Effect of Magnetic Field on Successive $\gamma \rightarrow \varepsilon' \rightarrow \alpha'$ Isothermal Martensitic Transformation in a SUS304L Stainless Steel

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(Received on January 11, 2012; accepted on February 23, 2012)

Effect of magnetic field on the $\gamma \rightarrow \varepsilon' \rightarrow \alpha'$ isothermal martensitic transformation in a solution-treated SUS304L stainless steel has been investigated. The $\gamma \rightarrow \varepsilon' \rightarrow \alpha'$ martensitic transformation shortens as the strength of magnetic field increases although the nose temperature does not depend on the magnetic field. Moreover, the width of the $\varepsilon'$ martensite including $\alpha'$ martensite becomes thinner as the strength of the applied magnetic field increases at a fixed temperature. This result implies that the potential barrier for the $\varepsilon' \rightarrow \alpha'$ transformation decreases with increasing magnetic field. We have explained this behaviour based on a model previously proposed by our group.

KEY WORDS: SUS304L stainless steel; isothermal martensitic transformation; athermal martensitic transformation; time-temperature-transformation diagram; magnetic field.

1. Introduction

Martensitic transformations are generally classified into two groups, athermal and isothermal martensitic transformations from the viewpoint of kinetics.\(^1\) The so-called athermal martensite transformation occurs instantaneously when the temperature reaches $M_s$ (martensite transformation start temperature). On the other hand, the so-called isothermal martensite transformation does not have a definite transformation temperature but occurs after some finite incubation time during isothermal holding.\(^2,3\)

Recently, we found the existence of an isothermal martensite transformation in a solution-treated SUS304L austenitic stainless steel. The transformation proceeds in two-step, $\gamma \rightarrow \varepsilon' \rightarrow \alpha'$ during isothermal holding at a constant temperature. The $\gamma \rightarrow \varepsilon'$ transformation is an isothermal transformation in which the width of the $\varepsilon'$ plate increases as time proceeds while the $\varepsilon' \rightarrow \alpha'$ transformation is an athermal transformation occurring instantaneously.\(^4,5\)

Considering previous studies on the effect of magnetic field on martensitic transformation in Fe-based alloys,\(^6-11\) it is expected that the $\varepsilon' \rightarrow \alpha'$ transformation is influenced by the application of magnetic field since the $\alpha'$ martensite is ferromagnetic, while the $\gamma \rightarrow \varepsilon'$ transformation is not affected by a magnetic field because the $\gamma$ and $\varepsilon'$ martensites are both paramagnetic. So, we can speculate that the magnetic field influences the $\gamma \rightarrow \varepsilon' \rightarrow \alpha'$ transformation diagram corresponding to 0.5 vol.% formation of the $\alpha'$ phase in the $\varepsilon'$ phase. However, such experiment has not been made yet.

In the present study, therefore, we examine the effect of magnetic field on $\gamma \rightarrow \varepsilon' \rightarrow \alpha'$ isothermal martensitic transformation in a solution-treated SUS304L austenitic stainless steel.

