18.0	8.0
18–8 steel with 0.1%C	0.10	18.0	7.7

Fig. 2. Setup used for the numerical simulations of intergranular $M_{23}C_6$ carbide precipitation at the austenite/carbide interface using the DICTRA code.

previously.⁹⁾ To consider the amount of carbon removed from the austenite matrix by the growth of $M_{23}C_6$ carbide, it is necessary to define a volume from which the carbon is drawn. In this study, a simple cubic model was used to represent a grain, where the six faces drew carbon from the same volume, and thus, the initial width of the austenite matrix was set to be a sixth of the grain size, following a previous treatment,⁹⁾ i.e., $d_a = 8.3 \mu\text{m}$ for 18–8 steel with 0.06%C and $d_a = 7.0 \mu\text{m}$ for 18–8 steel with 0.1%C. The effect of d_a on the annealing time for sensitization and self-healing for 18–8 steel with 0.06%C was also evaluated. On the other hand, since the diffusion in $M_{23}C_6$ carbide was not considered in this study, the initial width of carbide (d_c) was not of any importance to the final result, and thus, it was arbitrarily set to $d_c = 0.1 \mu\text{m}$. The initial composition of the austenite matrix was set to be that of the original steel composition. The initial composition of $M_{23}C_6$ carbide was evaluated using the Thermo-Cal software package, based on the operative tie-line (austenite + $M_{23}C_6$) representing the local equilibrium condition at the interface at the beginning of precipitation, which is connected with the isoactivity line for C that passes through the original steel composition, as discussed in the Introduction.

3. Results and Discussion

Figure 3 shows the calculated Cr concentration profiles after annealing for 1 s, 10 h, 100 h, and 1 000 h at 700°C for 18–8 steel with 0.06%C. According to the data in **Fig. 3**, the degree of precipitation of $M_{23}C_6$ carbide increased with increasing annealing time. In addition, the Cr content in $M_{23}C_6$ and in austenite at the austenite/carbide interface increased with annealing time, and this reflected the variation of the operative tie-line (austenite + $M_{23}C_6$) at the interface. The operative tie-line must shift toward the global equilibrium during the later precipitation stages. The calculated C content in austenite in the grain center at 816°C for 18–8 steel with 0.1%C is shown in **Fig. 4**, together with the experimental data.¹⁶⁾ The agreement between the calculated and the experimental values is satisfactory.

Figure 5 shows the calculated time-temperature-sensitization (TTS) diagram for 18–8 steel with 0.06%C. The time required for the loss of corrosion resistance was arbitrary, and an attempt was first made to adopt two criteria for the onset of sensitization: sensitization began (1) when a depleted

Fig. 3. (a) The calculated Cr concentration profiles after annealing at 1 s, 10 h, 100 h, and 1 000 h at 700°C for 18–8 steel with 0.06%C. (b) An enlarged view of (a) near the austenite/carbide interface.

zone with a Cr content < 12 mass% exceeded a thickness of 20 nm (after Stawström and Hillert¹⁾), or (2) when the average concentration of Cr over the first 25 nm of the austenite matrix in contact with $M_{23}C_6$ carbide was < 12 mass%Cr (after Sourmail *et al.*⁹⁾). Regarding the annealing time for restoring corrosion resistance (*i.e.*, self-healing), two criteria were applied, which were the opposite to those for sensitization. The experimental data from Wiester *et al.*¹¹⁾ are also shown in Fig. 5 for comparison, where the open circle, circle divided by a vertical line, half-filled circle, and solid circle denote no corrosion, weak corrosion, medium corrosion, and strong corrosion character in the corrosion test, respectively. The calculated results reproduced the experimental results of typical corrosion character trends with annealing time; however, the agreement between the calculated and the experimental results are not satisfactory. According to a previous study,¹⁾ a thickness of 20 nm for a Cr-depleted zone was arbitrary chosen in such a way that the calculated values agreed with the experimental data¹¹⁾ for sensitization. On the other hand, although the experimental data were closer to the onset of sensitization when evaluated based on an average Cr concentration criterion (broken line) than that evaluated based on a 20 nm-thick Cr-depleted zone criterion (dotted line), it seems to be difficult to use an average Cr concentration criterion because it was found that the averaged value decreased by more than 1 mass% for annealing time below 10 h in which the nose of TTS curve is located, as the distance over which the average was calculated decreased from 25 nm to 15 nm.⁹⁾ Then, a 10 nm-thick

