UDC 620 . 184 / . 186 : 620 . 192 . 45 : 669 . 14

Effect of Oxide on the Solidification Structure of Steel

Takashi MOROHOSHI* Tooru MATSUMIYA

Masafumi ZEZE

Abstract

Solidification structure control is important to improve the inner quality and performance of steel products. To increase equiaxed grains, catalysts for the nucleation of Fe were investigated. As a result, some catalysts are effective for the nucleation of δ -Fe, but the effective catalyst for γ -Fe is unknown. In this study, the effects of β -ZrO₂ and α -Al₂O₃ on the solidification structure and the undercooling of 0.75 mass%C steel were investigated. The results indicate that β -ZrO₂ acted as a heterogeneous nucleation site for γ -Fe. In discussion, the interfacial energy difference between liquid Fe and solid Fe both in the case of facing ZrO₂ and Al₂O₃ ($\gamma_{cL} - \gamma_{cS}$), which are key elements for nucleation capability, were estimated.

1. Introduction

Increasing equiaxed grains of solidification structure is effective to reduce center segregation and porosity of steel casting products. Consequently, electromagnetic stirring and low-temperature casting are widely applied in steel casting processes. In addition, there are studies on the possibility of using non-metallic inclusions (hereinafter, "inclusions") in molten steel as heterogeneous nucleation sites for Fe (catalysts) in solidification to promote equiaxed crystallization. When the lattice misfit between solid Fe and a catalyst is small, equiaxed grains increase.^{1,2)} There are two types of solidified primary grains depending on the steel components: δ -Fe(bcc) and γ -Fe(fcc). Since the crystal structure of δ -Fe differs from that of γ -Fe, the catalyst effective for each type may be different.

To date, many studies have been performed on components for which the solidified primary crystals are δ -Fe (δ -Fe solidification steel). There are reports that when TiN³⁻⁷ and REM₂O₃⁸ are formed in molten steel, equiaxed crystallization of the solidification structure is promoted—forming MgAl₂O₄ and MgO prior to crystallization of the TiN results in high fractions of equiaxed grains, in particular.⁵⁻⁷ In addition, the influence of catalysts on the nucleation of δ -Fe has been studied through the measurement of undercooling during solidification.^{1, 2, 9} Meanwhile, there are only a few reports on catalysts effective for the nucleation of γ -Fe^{9, 10} and there are no particular study reports on changes in the solidification structure. Therefore, catalysts that are effective for the equiaxed crystallization of components for which the solidified primary crystals are γ -Fe (γ -Fe solidification steel) and that are industrially useful have not been precisely specified. In this study, we calculated the lattice misfit between γ -Fe containing 0.75 mass%C and some inclusions to find effective catalysts. We studied possibly effective catalysts for 0.75 mass%C steel as an example of γ -Fe solidification steel using the lattice misfit as an indicator. From the results, we estimated that β -ZrO₂ would be effective as will be described later. In our experiments, Zr-deoxidized 0.75 mass%C steel of 20 kg was casted and undercooling of 500 g molten steel with a ZrO₂ tablet immersed was measured to study the heterogeneous nucleation capability of β -ZrO₂ experimentally from the viewpoints of changes in the solidification structure and undercooling.

To specify effective catalysts, the lattice misfit is evaluated in general. However, other factors may have influence.^{1, 2)} Accordingly, the contribution of the lattice misfit to heterogeneous nucleation was studied through estimation by dividing interfacial energy that works in heterogeneous nucleation into a structural energy term caused by the lattice misfit and another chemical energy term.¹¹⁾

2 Calculation of the Lattice Misfit between γ -Fe and β -ZrO,

The lattice misfit between γ -Fe and catalysts (inclusions) was calculated from the planar disregistry, δ (%), that was proposed by Bramfitt¹) and given by Equation (1). As a result, in the combination of β -ZrO₂ and γ -Fe, the value was small.¹²)

$$\delta_{(hkl)_{Fe}}^{(hkl)_{C}} = \frac{1}{3} \sum_{i=1}^{3} \frac{|(d_{[uvw]_{C}^{i}} \cos\theta) - d_{[uvw]_{Fe}^{i}}|}{d_{[uvw]_{Fe}^{i}}} \times 100$$
(1)

Where, $(hkl)_{c}$ is the plane index of the catalyst, $[uvw]_{c}$ is an orientation within the plane $(hkl)_{c}$, and $d_{[uvw]_{c}^{i}}$ is the interatomic spacing

^{*} Senior Researcher, Dr. Eng., Casting-Rolling Research Lab., Process Research Laboratories 20-1 Shintomi, Futtsu City, Chiba Pref. 293-8511

along $[uvw]_{C}$ (hkl)_{Fe} is the plane index of the Fe, $[uvw]_{Fe}$ is an orientation within the plane, and $d_{[uvw]_{Fe}^{i}}$ is the interatomic spacing along $[uvw]_{Fe}$. Also, θ is the angle between $[uvw]_{C}$ and $[uvw]_{Fe}$.