2. Experimental Procedure

The chemical composition of the SUS304L stainless steel used in the present study is 0.023C–0.48Si–1.07Mn–0.005S–8.47Ni–18.20Cr–Bal. Fe (mass%). The stainless steel was cold-rolled into a sheet, and specimens of $3 \times 3 \times 1$ mm in size were cut out. The specimens were solution-treated at 1 323 K for 0.5 h in vacuum, and then quenched into ice water. The oxidized surface layer was eliminated by electropolishing in an electrolyte composed of 85% C\(_2\)H\(_5\)OH and 15% HClO\(_4\) in volume. Isothermal holding experiments were carried out under magnetic fields of 1–7T in the temperature range between 70 and 170 K for various periods. The chamber for the isothermal holding experiment was filled with helium gas with a set temperature, and the magnetic field was applied to the chamber before inserting the specimen. Then the specimen was rapidly inserted to the chamber, kept for a predetermined holding time, and then rapidly pulled out of the chamber. Since a quantitative evaluation of a small fraction of the $\varepsilon'$ martensite is difficult, we evaluated only the fraction of the $\alpha'$ martensite by magnetization measurement. That is, the amount of the $\alpha'$ martensite ($f_{\alpha'}$) was obtained by a magnetization measurement under a low field at room temperature. Here, the measurement of magnetization was made at room temperature because the ferromagnetic $\alpha'$ martensite retains at room
temperature due to the large temperature hysteresis of the transformation. The fraction is evaluated as $f_{\alpha'} = M_0(T_R)/M_0'(T_R)$, where $M_0(T_R)$ and $M_0'(T_R)$ are the spontaneous magnetization of the specimen at room temperature of $T_R$ and that of the $\alpha'$ phase, respectively. The value of $M_0'(T_R)$ is approximated to be the value at 0 K ($M_0'(0) = 1.79 \mu B/atom$), which is obtained by the Slater-Pauling curve and their valence electron concentration although it is a rough approximation.\(^{12}\) The microstructure of the specimens was investigated by an optical microscope after the isothermal holding at 103 K under each magnetic field (1–7T). This temperature of 103 K is the nose temperature of a successive $\gamma \rightarrow \epsilon' \rightarrow \alpha'$ isothermal martensitic transformation in the present specimen. Incidentally, according to a previous study,\(^5\) the $\gamma \rightarrow \epsilon'$ transformation is an isothermal one, while the $\epsilon' \rightarrow \alpha'$ transformation is an athermal one. Consequently, the time dependence of the successive $\gamma \rightarrow \epsilon' \rightarrow \alpha'$ transformation is essentially due to time dependent nature of the $\gamma \rightarrow \epsilon'$ transformation. In addition, the time dependence of the $\gamma \rightarrow \epsilon'$ transformation is not measured directly, but is measured through the amount of $\alpha'$ martensite in the present study.

3. Results

3.1. Effect of Magnetic Field on TTT Diagram

In order to investigate the TTT diagram corresponding to 0.5 vol.% transformation of the $\alpha'$ phase within the $\epsilon'$ phase under a magnetic field, isothermal holding experiments have been made in the temperature range between 70 and 170 K. Figure 1 shows magnetization curves at $T_R = 300$ K after the isothermal holding at $T_h = 103$ K under the magnetic field of 1T for 70 s, 210 s, 760 s, 1680 s and 4860 s. We can evaluate the spontaneous magnetization from these curves. As an example, the spontaneous magnetization obtained after the holding for 4860 s is indicated with an arrow in the Fig. 1. It should be noted in the figure that the spontaneous magnetization increases with increasing isothermal holding time. This increase is due to the formation of the $\alpha'$ martensite during isothermal holding at 103 K.

The volume fraction of the $\alpha'$ martensite ($f_{\alpha'}$) can be evaluated using the spontaneous magnetization as described before. The fraction, $f_{\alpha'}$, obtained from Fig. 1 is shown with open circles as a function of holding time in Fig. 2. The same holding experiments at 103 K have been made under different magnetic fields, and the results are shown with solid squares (5T) and open squares (7T) in Fig. 2. In this figure, the result under 0 T (solid circles) reported previously is also shown for comparison. The amount of the $\alpha'$ martensite clearly depends on the magnetic field as well as the isothermal holding time. For example, the time required for the 0.5 vol.% formation of the $\alpha'$ martensite under magnetic fields of 0T, 1T, 5T and 7T is evaluated to be 6.1 ks, 3.5 ks, 3.0 ks and 2.8 ks, respectively and the time required for the 0.5 vol.% formation of the $\alpha'$ martensite decreases as the strength of the applied magnetic field increases.

