Determination of Free Energy of δ -Ferrite/ γ -Austenite Interphase Boundary of Low Carbon Steels by *In-situ* Observation

Hongbin YIN, Toshihiko EMI and Hiroyuki SHIBATA

Institute for Advanced Materials Processing, Tohoku University, Katahira, Aoba-ku, Sendai, Miyagi-ken, 980-8577 Japan.

(Received on February 26, 1998; accepted in final form on April 8, 1998)

Phase transformations of δ -ferrite/ γ -austenite in low carbon steels containing 0.017 mass% phosphorus are observed *in-situ* by using a combination of confocal scanning laser microscope with infrared image furnace. Dihedral angles at triple points of one high energy δ/δ grain boundary and two incoherent δ/γ interphase boundaries are measured by holding the sample at temperatures where δ - and γ -phases co-exist in quasi-equilibrium. From the average value of observed dihedral angles, free energy of γ/δ incoherent boundary for a steel with low sulfur content (0.007 mass%) is estimated to be 0.450 J/m² at *ca.* 1 700 K. The effects of temperature and sulfur content on the dihedral angle and free energy of incoherent δ/γ boundary are also discussed.

KEY WORDS: free energy; dihedral angle; interphase boundary; grain boundary; δ -ferrite; γ -austenite; low carbon steel; confocal scanning laser microscope.

1. Introduction

Studies on the free energy of interphase boundary (referred as IB hereafter) in metals and alloys become increasingly important in materials science and engineering. Nucleation, growth and morphology of precipitate phase during phase transformation of metals and alloys are all considered to be primarily controlled by interfacial free energy between the precipitate and matrix.

For producing low carbon steels with finer microstructure in integrated mills with hot-charge-rolling or hot-direct-rolling process and in mini-mills with thin-slab-casting process, finer austenite (γ) grains are prerequisite because most of ferrite (α) grains nucleate and grow at the γ -grain boundary (referred as GB hereafter). In this respect, nucleation and growth of γ -grains in δ -matrix and hence the free energy of δ/γ IB are of particular interest. During welding of steels, high temperature $\delta \rightarrow \gamma$ transformation in the periphery of weld can take place, which will have strong influence on the properties of welded steels. Also, high speed continuous casting of peritectic steels is still a problem to steelmakers as the formation of surface cracks upon solidification of these steel slabs is caused by large volume contraction arising from peritectic transformation, $L + \delta \rightarrow \gamma$. To understand the nucleation and growth behaviors during solidification of liquid peritectic steels, free energies of the interfaces of L/δ and L/γ as well as the δ/γ interphase boundary are required. The free energies of L/δ and L/γ interfaces have been given by Turnbull¹⁾ and Ono *et al.*²⁾ However, the free energy of δ/γ interphase boundary remains unknown due to the difficulties associated with accurate measurement, especially at high temperatures over *ca.* 1 663 K.

The free energy of GB can be measured by zero-creep method which was thoroughly reviewed by Murr.³⁾ The δ/δ and γ/γ GB free energies of iron at high temperatures were determined with the zero-creep method by Inman and Tipler⁴⁾ and Hondros⁵⁾ which are reproduced in Table 1. At lower temperatures where the zero-creep method does not work, Van Vlack⁶⁾ provided another method to measure the γ/γ GB free energy and estimate α/α GB free energy of Fe–S alloy as listed in Table 1. For the solid/solid IB free energy in iron, only attempt made was also by Van Vlack⁶⁾ who estimated the α/γ interphase boundary free energy (see Table 1) from observed γ/γ GB free energy of Fe–S alloy. Other relevant data of surface and interface free energy of iron are also listed in Table 1.

When an incoherent secondary phase precipitates at a high energy GB of matrix phase as shown in Fig. 1, the free energy, σ_{IB} , of the incoherent IB can be calculated

Table 1. Surface and interfacial free energy of iron.

