1. Introduction

Along with Mg and Ca, rare earth elements (REEs) such as Ce and La are typical elements present in commercial graphite nodularizing agents. Additions of REE-contained nodularizing agents are known to increase the number of graphite nodules1,2) and to promote the uniformity of graphite nodularity in ductile iron with thickness varied.3) Due to the strong affinities of REEs with dissolved oxygen4) and dissolved sulfur5) in molten iron, non-metallic inclusions such as RE oxides, sulfides, and oxy-sulfides are produced. In investigating the formation mechanism of nodular graphite, numerous studies have since identified the presence of these inclusions at the center of nodular graphite.6–8) Hence, it is ascertained that non-metallic inclusions of REEs could serve as effective heterogeneous sites for graphite nucleation. In studying the effects of non-metallic compounds on the nucleation of graphite in cast iron, Ueda et al. experimentally determined that compounds with low interfacial energy with the nucleated solids showed a stronger nucleating efficiency and, the interfacial energy between two solids were affected by crystallographic mismatch.9)

The general approach applied to specimen preparation in previous studies is nodularizing treatment.1–8) Considering that nodularizing treatment is a series of processes involving the dissolution/melting of nodularizing agent, followed by reactions with solutes (S, O etc.) to form inclusions and, finally, heterogeneous nucleation and growth of graphite, it is understandable that under such complexities, it is rather difficult to comprehensively evaluate the heterogeneous nucleation of graphite.

In attempting to overcome the limitations of previous studies, the main purpose of this study focuses on evaluating graphite nucleation on heterogeneous substrates during solidification of cast iron, and the central concept is illustrated in Fig. 1. Hypereutectic Fe–C–Si alloys are intentionally contact-melted and solidified on RE2O3 (RE; La, Yb) substrates. Because RE oxides are known heterogeneous nucleus materials of nodular graphite,6) it is predicted that graphite nucleates heterogeneously on the substrate during solidification of cast iron, and the central concept is illustrated in Fig. 1. Hypereutectic Fe–C–Si alloys are intentionally contact-melted and solidified on RE2O3 (RE; La, Yb) substrates. Because RE oxides are known heterogeneous nucleus materials of nodular graphite,6) it is predicted that graphite nucleates heterogeneously on the substrate.
solidification (Fig. 1(b)). Observations of the alloy/substrate interface, therefore, provide important information relating to the nucleation and development of graphite during solidification.

In the present investigation, 2 types of RE sesquioxides, La$_2$O$_3$ and Yb$_2$O$_3$, are selected as substrate materials. Despite sharing similar thermodynamic characteristics and empirical formula, La$_2$O$_3$ and Yb$_2$O$_3$ are crystallographically distinct; La$_2$O$_3$ has a type-A (hexagonal) structure whereas Yb$_2$O$_3$ has a type-C (cubic) structure. In the evaluation of graphite precipitation behavior, it is important to understand how such differences in crystal structure will affect the heterogeneous nucleation of graphite. In addition, the effects of 0.01 mass% S addition on the precipitation behavior of graphite are investigated.

2. Experiment Method

2.1. Base Alloys Preparation

To evaluate the heterogeneous nucleation of graphite on non-metallic substrates, the chemical composition of the base alloy was determined to be Fe-4.1mass%C-2.5mass%Si. The crystallization temperature of primary graphite at this composition is expected to be 1 365°C under equilibrium conditions. Besides, in investigating the effects of S on the precipitation behavior of graphite, another charge with 0.01% S addition was prepared. Raw materials used in the preparation of base alloys were: electrolytic iron (>99.5% purity, provided by Toho Zinc Co., Ltd.), graphite powder (>99.9% purity, Kojundo Chem. Lab. Co., Ltd.), metallic silicon (>99.999% purity, Kojundo Chem.) and FeS (>99% purity, Kojundo Chem.). Each charge weighed approximately 10 g and was heated in an alumina crucible (purity 99.6%, Nikkato Co.) to 1 500°C, held for 10 min, and furnace-cooled at a rate of approximately 200°C/min in Ar atmosphere (50 ml/min). The carbon and sulfur contents of the base alloys were quantified using the combustion/infrared absorption method (LECO CS600, LECO Co.), and the results are shown in Table 1.

