Effects of Heat Treatment, Pre-Strain and Magnetic Field on the Formation of α' Martensite in Fe-25.5Ni-4Cr and 304L Steels

Koji Shibata, Tadahiro Shimozone^{*1}, Yutaka Kohno^{*2} and Hideyuki Ohtsuka^{*3}

Department of Metallurgy, The University of Tokyo, Tokyo 113-8656, Japan

The effects of solution heat treatment temperature, cooling rate from this temperature, pre-strain and re-heating on α' martensite formation were examined in Fe-25.5Ni-4Cr steel and 304L steels. The distribution of the potential energy of nucleation sites for α' martensite was also estimated using results obtained in magnetic fields of up to 20.70 MA/m. In Fe-25.5Ni-4Cr steel, solution heat treatment temperature and cooling rate from this temperature had almost no effect on the amount of α' martensite formed in magnetic fields over about 8 MA/m. In contrast, the amount of α' martensite formed in magnetic fields lower than about 8 MA/m increased as solution heat treatment temperature increased and as cooling rate decreased. This cooling rate effect in Fe-25.5Ni-4Cr steel is opposite to that in 304L steel, and the reason for this remains to be clarified. In Fe-25.5Ni-4Cr steel, re-heating almost did not affect the amount of α' martensite. From this result, it was expected that internal strain or lattice defects generated by water-quenching almost do not act as nucleation sites in this steel. In Fe-25.5Ni-4Cr steel, pre-strain of up to about 10% suppressed the formation of α' martensite and pre-strain over 10% enhanced the formation of α' martensite. Such a change of the amount of α' martensite with pre-strain was reduced as the magnetic field increased. In Fe-25.5Ni-4Cr steel, it was predicted that specimens that were solution heat treated at higher temperatures would have two peaks on the curve of the potential energy distribution of nucleation sites and that the small peak with a high potential energy would be easily annihilated by a small pre-strain. However this peak was not thought to be annihilated by re-heating. On the other hand, the large peak was expected to increase at larger pre-strain. This enhancing effect of pre-strain was not observed in 304L steel even in high magnetic fields. This supported the view that pre-strain suppresses the formation of α' martensite not through work hardening but through the annihilation of nucleation sites. In contrast, in Fe-25.5Ni-4Cr steel, some strain concentration induced by a large pre-strain was expected to generate nucleation sites. As mentioned above, clear differences were revealed in the effects of heat treatments and pre-strain on the formation of α' martensite between Fe-25.5Ni-4Cr steel and 304L steel. This shows that the nature of the nucleation sites and the procedure for the formation of α' martensite differ between these two kinds of steels.

(Received March 24, 2000; Accepted June 2, 2000)

Keywords: solution heat treatment, cooling rate, re-heating, work hardening, potential energy of nucleation site, 77 K, ε martensite, stacking fault energy

1. Introduction

Type 304L steel is one of the steels that are used widely in various engineering fields. In this steel, α' martensite affects mechanical, physical and chemical properties; thus, the control of this phase is important. The research group of Shibata *et al.*¹⁻³⁾ clarified that the amount of α' martensite formed in this steel changed with solution heat treatment temperature, cooling rate from this temperature, pre-strain (the amount of plastic deformation at room temperature after solution heat treatment) and re-heating (heating after solution heat treatment). Such results are thought to be related to the nucleation sites and the transformation pathway of α' martensite. As for the transformation pathway, the following have been advocated for α' martensite formation in austenitic stainless steel to date.

- (1) ε martensite is generated from austenite, and is then transformed into α' martensite⁴⁻⁸⁾
- (2) α' martensite is generated at the ε martensite/austenite interface or the crossing point of two plates of ε martensite⁷⁻¹¹⁾
- (3) α' martensite is directly generated from austenite¹²⁻¹⁴⁾

It is generally known that ε martensite is not formed in

high-Ni low-Cr steel that has a high stacking fault energy. Therefore, it is conceivable that if α' martensite is formed mainly via pathway (3) in 304L steel, the effects of such heat treatments and pre-strain as mentioned above on the formation of α' martensite should be similar in both cases of high-Ni low-Cr steel and 304L steel. Hence, in the present research, effects of solution heat treatment temperature, cooling rate from this temperature, pre-strain and re-heating on α' martensite formation are examined in Fe-25.5Ni-4Cr steel, and the results are compared with those in 304L steel.

