Martensitic transformation behaviour in sensitized SUS304 austenitic stainless steel during isothermal holding at low temperature

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Abstract. We investigated martensitic transformation behaviour in sensitized SUS304 austenitic stainless steel to determine the stability of the austenitic phase at low temperatures. We found that a specimen that was sensitized at 973 K for 100 h exhibits an isothermal martensitic transformation when the specimen is held in the temperature range between 60 and 260 K. We constructed a time-temperature-transformation (TTT) diagram corresponding to the formation of 0.5 vol. % \(\alpha'\)-martensite. A magnetization measurement was used to evaluate the volume fraction of \(\alpha'\)-martensite. The TTT diagram shows a double-C curve with two noses located at about 100 and 200 K. In-situ optical microscope observations reveal that the double C-curve is due to two different transformation sequences. That is, the upper part of the C-curve is due to a direct \(\gamma \rightarrow \alpha'\) martensitic transformation and the lower part of the C-curve is due to a successive \(\gamma \rightarrow \varepsilon' \rightarrow \alpha'\) martensitic transformation. The direct \(\gamma \rightarrow \alpha'\) transformation occurs in the vicinity of grain boundaries while the successive \(\gamma \rightarrow \varepsilon' \rightarrow \alpha'\) transformation occurs near the centre of grains. A scanning electron microscope observation reveals that carbide particles of \(M_23C_6\) are formed in the grain boundaries. The concentration difference between the centre of the grains and regions near grain boundaries is the reason for the difference in the isothermal transformation sequence for the sensitized SUS304 stainless steel.

1. Introduction
Austenitic stainless steels are characterized by good corrosion resistance, excellent mechanical properties, superior weldability and nonmagnetic characteristics [1-2]. SUS304 stainless steel is extensively used in equipment for cryogenic applications such as tanks, piping systems and other equipment for handling condensed gases. The welding process is an essential factor for the use of this steel in these applications as thermal effects can result in sensitized zones where carbide precipitation (\(M_23C_6\)) at grain boundaries and chromium depletion in the vicinity of grain boundaries may occur [3-4]. Recently, we found that sensitized SUS304 stainless steel exhibits an isothermal martensitic transformation at cryogenic temperatures [5-6]. However, its time-temperature-transformation (TTT) diagram which contains important information relating to its isothermal transformations has not been constructed yet.

For this study we constructed a TTT diagram of the isothermal martensitic transformation in sensitized SUS304 stainless steel.

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2. Experimental Procedure
The material used in the study was SUS304 austenitic stainless steel with a composition of 0.06C-0.67Si-1.01Mn-0.029P-0.009S-8.5Ni-18.10Cr-Bal.Fe (mass %). Specimens of $3 \times 3 \times 1$ mm were cut from the sheet and solution-treated at 1323 K for 0.5 h in vacuum followed by quenching in ice water. Most specimens were sensitized by heat treatment at 973 K for 100 h. The oxidized surface layer was then eliminated by electropolishing in an electrolyte composed of 85 % C$_2$H$_5$OH and 15 % HClO$_4$ by volume. Isothermal holding was carried out without a magnetic field in the temperature range of 60 to 260 K. The volume fraction of the $\alpha'$-martensite that was formed by isothermal holding was obtained by a magnetization measurement as in a previous study [7]. The microstructure of the specimen was investigated by a scanning electron microscopy (SEM) and the change in morphology during isothermal holding was observed using an in-situ optical microscopy.

3. Results and Discussion
The microstructure near grain boundaries is shown in Figure 1 for as-sensitized SUS304 stainless steel. Some particles are present along the grain boundaries. These particles are mainly M$_{23}$C$_6$ type, as confirmed by electron diffraction and EDS analysis. From this observation, the concentration of chromium between the centre of grains and near grain boundaries has been partially altered by the formation of M$_{23}$C$_6$ carbide.