2.2. Substrates Preparation

La$_2$O$_3$ (>99.9%, Kojundo Chem.) and Yb$_2$O$_3$ (>99.9%, Wako Pure Chem.) powders were used in the present investigation. Due to the high activity of La$_2$O$_3$ to hydroxylation and carbonation, La$_2$O$_3$ powder was preheated at 950°C for 60 min and the powder was stored in a vacuum desiccator prior to shaping. La$_2$O$_3$ and Yb$_2$O$_3$ powders were isostatically pressed at 460 MPa into a size of 47.3% increase in total volume, causing the sintered substrates to expand and disintegrate over time. Consequently, overall observation and characterization of the alloy/substrate interface were viable without significantly damaging the interface. On the other hand, unlike type-A (A: La, Ce, Pr, Nd) sesquioxides, type-C (Dy, Ho, Yb) sesquioxides are less prone to hydroxylation and carbonation. As a result, complete separation of Yb$_2$O$_3$ substrates and the alloy was unattainable. Despite being partially covered in Yb$_2$O$_3$, overall observation and characterization of precipitated phases at the interface were feasible.

The alloy/substrate interfaces of the specimens were examined with SEM-EDS at an accelerating voltage of 20 kV (JSM-6510LA; JED-2300 AnalysisStation, JEOL Ltd.) and precipitated phases were characterized by XRD (Smart-Lab 3, Rigaku Corp.). In addition, to study the microstructure development of the contact-melted alloy, the specimens were fine-cut and the cross sections were investigated.

2.4. Image Processing

Quantitative analyses of the aspect ratio (AR) of precipitated graphite in base alloys and number of graphite nodules in contact-melted specimens were performed by analyzing 5 SEM images using image analysis software (ImageJ). SEM images were first subjected to image thresholding followed by binarization. The size of nodular graphite in the binary images was evaluated under the conditions stated in Table 2.

Table 1. Carbon and sulfur contents of base alloys.

| Base Alloy                  | C (mass%) | S (ppmw) |
|----------------------------|-----------|----------|
| Fe-4.1%C-2.5%Si (reference)| 4.00      | <9       |
| Fe-4.1%C-2.5%Si-0.01%S (0.01%S) | 4.00      | 95       |

Fig. 2. Schematic diagram of contact melting experiment.
3. Experimental Results

3.1. Microstructure of Base Alloys

Figure 3 shows SEM images of the base alloys. It can be seen that the morphologies of graphite mainly consisted of primary and eutectic graphite flakes (Figs. 3(a) and 3(b)). The microstructure obtained can be explained using time-resolved X-ray observations by Sugiyama et al.\textsuperscript{17} They observed that the solidification sequence of hypereutectic grey iron was initiated by the formation of primary graphite, followed by precipitation/growth of \(\gamma\)-dendrite, formation of fine graphite granules, and coupled growth of eutectic at the final stage of the solidification process.

The distribution of graphite AR of both base alloys is given in Fig. 4. Compared to the reference alloy, it is noticeable that the overall distribution of 0.01%S-added alloy shifted towards groups with a larger AR, indicating a thinning of graphite crystals as a result of S addition. Such changes in the precipitated graphite microstructures can be associated with the flake graphite promoting effects of S.\textsuperscript{18} Nevertheless, it can be concluded that the addition of 0.01%S alone does not contribute to the formation of nodular graphite in the microstructure.

3.2. Alloy/substrate Interface of Contact-melted Base Alloys on RE\textsubscript{2}O\textsubscript{3} (RE; La, Yb)

The SEM images and XRD patterns of the alloy/substrate interface of contact-melted base alloys are summarized in Figs. 5 and 6, respectively. As shown in Figs. 5(a) and 5(b), precipitates with grain sizes ranging from 100 to 300 \(\mu\text{m}\) were observed at the interface of contact-melted alloy on La\textsubscript{2}O\textsubscript{3}. Along with the XRD pattern obtained in Fig. 6(a), it is ascertained that the precipitates were graphite, which showed an overall crystallographic orientation in the c-direction ([0001] direction). In the case of Yb\textsubscript{2}O\textsubscript{3} substrate, despite being mainly covered in Yb\textsubscript{2}O\textsubscript{3}, graphite precipitation at the periphery of the interface was confirmed (Figs. 5(e) and 5(f)). In addition, the precipitated graphite also demonstrated an overall orientation in the c-direction (Fig. 6(c)). The above observations suggest that after the heterogeneous nucleation of graphite crystals on RE\textsubscript{2}O\textsubscript{3}, the crystals exhibited lateral growth behavior along the basal plane during solidification.