On the other hand, it is generally accepted that martensite in steel is formed heterogeneously on certain nucleation sites where it can nucleate at the driving free energy which is ΔG (hetero) lower than that in the case of homogeneous nucleation, although the details remain unknown.¹⁵⁻²¹⁾ In this paper, ΔG (hetero) will be called potential energy of the nucleation sites of α' martensite. The value of ΔG (hetero) is thought not to be unique but to show some distribution. It is thought that martensite nucleates earlier from sites with higher potential energy. In the present research, the distribution of the value of ΔG (hetero) is estimated using magnetic fields in order to know the details of effects of such heat treatments and pre-strain on the formation of α' martensite. An external magnetic field drives the transformation from non-Invar paramagnetic austenite to α' martensite by magnetic energy ΔG (mag), and this energy can be related mainly to the intensity of a magnetic field and the saturation magnetization of the martensite.²²⁾ Therefore, some information on the potential distribution of nucleation sites should be derived by

^{*1}Graduate Student, The University of Tokyo.

^{*2}Present address: Muroran Institute of Technology.

^{*3}High Magnetic Field Research Center, National Research Institute for Metals.

Fig. 1 Schematic distribution of potential energy ΔG (hetero) of nucleation sites of α' martensite. Martensite nucleates on the sites with potential energy higher than a certain value of A. When a magnetic field of which driving energy is ΔG (mag) is applied to the specimen, martensite nucleate on sites with the potential energy higher than the value of B.

examining how the amount of α' martensite increases with an increase in magnetic field. Figure 1 is a schematic curve of the distribution of ΔG (hetero) following Ghosh and Olson,²³⁾ although this curve is simplified and a real distribution is conceived to be more complicated. When a specimen is held at a certain temperature for a certain time in zero magnetic field, we can suppose that martensite nucleates on sites with potential energy higher than a certain value of A shown in Fig. 1. When a magnetic field with driving energy ΔG (mag) is applied to the specimen, martensite will nucleate on sites with potential energy higher than the value of B. In this consideration, the difference between application time of a magnetic field and soaking time in refrigerant is neglected for simplicity.

Heat treatments and pre-strain may change the shape and the position of the curve of potential distribution. For instance, two extremely simple changes (a) and (b) are shown in Fig. 2. Both changes in Fig. 2 decrease the amount of α' martensite in zero magnetic field. Following change (a), however, the application of a high magnetic field will lead to the recovery of the amount of α' martensite. On the other hand, following change (b), the amount of α' martensite is smaller even in high magnetic fields than that before the change. In the mentions above, the effects of heat treatments and pre-strain on the size of plate or lath of martensite are neglected for simplicity. In actual cases, however, these effects should be considered. As regards the effects of heat treatments, the mean volume $\bar{V}$ of plate or lath of martensite increases as solution treatment temperature increases and as austenitic grain size increases. Cooling rate from solution treatment temperature and re-heating after solution treatment are not thought to induce a noticeable change in volume $\bar{V}$ in such steels and experimental conditions as used in the present research. Concerning the effect of pre-strain, it is difficult to think that pre-strain increases volume $\bar{V}$.

2. Experimental Procedures

The chemical composition of the steels used is shown in Table 1. Fe-25.5Ni-4Cr steel was melted in a small vacuum induction furnace at the National Institute for Metals (NRIM) and was hot-rolled to a plate of 15 mm thickness. 304L (I) and 304L (II) steels were produced by Kobe Steel Corporation and Nippon Steel Corporation, respectively. They were used in previous reports¹⁻³⁾ and were used here for comparison. Round bar blanks cut from the hot-rolled plates were machined to tensile test specimens and round bar test pieces. The dimensions of the gage region of the tensile test specimen and the round bar test piece are 60 mm in length and 8 mm in diameter. Each of these was enclosed in a silica tube of which diameter and length were about 15 and 100 mm, respectively. Silica tubes were evacuated and then a small amount of high-purity Ar gas was introduced before sealing. Round bar test pieces were used for experiments on the effects of solution heat treatment temperature and cooling rate from this temperature. Silica tubes enclosing the round bar test pieces were heated in a horizontal electric furnace at 1473 and 1573 K for 1 h, and then air-cooled and water-quenched. Tensile test specimens were used for experiments on the effects of pre-strain and re-heating. Silica tubes enclosing the tensile test specimens were heated at 1573 K in the electric furnace for 5 h and water-quenched. Pre-strain was introduced using a tensile testing machine at room temperature at a crosshead speed of 83 $\mu\text{m/s}$. Rectangular parallelepiped blocks of $2.5 \times 2.5 \times 4 \text{ mm}^3$ size were cut from the tensile test specimens that were solution heat treated and pre-strained. These blocks were soaked in liquid nitrogen, and then a magnetic field was applied.