The crystal structure of ZrO, varies depending on the temperature. The liquidus line temperature of 0.75 mass%C steel calculated by Hirai's equation¹³⁾ is 1743 K. According to the O-Zr binary phase diagram¹⁴, the structure is β -ZrO₂ (tetragonal, 1478 to 2650 K) at this temperature. Figure 1^{12} shows the crystallographic relationship at the interface that is the combination of a crystal plane and orientation for which the lattice misfit between β -ZrO₂ and γ -Fe is the smallest. Figure 2^{12} shows that between α -Al₂O₂ and γ -Fe. Lattice constants at 1743 K were calculated; the planar disregistry between the (001) of β -ZrO₂ and the (001) of γ -Fe was 1.5%.¹² This value is smaller than the lattice misfit of $3.9\%^{1}$ between δ -Fe and TiN, which is effective as a heterogeneous nucleation site for δ -Fe. Therefore, β -ZrO, may be effective as a catalyst for γ -Fe (0.75 mass%C steel). On the other hand, the planar disregistry between α -Al₂O₂ and γ -Fe is large at 8.1%¹² and thereby it may not be so effective.

3. Experimental Procedures

3.1 Casting of 20-kg molten steel

Electrolytic iron was melted in Ar atmosphere with a high-frequency induction furnace and the molten iron was deoxidized with Al or Zr. The composition of the iron was adjusted targeting 0.75 mass%C and 20 kg ingots were made from them.

Table 1¹² lists the chemical composition of the ingots. The so-

[010]_{γ-Fe} [010]_{β-Zr02} [110]_{γ-Fe} [110]_{β-Zr02} [110]_{β-Zr02} [100]_{γ-Fe} [100]_{γ-Fe} [100]_{γ-Fe}

Fig. 1 Crystallographic relationship at the interface between the (001) of β -ZrO₂ and the (001) of γ -Fe¹²)

lidification structure of the cross sections was observed and the equiaxed grain ratio and equiaxed grain size were measured. Inclusions were observed with a scanning electron microscope (SEM) and the composition of each inclusion was analyzed.

3.2 Measurement of undercooling of 500 g molten steel

To simulate inclusions in molten steel, ZrO_2 tablets and Al_2O_3 tablets with a diameter of 6 mm and height of 2 mm were made from reagent powder. Each was set at the bottom of a crucible. With the tablet immersed in the molten steel, the undercooling was measured during furnace cooling. **Table 2**¹² lists the chemical composition of the ingots.

Usually, it is difficult to maintain the number density of inclusions in molten steel at the same level between all samples. Therefore, when only the deoxidizing element was added, not only the heterogeneous nucleation capability of each type of oxide but also the number density in the molten steel may affect the undercooling. The surface area of the tablet is significantly larger than that of inclusions in molten steel. Therefore, solidification may certainly occur on the surface of the tablet and thereby the heterogeneous nucleation capability of β -ZrO₂ and α -Al₂O₃ themselves may be evaluated separately from the effect of the number density in the molten steel.

4. Experimental Results

4.1 Solidification structure of the 20-kg ingots and inclusions in them

Figure 3 (a)¹² shows the solidification structure of the cross section on the left half of each ingot. Columnar grains were formed on the surface that was in contact with the mold and equiaxed grains



Fig. 2 Crystallographic relationship at the interface between the (0001) of α -Al,O₃ and the (111) of γ -Fe¹²)

Table 1	Chemical	composition	of 20 kg	ingots	(mass%) ¹²⁾
					· /

Sample	С	Si	Mn	Р	S	Al	Zr	Ν	T.O
Base	0.77	0.85	0.82	0.02	0.021	0.023	-	0.0061	0.0015
Z1	0.71	0.82	0.83	0.02	0.018	< 0.010	0.003	0.0056	0.0010
Z2	0.73	0.87	0.84	0.02	0.019	< 0.010	0.010	0.0028	0.0012
Z3	0.78	0.86	0.80	0.02	0.017	< 0.010	0.192	0.0050	0.0014

