Isothermal Martensitic Transformation in Sensitized SUS304 Austenitic Stainless Steel at Cryogenic Temperature

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We have investigated martensitic transformation behavior in a sensitized SUS304 austenitic stainless steel to know the stability of the austenitic phase at cryogenic temperatures. We found that the sensitized specimen exhibits an isothermal martensitic transformation when the specimen is held in the temperature range between 60 and 260 K. The time-temperature-transformation (TTT) diagram corresponding to the formation of 0.5 vol% of \( f' \)-martensite shows a double-C curve with two noses located at about 100 and 200 K. An in-situ optical microscope observation has revealed that the double-C curve is due to two different transformation sequences. That is, the upper part of the C-curve is attributed to the direct \( f(\text{fcc}) \rightarrow f'(\text{bcc}) \) martensitic transformation and the lower part of the C-curve is due to the successive \( f(\text{fcc}) \rightarrow f' \rightarrow f'' \) (hcp) \( \rightarrow f' \) (bcc) martensitic transformation. The direct \( f \rightarrow f' \) transformation occurs in the vicinity of grain boundaries, while the successive \( f \rightarrow f' \) transformation occurs near the center of each grain. The reason for appearing two types of isothermal transformation sequence in the sensitized SUS304 stainless steel will be due to the difference in concentration by sensitization heat-treatment.

(Received October 20, 2008; Accepted December 15, 2008; Published February 4, 2009)

Keywords: austenitic stainless steel, isothermal martensitic transformation

1. Introduction

Austenitic stainless steels, especially SUS304 stainless steel, are extensively used in wide range of industries owing to their good corrosion resistance, excellent mechanical properties, superior weldability and nonmagnetic characteristics.\(^{1-4}\) According to previous studies, the austenitic stainless steels are unstable upon some external fields, such as high stress and cryogenic temperature.\(^{5-7}\) Therefore, it is very important to clarify the stability of the austenitic phase under such environments because many of the excellent properties could be deteriorated if the austenitic phase transforms into martensite phases.\(^{8}\) For example, the non-magnetic property of the austenitic phase is lost when \( f' \)-martensite is formed.\(^{9,10}\)

Generally, welding process is essential to use the austenitic stainless steel in various industries, and it is widely known that welded austenitic stainless steels can develop a sensitized zone which consists of carbide precipitation (\( \text{M}_{23}\text{C}_6 \)) at grain boundaries and chromium depletion in the vicinity of grain boundaries.\(^{11-14}\) Recently, we found that the sensitized SUS304 stainless steel exhibits an isothermal martensitic transformation at cryogenic temperatures.\(^{15,16}\) However, its time-temperature-transformation (TTT) diagram, which is one of the most important information for isothermal transformations, has not been constructed yet.

In the present study, therefore, we have constructed the TTT diagram of the isothermal martensitic transformation in a sensitized SUS304 stainless steel.

2. Experimental Procedure

The chemical composition of a SUS304 austenitic stainless steel used in the present study is 0.06C-0.67Si-1.01Mn-0.029P-0.009S-8.5Ni-18.10Cr-Bal.Fe (mass%). The steel was cold-rolled into a sheet. From the sheet, specimens of \( 3 \times 3 \times 1 \) mm in size were cut out, and were solution-treated at 1323 K for 0.5 h in vacuum followed by quenching into iced water. Most of the specimens were sensitized by heat-treatment at 973 K for 100 h. Then the oxidized surface layer of all the specimens was eliminated by electropolishing, where an electrolyte composed of 85% \( \text{C}_2\text{H}_5\text{OH} \) and 15% \( \text{HClO}_4 \) in volume was used.