Re-heating after solution heat treatment (1573 K, WQ) was

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

Steel	Ni	Cr	C	N	Mn	Si
Fe-25.5Ni-4Cr	25.44	3.89	0.004	0.005	*	*
304L (I)	9.00	18.05	0.015	0.054	1.01	0.46
304L (II)	9.67	18.36	0.020	0.049	0.82	0.46

*: not alloyed

Fig. 2 Two extremely simple changes of potential energy distribution curve with heat treatments or pre-strain.

carried out as follows. Rectangular parallelepiped blocks of $2.5 \times 2.5 \times 4 \text{ mm}^3$ size were cut from tensile test specimens that were solution heat treated. These blocks were heated for 2 h using a constant temperature oven (in air) at temperatures up to 623 K, a salt bath at temperatures between 973 and 673 K and a horizontal electric furnace (in Ar gas) at temperatures higher than 1023 K. Cooling after re-heating involved water-quenching unless otherwise specified. These blocks were divided into two parts. Blocks of one part were re-heated and those of the other part were not re-heated. Both parts of blocks were soaked in liquid nitrogen and then a magnetic field was applied.

The application of a magnetic field was performed using a hybrid magnet and a superconducting magnet at NRIM. Figure 3 shows the time course of magnetic field application. While soaking in liquid nitrogen for 154 min, a static magnetic field was applied to specimen blocks for 1 h. However,

the soaking time was increased to 196 min when a magnetic field of over 15.92 MA/m was applied, because it required a longer time to increase and decrease such high magnetic fields. Some blocks were soaked in liquid nitrogen after the magnetic field was increased to a certain intensity.

Specimen blocks were taken out from liquid nitrogen and their surface layer was removed electrolytically. Then, saturation magnetization of the blocks was measured using a VSM (Vibrating Specimen Magnetometer) at room temperature. Considering the scatter in the data, saturation magnetization of at least three blocks was measured for one experimental condition. Volume fraction f (%) of α' martensite was obtained using eq. (1).

$$f(\%) = 100 \cdot (I_s'/I_s) \quad (1)$$

where I_s' is the value of saturation magnetization measured with a VSM and I_s is calculated saturation magnetization of the block which is assumed to be 100% transformed into α' martensite. The I_s value of 1.74 Wb/m^2 was obtained using the Slater-Pauling curve and substituted into eq. (1).

Using an optical microscope, microstructures were observed after the block was polished mechanically and then electrolytically. Chemical etching was carried out using the two steps described below.

1st step: $\text{1HNO}_3 + 2\text{HCl}$

2nd step: $\text{H}_2\text{O} + 30\%$ sodium bisulphite

3. Results

3.1 Effect of solution heat treatment temperature and cooling rate from this temperature

The result for Fe-25.5Ni-4Cr steel is shown in Fig. 4. The amount of α' martensite formed in magnetic fields over about 7.96 MA/m is almost unaffected by solution heat treatment temperature and cooling rate from this temperature. In mag-

Fig. 3 Some examples of time course of magnetic field application.

(a)

(b)

Fig. 4 Effect of solution heat treatment temperature and cooling rate from this temperature on the amount of α' martensite in Fe-25.5Ni-4Cr steel. Solution heat treatment time is 1 h.

Fig. 5 Correlation between re-heating temperature and amount of α' martensite in Fe-25.5Ni-4Cr steel. Re-heating time is 2 h.

Fig. 7 Correlation between pre-strain and the amount of α' martensite in 304L (II) steel.

Fig. 6 Correlation between pre-strain and the amount of α' martensite formed in Fe-25.5Ni-4Cr steel in magnetic fields from 3.98 to 19.10 MA/m.

netic fields lower than 7.96 MA/m, it seems that the amount of α' martensite increases as solution heat treatment temperature increases and as cooling rate decreases, although scatter in the data is fairly large.

3.2 Effect of re-heating

The relationship between re-heating temperature and the amount of α' martensite is shown in Fig. 5. The amount of α' martensite seems to increase slightly by re-heating in the case of application of 11.94 MA/m and 15.92 MA/m magnetic fields. However, the amount of α' martensite almost does not change with re-heating temperature.