Surface or interface		Free energy (J/m ²)	Temperature (K)	Ref. No.
Surfaces	Liquid	1.902	1 808	7)
	δ -ferrite	1.950	1 723	4), 5)
	γ -austenite	2.100	1 623	4), 5)
Grain boundaries	α/α	0.765	1 378	6)*
	γ/γ	0.850	1 378	6)*
	γ/γ	0.756	1 623	4), 5)
	δ/δ	0.468	1 723	4), 5)
Interphase boundaries	Liquid/Solid	0.204	1 808	1)
	α/γ	0.612	1 378	6)*

* Fe–S alloy.

Fig. 1. Schematic diagram of force balance at a triple point of an incoherent precipitate at a high energy grain boundary.

from the force balance by Eq. (1) with observed dihedral angle, θ , at a triple point when the system reaches equilibrium:

$$\sigma_{IB} = \frac{\sigma_{GB}}{2 \cdot \cos(\theta/2)} \quad \text{.....(1)}$$

Here it is assumed that the free energy, σ_{GB} , of high energy GB is known and the strain energy of IB due to the volume change during transformation is negligible. In practice, however, it is difficult to observe the co-existing two phases at high temperatures. Quenching is an effective method for some metals and alloys to retain the high temperature microstructure and dihedral angles to room temperature, making the post-mortem determination possible. Unfortunately, δ/γ interphase boundary is hardly retained in low carbon steels during quenching because of the unavoidable $\gamma \rightarrow \alpha$ phase transformation. In this case, an *in-situ* observation method is definitely required.

In the present work, a Confocal Scanning Laser Microscope (CSLM) combined with an infrared image furnace is implemented with which the *in-situ* observation of the dynamic behaviors of grain and interphase boundaries of low carbon steels is made possible at high temperatures. The dihedral angles at triple points under quasi-equilibrium condition were measured and the free energy of δ/γ IB is determined.

2. Experimental

Detailed characteristics of the CSLM with infrared image furnace used in this study were described elsewhere.⁸⁾ The laser beam was confocally focused and scanned the sample surface, and reflecting beam from the sample surface was detected by a CCD image sensor and displayed on CRT monitor at a magnification of up to 2 100. Because of the confocal function of the CSLM, shallow undulation of the sample surface induced a marked intensity difference of the reflecting beam, which was shown on CRT brighter or darker than the flat area of sample surface. Also, small difference in reflectivity of a secondary phase from matrix surface affected the intensity of reflecting beam and was sensitively detected by the CCD image sensor. These two advantages of the CSLM made it possible to observe the phase transformation processes real-time and *in-situ* at high temperatures up to 1650°C. The different phases at the sample surface with varied reflectivities and heights that is caused by the volume change during transformation were clearly distinguishable. As an important comple-

Table 2. Composition of steel samples. (mass%)

Samples	C	Si	Mn	S	P	sol. Al
LC1	0.044	0.01	0.22	0.007	0.017	0.040
LC2	0.045	0.01	0.21	0.014	0.017	0.036
LC3	0.044	0.01	0.21	0.021	0.017	0.039

ment, the grain and interphase boundaries at the surface were also clearly observable both in static and dynamic states as grooves caused by interfacial tension acting at these boundaries inwardly against the bulk of sample. The dynamic picture of the sample surface was simultaneously recorded on videotape at a rate of 30 frames per second. The minimum and maximum view fields were $120 \times 90 \mu\text{m}^2$ and $960 \times 720 \mu\text{m}^2$, respectively.

The steel sample was machined into a disc ($\phi 4.3 \text{ mm} \times 2 \text{ mm}$), mirror polished, and set into a high purity alumina crucible ($\phi 5.5 \text{ mm} \times \phi 4.5 \text{ mm} \times 3 \text{ mm}$). The sample and crucible were installed into the furnace at one focal point of the gold plated ellipsoidal chamber. Then, the furnace chamber was evacuated to desorb gases from the surface of the sample and crucible. During experiment, ultra pure argon gas containing *ca.* 10 ppb of $\text{CO} + \text{CO}_2 + \text{H}_2\text{O} + \text{O}_2$ was further deoxidized with Mg powder (500°C) and subsequently with Ti foil (*ca.* 1400°C), and introduced into the chamber to prevent the sample surface from reoxidation. The sample was then heated to a desired temperature by a halogen lamp (max. 650 W) placed at the other focal point of the chamber at a program-controlled heating rate. Once the aimed temperature of the sample was reached, it was kept constant within $\pm 1 \text{ K}$ by an advanced computer control of heating power input. If needed, the sample was cooled at a precisely controlled cooling rate.