Phase stability in the cryogenic temperature range was examined by the magnetic susceptibility measurement with a constant cooling and heating rate of 1 K/min in the temperature range between 4.2 and 300 K. Isothermal holding experiment was carried out under no magnetic field in the temperature range between 60 and 260 K for various holding times. The volume fraction of the \( f' \)-martensite, \( f'_{\text{v}} \), formed by the isothermal holding was evaluated by a magnetization measurement at 300 K (= \( T_K \)). Details of this method were described elsewhere.\(^{17}\)

Change in morphology during the isothermal holding experiment was observed by in-situ optical microscopy (OM). Morphology of the martensite phase formed by isothermal holding experiment was investigated by using a transmission electron microscope (TEM). Specimens for TEM observation were prepared by electropolishing using an electrolyte consisting of 85% \( \text{CH}_3\text{COOH} \) and 15% \( \text{HClO}_4 \) in volume. TEM observation was made with an accelerating voltage of 200 kV.

3. Results and Discussion

3.1 Construction of TTT diagram

In order to investigate the martensitic transformation and magnetic properties of the present SUS304 stainless steel, we have carried out magnetic susceptibility measurement in the temperature range between 4.2 and 300 K by applying a low magnetic filed of 79.6 kA/m. Figure 1 shows temperature dependence of magnetic susceptibility, \( \chi \), of the solution-treated and the sensitized SUS304 stainless steel. The \( \chi-T \) curve of the solution-treated SUS304 shows a peak at about...
40 K due to a paramagnetic to anti-ferromagnetic transition of the \( \gamma \)-phase and there is no hysteresis between heating and cooling processes, being in agreement with a previous study.\(^{15,16}\) On the other hand, the \( \chi-T \) curve of the sensitized SUS304 starts to increase at about 260 K in the cooling process as indicated with “A”. Such increase of \( \chi \) means that the ferromagnetic \( \alpha' \)-martensite was formed during the cooling process. In the heating process, the \( \chi-T \) curve starts to increase at about 60 K, meaning that the \( \alpha' \)-martensite was also formed in the heating process. This result implies that the martensitic transformation of the sensitized SUS304 proceeds isothermally in the temperature range between 60 and 260 K. Furthermore, we notice that the \( \chi-T \) curve increase in two step in the cooling process as indicated by “A” and “B”, respectively. This result suggests that there are two kinds of isothermal martensitic transformations in the sensitized SUS304 stainless steel.

In order to construct the \( T-T-T \) diagram, we have made isothermal holding experiment in the absent of magnetic field at several temperatures in the temperature range between 60 and 260 K, followed by magnetization measurement at room temperature. Figure 2 shows typical magnetization curves (\( M-H \) curves) after isothermal holding experiments of at 200 K. We know from Fig. 2 that the magnetization increases with increasing isothermal holding time, meaning that the amount of the ferromagnetic \( \alpha' \)-martensite increases by isothermal holding at 200 K. We can evaluate the volume fraction of the \( \alpha' \)-martensite by using the value of the spontaneous magnetization, where the value of the spontaneous magnetization is estimated as indicated with an arrow in Fig. 2(g). We notice in Fig. 2(a) that the spontaneous magnetization exists even after isothermal holding for 0 s. This result is probably attributed to the spontaneous magnetization of the carbide \( M_23C_6 \) formed by the sensitization treatment.\(^{18}\) From the values of spontaneous magnetization, the volume fraction of \( \alpha' \)-martensite, \( f_{\alpha'} \), can be obtained quantitatively. That is, \( f_{\alpha'} = (M_0(T_R) - M^\text{Carbide}(T_R))/M^\text{Carbide}(T_R) \), where \( M_0(T_R) \) is the spontaneous magnetization at room temperature of the specimen after isothermal holding, \( M_0^\text{Carbide}(T_R) \) is that of the as-sensitized specimen, and \( M^\text{Carbide}(T_R) \) is that of the \( \alpha' \)-martensite. Here, the value of \( M^\text{Carbide}(T_R) \) can be approximated as the value at 0 K, \( M_0^\text{Carbide}(0 \text{ K}) \), because the Curie temperature is far above room temperature. Also, \( M_0^\text{Carbide}(0 \text{ K}) \) is estimated to be 1.79 \( \mu_B \) / atom considering the Slater-Pauling curve and their valence electron concentration.\(^{19,20}\) The volume fraction thus obtained at 200 K is plotted as a function of holding time in Fig. 3, together with the results obtained at 140 and 100 K. We know from the result that the \( f_{\alpha'} \) obviously depends on isothermal holding temperature as well as isothermal holding time. From the curve in Fig. 3, we have constructed the \( T-T-T \) diagram of 0.5 vol% of \( \alpha' \)-martensite. The time required for the formation of 0.5 vol% of \( \alpha' \)-martensite is evaluated to be 860, 2320 and 770 s for isothermal holding temperature at 200, 140 and 100 K, respectively. The same experiments have been made in the temperature range between 260 and