3.3 Effect of pre-strain

Figure 6 shows the relationship between pre-strain and the amount of α' martensite formed at 77 K in magnetic fields from 3.98 to 19.10 MA/m. In zero magnetic field, α' martensite was not formed in all pre-strained specimens. The formation of α' martensite is suppressed as the pre-strain is increased up to about 10%. However, the amount of α' martensite increases again when the pre-strain exceeds 10%. Such a change of the amount of α' martensite with pre-strain is reduced as the magnetic field is increased.

Figure 7 shows the relationship between pre-strain and the amount of α' martensite in 304L (II) steel. In water-quenched specimens, α' martensite is formed even in zero magnetic field. Pre-strain suppresses the formation of α' martensite and α' martensite is not formed even in a magnetic field of 20.70 MA/m when pre-strain exceeds about 5%. In air-cooled specimens, α' martensite is not formed even in a magnetic field of 7.96 MA/m.

4. Discussion

4.1 Effect of solution heat treatment temperature and cooling rate from this temperature

Figure 8 shows results that were previously obtained for 304L (I) steel.^{2,3)} The amount of α' martensite increases as solution heat treatment temperature and cooling rate increase, although the amount is saturated at high magnetic fields. Figure 7 shows clearly that the amount of α' martensite also increases as cooling rate increases in the case of 304L (II) steel. On the other hand, Fig. 4 shows that in Fe-25.5Ni-4Cr steel, solution heat treatment temperature and cooling rate from this temperature almost do not affect the formation of α' martensite in magnetic fields over about 7.96 MA/m. In magnetic fields lower than 7.96 MA/m, it seems that the amount of α' martensite increases as solution heat treatment

Fig. 8 Correlation between re-heating temperature and cooling rate from this temperature on amount of α' martensite in 304L (I) steel.

Fig. 9 Simplified curves showing effects of cooling rate on the potential energy distribution of nucleation sites in 304L (I) steel.

Fig. 10 Simplified curves showing effects of cooling rate on the potential energy distribution of nucleation sites in 304L (II) steel.

temperature increases and as cooling rate decreases, although the scatter in data is large. This effect of cooling rate is the reverse of that on 304L steel, although the reason for this remains unknown. It is obvious that the effects of solution heat treatment temperature and cooling rate differ between 304L and Fe-25.5Ni-4Cr steels.

Figure 9 shows schematically the effects of cooling rate on the potential energy distribution of nucleation sites in 304L (I) steel. The solid curve represents the air-cooled (or heated at lower solution heat treatment temperature) specimen and dotted lines represent water-quenched (or heated at higher solution heat treatment temperature) ones. Distribution (a) shows the case in which the total number of nucleation sites is large compared with that of the air-cooled specimen, while distribution (b) shows the case in which the total number of nucleation sites is similar to that of the air-cooled specimen. In both distributions of (a) and (b), the amount of α' martensite formed in zero magnetic field in water-quenched specimens is large compared with that formed in the air-cooled speci-

men. However, in distribution (b), the amount of α' martensite formed in a high magnetic field is similar to that formed in the air-cooled specimen; this conflicts with the results shown in Fig. 8. That is to say, in 304L (I) steel, water-quenching should have the effect of increasing the total number of nucleation sites.

In the case of 304L (II) steel, information about the potential energy distribution of air-cooled and water-quenched specimens is not sufficient; thus it is difficult to visualize the potential energy distribution. Figure 10 shows simplified schematic potential energy distribution curves estimated for air-cooled and water-quenched 304L (II) steels. In the water quenched specimen, the amount of α' martensite is slightly increased by the application of a magnetic field. In the air-cooled specimen, α' martensite does not nucleate even in a magnetic field of 7.96 MA/m. In Fig. 10, a small amount of α' martensite is estimated to form in very high magnetic fields, although it remains to be confirmed whether or not α' martensite can nucleate in magnetic fields over 7.96 MA/m.

Fig. 11 Simplified curves showing effects of cooling rate on the potential energy distribution of nucleation sites in Fe-25.5Ni-4Cr steel.

It is clear that there is a very large difference in the position and shape of the potential energy distribution curves between 304L (I) and 304L (II) steels even if they have similar chemical composition.

Figure 11 shows simplified curves of the potential energy distribution of air-cooled and water-quenched Fe-25.5Ni-4Cr steels. The details of the distribution curve of water-quenched Fe-25.5Ni-4Cr steel will be discussed in Section 4.3.