In 0.01%S added specimens, it is observed that the precipitation of graphite at the interface was significantly weakened (Figs. 5(c) and 5(g)). Besides, the element maps in Figs. 5(d) and 5(h) confirmed the presence RE–O–S compounds at the contact interface. By matching the elemental mapping results with the XRD patterns obtained in Figs. 6(b) and 6(d), several non-metallic compounds such as La\textsubscript{2}O\textsubscript{2}S, Yb\textsubscript{2}O\textsubscript{2}S, and YbS were identified. The above results indicate that desulfurization reactions occurred at the interface during the contact-melting/solidification process.

To further investigate the development of graphite at the interface, the cross sections near the alloy/substrate interface were observed and the SEM images are shown in Fig. 7. In the case of reference alloy on La\textsubscript{2}O\textsubscript{3} (Fig. 7(a)), we were
unable to identify the graphite formed at the interface from the cross-sectional observation. This is likely to be due to the loss of the graphite layer from the interface during mechanical/mirror polishing of the cross section. On the other hand, precipitation of graphite on Yb2O3 is observed in Fig. 7(c). It is worth noting that there is a region where Yb2O3 substrate was infiltrated by the alloy. It is considered that the dissolution of Yb2O3 into the molten alloy at an elevated temperature resulted in the formation of such a region.

From the observations in Figs. 7(b) and 7(d), it is observed that the morphology of precipitated graphite appeared hemispherical when using the La2O3 substrate, whereas Yb2O3 substrate created a comparatively planar morphology. Because the surface roughness of the substrates inevitably affects the morphology of the precipitated graphite, it is
considered that the severe structural non-uniformity of the La–O–S phase resulted in graphite with a hemispherical morphology, whereas a comparatively uniform Yb–O–S phase precipitated graphite with a relatively planar structure.

The above observations clearly indicate that in addition to RE\(_2\)O\(_3\), RE oxysulfides (La\(_2\)O\(_2\)S and Yb\(_2\)O\(_2\)S) and RES (YbS) could also act as potent heterogeneous sites for graphite nucleation.

### 3.3. Bulk Alloy of Contact-melted Base Alloys on RE\(_2\)O\(_3\) (RE; La, Yb)

Cross-sectional images of the bulk alloy of contact-melted base alloys on La\(_2\)O\(_3\) and Yb\(_2\)O\(_3\) are shown in Figs. 8(a)–8(b) and 8(c)–8(d), respectively. From the figures, it is worth noting that a rearrangement of graphite microstructures, from flake (in Fig. 3(a)) towards nodular, was observed. This clearly indicates a significant change in graphite precipitation behavior in the bulk alloy as a result of contact-melting on RE\(_2\)O\(_3\). In addition, the results of a statistical analysis, shown in Fig. 8, indicate that adding 0.01%S to the base alloy significantly increased the number of graphite nodules: from 101 to 903 mm\(^{-2}\) and from 138 to 631 mm\(^{-2}\) in the contact-melted alloys on La\(_2\)O\(_3\) and Yb\(_2\)O\(_3\), respectively. Meanwhile, the average diameter of graphite nodules changed from 13.2 to 8.0 \(\mu\)m and from 10.3 to 10.4 \(\mu\)m in the contact-melted alloys on La\(_2\)O\(_3\) and Yb\(_2\)O\(_3\), respectively. Both observations and quantitative analysis suggest that finer graphite nodules were distributed more evenly throughout the specimens with 0.01%S addition.