**Fig. 1** Magnetic susceptibility curves of solution-treated and sensitized SUS304 stainless steel. Measurements were made in the cooling process and then in the heating process.

**Fig. 2** Magnetization curves obtained at 300 K for the sensitized SUS304 stainless steel after isothermal holding at 200 K for 0 s (a), 300 s (b), 900 s (c), 1800 s (d), 3600 s (e), 5400 s (f) and 7200 s (g).

**Fig. 3** Volume fraction of \( \alpha' \)-martensite formed by isothermal holding at 200, 140 and 100 K in the sensitized SUS304 stainless steel. The curves are guide for eyes.
60 K, and we have obtained the time required for the formation of 0.5 vol% of \(\alpha'\)-martensite at these temperatures. Using these times obtained from the evaluation, we have constructed the TTT diagram of \(\alpha'\)-martensite as shown in Fig. 4. It should be noted that the TTT diagram shows double C-curve with two noses located at about 100 and 200 K as indicated by arrows. This result is completely different from the TTT diagram of the solution-treated SUS304L stainless steel, in which only one nose appears.\(^{17}\)

### 3.2 Morphologies of martensites formed during isothermal holding

In order to know the reason why two noses appear in the TTT diagram, we have made \textit{in-situ} optical microscope observation during the isothermal holding at the nose temperatures, 100 and 200 K, of the double C-curve. Figures 5 and 6 show a series of optical micrographs during the isothermal holding at 200 K related to the upper part of the double C-curve. After isothermal holding for 300 s, we can see that wedge-shaped plates, indicated by “A”, forms directly in the matrix (\(\gamma\)-phase) in the vicinity of grain boundaries as shown in Fig. 5(b). These plates are \(\alpha'\)-martensite because the wedge-shaped morphology is characteristic to the \(\alpha'\)-martensite.\(^{10,21}\) We notice that the number of \(\alpha'\)-plates increases near the grain boundaries gradually with increasing the isothermal holding time. In addition, the size of \(\alpha'\)-martensite gradually increases with increasing the isothermal holding time. The gradual growth is clearly seen in Fig. 6, which is taken from a different region. In the figure, the \(\alpha'\)-plate indicated by an arrow obviously grows with increasing holding time. Such a gradual growth of the \(\alpha'\)-plate resembles that reported in an Fe-Ni-Mn alloy.\(^{22}\) From the above results, we suggest that the upper part of the double C-curve should be related to the direct \(\gamma \rightarrow \alpha'\) martensitic transformation induced isothermally in the vicinity of grain boundary during the isothermal holding experiment.

On the other hand, Fig. 7 shows a series of optical micrographs taken during the isothermal holding experiment at 100 K, the nose temperature of the lower part of the double C-curve. After isothermal holding for 10 min, a banded plate (characteristic to the \(\epsilon'\)-martensite) appears gradually near the center of grains indicated by a dashed rectangle in Fig. 7(c). Similar microstructure has been observed in the solution treated SUS304L after isothermal

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**Fig. 4** TTT diagram of the isothermal martensitic transformation in the sensitized SUS304, and dashed line is guide for eyes.