In 304L steel, the present authors showed in their previous paper¹⁾ that some internal strain or lattice defects are generated by water-quenching through thermal stress, and these act as nucleation sites for α' martensite. Similar internal strain or lattice defects are also thought to be induced in Fe-25.5Ni-4Cr steel by water-quenching. Therefore it is expected that internal strain or lattice defects generated in this steel do not act as nucleation sites.

On the other hand, in Fig. 7, the amount of α' martensite formed in zero magnetic field is larger than that reported in previous papers.^{2,3)} It is thought that this difference can be attributed to the difference in the method of water-quenching. That is to say, in previous studies, the silica tube was broken using a hammer in water about 5 s after it was taken out of the furnace. In the present research, the silica tube was broken using a hammer and a steel plate, which was set in water, about 3 s after it was taken out of the furnace; the cooling rate by water-quenching was higher in the present study than in the previous one.

In Fig. 4, there is a large scatter in data when the applied magnetic field is lower than around 6.37 MA/m. In order to determine the reason for this scatter, some blocks were soaked in liquid nitrogen after the magnetic field was raised to a certain intensity and held at this intensity. After soaking in liquid nitrogen for a certain time, saturation magnetization of the blocks was measured at room temperature, and then these procedures were repeated several times using the same specimen blocks. The results are shown in Fig. 12. The transformation proceeds isothermally and the incubation period differs for each block. Therefore, it was found that scatter in the amount of the martensite is large when the soaking time is short. As

Fig. 12 Isothermal transformation curves of Fe-25.5Ni-4Cr steel water-quenched after heating at 1573 K for 5 h. Each curve was obtained by the repetition of magnetic application at 77 K and measuring of amount of α' martensite at room temperature.

the magnetic field increases, the incubation period is thought to shorten and the scatter is reduced even when the soaking time is short.

4.2 Effect of re-heating

In their previous paper,¹⁾ the authors showed that the amount of α' martensite in 304L (II) steel is strongly affected by reheating: the amount of α' martensite slightly increases initially with re-heating temperatures up to 523 K, decreases markedly at re-heating temperatures between 523 and 773 K, and increases again above 773 K. They concluded that the decrease in the amount of α' martensite between 523 and 773 K was caused by the decrease in the number of nucleation sites through annihilation of some lattice defects induced by water-quenching. The occurrence of such annihilation was supported by the following two results: one was that the apparent activation energy was estimated to be about 200 kJ/mol for the decrease in the amount of α' martensite around 773 K; this value is similar to the activation energy for the diffusion of Fe, Cr and Ni in austenitic stainless steels.²⁴⁾ The other was that in the specimen re-heated at temperatures between 523 and 773 K, the amount of α' martensite does not increase even by applying a magnetic field of 20.70 MA/m. The increase in the amount of α' martensite above 773 K was attributed to lattice defects and/or residual strain induced by cooling process after re-heating, because the increase was not observed in specimens air-cooled from such reheating temperatures and the water-quenching rate from re-heating temperatures increased as the temperature increased.

As shown in Fig. 5, in Fe-25.5Ni-4Cr steel, re-heating after water-quenching from solution heat treatment temperature increases the amount of α' martensite slightly but the reheating temperature has little effect on the amount of α' martensite. From the latter result, it is expected that internal strain or lattice defects generated by water-quenching almost do not act as nucleation sites for the formation of α' martensite in this steel. Therefore, even if such internal strain or lattice defects were annihilated by re-heating, the amount of α' martensite would not be affected.

4.3 Effect of pre-strain

In Fe-25.5Ni-4Cr steel, a pre-strain of up to about 10% suppresses the formation of α' martensite and pre-strain larger than 10% enhances the formation of α' martensite (Fig. 6).

Regarding the former effect, pre-strain suppresses the formation of α' martensite also in 304L steel, although a very small pre-strain seems to increase the amount of α' martensite in a water-quenched specimen under a certain condition.^{2,3)} However, in the pre-strained 304L steel, the amount of α' martensite is hardly increased by the application of a magnetic field of 20.70 MA/m (Fig. 7), whereas the application of a magnetic field can easily increase the amount of α' martensite in the pre-strained Fe-25.5Ni-4Cr steel (Fig. 6).