Table 2 Chemical composition of 500g ingots for undercooling measurement (mass%)¹²⁾

Tablet	С	Si	Mn	Р	S	Al	Zr	T.O
Al ₂ O ₃	0.71-0.73	0.71-0.81	0.74-0.75	0.018-0.020	0.0006-0.0011	0.052 - 0.057	-	< 0.001
ZrO_2	0.72-0.74	0.72-0.75	0.70-0.78	0.019-0.022	0.0010-0.0012	0.043-0.066	0.077 - 0.089	< 0.001-0.0013

were formed within the areas indicated by the arrows in the figure. Figure $3(b)^{12}$ shows enlarged views of the equiaxed grains at the center of the ingots. In the case of the sample without Zr addition, coarse branched dendrite structure was observed while in the case of the sample with Zr addition, fine globular grains were observed. **Figure 4**¹² shows the ratio of the thickness of the equiaxed grain zone to that of each ingot. **Figure 5**¹² shows the equivalent circle diameters of the equiaxed grains. The mean equivalent circle diameter of the branched dendrite structure of the sample without Zr addition was approximately 5 mm, while that of the globular grains of the sample with Zr addition was approximately 1 mm. Thus, adding



Fig. 3 Solidification structure of 20kg ingots, (a) Half cross section of ingots, (b) Enlarged parts of (a)¹²



Fig. 4 Equiaxed grain ratio of 20 kg ingots¹²⁾



Fig. 5 Equivalent circle diameter of equiaxed grain¹²⁾

Zr increased the equiaxed grain ratio and fine globular grains.

Figure 6¹²⁾ shows SEM images (backscattered electron (BSE) images) of inclusions observed in the 0.192 mass%Zr steel along with the elemental maps for Zr and O. In each figure, three agglomerated square-shaped inclusions are observed. These figures indicate that all of them are ZrO_2 . On the other hand, for the comparative sample with Al addition, Al_2O_3 was formed. The results above suggest that for the sample with Zr addition, ZrO_2 that had been formed in the molten steel acted as a heterogeneous nucleation site (a catalyst) for γ -Fe, which increased the equiaxed grain ratio.

4.2 Measurement results of the undercooling of the 500-g molten steel

Figures 7¹²⁾ and **8**¹²⁾ show the undercooling measurement results. Figure 7¹²⁾ shows the thermal history of the steel with the Al₂O₃ tablet immersed. Figure 8¹²⁾ shows that of the steel with the ZrO₂ tablet immersed. The horizontal axis shows the time elapsed after the furnace was turned off. After approximately 120 s from the start of furnace cooling, the two lines are linear for a few tens of seconds. The cooling rates are 0.7 K/s for both cases. However, the temperature changes before the temperature reaches the minimum value around 200 s differ between them. For the experiment using the Al₂O₃ tablet (Fig. 7¹²⁾), the cooling rate after approximately 120 s is retained at 0.7 K/s and the temperature reaches the minimum value of 1 720.6 K at 204 s. Immediately after that, the temperature for 10 s



Fig. 6 BSE image of ZrO, and elemental maps for Zr or O¹²⁾



Fig. 7 Thermal history of 0.75 mass%C steel with an Al₂O₃ tablet¹²⁾



Fig. 8 Thermal history of 0.75 mass%C steel with a ZrO, tablet¹²⁾

(liquidus line temperature).

On the other hand, for the experiment using the ZrO_2 tablet (Fig. 8¹²⁾), the cooling rate starts decreasing before the temperature reaches the minimum value as its characteristic. Specifically, at point (s) (192 s) in the figure at which the temperature is 1733.5 K, the line starts deviating from the straight line; and as the cooling rate gradually decreases, the temperature reaches the minimum value of 1724.4 K. After that, the temperature increases at a slower rate than that in Fig. 7¹²⁾ and reaches the maximum temperature. In the experiment using the ZrO_2 tablet, solidification may have started at point (s) in the figure at which the cooling rate started decreasing. On the other hand, in the experiment using the Al_2O_3 tablet, since the time interval from when the cooling rate starts decreasing to when the temperature reaches the minimum value is significantly short, deviation of the line from the straight line may not be observed.