It was found that real temperature of the sample was different from the indication of thermocouple which was placed on crucible holder made of Pt sheet and used to control the furnace temperature during experiment. Therefore, the temperature of sample was calibrated by using another thermocouple placed at the sample surface in a preliminary experiment. The real sample temperature was corrected by the calibration results, accordingly. It was difficult to carry out experiment with the surface thermocouple simultaneously as the thermocouple wires impaired the quality of scanning image.

The compositions of three cold-worked low carbon steel samples, LC1, LC2 and LC3, utilized in this study are listed in Table 2. Except for the content of sulfur, the composition is the same for the three samples.

3. Results

3.1. The Dihedral Angles during δ/γ Phase Transformation

3.1.1. $\gamma \rightarrow \delta$ Phase Transformation

The $\gamma \rightarrow \delta$ transformation was observed at two holding temperatures after samples were heated at 100 K/min: one was at 1716 K, *ca.* 5 K above the upper limit of equilibrium temperature range where δ and γ co-exist (denoted Gamma I pattern), the other was at 1706 K,

ca. 5 K below that (denoted Gamma II pattern). It was assumed here that the equilibrium phase transformation temperatures are the same for the three samples.

When an LC3 sample was heated with Gamma I pattern shown in Fig. 2, the $\gamma \rightarrow \delta$ transformation took place at 1695 K with very quick growth of δ -phase in γ -matrix. It was ca. 5 K above the equilibrium temperature of $\gamma \rightarrow \delta$ transformation. After the temperature of the sample reached the aimed holding temperature of 1716 K, the transformation was almost completed leaving only small fraction of γ -phase with decreased δ/γ IB migration rate. At this stage, some δ -grains met each other and formed δ/δ GBs. In the places where the

Fig. 2. Gamma I and Gamma II temperature patterns and the times for pictures taken sequentially in Fig. 3 for an LC3 experiment with Gamma I pattern.

δ -grains had not touched yet, remaining γ -phase was squeezed between δ/γ IBs and gradually disappeared, leaving the δ/δ GBs behind. This process is illustrated in Fig. 3 in detail.

In Fig. 3(a), one second after the temperature reached the aimed 1716 K, three δ -grains met each other and formed three grain boundaries, lines AD, BE and CF, on the sample surface, thereby leaving γ -phase placed at the corners of the three δ -grains. At the three triple points, A, B and C, of the δ/δ GBs with γ -phase, three dihedral angles, θ_A , θ_B and θ_C were formed which were measured to be 108° , 113° and 128° , respectively. Four seconds later in Fig. 3(b), the shrinkage of γ -phase proceeded and two δ/δ GBs, BE and CF, met each other at point B. Simultaneously, dihedral angles of θ_B and θ_C were gone and a new dihedral angle, θ_B' , was formed at the new triple point. After that, the γ -phase only existed in one δ/δ GB, BD, as shown in Fig. 3(c), and two remaining dihedral angles, θ_A and θ_B' , were found to be almost constant with near identical values of 108° and 106° till the γ -phase totally disappeared after another 2 sec in Fig. 3(d).

At such a high temperature of over 1700 K, the strain energy caused by volume change during transformation at δ/γ IBs at free surface of the sample is expected to be small and easily relieved, and hence is ignored here. Under such circumstances, the three δ -GBs in Fig. 3 are high energy boundaries and the three δ/γ IBs are incoherent interfaces all with curved feature. Therefore, the three dihedral angles, θ_A , θ_B and θ_C in Fig. 3(a) should be the same according to Eq. (1) because the free energies of high energy boundary (σ_{GB}) and of incoherent interface (σ_{IB}) do not change much from one another.⁹⁾ The

Fig. 3. Sequence of disappearance of a γ -grain at δ/δ grain boundary during $\gamma \rightarrow \delta$ transformation while temperature of LC3 sample was held at 1716 K (Gamma I pattern). The time for each picture is counted from the start of isothermal holding and shown in Fig. 2.