Similar experiments have been made in the temperature range between 70 and 170 K, and the time required for the 0.5 vol.% formation of the $\alpha'$ martensite under the magnetic field of 1T (open circles), 5T (solid squares) and 7T (open squares) is shown in Fig. 3. In this figure, the result under 0 T (solid circles) reported previously is also shown for comparison. As known from Fig. 3, the incubation time of the successive $\gamma \rightarrow \epsilon' \rightarrow \alpha'$ martensitic transformation shortens with increasing the strength of magnetic field. On the other hand, the nose temperature of the isothermal transformation does not change significantly by the application of
magnetic field. This result is different from the magnetic field dependence of nose temperature of direct $\gamma \rightarrow \alpha'$ martensitic transformations reported in some Fe-based alloys, where the nose temperature decreases with increasing magnetic field. The reason for such difference will be discussed later.

3.2. Morphologies of Martensites Formed during Isothermal Holding under Magnetic Field

Figure 4 shows the optical micrographs of the surface of the specimens taken after the isothermal holding at 103 K under different magnetic fields. The holding times are 12.4 ks under 0 T, 7.4 ks under 1 T, 6.3 ks under 5 T and 5.6 ks under 7 T. These holding times correspond to the time required for the 1 vol.% formation of the $\alpha'$ martensite determined from Fig. 2. Incidentally, we show the results of 1 vol.% formation of the $\alpha'$ instead of 0.5 vol.% formation because the amount of martensite is not sufficient for optical microscope observation in case of 0.5 vol.% formation.

As known from Fig. 4, wedge-shaped plates ($\alpha'$ martensite) are observed in a banded plate of $\varepsilon'$ phase irrespective of magnetic field strength. And the width of the $\varepsilon'$ martensite, including the $\alpha'$ martensite inside (hereafter, the width will be expressed as $d_{\varepsilon' \rightarrow \alpha'}$), is 33.1 $\mu$m at 0 T, 18.2 $\mu$m at 1 T, 12.9 $\mu$m at 5 T and 7.3 $\mu$m at 7 T. Obviously, $d_{\varepsilon' \rightarrow \alpha'}$ decreases with increasing the strength of the applied magnetic field. We will discuss later the effect of magnetic field on the morphology of martensities formed during isothermal holding.

4. Discussion

In the present study, we have found that the incubation time of the successive $\gamma \rightarrow \varepsilon' \rightarrow \alpha'$ martensitic transformation shortens with increasing the strength of magnetic field, but the nose temperature of the C-curve does not change. In this section, we will discuss the reason of these behaviors in the incubation time and the nose temperature of the successive $\gamma \rightarrow \varepsilon' \rightarrow \alpha'$ martensitic transformation using a phenomenological model for the kinetics of martensitic transformation proposed by our group. According to the model, the probability, $P$, of the occurrence of a martensitic transformation is expressed as,

$$P = A \cdot \exp \left( -\frac{m^* \Delta}{k_B T} \right) \exp \left( -B \cdot \exp \left( -\frac{\Delta}{k_B T} \right) \right),$$

where $\Delta$ is the potential barrier between the parent phase and the martensite phase, $k_B$ is the Boltzmann constant, and $T$ is the temperature. In addition, $m^*$ is the minimum number of particles consisting of the cluster necessary for the martensite transformation to start, $A$ and $B$ are constants. In this model, the incubation time of martensitic transformation is proportional to $P^{-1}$. As described in a previous paper, a magnetic field influences the incubation time when $\Delta$ is affected by the magnetic field. In the case of an isothermal $\gamma \rightarrow \varepsilon'$ transformation, however, $\Delta$ is not affected by the magnetic field since both the $\gamma$ and $\varepsilon'$ phases are paramagnetic. Therefore, both the incubation time and the nose temperature of the $\gamma \rightarrow \varepsilon'$ transformation will not be influenced by the magnetic field. This is the reason why the nose temperature of the successive $\gamma \rightarrow \varepsilon' \rightarrow \alpha'$ martensitic transformation does not change by the application of magnetic field as seen in Fig. 3. However, although the $\gamma \rightarrow \varepsilon'$ martensitic transformation is not influenced by the application of magnetic field, the incubation time for the successive $\gamma \rightarrow \varepsilon' \rightarrow \alpha'$ transformation shortens as the strength of the applied magnetic field increases as shown in Fig. 3.