Accordingly, undercooling was defined as follows: For the case using an Al₂O₃ tablet, undercooling was defined as the difference between the minimum temperature and the maximum temperature after the temperature started increasing again (recalescence); for the case using the ZrO₂ tablet, it was defined as the difference between the temperature at point (s) in the figure at which the cooling rate started decreasing and the maximum temperature. **Figure 9**¹² shows the undercooling measured based on the definitions. The white circles indicate individual measured values and the black circles indicate mean values. The error bars show $\pm 1 \cdot \sigma$ with the standard deviation as σ . The undercooling in the experiment using the Al₂O₃ tablet is 17.7±5.0 K while in the experiment using the ZrO₂ tablet, it is 8.9±5.0 K. The undercooling in the latter case is smaller. These results show that ZrO₂ is more effective than Al₂O₃ as a catalyst for 0.75 mass%C steel.

5. Discussions

Figure 10 illustrates heterogeneous nucleation. The equilibrium of interfacial energy is expressed by the following Young's equation.

 $\begin{array}{l} \gamma_{\rm CL} = \gamma_{\rm CS} + \gamma_{\rm SL} \cdot \cos\theta_{\rm CSL} \qquad (2) \\ \mbox{Where, } \gamma_{\rm CL} \mbox{ is the interfacial energy between the catalyst and liquid phase, } \gamma_{\rm CS} \mbox{ is that between the catalyst and solid phase, } \gamma_{\rm SL} \mbox{ is that between the catalyst and solid phase, } \gamma_{\rm SL} \mbox{ is that between the catalyst and solid phase, } \gamma_{\rm SL} \mbox{ is that between the catalyst and solid phase, } \gamma_{\rm SL} \mbox{ is that between the catalyst and solid phase, } \gamma_{\rm SL} \mbox{ is that between the catalyst and solid phase, } \gamma_{\rm SL} \mbox{ is that between the solid phase and liquid phase, and } \theta_{\rm CSL} \mbox{ is the contact angle of the solid phase on the catalyst. The smaller the contact angle, } \theta_{\rm CSL}, \mbox{ the easier the nucleation occurs. Equation (2) indicates that the larger the value of (} \gamma_{\rm CL} - \gamma_{\rm CS} \mbox{), the smaller } \theta_{\rm CSL} \mbox{ is. However, there are only a few measurement results for the } \gamma_{\rm CS} \mbox{ between solid Fe and an oxide^{15,16} \mbox{ and there are no reports on the } \gamma_{\rm CS} \mbox{ between solid Fe and } \mbox{ and } \gamma_{\rm CS} \mbox{ between solid Fe and an oxide^{15,16} \mbox{ and there are no reports on the } \gamma_{\rm CS} \mbox{ between solid Fe and } \mbox{ and } \gamma_{\rm CS} \mbox{ between solid Fe and } \mbox{ and } \gamma_{\rm CS} \mbox{ between solid Fe and } \mbox{ and } \gamma_{\rm CS} \mbox{ between solid Fe and } \mbox{ and } \gamma_{\rm CS} \mbox{ between solid Fe and } \mbox{ and } \gamma_{\rm CS} \mbox{ between solid Fe and } \mbox{ and } \gamma_{\rm CS} \mbox{ between solid Fe and } \mbox{ and } \gamma_{\rm CS} \mbox{ between solid Fe and } \mbox{ and } \gamma_{\rm CS} \mbox{ between solid Fe and } \mbox{ and } \gamma_{\rm CS} \mbox{ between solid Fe and } \mbox{ and } \gamma_{\rm CS} \mbox{ between solid Fe and } \mbox{ and } \gamma_{\rm CS} \mbox{ between solid Fe and } \mbox{ and } \gamma_{\rm CS} \mbox{ between solid Fe and } \mbox{ and } \gamma_{\rm CS} \mbox{ between solid Fe and } \mbox{ and } \gamma_{\rm CS} \mbox{ between solid Fe and } \mbox{ and } \gamma_{\rm CS} \mbox{ and } \gamma_{\rm CS} \mbox{ and } \gamma_{\rm CS} \mbox{ and } \gamma_{\rm CS$



Fig. 9 Undercooling for nucleation of γ -Fe with an Al₂O₃ tablet or with a ZrO₂ tablet¹²⁾

ZrO₂.