observed difference among θ_A , θ_B and θ_C is, therefore, believed to be due to shape effect because the length of the IB, BC, is too short in Fig. 3(a). The fact that both θ_B and θ_C are high implies that the free energy of boundary BC (σ_{BC}) is high. The total free energy of boundary BC (E_{BC}) is given by

$$E_{BC} = l_{BC} \times \sigma_{BC} \dots\dots\dots(2)$$

where l_{BC} is the length of boundary BC. To minimize the total energy E_{BC} , the length l_{BC} and the free energy σ_{BC} will adjust together dynamically. Although the value of σ_{BC} increases, the value of l_{BC} decreases, making the total energy lowest possible. With regard to the influence of the shape effect on the free energy of incoherent interface, the two angles, θ_B and θ_C in Fig. 3(a), cannot be used to analyze the normal free energy of δ/γ IB.

In the case where the γ -phase remained at a single δ/δ

GB [Fig. 3(c)], θ_A and θ_B did not change much while the γ -phase shrunk away, and hence they are thought to be the intrinsic dihedral angles. Unfortunately, however, such γ -grains as surrounded by two δ/γ IBs were rarely observed during $\gamma \rightarrow \delta$ transformation. Instead, they were found frequently surrounded by more than two δ/γ IBs both in the experiments with patterns Gamma I and Gamma II, as typically shown in Figs. 4, 5 and 6.

As shown in Fig. 4, when another LC3 sample was heated with Gamma I pattern, remained γ -phase was observed to disappear just at the three δ -grain corners. Start of this sequence in Fig. 4 was 10 sec after the beginning of isothermal holding. Three dihedral angles, 1, 2 and 3 were measured to be 113° , 99° and 103° in Fig. 4(a), respectively, and did not change much with time until the γ -phase totally disappeared. It is clear that the three δ/δ GBs are not in three-fold symmetry, i.e., the angles between these GBs are not equal to the same 120° to each other. Thus, the shape effect may contribute to the difference in the dihedral angles as mentioned above although the differences are small. Also in Fig. 5 for an LC3 sample heated with Gamma II pattern and

Fig. 4. Sequence of disappearance of a γ -grain at three δ -grain corners during $\gamma \rightarrow \delta$ transformation while LC3 sample was held at 1716 K (Gamma I pattern). The sequence started 10 sec after temperature reached the aimed 1716 K.

Fig. 6. An example of γ -grain surrounded by four δ -grains after LC1 sample was held at 1706 K (Gamma II pattern) for 5 min. Among the four interphase boundaries, a semi-coherent interphase boundary (the upper one) appears, resulting in smaller angles, 1 and 2, than the other two, 3 and 4.

Fig. 5. An example of γ -grain surrounded by five δ -grains after LC3 sample was, (a) held at 1706 K (Gamma II pattern) for 10 min, and (b) cooled at 50 K/min after holding. All interphase boundaries show a curved feature with sharper dihedral angles.

Fig. 7. Sequence of γ -grain precipitation at δ/δ grain boundary during $\delta \rightarrow \gamma$ transformation while LC1 sample was held at 1700 K. The time for each picture started when the γ -grain became discernible ($\geq 0.5 \mu\text{m}$).

held for 10 min, observed γ -phase was surrounded by five δ -grains. In this case, the shape effect is believed to be much stronger, and hence the dihedral angles are considered not intrinsic ones. All δ/γ IBs in this case are incoherent interfaces because they changed their morphology to curved ones during cooling at 50 K/min as shown in Fig. 5(b). At the same time, quicker migration of the δ/γ interphase boundaries was observed locally at the δ/δ GBs, and all of the dihedral angles became sharper during the growth of the γ -grain, suggesting that the diffusion of carbon along the δ/δ GBs was quicker than that in the bulk.

