Estimation of the System Free Energy of Martensite Phase in an Fe–Cr–C Ternary Alloy

Tomonori KUNIEDA, Masaaki NAKAI, Yoshinori MURATA,1) Toshiyuki KOYAMA2) and Masahiko MORINAGA1)

Graduate Student of Nagoya University, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603 Japan.
1) Department of Materials, Physics, and Energy Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603 Japan. 2) National Institute for Materials Science, Tsukuba 305-0047 Japan.

(Received on July 19, 2005; accepted on September 13, 2005)

The system free energy was estimated for the martensite phase of an Fe–Cr–C ternary alloy. The system free energy of the martensite phase is defined as, \( G_{sys} = G_0 + E_{surf} + E_{str} \), where \( G_0 \) is the chemical free energy, \( E_{surf} \) is the interfacial energy for the boundaries in the martensite microstructure, and \( E_{str} \) is the elastic strain energy due to the dislocations in the martensite phase. From the experimental results on SEM/EBSD, the interfacial energy was estimated to be 0.05 J/mol for the prior austenite boundary, 0.11 J/mol for the martensite packet boundary and 0.32 J/mol for both the martensite block and the lath boundaries in the quenched specimen. The total decrement in the interfacial energy accompanying annealing at 873 K for 100 h after quenching was estimated to be about 0.1 J/mol. Also, the elastic strain energy of the as-quenched specimen was estimated to be 7.1 J/mol. The total microstructural energy of the martensite phase was about 10 J/mol, which operates as a driving force for the microstructure evolution, e.g., recovery of dislocations and the coarsening of the sub-structures such as martensite-packet, -block and -lath.

KEY WORDS: martensite phase; heat-resistant steel; dislocation density; interfacial energy; system free energy; microstructure evolution.

1. Introduction

It is generally known that the creep strength of materials is related closely to their microstructures. The quantitative estimation of microstructure evolution (e.g., recovery of dislocations, coarsening of grain and coalescence of precipitates, etc.) is so important for the understanding of the long-term creep strength for high Cr ferritic steels consisting of the complicated microstructures. Namely, their microstructures are composed of the martensite phase, M\(_{23}C_6\) carbide, MX carbonitrides and intermetallic compounds (e.g., the Laves phase) as well as the ferritic phase.\(^1,2\) The creep strength of these steels was affected by the structural change of the martensite phase and the coalescence of both the Laves phase and the M\(_{23}C_6\) carbide. Recently, it has been reported that their long-term creep strength at 923 K is much smaller than the value extrapolated from a short-term creep strength. Such a large decrease in the long-term creep strength is interpreted as due to the inhomogeneous microstructure evolution during creep.\(^3\) Thus, one of the subjects of important in these days is in how to quantify the microstructure of the steels.

Recently, we have proposed that the system free energy concept is useful for the quantitative estimation of the microstructure evolution in the steels.\(^4\) This concept was made on the basis of the total energy change attendant on the microstructural energy change.\(^5\) In our previous study, the microstructure evolution of the Laves phase was elucidated with the aid of this system free energy concept. The purpose of this study is to estimate the system free energy change in the course of the microstructure evolution of the martensite phase in a high Cr heat resistant ferritic steel.\(^5\)

2. Theory of the System Free Energy

2.1. System Free Energy of the Martensite Phase

The system free energy is defined by the sum of a chemical free energy, \( G_0 \), an interfacial energy, \( E_{surf} \), and an elastic strain energy, \( E_{str} \). Then, the system free energy of the martensite phase is expressed by the following equation,

\[
G_{sys} = G_0 + E_{surf} + E_{str}
\] ............................(1)

Here, the chemical free energy, \( G_0 \), was set to be zero, because only the ferrite phase was treated in this study and the \( G_0 \) of the ferrite phase was employed as a standard of \( G_{sys} \), i.e. zero. In this study, we estimated the tempered martensite phase precipitating the M\(_{23}C_6\) carbide completely, as will be mentioned with experimental results. Therefore, carbon content of the standard ferrite phase corresponds to that of the tempered martensite phase. The interfacial energy \( E_{surf} \) was estimated in terms of the area fraction obtained from the experimental results as explained later. The elastic strain energy \( E_{str} \) was calculated from the dislocation density in the martensite lath. The low carbon martensite such as the experimental steel is a lath martensite which contains dislocations but no twins, so that the
elastic strain energy caused by the martensite transformation was assumed to be stored as the dislocation strain energy in the lath martensite. In such a case, the microstructure evolution from the martensite phase to the ferrite phase proceeds by the driving force of $E_{\text{surf}} + E_{\text{str}} (= G_{\text{sys}} - G_0)$. Therefore it is expected that the estimation of $G_{\text{surf}} + G_{\text{str}}$ makes it possible to predict the microstructure evolution.