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**Fig. 5** A series of \textit{in-situ} optical micrographs of sensitized SUS304 stainless steel during isothermal holding at 200 K.
holding in the previous report. This result suggests that the \( \gamma \rightarrow \varepsilon' \) martensitic transformation proceeds isothermally. Figure 7(d) shows the microstructure taken 5 sec after observing Fig. 7(c). We notice wedge-shaped plates (\( \alpha' \)-martensite) instantaneously form in the banded \( \varepsilon' \)-martensite. That is, the \( \varepsilon' \rightarrow \alpha' \) martensitic transformation proceeds athermally. In this way, it was confirmed that the lower part of double C-curve is related to the successive \( \gamma \rightarrow \varepsilon' \rightarrow \alpha' \) martensitic transformation induced near the center of grains during the isothermal holding experiment. Incidentally, we can also observe the \( \alpha' \)-martensites formed directly in the vicinity of the grain boundaries after isothermal holding for 5 min in Fig. 7(b), as indicated by “A”. This morphology is similar to the result obtained at 200 K. However, the amount of \( \alpha' \)-martensites formed directly from grain boundary does not increase on further increasing the isothermal holding time at 100 K. Therefore, it is likely that such direct \( \alpha' \)-martensites shown in Fig. 7(b) had been formed at about 200 K during the cooling process.

To understand the martensitic transformation sequence in the sensitized SUS304 stainless steel further, the microstructure formed by isothermal holding experiment is examined by using TEM. Figure 8(a) shows a bright field image obtained from the as-sensitized specimen. We can see a grain boundary and some precipitates along the grain boundary. The electron diffraction pattern of these precipitates (Fig. 8(d)) can be indexed with the carbide \( \text{M}_{23}\text{C}_6 \).
which is formed by sensitization. This result strongly suggests that the chemical composition of the matrix near the grain boundaries should be different from that of the center of grains. In fact, a EDS (energy dispersive spectroscopy) analysis of the specimen revealed that Cr and Ni are depleted in the vicinity of the grain boundaries. Figure 8(b) shows a bright field image after isothermal holding at 200 K. The carbide precipitates are also observed along the grain boundary. In addition, we notice that \( \alpha' \)-martensite is formed near the grain boundary, which is known from the electron diffraction pattern corresponding to the encircled area (Fig. 8(e)). This result also confirms that the martensitic transformation sequence on the upper nose of double C-curve is direct \( \gamma \rightarrow \alpha' \) martensitic transformation. Figure 8(c) shows the bright field image of the specimen after isothermal holding at 100 K. The image was obtained from the inner region of a grain. We can see that some banded plates of the \( \varepsilon' \)-phase are formed from \( \gamma \)-phase, and \( \alpha' \)-phase is induced inside the banded \( \varepsilon' \) plates. Such a coexistence with \( \gamma' \), \( \varepsilon' \) and \( \alpha' \)-phase suggests that the martensitic transformation sequence on the lower nose of the double C-curve is successive \( \gamma \rightarrow \varepsilon' \rightarrow \alpha' \) martensitic transformation.

4. Conclusions

We have investigated martensitic transformation behavior in the sensitized SUS304 austenitic stainless steel at cryogenic temperatures. Following results have been obtained.

1. Sensitized SUS304 stainless steel exhibits an isothermal martensitic transformation when the specimen is held in the temperature range between 60 and 260 K.

2. TTT diagram of the martensitic transformation shows a double-C curve with two noses located at about 100 and 200 K due to two different transformation sequences: the upper and lower parts of the double C-curve are ascribed to the direct \( \gamma \rightarrow \alpha' \) martensitic transformation in the vicinity of grain boundaries and the successive \( \gamma \rightarrow \varepsilon' \rightarrow \alpha' \) martensitic transformation near the center of grains, respectively.

Acknowledgements

This study was supported by Priority Assistance for the Formation of Worldwide Renowned Centers of Research-The Global COE Program (Project: Center of Excellence for Advanced Structural and Functional Materials Design) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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