Turnbull¹¹ divided $\gamma_{\rm CS}$ into a structural energy term, $\gamma_{\rm CS}^{\rm str}$, and chemical energy term, $\gamma_{\rm CS}^{\rm ch}$.

$$\gamma_{\rm CS} = \gamma_{\rm CS}^{\rm str} + \gamma_{\rm CS}^{\rm och} \tag{3}$$

The structural energy term is interfacial energy to be generated by structural irregularities in atomic arrangement (lattice misfit). The chemical energy term is interfacial energy to be generated by differences in the bond energy of various types of atomic species.¹⁷) Therefore, the lattice misfit can be regarded as an indicator for $\gamma_{\rm CS}^{\rm str}$. $\gamma_{\rm CS}^{\rm str}$ and $\gamma_{\rm CS}^{\rm ch}$ were estimated using models and the influence of the lattice misfit on interfacial energy and heterogeneous nucleation was discussed as shown below.

5.1 Estimation of the structural energy term, $\gamma_{\rm CS}^{~~str12)}$

Van der Merwe¹⁸⁾ calculated the interfacial energy caused by dislocations arranged periodically in one direction along an interface between two crystals A and B having different lattice constants.

$$\gamma_{CS}^{\text{str}}_{\text{one direction}} = (\mu c/4\pi^2) [1 + \beta - (1 + \beta^2)^{1/2} - \beta \ln \{2\beta (1 + \beta^2)^{1/2} - 2\beta^2\}]$$
(for along one direction) (4)
$$\beta = 2\pi (c/p) (\lambda_{+}/\mu)$$
(5)
$$p = ab/(b-a)$$
(6)

Where, p is the distance between the dislocations, a is the lattice constant of crystal A, and b is that of crystal B ($a \le b$).

$$2/c = 1/a + 1/b$$
(7)
Where c is a reference lattice constant

$$1/\lambda_{+} = (1 - v_{a})/\mu_{a} + (1 - v_{b})/\mu_{b}$$
(8)

Where, λ_{+} is an effective elastic constant, v_{a} is the Poisson's ratio of crystal A (=0.3), v_{b} is that of crystal B (=0.3), μ_{a} is the modulus of rigidity of crystal A, and μ_{b} is that of crystal B.

$$\mu = (\mu_a + \mu_b)/2$$
(9)
Where, μ is the interfacial rigidity modulus.
$$\mu = E/2 (1+\nu) \quad (i=a,b)$$
(10)

 $\mu_{i} = E_{i}/2(1+v_{i}) \quad (i=a,b)$ (10) Where, E_{i} is the Young's modulus of crystal A and B.

The first half, $1+\beta-(1+\beta^2)^{1/2}$, in the bracket in Equation (4) indicates the dislocation core energy. The latter half, $-\beta \ln \{2\beta(1+\beta^2)^{1/2} - 2\beta^2\}$, in the bracket indicates the energy of the elastic strain field.

Equation (6) expresses the distance between the dislocations, p, using lattice constants a and b. Since a is smaller than b, dislocations have been introduced into crystal A and p=(P+1)a=Pb (P is a positive integer). Equation (6) is obtained using P=a/(b-a), which was obtained by modifying the second and third sides in the aforementioned equation.

Equation (7) is a definition of reference lattice constant c. The number of lattice planes included in p is p/a for crystal A and p/b for crystal B. The number of lattice planes with the spacing c included in p is the mean value of the two crystals, (p/a+p/b)/2=p/c.

Equation (9) is the modulus of rigidity of the interface that is the mean modulus of rigidity of crystals A and B.

To calculate $\gamma_{\rm CS}^{\rm str}$ using Van der Merwe's model, the lattice constants of the solid Fe and catalyst, and modulus of rigidity or Young's modulus at the solidification temperature (1743 K in this study) are required.



Fig. 10 Interfacial energy acting for the heterogeneous nucleation

The calculation was performed on the interface that was a combination of a lattice plane and orientation for which the lattice misfit was the smallest. Therefore, as a and b in Equations (6) and (7), interatomic spacing $d_{[uvw]_{oxide}}$ and $d_{[uvw]_{\gamma\text{-}Fe}}$ shown in Fig. 1 $^{12)}$ and Fig. 2^{12} were used.

The Young's moduli of Al₂O₃ and ZrO₂ at 1743 K were obtained as follows: Values in a literature for Al₂O₂ and 5 mass%CaO-ZrO₂¹⁹⁾ were referred to; and the values within the range where the temperature dependency is in a linear relationship (for Al₂O₂, 673 to 1223 K and for 5 mass%CaO-ZrO2, 873 to 1173 K) were used for extrapolation.