Because the number of graphite nodules can be directly correlated with the number of effective nucleation sites formed during solidification, it can be inferred that the number of effective nucleation sites in the bulk alloy increased as a result of S addition. Examples of heterogeneous nuclei observed in nodular graphite are shown in Fig. 9. With the exception of the contact-melted reference alloy on Yb\(_2\)O\(_3\), we identify several heterogeneous nuclei of nodular graphite in specimens. The results of an EDS point analysis show that the heterogeneous nuclei mainly consisted of RE and S, suggesting rare earth sulfides as possible heterogeneous nuclei.

Figures 10(a) and 10(b) show backscattering electron (BSE) images of the bulk alloy of contact-melted Fe-4.1%C-2.5%Si base alloy on La\(_2\)O\(_3\) and Yb\(_2\)O\(_3\), respectively. From the figure, segregation of RE-contained compounds in the coupled eutectic region is observed. It is considered that these RE-contained compounds are probably RE–Fe–Si intermetallic compounds or RE carbides because REEs are known to form several intermetallic compounds with Fe and Si\(^{19,20}\) as well as RE carbides\(^{21,22}\). In addition, it is observed that the contact-melted alloy on Yb\(_2\)O\(_3\) has a higher proportion of RE-rich compounds in the coupled eutectic region. It is known that the reducibility of metal oxide is affected by parameters such as particle size\(^ {23}\) and porosity\(^ {24}\). These factors might contribute to the increased formation of RE-rich compounds in contact melted alloy on Yb\(_2\)O\(_3\). In addition,
several studies show that REEs in excessive concentrations degenerate the shape of nodular graphite.\textsuperscript{25–27} It is considered that the formation of degenerated graphite, as observed in Figs. 8(c) and 8(d), may be related to a higher proportion of dissolved Yb in the bulk alloy.

4. Discussion

4.1. Thermodynamic Consideration

4.1.1. Desulfurization Reactions at the Alloy/substrate Interface

As given in Figs. 6(b) and 6(d), the formation of product compounds consisting of RE sulfides and oxysulfides was confirmed in 0.01%S added specimens. In evaluating the desulfurization reactions at the interface, due to insufficient thermodynamic data for the Yb–O–S system, the La–O–S system was evaluated as described below.

Using the thermodynamic parameters available in Table 3, the desulfurization diagram of La\textsubscript{2}O\textsubscript{3} in molten Fe-4.1%C-2.5%Si at 1 500°C is shown in Fig. 11. In the figure, $p_i$ is the partial pressure of gas $i$ in atm and [mass% $i$] is the mass percent of component $i$ dissolved in liquid iron. At a S concentration of 0.01% (log[mass% S] = −2), it can be seen that sulfurization of La\textsubscript{2}O\textsubscript{3} forms either La$_2$O$_2$S (for log$p_{CO} >$−1) or LaS$_2$ (for log$p_{CO} <$−1) at equilibrium. Given that the product formed at the interface is determined to be La$_2$O$_2$S (Fig. 6(b)), it is reasonable to estimate that the $p_{CO}$ developing during the process is likely to be larger than 0.1 atm but smaller than 1.0 atm because bubbles were not observed to be generated in the experiment.

Another important item of information that can be drawn from Fig. 11 is that, under the evaluated $p_{CO}$ range and temperature, the sulfurization of La$_2$O$_3$ is predicted to proceed for log[mass% S] greater than −9.5. This suggests that under normal experimental conditions, the formation of lanthanum oxysulfides and sulfides as a result of La$_2$O$_3$ sulfurization is imminent.

4.1.2. Formation of Rare Earth Sulfides in the Bulk Alloy.

From the observation in Fig. 9(a), it is found that RE sulfide acts as a heterogeneous site for graphite nucleation, despite the low S concentration (less than 9 ppmw) in the reference alloy. The source of S is likely to originate from the raw materials used in the present investigation.