Cr-depleted zone criterion was applied in the present study, and the calculated result is shown in Fig. 5 by the solid line. Although the present criterion is better suited than the other two criteria in the vicinity of the nose, there was still a relatively large discrepancy in the onset of sensitization at lower temperatures, and the calculated annealing time for sensitization was longer than the experimentally observed results. This may be because grain boundary diffusion, which becomes dominant at lower temperatures, was not taken into account in our simulations.

Figure 6 shows the effect of the initial width of the austenite matrix, d_a , on the calculated annealing time at 700°C for sensitization and self-healing, as evaluated using a 10 nm-thick Cr-depleted zone criterion for 18–8 steel with 0.06%C. From this result, the annealing time for both sensitization and self-healing was strongly dependent on d_a . The annealing time for sensitization decreased from approx. 10^0 h for $d_a = 2 \mu\text{m}$ to approx. 10^{-4} h for $d_a = 25 \mu\text{m}$, whereas the self-healing time increased from approx. 10^2 h for $d_a = 2 \mu\text{m}$ to approx. 10^4 h for $d_a = 25 \mu\text{m}$. According to the TTS diagram for 18–8 steel with 0.06%C shown in Fig. 5, the calculated annealing time for sensitization and self-healing at 700°C was approx. 10^0 h and 10^3 h, respectively, and these values agree well with the experimental results. Despite the simple treatment used, a reasonable approximation is to regard the initial width of the austenite matrix as being a sixth of the grain size.

Figure 7 shows the calculated TTS diagram for 18–8

Fig. 4. The calculated carbon content in austenite in the grain center at 816°C for 18–8 steel with 0.1%C, together with the experimental data.¹⁶⁾

Fig. 5. The calculated time-temperature-sensitization diagram for 18–8 steel with 0.06%C, together with the experimental data.¹¹⁾

Fig. 6. Effect of the initial width of the austenite region, d_a , on the calculated annealing time at 700°C for sensitization and self-healing for 18–8 steel with 0.06%C, evaluated based on a 10 nm-thick Cr-depleted zone criterion.

Fig. 7. The calculated time-temperature-sensitization diagram for 18–8 steel with 0.1%C, together with the experimental data.¹⁾

steel with 0.1%C, together with the experimental data.¹⁾ As in the case of the 18–8 steel with 0.06%C, the calculated results based on a 10 nm-thick Cr-depleted zone criterion (solid line) are in line with the experimental values near the nose of the TTS curve. Furthermore, it can be clearly seen that the onset of sensitization for 18–8 steel with 0.1%C shifts to shorter times and to higher temperatures compared with the onset for 18–8 steel with 0.06%C, and the calculated results is consistent with the experimental observation.¹⁷⁾

4. Conclusions

Simulations of the intergranular precipitation of $M_{23}C_6$ carbide were carried out using the DICTRA software package employing kinetic and thermodynamic databases. The calculated TTS diagrams for two types of 18–8 stainless steel with different C content were compared with the reported experimental data obtained from corrosion tests. The results obtained are summarized as follows:

(1) The simulations reproduced the sensitization and self-healing behavior well, and the calculated time-temperature-sensitization (TTS) diagrams were in line with the experimental results of typical corrosion character trends with annealing time.

(2) The annealing time for both sensitization and self-healing was influenced significantly by the initial width of the austenite matrix (d_a) from which the carbon was drawn in our simulations. By considering the fact that the agreement between the calculated and the experimental results, a reasonable approximation is to use a sixth of the austenite grain size for d_a .

(3) It was confirmed that the increase in C content from 0.06 mass% to 0.1 mass% shifted the onset of sensitization to shorter times and higher temperatures.

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