2.2. Interfacial Energy for the Martensite Phase

The interfacial energy $E_{\text{surf}}$ was estimated by using the following equation,

$$E_{\text{surf}} = A \cdot \varepsilon_i \cdot V_i$$ \hspace{1cm} (2)

where $A$ is the interfacial area per unit volume, $\varepsilon_i$ is the energy density for the boundaries, $i$ is the type of boundaries and $V_i$ is the molar volume. The martensitic steels consist of the multi boundaries, i.e., the prior austenite phase boundary and the martensite packet-, block- and lath-boundaries. Then, Eq. (2) is modified into the following equation,

$$E_{\text{surf}} = (A_a \times \varepsilon_b + A_p \times \varepsilon_p + A_b \times \varepsilon_b) \times V_r$$ \hspace{1cm} (3)

Here, the subscripts, $a$, $p$, and $b$, indicate the prior austenite grain boundary, the martensite packet boundary and the block boundary, respectively. Both the lath and block boundaries are regarded as small-angle boundaries or twin boundaries, and sometimes these two boundaries are hard to be distinguished with each other. In this study, the values of $\varepsilon_b$, $\varepsilon_p$ and $\varepsilon_a$ in Eq. (3) are set to be $0.10 \text{J/m}^2$, $0.468 \text{J/m}^2$, and $0.76 \text{J/m}^2$, respectively.\(^6\)

2.3. Elastic Strain Energy for the Martensite Phase

As mentioned in Sec. 2.1, it was assumed that the elastic strain energy of the martensite phase could be approximate equivalent of the dislocation strain energy. Then, the elastic strain energy is expressed by the following equation,\(^7\)

$$E_{\text{dis}} = \frac{\mu b^2}{4\pi} \ln \frac{R_s}{r} \times \rho$$ \hspace{1cm} (4)

where, $\mu$ is the shear modulus and the value of pure iron $\mu = 8.0 \times 10^{10} \text{N/m}^2$ was used in this study,\(^9\) $b$ is the magnitude of the Burgers vector, i.e. $b=0.284 \text{nm}$ for iron, and $r$ is the radius of dislocation core to be set at $0.284 \text{nm}$ for iron. $R_s$ is the outer cut-off radius for calculating the strain energy around a dislocation, and $\rho$ is the dislocation density. Both $R_s$ and $\rho$ can be determined using experimental data.

3. Experimental Procedure

3.1. Steel Preparation

An Fe-11Cr-0.1C (mass%) ternary alloy was used in this study. The analyzed result of the chemical composition is listed in Table 1. The ingot of this alloy was prepared by vacuum induction melting and processed by hot-forging in a conventional way. In order to control the grain size to be about 100 mm, this alloy was normalized at 1 373 K for 5 h, followed by the tempering at $993 \text{K}$ for 20 h. Subsequently, it was cut into a plate with the size of $5 \times 5 \times 10 \text{mm}^3$. The plate was austenitized at 1 323 K for 5 h followed by quenching into water and then into liquid nitrogen. After this quenching treatment, the plate was annealed at $873 \text{K}$ for various times from 2 h to $1 000 \text{h}$. Also, a specimen annealed at $923 \text{K}$ for 1 year was prepared as a full-annealed specimen in order to use as a reference, i.e., the strain free ferrite phase.

3.2. Microstructure Observation

The specimen was polished mechanically with emery papers down to $\phi 2 000$ followed by the buff polishing with $\text{Al}_2\text{O}_3$ powders down to $0.3 \mu \text{m}$. In order to observe the prior austenite grain boundary, it was etched in a Vilella’s reagent with a $50 \text{mol}%-\text{glycerin}$, $17 \text{mol}%-\text{nitric acid}$ and $33 \text{mol}%-\text{hydrochloric acid}$. After the etching, the microstructure in the specimen was observed with an optical microscope (OM), a scanning electron microscope (SEM) equipped with an instrument for taking electron backscattered diffraction pattern (EBSD).