To evaluate the formation of lanthanum sulfides, it is necessary first to determine the concentration of dissolved La in the molten alloy. The equilibrium reaction of La$_2$O$_3$...
in C-rich molten alloy can be expressed as

$$\text{La}_2\text{O}_3(s) + 3\text{C} = 2\text{La} + 3\text{CO}(g)$$ (1)

Assuming the activity of the pure component can be treated as unity, the equilibrium constant, $K$ in Eq. (1) is given as

$$K_1 = \frac{p_{\text{CO}}a_{\text{La}}^2}{a_{\text{C}}^3}$$ (2)

where $a_i$ is the Henrian activity of $i$ in mass%. Assuming $K_1$ is applicable to Fe-4.1%C-2.5%Si system after taking the interactions between dissolved elements into consideration, $K_1$ in Eq. (2) can be expressed as

$$\log K_1 = 3\log p_{\text{CO}} + 2\log[\text{mass% La}]$$

$$+ \left(2e_{\text{Si}}^c - 3e_{\text{Si}}^i\right)[\text{mass% Si}] + 2e_{\text{C}}^c[\text{mass% C}]$$

$$- 3\log[\text{mass% C}] - 3\log f_{j}^c + \left(2e_{\text{La}}^c - 3e_{\text{La}}^i\right)[\text{mass% La}]$$

where $f_{j}^c$ is the Henrian activity coefficient of $i$ in carbon-saturated iron and $e_{i}^j$ is the first-order interaction parameter of element $j$ on element $i$ in mass percent. Assuming $K_1$ is applicable to Fe-4.1%C-2.5%Si system after taking the interactions between dissolved elements into consideration, $K_1$ in Eq. (2) can be expressed as

$$\log K_1 = 3\log p_{\text{CO}} + 2\log[\text{mass% La}]$$

$$+ \left(2e_{\text{Si}}^c - 3e_{\text{Si}}^i\right)[\text{mass% Si}] + 2e_{\text{C}}^c[\text{mass% C}]$$

$$- 3\log[\text{mass% C}] - 3\log f_{j}^c + \left(2e_{\text{La}}^c - 3e_{\text{La}}^i\right)[\text{mass% La}]$$

where $f_{j}^c$ is the Henrian activity coefficient of $i$ in carbon-saturated iron and $e_{i}^j$ is the first-order interaction parameter of element $j$ on element $i$ in mass percent. Using the thermodynamic parameters available in Table 3, the relationship between log$p_{\text{CO}}$ and log[mass% La] at various temperatures is shown in Fig. 12. Assuming $p_{\text{CO}}$ was constant and can be treated as 0.1 atm (log$p_{\text{CO}}=-1$), the concentration of La is estimated to be between 8 and 437 ppmw ($-3.09 < \text{log[mass% La]} < -1.36$) at a temperature range of 1 350–1 500°C.

In determining the stability of rare earth sulfides, the equilibrium between LaS and La$_2$S$_3$ is considered:

$$2\text{LaS}(s) + \text{S} = \text{La}_2\text{S}_3(s)$$ (4)

Using the thermodynamic parameters available in Table 3, it is estimated that Eq. (4) spontaneously shifts to the right side only if $S$ is greater than 41 and 38 ppmw at 1 350°C and 1 500°C, respectively. Provided the S content in the reference alloy is less than 9 ppmw (Table 1), it can be inferred that LaS is more likely to be the heterogeneous nucleus observed in Fig. 9(a). Whereas, in the case of the 0.01%S-added specimen, given that a significant amount of initial S content is consumed as a result of La$_2$O$_3$ sulfurization in the process, the formation of La$_2$S$_3$ from LaS is considered to be less likely under such a low concentration of S.

The formation of LaS in molten iron is described by Eq. (5).

$$\text{La} + \text{S} = \text{LaS}(s)$$ (5)

After considering interactions with other solutes in the molten alloy, the solubility constants in Eq. (5), $K_5$ can be expressed as:

$$\log K_5 = -\left[\text{log[mass% La]} + \text{log}\left(f_{j}^c[\text{mass% Si}]\right) + \left(e_{\text{Li}}^c[\text{mass% C}] + \left(e_{\text{Si}}^c + e_{\text{Si}}^i\right)[\text{mass% Si}] + \left(e_{\text{La}}^c + e_{\text{La}}^i\right)[\text{mass% La}]\right)\right]$$

The relationship between log[mass% S]-log[mass% La] for Eq. (5) is shown in Fig. 13. Using the estimated value of $\text{La}$ obtained in Fig. 12, it is predicted that LaS will precipitate readily even at 1 500°C. Considering the precipita-

### 4.2. Evaluation of Heterogeneous Nucleation of Graphite on RE Compounds

From the observations, it can be concluded that the initial stage in the formation of nodular graphite is heterogeneous nucleation. Because heterogeneous nucleation is a process that involves two phases with different atomic arrangements coming into contact, a certain degree of lattice mismatch between the nucleated solid and the substrate is expected. The magnitude of the mismatch is, therefore, dependent on the relative crystal orientation of the two phases. It has been validated experimentally and theoretically that the lattice mismatch significant impacts the catalytic efficiency of a heterogeneous substrate.