The Young's modulus of Fe at 1743 K was obtained as follows: Among the experimental values by Mizukami et al.,²⁰⁾ the values at the temperature lower than the zero-ductility temperature (ZDT) were used to obtain a regression line; and it was used for extrapolation. Data on all the three steel grades was used since there was no significant difference between the steel grades.

Equation (4) expresses the structural energy caused by the arrangements of dislocations in the one axial direction. However, an interface is two dimensional. Therefore, dislocations may be arranged in independent two axial directions. Accordingly, assuming that there is no interaction between the dislocations in the two directions, the result for the one axial direction calculated using Equation (4) was doubled and the value was used as the structural energy term value of the interface between the catalyst and solid Fe. As a result, $\gamma_{\rm CS}^{\rm str}_{(\beta-ZrO_2/\gamma-Fe)}$ of the interface between β -ZrO₂ and γ -Fe was 51 mJ/m² and $\gamma_{CS}^{\text{max}}(\alpha,A_{1,O_{3}/\gamma},F_{e})$ of the interface between α -Al₂O₃ and γ -Fe was 319 mJ/m².¹²⁾ The former is approximately one sixth (1/6) of the latter.

5.2 Estimation of the chemical energy term, $\gamma_{\rm CS}^{~~ch12)}$

Ohta et al.²¹⁾ used Kaptay's equation²²⁾ shown below to estimate the interfacial energy between ZrO₂ and solid Fe and between Al₂O₂ and solid Fe.

$$= \gamma_{cr} + \gamma_{r} (0.01 - 0.11 \cdot \cos\theta_{cr})$$
(11)

 $\gamma_{\rm CS}$ Where, γ_{CL} is the interfacial energy between the inclusion and liquid phase, $\gamma_{\rm L}$ is the surface energy of the liquid phase, and $\theta_{\rm CL}$ is the contact angle of the liquid phase on the inclusion. In the derivation of Equation (11), the lattice misfit has not been considered and the equation expresses interfacial energy of an ideally coherent interface. That is to say, since γ_{CS}^{str} has not been considered, Equation (11) expresses the chemical energy term, $\gamma_{\rm CS}^{~~{\rm ch}}$. This can be confirmed from the facts that $\gamma_{\rm CL}$, $\gamma_{\rm L}$, and $\theta_{\rm CL}$ in Equation (11) are the physical properties of liquid metals and thereby they are not related to the crystal structure of a solid.

According to the results calculated by Ohta et al.,²¹⁾ the chemical energy term, $\gamma_{\rm CS}^{\rm ch}_{\rm (ZrO_2/Fe)}$, of the interfacial energy between ZrO₂ and solid Fe is 1760 mJ/m²; and the chemical energy term, $\gamma_{\rm CS}^{\rm ch}_{\rm (Al_2O_3/Fe)}$, of the interfacial energy between Al₂O₃ and solid Fe is 2480 mJ/m². 5.3 Influence of the structural energy and chemical energy

terms on heterogeneous nucleation¹²⁾

The Young's equation (Equation (2)) in heterogeneous nucleation indicates that as $(\gamma_{\rm CL} - \gamma_{\rm CS})$ is larger, the contact angle, $\theta_{\rm CSL}$, is smaller, thus, the heterogeneous nucleation capability is higher. Therefore, $(\gamma_{CL} - \gamma_{CS})$ can be regarded as an indicator for heterogeneous nucleation capability. The following equation was obtained by dividing $(\gamma_{\rm CL} - \gamma_{\rm CS})$ into a structural energy term and chemical energy term and organizing them.

$$\gamma_{\rm CL} - \gamma_{\rm CS} = (\gamma_{\rm CL}^{\rm ch} + \gamma_{\rm CL}^{\rm str}) - (\gamma_{\rm CS}^{\rm ch} + \gamma_{\rm CS}^{\rm str}) = (\gamma_{\rm CL}^{\rm ch} - \gamma_{\rm CS}^{\rm ch}) + (-\gamma_{\rm CS}^{\rm str})$$
(12)

Where, since at the interface between the catalyst and liquid metal, no structural energy works, $\gamma_{\rm CL}$ str was determined as zero. Since $\gamma_{\rm CS}^{\rm str}$ is always equal to or larger than zero, Equation (13) holds.