3.3. Analysis of X-ray Diffraction Peak Profile

Dislocation density of each specimen was measured by the X-ray diffraction, using a modified Williamson–Hall plot as well as a modified Warren–Averbach plot.\(^5\)\(^–\)\(^13\) The procedure is as follows; (i) Peak profiles of (110), (200), (211), (220), (310) and (222) reflections were measured with the Cu target operated at 40 kV and 30 mA. (ii) Integrated intensities of each reflection were normalized by the following equation,

$$\int_{-\infty}^{+\infty} I(\theta)d\theta = 1$$ \hspace{1cm} (5)

where $I(\theta)$ is the X-ray intensity and $\theta$ is the diffraction angle.\(^9\) Then the profiles were fitted by the pseudo-Voigt function.\(^14\) The normalized profiles were expanded into the Fourier series which gave the real part of the Fourier coefficients, $A(L)$ for each peak. (iii) The full-width at half-maximum (FWHM) of the normalized peaks can be evaluated by the modified Williamson–Hall plot,\(^11\)

$$\Delta K \equiv \frac{0.9}{D} + \frac{\pi M^2 b^2}{2} - \rho^{1/2} \sqrt{K C} + O(K^2 \sqrt{C})$$ \hspace{1cm} (6)

Here, the first term is related to the crystal size, and both the second and third terms are related to the dislocation density. $K = 2\sin \theta / \lambda$, and $\Delta K = 2\cos \theta (\Delta \theta / \lambda)$ is the magnitude of FWHM. $\lambda$ is the X-ray wavelength. $D$, $\rho$ and $b$ are the average particle size, the average dislocation density and the magnitude of the Burgers vector, respectively. Both $M$ and $O$ are the constants depending on the effective outer cut-off radius ($R_s$) of dislocations. $\bar{C}$ is the contrast factor of dislocations, which is the value depending on the elastic constants of the crystal.\(^13\) The average dislocation contrast factors, $\bar{C}_{\text{hkl}}$, for the specific (hkl) reflection can be represented as,

$$\bar{C} = \bar{C}_{\text{hkl}} (1 - qH^2)$$ \hspace{1cm} (7)

---

Table 1. Chemical composition of alloy investigated in this study, (mass%).

| Element | C | Cr | Fe |
|---------|---|----|----|
| %       | 0.10 | 11.01 | Bal. |

N: 11 ppm as an impurity.
where $C_{h00}$ is the average dislocation contrast factor for $(h00)$ reflections, and $H^2$ is expressed as $H^2 = (h^2k^2 + h^2l^2 + k^2l^2)$. $q$ is a parameter depending on the elastic constants of the crystal and the character of the dislocations in the crystals. The value of $C_{h00}$ is determined from the calculation based on elastic constants. The value of $C_{h00} = 0.285$ for pure iron was used in the present analysis. Equation (6) was converted into the quadratic form. In this form, the high-order term of Eq. (6) became negligible. By inserting Eq. (7) into the quadratic form, the following equation was obtained:

$$[(A k^2 - \alpha)/K^2 \equiv \pi M^2 b^2 \rho C_{h00}(1 - qH^2)/2]$$

Here, $\alpha$ is equal to $(0.9/D)^2$, and the value of $\alpha$ was set so as to obtain a linear relationship between the left side of Eq. (8) and $H^2$. As a result, the parameter $q$ can be determined experimentally. Now, $C$ is known and the dislocation density can be obtained by the modified Warren–Averbach method,

$$\ln A(L) \equiv \ln A'(L) - \rho B L^3 \ln \left(\frac{R}{L}\right)(K' C^2 + Q(K' C^2)^2)$$

where $A(L)$ is the real part of the Fourier coefficients, $A'$ is the size Fourier coefficient as defined by Warren, $B = \pi b^2/2$, $R$ is the effective outer cut-off radius of dislocations and $Q$ stands for the second-order terms of $K' C^2$ i.e., $K' C^2$. $L$ is the Fourier length defined as $L = n a_0$, where $a_0 = \lambda/2(\sin \theta_1 - \sin \theta_2)$, $n$ are integers starting from zero and $(\theta_2 - \theta_1)$ is the angular range of the measured diffraction profile. The dislocation density can be obtained from the coefficient of the second term in Eq. (9).