It is concluded, therefore, that the use of the observed results of $\gamma \rightarrow \delta$ transformation is not suited to obtain intrinsic dihedral angle at the triple point of one high energy δ/δ GB and two incoherent δ/γ IBs. It should be mentioned here that the semi-coherent δ/γ interface and low energy δ/δ grain boundary were occasionally found in experiments. One example of the semi-coherent δ/γ IB is shown in Fig. 6 in an experiment for LC1 with Gamma II pattern, where angles 1 and 2 are smaller than angles 3 and 4. The reason for this may be due to the fact that the free energy of semi-coherent interface is generally lower than that of incoherent interface. Semi-coherent interface will not be studied in the present work since its free energy depends much on the orientation between δ and γ , which cannot be determined during the high temperature experiment. For common materials like the low carbon steels investigated here, the high energy grain boundary and incoherent interphase boundary are much more important than the low energy grain boundary and semi-coherent interphase boundary.

3.1.2. $\delta \rightarrow \gamma$ Phase Transformation

The $\delta \rightarrow \gamma$ transformation experiments were carried out by cooling the sample quickly to temperatures below the upper limit of equilibrium temperature range, in

Fig. 8. Sequence of γ -grain precipitation at three δ -grain corners during $\delta \rightarrow \gamma$ transformation while LC3 sample was held at 1703 K. The sequence starts when the γ -grain became discernible ($\geq 0.5 \mu\text{m}$).

which the γ and δ co-exist, after holding the sample for 10 min at 1716 K, *ca.* 5 K above the upper limit.

The growth of δ -grains still went on as mentioned before in the very beginning of holding at 1716 K, leaving some fraction of γ -phase at the corners of δ -grains. After these γ -grains totally disappeared within one minute of holding, the migration of δ/δ GBs was quick at first, then slowed down and finally stopped within 5 min. This is clearly the stabilization of δ -grains; some small grains are eaten up by larger ones and all grains are eventually almost equal-sized with honeycomb structure as commonly seen. Once the boundaries became stagnant there, they developed much deeper and clearer because of the GB tension acting at the free surface inwardly against the bulk of sample. Another 5 min later, the sample was ready to be cooled to the lower temperatures.

During holding after the cooling, the nuclei of γ -phase were always observed to grow at the δ/δ GBs and at the junctions of three δ/δ GBs because they provide γ -phase with favorable nucleation sites on free surface.^{10,11)} In Fig. 7 where an LC1 sample was held at 1700 K, a γ -grain nucleated at δ/δ GB grew quickly to its mature size of $165 \mu\text{m}$ in long-axis within 5 min. At this period, the dihedral angles were a little sharper than the mature ones and increased with time [Fig. 7(b)], but, once the γ -grain reached the mature size [Fig. 7(c)], its shape and the dihedral angles hardly changed even during a long period of holding [Fig. 7(d)], indicating that the system was close to its equilibrium. The dihedral angles in the quasi-equilibrium state in Fig. 7(d) are thought to be intrinsic ones which can be used to calculate the free energy of incoherent δ/γ IBs. Again, the strain energy at the δ/γ IBs will be neglected in the calculation.

An example of γ -grain precipitating at the junction of

Fig. 9. Sequence of γ -grain growth in δ/δ grain boundary during $\delta \rightarrow \gamma$ transformation while LC1 sample was held at different temperatures from 1705 to 1695 K. Times when each picture was taken are shown in Fig. 10.

Fig. 10. Relationship between holding temperatures and observed dihedral angle of the same γ -grain as shown in Fig. 9.

three δ/δ GBs is shown in Fig. 8, where an LC3 sample was held at 1703 K. The three δ/δ GBs were found to be of almost identical angles of *ca.* 120° to each other. The γ -grain also grew to its mature size within 5 min and the dihedral angles at the δ/γ junction did not change much during the growth of the γ -grain. The dihedral angles observed at 600 sec at each triple point are considered to be intrinsic ones, accordingly.

It should be noted here that when samples were cooled from one holding temperature to another, the angles rarely varied with different holding temperatures as shown for example in Figs. 9 and 10 for LC1. While the γ -grain was growing, the δ/γ IBs moved stepwise, leaving the traces of the growth steps as grooves on the free surface of the sample. From these traces behind the δ/γ IBs, it is also confirmed that the dihedral angle does not change even during the growth of γ -grain at such slow cooling condition. The dihedral angles were observed to decrease temporarily during rapid cooling as shown in Fig. 5. Once the cooling stopped, however, the angles gradually resumed its original value at the higher holding temperature, indicating that the tempera-

ture does not affect the dihedral angle. Comparison of Fig. 5 with Fig. 9 suggests that, although the diffusion in GB is generally thought to be faster than that in bulk, relatively large undercooling attained by higher cooling rate is needed to induce quicker diffusion of carbon at δ/δ GB. If this is the case, the γ -grains should grow faster along the δ/δ GB to make dihedral angles sharper.