Next, we will discuss the reason why the incubation time of the $\gamma \rightarrow \varepsilon' \rightarrow \alpha'$ martensitic transformation in solution-treated SUS304L austenitic stainless steel depends on a magnetic field. According to a previous study, the $\gamma \rightarrow \varepsilon'$ transformation has an isothermal nature, and the width of the $\varepsilon'$ martensite, $d$, increases with increasing holding time. This behavior is schematically shown in Fig. 5(a). On the other hand, the
The transformation occurs instantaneously (athermally) when the width of the ε' martensite reaches a critical width, which is indicated as $d^{H=0}_{\epsilon'\rightarrow\alpha'}$. Such instantaneous transformation implies that the potential barrier $\Delta$ for the $\epsilon'\rightarrow\alpha'$ transformation becomes zero\(^b\) at the critical width $d^{H=0}_{\epsilon'\rightarrow\alpha'}$. That is, the potential barrier $\Delta$ for the $\epsilon'\rightarrow\alpha'$ transformation depends on the width of $\epsilon'$ martensite; it decreases with increasing the width of the $\epsilon'$ martensite, $d$, and becomes zero at the critical width, $d^{H=0}_{\epsilon'\rightarrow\alpha'}$, as schematically shown in Fig. 5(b) ($H = 0$). Then we consider the relation between the potential barrier $\Delta$ for the $\epsilon'\rightarrow\alpha'$ transformation and the width of the $\epsilon'$ martensite under magnetic field. Here we assumed that growth rate of $\epsilon'$ martensite is independent of magnetic field. The application of a magnetic field of $H_1$ lowers the free energy of the $\alpha'$ martensite relative to the $\epsilon'$ martensite because the magnetization of the ferromagnetic $\alpha'$ martensite is much larger than that of the paramagnetic $\epsilon'$ martensite. Thus, in association with the decrease in the free energy of the $\alpha'$ martensite, the potential barrier $\Delta$ for the $\epsilon'\rightarrow\alpha'$ transformation should also decrease as illustrated by the dotted arrow in Fig. 5(b) ($H = H_1$). Therefore, the critical width of the $\epsilon'$ plate under the magnetic field, $d^{H=H_1}_{\epsilon'\rightarrow\alpha'}$, when the $\epsilon'\rightarrow\alpha'$ transformation occurs instantaneously is smaller than that under no magnetic field; $d^{H=0}_{\epsilon'\rightarrow\alpha'} < d^{H=H_1}_{\epsilon'\rightarrow\alpha'}$ as seen in Fig. 5(b). The decrease in the width of the $\epsilon'$ martensite, including the $\alpha'$ martensite inside, by the application of the magnetic field can be seen in Fig. 4. Then, the holding time necessary to grow the $\epsilon'$ martensite to the critical width $d^{H=0}_{\epsilon'\rightarrow\alpha'}$ is $t_0$ and that to the width $d^{H=H_1}_{\epsilon'\rightarrow\alpha'}$ is $t_1$ as seen in Fig. 5(a), where $t_1 < t_0$. Consequently, the holding time for the formation of $\alpha'$ martensite shortens by the application of the magnetic field. For further discussion, we need to construct the TTT diagram for the $\gamma\rightarrow\varepsilon'$ transformation.

5. Conclusions

We have investigated effect magnetic field on TTT diagram of successive $\gamma\rightarrow\varepsilon'\rightarrow\alpha'$ martensitic transformation in a solution-treated SUS304L stainless steel, and following results have been obtained.

(1) The nose temperature of the successive $\gamma\rightarrow\varepsilon'\rightarrow\alpha'$ martensitic transformation does not change under the magnetic field. However, incubation time shortens with increasing the strength of magnetic field. This result is explained by size effect of martensitic transformation.

(2) The width of the $\epsilon'$ martensite, including the $\alpha'$ martensite inside, decreases with increasing magnetic field.

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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