4. Experimental Results

4.1. Microstructure Observation

It was confirmed by the optical microscopic observation that the as-quenched specimen exhibited only the martensite single phase without any retained austenite phase. Figure 1 shows the typical OM and SEM images taken from the specimens annealed at 873 K for 2 h and 100 h. The precipitates observed in SEM images in Fig. 1 were identified as $M_23C_6$ carbide by the X-ray diffraction experiment using the extracted residues. In order to obtain the area fraction of each boundary, the average sizes of the prior austenite grain, martensite packet, block and lath with annealing time at 873 K are shown in Fig. 2. The every size increased with annealing time. Here, the prior austenite grain was the largest as might be expected. On the other
hand, the martensite block was the smallest. The interfacial energy of each interface in unit volume was calculated by Eq. (2) using the measured sizes shown in Fig. 2. The interfacial energy versus annealing time is shown in Fig. 3. It was found that the martensite block exhibited the largest interfacial energy, and the value was about 0.2 J/mol after annealing for 2 h. On the other hand, the prior austenite grain showed the smallest interfacial energy of about 0.05 J/mol after annealing for 2 h. This difference is attributed mainly to the difference in the area fraction. Therefore, it was found that the microstructure change of the martensite phase in the Fe–Cr–C alloy would be caused by the growth of the martensite block.

As shown in Fig. 4, the total interfacial energy decreased quickly in the initial stage of annealing, but slowly in the later stage. The decrement was about 0.15 J/mol. Here, \( E_{\text{surf}} \) of the as-quenched specimen could not be measured directly because of too fine microstructure. However, it can be estimated roughly to be 0.5 J/mol using the data shown in Figs. 2 and 3.

### 4.2. Estimation of the Elastic Strain Energy

Figure 5 shows the representative normalized (200) peak profiles. It was seen clearly that the as-quenched specimen exhibited a broad line profile. The FWHM decreased with increasing annealing time. The plot of the FWHM according to Eq. (8) is shown in Fig. 6, where used were \( (110), (200), (211), (220), (310) \) and \( (222) \) profiles in the as-quenched specimen. Using Eqs. (7) and (8), for the as-quenched specimen, the value \( q = 2.01 \) was obtained from the intercept point in the horizontal scale in Fig. 6. On the other hand, the Fourier coefficient of real parts \( A(L) \) was calculated by Fourier transformation from the normalized profiles shown in Fig. 5. Using the \( q \) value and \( A(L) \) value, the \( \ln A(L) \) versus \( K^2 \bar{C} \) plot was obtained according to Eq. (9). The fitting curve is the second-order of \( K^2 \bar{C} \). Figure 7 shows the result for the five reflections at different \( L \) value.
Now, the parameter \( Y = \rho B L^2 \ln (R_e/L) \) was set in Eq. (9) and reformed to the expression as follows,

\[
\frac{Y}{L^2} = \rho B \ln R_e - \rho B \ln L \quad \ldots \ldots \ldots (10)
\]

From Eq. (10), \( \rho \) and \( R_e \) were derived from the plot of \( Y/L^2 \) against \( \ln L \) as shown in Fig. 8, and \( \rho \) and \( R_e \) were estimated to be \( 5.4 \times 10^{14} \text{ m}^{-2} \) and 120 nm, respectively, for the as-quenched specimen. Table 2 shows the estimated values of \( R_e \) and \( \rho \) for the experimental specimen. It was found that compared with the value for the as-quenched specimen, the dislocation density decreased by about 80% after 2 h annealing.

The change in the total elastic strain energy per unit volume with annealing time is shown in Fig. 9. The elastic strain energy of the as-quenched specimen was about 7.1 J/mol. It decreased drastically in the initial stage of annealing. But the change became quite slow after 4 h annealing, although the value did not reach the equilibrium one, i.e. about 0.30 J/mol of the full-annealed ferrite phase.

5. Discussion

The elastic strain energy \( (E_{str}) \) of the as-quenched specimen was about 7.1 J/mol, whereas the interfacial energy \( (E_{int}) \) was about 0.5 J/mol. Thus the elastic strain energy was larger by an order of magnitude than the interfacial energy in the as-quenched specimen. In other words, most of the system free energy was the elastic strain energy in the as-quenched ternary alloy. Here, as shown in Fig. 6, the experimental value of \( q \) was obtained to be 2.01 in the as-quenched specimen. This \( q \) value is known to be a measure of the dislocation character. Values calculated theoretically in pure iron are 1.2 for pure edge dislocation and 2.8 for screw dislocation, respectively. Therefore, the result obtained in this study suggests that the amounts of the screw and edge dislocations are almost equal in the as-quenched specimen.