To investigate the magnetic properties and the martensitic transformation we carried out a magnetic susceptibility measurement in the temperature range between 4.2 and 300 K. Figure 2 shows the temperature dependence of the magnetic susceptibility for sensitized SUS304 stainless steel. The value of $\chi$ starts to increase at about 260 K during the cooling process as indicated by “A”. Such an increase in the value of $\chi$ means that the ferromagnetic $\alpha'$-martensite is formed during the cooling process. During the heating process the value of $\chi$ starts to increase at about 60 K indicating that $\alpha'$-martensite is also formed during the heating process. This result suggests that the martensitic transformation of the sensitized SUS304 stainless steel proceeds isothermally in the temperature range between 60 and 260 K. Furthermore, we notice that the value of $\chi$ increased by about 125 K during the cooling process and is indicated by “B”. This result implies that two types of martensitic transformations exist for the sensitized SUS304 stainless steel. The value of $\chi$ has a peak at about 40 K because of a paramagnetic to anti-ferromagnetic transition of the $\gamma$-phase.

To investigate the isothermal nature further we conducted isothermal holding experiments at several temperatures between 60 and 260 K to construct a $TTT$ diagram. We then carried out magnetization measurements at room temperature to evaluate the amount of $\alpha'$-martensite from the spontaneous magnetization, as described elsewhere [7]. We obtained the time required for the formation of 0.5 vol. % $\alpha'$-martensite for each temperature. Using these times we constructed the $TTT$ diagram for $\alpha'$-martensite as shown in Figure 3. It should be noted that the $TTT$ diagram shows a double C-curve with two noses located at about 100 and 200 K as indicated by the arrows. This result is completely
different from the TTT diagram of solution-treated SUS304L stainless steel in which only one nose is present [7].

To determine why two noses appear in the TTT diagram we conducted in-situ optical microscopy during isothermal holding at the nose temperatures of 100 and 200 K. Figure 4 shows a series of optical micrographs taken during the isothermal holding at 200 K. After isothermal holding for 30 min wedge-shaped plates were formed directly from the γ-phase in the vicinity of the grain boundaries. These plates are α′-martensite because the wedge-shaped morphology is characteristic of α′-martensite [8]. The amount of α′-martensite gradually increased near the grain boundaries as the isothermal holding time increased. The above result implies that the upper part of the double C-curve is related to the direct γ → α′ martensitic transformation that was induced isothermally in the vicinity of a grain boundary during the isothermal holding.

On the other hand, Figure 5 shows a series of optical micrographs taken during isothermal holding at 100 K and the nose temperature of the lower part of the double C-curve. After isothermal holding for 10 min, a banded plate (characteristic of ε′-martensite) gradually appears near the centre of the grains as indicated by the dashed rectangle in Figure 5 (b). This result suggests that the γ → ε′ martensitic transformation proceeds isothermally. Figure 5 (c) shows a micrograph of the

Figure 2. The magnetic susceptibility curve of sensitized SUS304 stainless steel. The measurement was made during the cooling process and also during the heating process.

Figure 3. The TTT diagram of the isothermal martensitic transformation for sensitized SUS304 stainless steel. The dashed line is a guide.

Figure 4. A series of in-situ optical micrographs of sensitized SUS304 stainless steel showing a direct γ → α′ transformation during isothermal holding at 200 K.
We notice that $\alpha'$-martensites instantaneously forms within the banded $\varepsilon'$-martensite. The $\varepsilon' \rightarrow \alpha'$ martensitic transformation thus proceeds athermally. This result confirms that the lower part of the double C-curve is related to the successive $\gamma \rightarrow \varepsilon' \rightarrow \alpha'$ martensitic transformation that was induced near the centre of the grains during the isothermal holding experiment.

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.

4. Conclusions
We investigated martensitic transformation behaviour in sensitized SUS304 austenitic stainless steel at low temperatures and the following results were obtained.
(i) Sensitized SUS304 stainless steel exhibits an isothermal martensitic transformation when a specimen is held in a temperature range between 60 and 260 K.
(ii) The $TTT$ diagram of the martensitic transformation shows a double C-curve with two noses located at about 100 and 200 K because of two different transformation sequences: the upper and lower parts of the double C-curve are assigned to a direct $\gamma \rightarrow \alpha'$ martensitic transformation in the vicinity of the grain boundaries and the successive $\gamma \rightarrow \varepsilon' \rightarrow \alpha'$ martensitic transformation near the centre of grains, respectively.

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