 $\gamma_{\rm CL} - \gamma_{\rm CS} \leq \gamma_{\rm CL}^{\rm ch} - \gamma_{\rm CS}^{\rm ch}$ (13) This equation shows that the upper limit of $(\gamma_{\rm CL} - \gamma_{\rm CS})$, i.e., the lower limit of θ_{CSL} , $\theta_{CSL\ min}$, is determined by $(\gamma_{CL}^{ch} - \gamma_{CS}^{ch})$ consisting of only the chemical energy terms. Due to $(-\gamma_{CS}^{ch})$ added to $(\gamma_{CL}^{ch} - \gamma_{CS}^{ch})$ $\gamma_{\rm CS}^{\rm \ ch}$), the contact angle, $\theta_{\rm CSL}$, becomes larger than the lower limit.

Table 3¹²⁾ lists the calculation results of $(\gamma_{CL}^{ch} - \gamma_{CS}^{ch}), (\gamma_{CL}^{c} - \gamma_{CS}),$ and $(-\gamma_{\rm CS}^{\rm str})/(\gamma_{\rm CL}^{\rm }-\gamma_{\rm CS})$ for the β -ZrO₂/ γ -Fe interface and α -Al₂O₃/ γ -Fe interface. $(-\gamma_{CS}^{str})/(\gamma_{CL}^{-}-\gamma_{CS}^{-})$ can be regarded as an indicator that shows the contribution of the structural energy term to heterogeneous nucleation capability. The table shows that the values of both $(\gamma_{CL}^{ch} - \gamma_{CS}^{ch})$ and $(-\gamma_{CS}^{str})$ are larger in the case of the β -ZrO₂/ γ -Fe interface; as a result, the value of $(\gamma_{\rm CL} - \gamma_{\rm CS})$ in the case of the β -ZrO₂/ γ -Fe interface is larger than that in the case of the α -Al₂O₃/ γ -Fe interface; and the contribution of $(-\gamma_{\rm CS}^{\rm str})$ to $(\gamma_{\rm CL}^{\rm }-\gamma_{\rm CS}^{\rm })$ is lower in the case of the β -ZrO₂/ γ -Fe interface, being less than 30%. Thus, β -ZrO₂ is more effective as a catalyst than α -Al₂O₂ from the viewpoints of both chemical energy and structural energy terms.

5.4 Relationship between heterogeneous nucleation capability and dispersiveness of catalysts in molten steel

This paper discussed nucleation capability of a single catalyst. To make a steel ingot with high fractions of equiaxed grains, it is important for many effective catalysts to disperse in molten steel. To realize this, the wettability between catalysts (inclusions) and molten steel must be good. The following equation is obtained by modifying Equation (11).

$$\gamma_{\rm CL}^{\rm ch} - \gamma_{\rm CS}^{\rm ch} = -\gamma_{\rm L} (0.01 - 0.11 \cdot \cos\theta_{\rm CL}) \tag{14}$$

This equation shows that the smaller the contact angle, θ_{CI} , of the liquid metal on the catalyst and the more easily the catalyst gets wet with the molten steel, the larger the value of $(\gamma_{CL}^{\ ch} - \gamma_{CS}^{\ ch})$ is. For the catalyst with large $(\gamma_{CL}^{ch} - \gamma_{CS}^{ch})$, $\theta_{CSL_{min.}}$ (the lower limit of θ_{CSL}) is small as described above. Therefore, $\bar{\theta_{\rm CSL}}$ may be small even when a structural energy term is added. For that, it is important for the catalyst to have a low-index plane for which the lattice misfit with solid Fe is small. Thus, as a rough trend, effective catalysts may tend to disperse in molten steel and heterogeneous nucleation capability and dispersiveness may be realized at the same time to the extent possible.

6. Conclusions

(1) A catalyst effective for equiaxed crystallization of 0.75 mass%C steel for which the primary crystal is y-Fe was studied by calculation of the planar disregistry as an indicator and

Table 3 Calculation of $(\gamma_{CL}^{ch} - \gamma_{CS}^{ch})$, $(\gamma_{CL}^{-} - \gamma_{CS}^{ch})$ and $(-\gamma_{CS}^{str})/(\gamma_{CL}^{-} - \gamma_{CS}^{ch})^{12}$

Interface	$\gamma_{\rm CL}^{\rm ch21)}$	$\gamma_{\rm CS}^{\rm ch21)}$	$\gamma_{\rm CL}^{\rm ch} - \gamma_{\rm CS}^{\rm ch}$	$-\gamma_{\rm CS}^{\rm str12)}$	$\gamma_{\rm CL} - \gamma_{\rm CS}$	$(-\gamma_{\rm CS}^{\rm str})/(\gamma_{\rm CL}-\gamma_{\rm CS})$
	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)	(-)
β -ZrO ₂ / γ -Fe	1630	1 760	-130	-51	-181	0.28
α -Al ₂ O ₃ / γ -Fe	2290	2480	-190	-319	-509	0.63

 β -ZrO₂ for which the value was 1.5% was selected. Zr was added to 20 kg molten steel to form ZrO₂ in the steel and it was cast. The equiaxed grain ratio significantly increased.