Although the elastic strain energy accounts for the major part of the system free energy in the as-quenched state, it decreased abruptly to about 1.1 J/mol with annealing at 873 K for a few hours, and then decreased very slowly during the subsequent annealing. As a result, although the ratio of the interfacial energy to the total system free energy was very small in the as-quenched state, it increased and became about twenty percent after annealing at 873 K for 100 h. This result indicates that the role of the interfacial energy on the microstructure evolution becomes large in the later stage of creep. In other words, it is considered that the strength of the martensite phase in the high Cr steels is subject to both the interfacial energy and the elastic strain energy in the later stage of creep.

When the standard energy level of the system free energy was set at that of the ferrite phase, the system free energy in the full annealed Fe–Cr–C alloy was about 0.30 J/mol. On the other hand, the system free energy after 1000 h anneal-
ing at 873 K was about 1.15 J/mol as shown in Fig. 10. Thus, the total free energy decreased very slowly during the subsequent annealing. Therefore, inhomogeneous nucleation of the ferrite phase might be necessary so as to approach the equilibrium value (the full annealing state) for a finite annealing time. This is probably the reason why the inhomogeneous microstructure evolution is observed frequently in high Cr ferritic steels.

6. Conclusion

The system free energy of the martensite phase in an Fe–Cr–C ternary alloy was estimated quantitatively. The results are summarized as follows.

The total system free energy of the martensite phase was about 7.6 J/mol in the as-quenched stage compared to the full annealed ferrite phase as the standard energy level. When the as-quenched specimen was annealed at 873 K for a few hours, the elastic strain energy decreased drastically from 7.1 J/mol to about 1 J/mol, and then kept decreasing very slowly during the subsequent annealing. As a result, the ratio of the interfacial energy to the total system free energy increased up to about 20% during the subsequent annealing. This value, 1 J/mol, worked as a driving force of the microstructure evolution during the subsequent annealing.

Acknowledgements

The authors would like to thank Dr. Azuma and Mr. Miki of the Japan Steel Works Ltd., for providing us the experimental steels. Also, we are grateful to Dr. M. Suganuma in the Aichi Industrial Technology Institute for his kind support to use the X-ray diffractometry and his useful discussion for the analysis. This work was supported in part by the Grant-in-Aid for Scientific Research of the Japan Society for the Promotion of Science (JSP), and also by “Nanotechnology Support Project of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan” in the Research Center for Ultrahigh Voltage Electron Microscopy, Osaka University.

REFERENCES
1) T. Fujita: *ISIJ Int.*, 32 (1992), 175.
2) Y. Murata, M. Morinaga, R. Hashizume, K. Takami, T. Azuma, Y. Tanaka and T. Ishiguro: *Mater. Sci. Eng. A*, A136 (2000), 251.
3) H. Kushima, K. Kimura and F. Abe: *Tetsu-to-Hagané*, 85 (1999), 841.
4) Y. Murata, T. Koyama, M. Morinaga and T. Miyazaki: *ISIJ Int.*, 42 (2002), 1423
5) T. Miyazaki and T. Koyama: *Mater. Sci. Eng. A*, A136 (1991), 151.
6) Y. Ono, K. Kimura and T. Watanabe: Computer Assisted Microstructure Control of Steels, ISIJ, Tokyo, (2000), 99.
7) H. Suzuki: Teni-ron Nyumon, Agn, Japan, (1967), 70.
8) Kinzoku Data Book, The Japan Institute of Metals, Sendai, (1984), 35.
9) M. Wilkens: *Phys. Status. Solid.*, 2 (1970), 359.
10) T. Ungar, I. Dragomir, A. Revesz and A. Borbely: *J. Appl. Crystallogr.*, 32 (1999), 992.
11) F. Yin, T. Hanamura, O. Umezawa and K. Nagai: *Mater. Sci. Eng. A*, A354 (2003), 31.
12) T. Unger, J. Gubicza, G. Ribarik and A. Borbely: *J. Appl. Crystallogr.*, 34 (2001), 298.
13) T. Unger and G. Tichy: *Phys. Status. Solid.*, 171 (1999), 425.
14) P. Dasgupta: *Fizika A* (Zagreb), 9 (2000), 2, 61.