Regarding these dynamic features of δ/γ IBs in the $\delta \rightarrow \gamma$ transformation experiments, measurement of the dihedral angles was made 10 min after the transformation occurred, at which the system is assumed to be in a quasi-equilibrium state. The difference in the angles for same sample, even for same γ -grain, still exists as shown in Figs. 7 and 8. This difference is believed to be caused by the difference in the free energies of GBs and IBs at different triple points. Microscopically, the free energies of high energy GB and incoherent IB will be different at different locations of these boundaries because the arrangement of atoms at these boundaries varies from place to place. Therefore, such variation of dihedral angles is difficult to predict in terms of the difference in the arrangement of atoms. Furthermore, the segregation of solute elements, like P, S and C, at δ/δ GBs and δ/γ IBs may vary at different locations, leading to the local fluctuation of the free energies at these boundaries. Statistically, however, the average of dihedral angles will provide useful information on the free energy of δ/γ IB, at least in the engineering application. In fact, the free energy of δ/δ GB listed in Table 1 is an averaged value. If the averaged value is used to calculate the σ_{IB} by Eq. (1), the angle should also be taken as an averaged one.

3.2. Dihedral Angles of Different Steels

The dihedral angles observed on the three kinds of steel samples are shown in Fig. 11. The average values of the dihedral angle for LC1, LC2 and LC3 are 131.5°, 118.3° and 107.3°, respectively, which are plotted in Fig. 12 vs. sulfur content of these samples. The value of dihedral angles decreases substantially with increasing sulfur content.

4. Discussion

The temperature coefficient of the free energy of high energy δ/δ GB in iron was determined by Inman and Tipler⁴⁾ to be $-0.25 \times 10^{-3} \text{ J/m}^2 \cdot \text{K}$. In the temperature range of 1690–1711 K where δ and γ are in equilibrium, the δ/δ GB free energy should change little from 0.476 to 0.471 J/m² with this temperature coefficient. Thus, the average δ/δ GB free energy of iron is taken to be a constant 474 J/m² within 1695–1705 K where the dihedral angles were measured in the present experiments. Hondros⁵⁾ found that the phosphorus in iron has marked effect on the free energy of δ/δ GB due to substantial segregation of phosphorus at δ/δ GB. The free energy data given by Hondros⁵⁾ are reproduced in Fig. 13 by assuming that the temperature coefficients of δ/δ GB free energy of Fe–P alloys are the same as that of iron, *i.e.*, $-0.25 \times 10^{-3} \text{ J/m}^2 \cdot \text{K}$. From Fig. 13, the free energy of high energy δ/δ GB of LC1 at 1695–1705 K is estimated to be about 0.370 J/m².

Fig. 11. Distribution of observed dihedral angles for LC1, LC2 and LC3 specimens in quasi-equilibrium state at 1695–1705 K.

Fig. 12. Average dihedral angles vs. sulfur contents for LC1, LC2 and LC3 specimens.

Fig. 13. Influence of phosphorus content on the free energy of high energy grain boundary of δ -iron at 1695–1705 K.

Here the effect of other solute elements in LC1 on δ/δ GB free energy should also be considered since they may segregate at δ/δ GB. So far, no data have been reported on the segregation of C, Mn, Si and S at δ/δ GB of iron at temperatures of the present experiments. Generally, Mn is neither surface active nor segregating, having a high solubility in iron. At 0.2 mass%, the effect of Mn on δ/δ GB free energy may be neglected at such high temperatures of *ca.* 1700 K.

Segregation of Si in b.c.c. α -Fe at low temperatures (*ca.* 700 K) was observed by Faulkner *et al.*¹²⁾ According to Viefhaus and Richarz's work,¹³⁾ however, if P presents in iron, Si will be rejected away from GB. This was confirmed by Erhart *et al.*¹⁴⁾ who found no segregation of Si at GB in Fe–P–Si alloys. Thus, the effect of Si on δ/δ σ_{GB} can also be ignored because of the presence of P in LC1.