- (2) In the measurement of undercooling, a ZrO_2 tablet or an Al_2O_3 tablet simulating inclusions was immersed into 500 g molten steel containing 0.75 mass%C. As a result, the undercooling was smaller in the case using the ZrO_2 tablet than that in the case using the Al_2O_3 tablet. ZrO_2 may be more effective as a catalyst for the nucleation of γ -Fe.
- (3) $(\gamma_{CL} \gamma_{CS})$ that affects the contact angle, θ_{CSL} , was divided into $(\gamma_{CL} \gamma_{CS} \gamma_{CS} \gamma_{CS})$ consisting of chemical energy terms and $(-\gamma_{CS} \gamma_{CS})$ that is a structural energy term and they were estimated. As a result, both values were larger in the case of the β -ZrO₂/ γ -Fe interface than those in the case of the α -Al₂O₃/ γ -Fe interface. These results show that β -ZrO₂ is effective as a catalyst from the viewpoints of both chemical energy and structural energy terms.

References

1) Bramfitt, B.L.: Metall. Trans. 1, 1987 (1970)

- 2) Ohashi, T. et al.: Tetsu-to-Hagané. 62, 614 (1976)
- 3) Itoh, Y. et al.: Tetsu-to-Hagané. 66, 710 (1980)
- 4) Takeuchi, H. et al.: Tetsu-to-Hagané. 66, 638 (1980)
- 5) Fujimura, H. et al.: Tetsu-to-Hagané. 87, 707 (2001)
- 6) Kimura, K. et al.: Tetsu-to-Hagané. 98, 601 (2012)
- 7) Isobe, K.: ISIJ Int. 50, 1972 (2010)
- 8) Nuri, Y. et al.: Tetsu-to-Hagané. 66, 628 (1980)
- 9) Nakajima, K. et al.: Metall. Mater. Trans. B. 34B, 539 (2003) 10) Nakajima, K. et al.: ISIJ Int. 46, 807 (2006)
- 11) Turnbull, D.: Impurities and Imperfections. Cleveland, USA, ASM,
- 1955, p. 121
- 12) Morohoshi, T. et al.: Tetsu-to-Hagané. 105, 502 (2019)
- 13) Edited by the Iron and Steel Institute of Japan: Tekko-Binran (Handbook of Iron and Steel). Vol. I. Basic. 3rd ed. Tokyo, Maruzen, 1981, p.205
- 14) Massalski, T.B.: Binary Alloy Phase Diagrams Vol. 2. Ohio, USA, ASM, 1986, p.1797
- 15) Pilliar, R. M. et al.: J. Phil. Mag. 16, 181 (1967)
- 16) Murr, L. E.: Mater. Sci. Eng. 12, 277 (1973)
- 17) Enomoto, M.: Bull. Iron Steel Inst. Jpn. 11, 294 (2006)
- 18) Van der Merwe, J. H.: J. Appl. Phys. 34, 117 (1963)
- 19) Wachtman, J.B. et al.: J. Am. Ceram. Soc. 42, 254 (1959)
- 20) Mizukami, H. et al.: Tetsu-to-Hagané. 81, 792 (1995)
- 21) Ohta, H. et al.: ISIJ Int. 46, 22 (2006)
- 22) Kaptay, G.: Metall. Mater. Trans. A. 32A, 993 (2001)



Takashi MOROHOSHI Senior Researcher, Dr. Eng. Casting-Rolling Research Lab. Process Research Laboratories 20-1 Shintomi, Futtsu City, Chiba Pref. 293-8511



Masafumi ZEZE Dr. Eng. Nishinippon Institute of Technology (Formerly Chief Researcher, Yawata R & D Lab.)



Tooru MATSUMIYA Formerly Senior Advisor, Sc. D. Research & Development Nippon Steel & Sumitomo Metal Corporation