Suppression of the formation of α' martensite by pre-strain has already been reported by several researchers.^{4,23,25,26)} Lagneborg⁴⁾ attributed this suppression to a decrease in the number of nucleation sites, while other researchers attributed this suppression to the work hardening of the matrix. When the work hardening suppresses the formation of α' martensite, the formation can be induced by the application of a magnetic field of which driving energy $\Delta G(\text{mag})$ is larger than the energy due to the work hardening of the matrix $\Delta G(\text{w.h.})$. In 304L steel pre-strained by more than about 5%, the amount of α' martensite almost cannot be increased by such a high magnetic field as 20.70 MA/m (Fig. 7). This fact supports Lagneborg.⁴⁾ The effect of pre-strain in 304L steel can be explained using Fig. 2. That is to say, in 304L steel, pre-strain suppresses the formation of α' martensite not by decreasing the potential energy of the nucleation sites generated by water-quenching (curve (a) in Fig. 2), but by reducing the number of nucleation sites (curve (b) in Fig. 2).

In order to confirm this hypothesis, values of $\Delta G(\text{mag})$ and $\Delta G(\text{w.h.})$ are estimated and compared. The value of $\Delta G(\text{mag})$ is calculated using eq. (2).²⁰⁾

$$\Delta G(\text{mag}) = H \cdot (J(\alpha') - J(\gamma)) \quad (2)$$

where H is the intensity of a magnetic field. $J(\alpha')$ is the saturation magnetization of martensite and is determined from the Slater-Pauling curve as mentioned in Chapter 2. $J(\gamma)$ is the saturation magnetization of austenite and is approximated to be zero.²⁰⁾

The value of $\Delta G(\text{w.h.})$ is estimated using eq. (3).

$$\Delta G(\text{w.h.}) = \Delta\tau \cdot S \quad (3)$$

where $\Delta\tau$ is the work hardening of austenite and S is the lattice shear strain which is thought to occur during the formation of α' martensite. The value of $\Delta\tau$ is determined from the increase in tensile stress ($\Delta\sigma$) in the stress-strain curve at room temperature; $\Delta\tau = (1/2) \cdot \Delta\sigma$. Temperature dependence of the work hardening of austenite is neglected.

As for S , several values have been proposed: 0.236 for the shear of $a/18\langle 112 \rangle$ on the $\{111\}$ plane of austenite (after Bogers and Burgers²⁷⁾) and 0.707 for the shear of $a/6\langle 112 \rangle$ on the $\{111\}$ plane of austenite (after Higo *et al.*²⁸⁾). Patel and Cohen²⁹⁾ assumed 0.2 for the shape shear strain in the formation of α' martensite. In the present study, 0.707 was used in order to estimate the largest value of $\Delta G(\text{w.h.})$.

Figures 13 and 14 show the correlation among $\Delta G(\text{mag})$,

Fig. 13 Correlation among $\Delta G(\text{mag})$, $\Delta G(\text{w.h.})$ and the formation of α' martensite in 304L (II) steel. Symbol $\bigcirc$ shows formation of α' martensite and symbol $\times$ shows the martensite does not form. Size of these symbols exhibits schematically amount of the martensite.

Fig. 14 Correlation among $\Delta G(\text{mag})$, $\Delta G(\text{w.h.})$ and the formation of α' martensite in Fe-25.5Ni-4Cr steel. Symbol $\bigcirc$ shows formation of α' martensite and symbol $\times$ shows the martensite does not form. Size of these symbols exhibits schematically amount of the martensite.

$\Delta G(\text{w.h.})$ and the formation of α' martensite in 304L (II) steel and Fe-25.5Ni-4Cr steel, respectively. In 304L steel, the formation of α' martensite is suppressed even in magnetic fields of which $\Delta G(\text{mag})$ is higher than $\Delta G(\text{w.h.})$ as shown by the plots in Fig. 13 for the specimen pre-strained by 5% and exposed to a magnetic field of 19.10 MA/m. This trend would be much clearer if 0.2 or 0.236 were adopted as the value of S in stead of 0.707.

On the other hand, in Fe-25.5Ni-4Cr steel, the formation of α' martensite can occur upon the application of magnetic fields of which $\Delta G(\text{mag})$ is much lower than $\Delta G(\text{w.h.})$. Therefore, in this steel, it is thought that the actual lattice strain must be smaller than 0.707. However, if the pre-strain has only the effect of suppressing the formation of α' martensite, higher magnetic fields should be necessary for the formation of α' martensite in the specimen subjected to a larger pre-strain. In contrast, Fig. 14 shows that α' martensite can be formed by the application of a 7.96 MA/m magnetic field even in the specimen pre-strained by 20%.