The lattice mismatch is evaluated using the concept of planar disregistry, $\delta$, proposed by Bramfitt. The equa-

![Fig. 12. Relationship between log$p_{\text{CO}}$ and log[mass% La] in molten Fe-4.1%C-2.5%Si at various temperatures.](image)

![Fig. 13. Estimated solubility of LaS in molten Fe-4.1%C-2.5%Si at various temperatures.](image)
tion is applicable to crystallographic combinations of two phases with planes of differing atomic arrangements, while taking into consideration the angular difference between the crystallographic directions within the planes. The planar disregistry equation is defined as follows:

$$\delta^{\text{hlh}}_{\text{substrate}} = \sum_{i=1}^{3} \frac{100}{3} \times \frac{d_{\text{hlh}} - d_{\text{hlh}}}{d_{\text{hlh}}} \cos \theta \quad (\%) \quad (7)$$

Where (hkl) is a low-index plane of the substrate, (hkl) is a low-index plane of the nucleated solid, [uvw], is a low-index direction in (hkl), [uvw], is a low-index direction in (hkl), $d_{\text{hlh}}$ is the interatomic spacing of substrate along [uvw], and $d_{\text{hlh}}$ is the interatomic spacing of nucleated solid along [uvw]. According to Bramfitt,\(^{46}\) $\delta$ with a value of less than 6% has the highest efficiency in promoting heterogeneous nucleation. $\delta$ with a value of 6–12% is considered to be effective, while $\delta$ larger than 12% is generally considered to be least effective.

In the determination of planar disregistry between graphite and rare earth compounds, because the heterogeneous nucleation of graphite occurs at a high temperature, the effects of thermal expansion on the lattice constant of each compound were considered. In the calculations, the temperature was set at 1 365°C (primary graphite precipitation temperature\(^{3,14}\)) and the lattice constant of graphite was treated as a constant (2.462 Å [a-axis])\(^{23}\) and a. Approximated value using the coefficient thermal expansion, $\alpha$, of CeS ($\alpha_{\text{CeS}} = 11.1 \times 10^{-6} \text{ K}^{-1}$)\(^{43}\) b. Approximated value using the coefficient thermal expansion of La$_2$O$_3$ and Yb$_2$O$_3$ ($\alpha_{\text{La}_2\text{O}_3,0\text{-axis}} = 10.6 \times 10^{-6} \text{ K}^{-1}$; $\alpha_{\text{Yb}_2\text{O}_3} = 8.4 \times 10^{-6} \text{ K}^{-1}$)\(^{44}\).

The estimated planar disregistry between graphite and RE compounds identified in this study are listed in Table 4. Based on the calculations, it is determined that planar disregistry irreducible factors were considered in the disregistry between (0001)$_{\text{graphite}}$ and (111)$_{\text{La,La,O}_2\text{S}}$, (0001)$_{\text{La,La,O}_2\text{S}}$, (111)$_{\text{YbS}}$, (0001)$_{\text{La,O}_2\text{S}}$, (111)$_{\text{YbS}}$, and (0001)$_{\text{Yb,O}_2\text{S}}$ have values of 1.4%, 3.9%, 4.3%, 6.2%, 6.6%, and 11.1%, respectively. The evaluated disregistry is obviously lower than the critical value (12%) proposed by Bramfitt, below which the substrate is sufficiently potent to promote heterogeneous nucleation.