Carbon is known to have a strong tendency to segregate at GB of b.c.c. iron. However, Hansel and Grabke¹⁵⁾ confirmed that, unlike the segregated P at GB, C does not decrease the GB cohesion, and hence, the δ/δ

σ_{GB} may not be affected by C in LC1.

Generally speaking, S is a strong surface active element and easily segregates at GB of iron. However, its segregation is greatly influenced by its solubility in iron with temperature. Briant¹⁶⁾ pointed out that sulfur segregation at GB of iron decreased with increasing temperature if bulk S content is less than the solubility limit. Under the present experimental conditions, the solubility limit of sulfur in δ -Fe at 1700 K is calculated after Turkdogan *et al.*¹⁷⁾ as 0.032 mass% for 0.2 mass% Mn. This concentration is much higher than the S content of 0.007 mass% in LC1. Therefore, the S segregation in δ/δ GB of iron is expected to be low at *ca.* 1700 K. Furthermore, if C exists in iron, the site competition between C and S atoms will occur at GB,^{18,19)} making the segregation of S much lower at δ/δ GB of LC1.

Neglecting the effects of Mn, Si, C and S in LC1 on σ_{GB} , σ_{GB} for LC1 equals 0.370 J/m² as estimated from Fig. 13 at 1695–1705 K. It can also be expected that Mn, Si and C will not much influence the free energy of incoherent δ/γ IB for the same reasons mentioned above. For S, however, careful analysis should be done because

Fig. 14. Free energy of incoherent δ/γ interphase boundary vs. sulfur contents of low carbon steels with 0.017 mass% phosphorus.

the solubility of S in δ - and γ -Fe is much different. After Turkdogan *et al.*,¹⁷⁾ the solubility limit of S in γ -Fe of LC1 is determined to be 0.022 mass% which is also much greater than the S content of LC1. The influence of S on σ_{IB} of LC1 is thus ignored. Accordingly, the free energy of incoherent δ/γ IB of LC1 is calculated by Eq. (1) with the observed average dihedral angle (131.5°) and the estimated σ_{GB} (0.370 J/m²) to be 0.450 J/m² which is higher than σ_{GB} .

For LC2 and LC3 containing, respectively, 0.014 and 0.021 mass% S, however, the effect of sulfur may not be neglected even though the effects of Mn, Si and C on both σ_{GB} and σ_{IB} are taken to be small. From the observed average value of dihedral angle of LC2 (118.3°) and LC3 (107.3°), it can be seen that the effect of sulfur on the σ_{IB} of δ/γ interphase boundary is much higher than that on the σ_{GB} of δ -Fe. From Eq. (1), the ratio of σ_{GB} to σ_{IB} is given by:

$$\frac{\sigma_{GB}}{\sigma_{IB}} = 2 \cdot \cos\left(\frac{\theta}{2}\right) \dots\dots\dots(3)$$

Assuming that the increase of S from 0.007 to 0.021 mass% will result in the reduction of both σ_{GB} and σ_{IB} , σ_{GB}/σ_{IB} will increase from 0.82 to 1.19 while θ decreases from 131.5° (LC1) to 107.3° (LC3), indicating that a larger reduction of σ_{IB} is caused by increasing S content. This may be due to the segregation of S at δ/γ IB, which is much greater for LC3 because the bulk concentration of S in LC3 (0.021 mass%) is almost the same as the solubility limit of S in γ -Fe (0.022 mass%). Thus, a large amount of S atoms will be rejected from γ -Fe and accumulates at δ/γ interphase boundary during the $\delta \rightarrow \gamma$ transformation. This will cause the sharp decrease in the free energy of δ/γ IB.