Therefore, it can be thought that pre-strain in Fe-25.5Ni-4Cr steel also has some effect of enhancing the formation of

Fig. 15 The amount of α' martensite formed in Fe-25.5Ni-4Cr steel subjected to various pre-strains after solution treated at 1573 K for 5 h and water-quenched as a function of magnetic field.

Fig. 16 Simplified potential distribution curves expected from Fig. 15 as one of possibilities for the Fe-25.5Ni-4Cr steel.

α' martensite. Figure 15 shows the amount of α' martensite formed in specimens subjected various pre-strains as a function of magnetic field. Each plot represents the mean value of data shown in Fig. 6. Following Fig. 15, the potential energy distribution curves shown in Fig. 16 are assumed for water-quenched and pre-strained Fe-25.5Ni-4Cr steel. The curve for the not pre-strained, as-solution heat treated steel is assumed to have two peaks: one peak is small and its potential energy is high, while the other is large and its potential energy is low. From Fig. 15, it is expected that the small peak is easily annihilated by a small pre-strain. However, this peak is not thought to be annihilated by re-heating, because no reduction in the amount of α' martensite is observed in specimens that were re-heated after water-quenching as shown in Fig. 5. The large peak in Fig. 16 can be expected from Fig. 15 to enlarge

a little by large pre-strain. Some strain concentration induced by a large pre-strain is thought to play the role of a nucleation site. Figure 17 shows the effect of pre-strain on the microstructures of Fe-25.5Ni-4Cr steel exposed to 5.97 MA/m magnetic field. Compared with the steel that was not pre-strained, the size of α' martensite plate or lath is small and the number of plates or laths is large in the steel pre-strained by about 40%. Therefore, Fig. 17 reveals that a large pre-strain increases the number of nucleation sites. However, Fig. 17 shows that α' martensite cannot be observed in some austenite grains of the pre-strained specimen, whereas in specimen that was not pre-strained, plates or laths of martensite are observed in almost all austenite grains. Considering this result, it is expected that a large pre-strain generates nucleation sites heterogeneously.

Fig. 17 Effects of pre-strain on microstructures of Fe-25.5Ni-4Cr steel applied a 5.97 MA/m magnetic field at 77 K. (a) not pre-strained ($f = 23.2\%$), (b) pre-strained by 9.6% ($f = 4.3\%$) and (c) pre-strained by 39.3% ($f = 23.3\%$)

5. Conclusion

The effects of solution heat treatment temperature, cooling rate from this temperature, pre-strain and re-heating on α' martensite formation were examined in Fe-25.5Ni-4Cr steel and 304L steel. The distribution of potential energy of nucleation sites for α' martensite was also estimated using experimental results obtained in magnetic fields of up to 20.70 MA/m. The main results are summarized as follows.

(1) In Fe-25.5Ni-4Cr steel, solution heat treatment temperature and cooling rate from this temperature have little effect on the formation of α' martensite at 77 K in magnetic fields over about 8 MA/m.

(2) In Fe-25.5Ni-4Cr steel, the amount of α' martensite increases as solution heat treatment temperature increases and as cooling rate decreases in magnetic fields lower than about 8 MA/m.

(3) In 304L steel, the amount of α' martensite increases as solution heat treatment temperature increases and as cooling rate increases. Therefore, the effect of cooling rate from solution heat treatment temperature in Fe-25.5Ni-4Cr steel is different from that in 304L steel, although the reason for this difference has not been clarified.

(4) In Fe-25.5Ni-4Cr steel, re-heating temperature has little effect on the amount of α' martensite. From this result, it is expected that internal strain or lattice defects generated by water-quenching almost do not act as nucleation sites for the formation of α' martensite in this steel. Therefore, even if such internal strain or lattice defects were annihilated by re-heating, the amount of α' martensite would not be affected.

(5) In Fe-25.5Ni-4Cr steel, pre-strain of up to about 10% suppresses the formation of α' martensite and pre-strain over 10% enhances its formation. Such a change of the amount of α' martensite with pre-strain is reduced as the magnetic field is increased.

(6) In Fe-25.5Ni-4Cr steel, it is expected that specimens solution heat treated at higher temperatures have two peaks on the potential energy distribution curve of nucleation sites and that the small peak is easily annihilated by a small pre-strain. However, this peak is not thought to be annihilated by re-heating. The large peak is expected to enlarge at larger pre-strain.

(7) The enhancing effect of pre-strain is not observed in 304L steel even in high magnetic fields. This supports the view that pre-strain suppresses the formation of α' martensite not through work hardening but through the annihilation of nucleation sites. In contrast, in Fe-25.5Ni-4Cr steel, it is expected that some strain concentration induced by a large pre-strain generates nucleation sites.