In addition, there is a trend that, with the exception of Yb$_2$O$_3$S, RES and RE$_2$O$_3$S have lower planar disregistry values compared to RE$_2$O$_3$. Because a lower planar disregistry also implies a smaller interfacial free energy at the nucleating interface,\(^{44,56}\) it is considered that RES and RE$_2$O$_3$S are generally more effective in promoting the heterogeneous nucleation of graphite than RE$_2$O$_3$. In other words, graphite preferentially nucleates on RES and RE$_2$O$_3$S over RE$_2$O$_3$ during solidification. Such differences in the nucleating efficiency of the substrates could explain the observed graphite precipitation behavior, as observed in Figs. 5 and 8. Adding 0.01%S significantly increases the number of effective nucleation sites (RES) in the bulk alloy during solidification. Because RES were determined to be the most effective graphite nucleating compounds among the evaluated species, an increase in the number of RES in S-added specimens enhances the precipitation of graphite in the bulk alloy. Considering the amount of C that could precipitate as graphite is limited, enhanced formation of nodular graphite in the bulk is considered to weaken graphite precipitation on the less effective alloy/RE$_2$O$_3$–RE$_2$O$_3$S substrate interface as observed in Fig. 5.

5. Conclusions

The contributions of several RE compounds, i.e., RE$_2$O$_3$, RES, and RE$_2$O$_3$S (RE; La, Yb), to the heterogeneous nucleation of graphite during solidification of Fe-4.1%C-2.5%Si melts were investigated using contact-melting methodology. Employing the method presented, we observed and evaluated the precipitation of graphite when a heterogeneous substrate was intentionally provided. Our major findings are listed as follows.

(1) Precipitation of graphite that demonstrated an overall crystallographic direction on the c-axis ([0001]) was observed at the alloy/RE$_2$O$_3$ interface. Considering the sizes of the graphite grains observed, it can be concluded that after heterogeneous nucleation of graphite, graphite crystals grew laterally on the surface of RE$_2$O$_3$ along the basal plane during solidification.

(2) In 0.01%S-added specimens, formation of RES and RE$_2$O$_3$S at the alloy/substrate interface was identified, indicating desulfurization reactions took place at the interface.

| Plane form | Nucleated solid | Substrate | $d_{[uvw]}$ @ 1 365°C (Å) | $\theta$ | $\delta^{\text{hlh}}_{\text{substrate}}$ (%) | Lattice parameter (Ref.) | Coefficient of thermal expansion (Ref.) |
|------------|----------------|-----------|--------------------------|--------|-----------------------------|-------------------------|-----------------------------------|
| (111)$_{\text{La,La,O}_2\text{S}}$ | [0T1]$_{\text{La,La,O}_2\text{S}}$ | 4.205 | 0 | 1.4 | 39 | a |
| (111)$_{\text{YbS}}$ | [0T1]$_{\text{YbS}}$ | 4.081 | 0 | 4.3 | 40 | b |
| (0001)$_{\text{La,O}_2\text{S}}$ | [1T00]$_{\text{La,O}_2\text{S}}$ | 4.097 | 0 | 3.9 | 41 | |
| (0001)$_{\text{Yb,O}_2\text{S}}$ | [1T00]$_{\text{Yb,O}_2\text{S}}$ | 3.790 | 0 | 11.1 | 42 | |
| (0001)$_{\text{La}_2\text{O}_3}$ | [011]$_{\text{La}_2\text{O}_3}$ | 4.264 | 3.999 | 6.2 | 11 | |
| (111)$_{\text{YbS}}$ | [0T1]$_{\text{YbS}}$ | 4.000 | 0 | 6.6 | 12 | 44 |
| (111)$_{\text{La,O}_2\text{S}}$ | [0T1]$_{\text{La,O}_2\text{S}}$ | 4.000 | 0 | 6.6 | 12 | 44 |

Table 4. Estimated planar disregistry between graphite and various RE non-metallic compounds.
In addition, precipitation of graphite on these compounds was also observed. This suggests that RES and \(\text{RE}_2\text{O}_2\text{S}\) exerted strong catalytic efficiencies in nucleating graphite. The significant increase in the total number of graphite nodules in the bulk alloy can be attributed mainly to the increasing formation of RES.

(3) The planar disregistry \(\delta\) between graphite and RES were determined to be lowest among \(\text{RE}_2\text{O}_2\text{S}\) and \(\text{RE}_2\text{O}_3\). Due to excellent lattice coherency, heterogeneous nucleation of graphite was expected to occur preferentially on RES over other non-metallic inclusions.

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