The S content is high in LC2 and LC3, but it is still less than the solubility limit of S in δ -Fe (0.032 mass%). If S content in LC3 does not affect σ_{GB} much, σ_{GB} of LC1 (0.370 J/m²) may be used for LC3. Then, σ_{IB} of LC3 is calculated to be 0.312 J/m² that is much smaller than σ_{GB} as illustrated in Fig. 14. For LC2, σ_{IB} is estimated to be 0.361 J/m² (also shown in Fig. 14) in the same way

as above, which is almost the same as σ_{GB} . It shows in Fig. 14 that the S content may have great influence on the value of free energy of incoherent δ/γ interphase boundary.

5. Conclusions

The δ/γ phase transformation process, nucleation and growth of δ -phase in γ -matrix or γ -phase in δ -matrix, of low carbon steels was *in-situ* observed with Confocal Scanning Laser Microscope. Focused on the static and dynamic dihedral angle measurements during $\delta \rightarrow \gamma$ transformation, the following results are obtained:

(1) The free energy of incoherent δ/γ interphase boundary of a low carbon steel (0.044 mass% C, 0.01% Si, 0.22% Mn, 0.007% S and 0.017% P) is calculated to be *ca.* 0.450 J/m² from the observed dihedral angles at triple point of one high energy δ/δ grain boundary and two incoherent δ/γ interphase boundaries.

(2) The dihedral angle is not affected by temperature in the narrow temperature range of δ/γ equilibrium, and hence, the free energy of incoherent δ/γ interphase boundary is almost the same in this temperature range.

(3) The dihedral angle strongly depends on the S content of low carbon steels. Increase of S content from 0.007 to 0.014 % then to 0.021 % decreases the averaged dihedral angle from 131.5° to 118.3° then to 107.3°. This indicates that the free energy of incoherent δ/γ interphase boundary will be reduced greatly by increasing sulfur in these low carbon steels.

Acknowledgements

The authors thank The Iron and Steel Institute of Japan (the 7th ISIJ Research Promotion Grant) and the Ministry of Education, Science, Sports and Culture, Japan [Grant in Aid Scientific Research (c) 09650804] for their financial support.

REFERENCES

- 1) D. Turnbull: *J. Appl. Phys.*, **21** (1950), 1022.
- 2) T. Ono, T. Umeda and Y. Kimura: Jpn. Soc. Promoting Sci., 19th Committee, 19-10403 (1982), Solidification-313.
- 3) L. E. Murr: *Interfacial Phenomena in Metals and Alloys*, Addison-Wesley, London, (1975), 130.
- 4) M. C. Inman and H. R. Tipler: *Met. Rev.*, **8** (1963), 105.
- 5) E. D. Hondros: *Proc. R. Soc., Ser. A*, **286** (1965), 479.
- 6) L. H. Van Vlack: *Trans. AIME*, **191** (1951), 251.
- 7) D. R. Poirier, H. Yin, M. Suzuki and T. Emi: *ISIJ Int.*, **38** (1998), 229.
- 8) H. Chikama, H. Shibata, T. Emi and M. Suzuki: *Mater. Trans., JIM*, **37** (1996), 620.
- 9) D.A. Porter and K.E. Easterling: *Phase Transformation in Metals and Alloys*, Chapman & Hall, London, (1992).
- 10) J. W. Cahn: *Acta Metall.*, **4** (1956), 449.
- 11) W. Huang and M. Hillert: *Metall. Mater. Trans.*, **27A** (1996), 480.
- 12) R. G. Faulkner, E. A. Little and T. S. Morgan: *J. Nucl. Mater., PT.B.*, **191-194** (1992), 858.
- 13) H. Viehhaus and B. Richarz: *Mater. Corros.*, **46** (1995), 306.
- 14) H. Erhart, H. J. Grabke and R. Moller: *Arch. Eisenhüttenwes.*, **52** (1981), 451.
- 15) H. Hansel and H. J. Grabke: *Scr. Metall.*, **20** (1986), 1641.
- 16) C. L. Briant: *Acta Metall.*, **33** (1985), 1241.
- 17) E. T. Turkdogan, S. Ignatowicz and J. Pearson: *J. Iron Steel Inst.*, **180** (1955), 349.
- 18) K. S. Shin and B. H. Tsao: *Scr. Metall.*, **22** (1988), 585.
- 19) S. Suzuki, S. Tani, K. Abiko and H. Kimura: *Metall. Trans. A*, **18A** (1987), 1109.