(8) The effects of heat treatment and pre-strain on the

formation of α' martensite are clearly different between Fe-25.5Ni-4Cr steel and 304L steel. This shows that the nature of the nucleation sites and the procedure for the formation of α' martensite differ between these two kinds of steels.

Acknowledgements

The authors are grateful to Kobe Steel Corporation, Nippon Steel Corporation, and Messrs. T. Saito, T. Shimizu and T. Mitsui, NRIM, for preparing the steels. They also wish to thank Dr. H. Wada, Messrs. M. Kosuge and M. Yuyama, the High Magnetic Field Research Station, NRIM, for their assistance in the experiments in high magnetic fields.

REFERENCES

- 1) Y. Kohno, H. Konishi, K. Shibata, K. Watanabe and S. Awaji: *Materials Science & Engineering*, **273-275** (1999), 333-338.
- 2) Y. Murakami, K. Shiabata, K. Watanabe and S. Awaji: *Netsu-syori*, **35** (1995), 335-340. (Japanese)
- 3) T. Shimozono, Y. Kohno, H. Konishi, K. Shibata, H. Ohtsuka and H. Wada: *Materials Science & Engineering*, **273-275** (1999), 337-341.
- 4) R. Lagneborg: *Acta Metal.*, **12** (1964), 823-843.
- 5) P. L. Mangonon, Jr. and G. Thomas: *Met. Trans.*, **1** (1970), 1577-1586.
- 6) B. Cina: *Acta Met.*, **6** (1958), 748-762.
- 7) H. Fujita and S. Ueda: *Acta Met.*, **20** (1972), 759-767.
- 8) T. Katayama and H. Fujita: *J. Japan Inst. Metals*, **52** (1988), 935-944. (Japanese)
- 9) J. A. Venables: *Phil. Mag.*, **7** (1962), 35-44.
- 10) P. M. Kelly: *Acta Met.*, **13** (1965), 635-646.
- 11) J. F. Breedis: *Trans. AIME*, **230** (1964), 1583-1596.
- 12) J. Dash and H. M. Otte: *Acta Met.*, **11** (1963), 1169-1178.
- 13) A. J. Goldman, W. D. Robertson and D. A. Koss, *Trans. AIME*, **230** (1964), 240-241.
- 14) T. Katayama and H. Fujita: *J. Japan Inst. Metals*, **52** (1988), 8-17. (Japanese)
- 15) Z. Nishiyama: *Martensitic Transformation*, New York, Academic Press, (1978).
- 16) K. C. Russell: *Metall. Trans.*, **2** (1971), 5-12.
- 17) M. Suezawa and H. E. Cook: *Acta Metall.*, **28** (1980), 423-432.
- 18) N. Lin, G. B. Olson and M. Cohen: *Metall. Trans.*, **23A** (1992), 2987-2998.
- 19) G. B. Olson and A. L. Roitburd: *Martensite*, ed. by G. B. Olson and W. S. Owen, ASM International, (1992), 149-174.
- 20) T. Kakeshita, K. Shimizu, S. Funada and M. Date: *Acta Metall.*, **33** (1985), 1381-1389.
- 21) K. Tsuzaki, N. Harada and T. Maki: *Supplement au J. de Physique*, **3**, **5** (1995), C8-167-172.
- 22) T. Kakesita, T. Saburi and K. Shimizu: *Materials Science & Engineering*, **273-275** (1999), 21-39.
- 23) G. Ghosh and G. B. Olson: *Acta Metall. mater.*, **42** (1994), 3371-3379.
- 24) Y. Iijima and K. Hirano: *Diffusion Process in Nuclear Materials*, ed. by R. P. Agarwala, Elsevier Science Publishers B. V., (1992), 169-200.
- 25) H. C. Fiedler, B. L. Averbach and M. Cohen: *Trans. ASM*, **47** (1955), 267-290.
- 26) P. M. Kelly and J. Nutting: *J. Iron St. Inst.*, **197** (1961), 199-211.
- 27) A. J. Bogers and W. G. Burgers: *Acta Met.*, **12** (1964), 255-261.
- 28) Y. Higo, F. Lecroisey and T. Mori: *Acta Met.*, **22** (1974), 313-323.
- 29) J. R. Patel and M. Cohen: *Acta Met.*, **1** (1953), 531-538.