

Time-Dependent Evolution of Ti-Bearing Oxide Inclusions During Isothermal Holding at 1573 K (1300 °C)



MINGGANG LI, HIROYUKI MATSUURA, and FUMITAKA TSUKIHASHI

Ti-bearing oxide inclusions are utilized to enhance the properties of steel used in shipbuilding, multi-purpose gas carriers, and pipelines in accordance with the principles of oxide metallurgy. Conventionally, Ti-bearing oxide inclusions have been assumed to be stable during isothermal holding. The authors propose the possibility of modifying Ti-bearing oxide inclusions by appropriate heat treatment. To provide fundamental information on the evolution of Ti-bearing inclusions in solid steel during isothermal holding, the effect of the isothermal holding time on their evolution at 1573 K (1300 °C) was studied systematically. For heterogeneous phase Al + Ti oxide in the as-cast alloys, the composition and size distribution were maintained during isothermal holding. In contrast, homogeneous phase Al-Ti oxide in the as-cast alloys changed to a heterogeneous oxide consisting of an Al-rich part and a Ti-rich part and its shape changed from spherical to irregular. The composition of the Al-Ti oxide changed upon isothermal holding for 0.5 hour, and it occurred earlier in the Al-Ti oxide with a higher Al content. The evolution mechanism is considered to involve the precipitation of Al₂O₃ from the Al-Ti oxide owing to crystallization of glassy oxide during isothermal holding. The results challenge the long-held opinion that Ti-bearing oxide inclusions are maintained in solid steel during isothermal holding, which is the first step toward modifying oxide inclusions by heat treatment as a new concept in oxide metallurgy.

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I. INTRODUCTION

TI-BEARING oxide inclusions enable the formation of the intragranular acicular ferrite (IAF), in accordance with the principles of oxide metallurgy, which greatly enhance the strength and toughness of steel used in shipbuilding, multi-purpose gas carriers, and pipelines. The mechanism by which IAF is formed has not yet been clarified. Previous studies suggested that the formation is affected by the composition and structure of inclusions,^[1–3] the formation of a Mn depletion zone near the inclusions,^[4–6] and the grain size of the prior austenite.^[7,8] These studies were conducted on the assumption that Ti-bearing oxide inclusions themselves are stable. There have been no reports on the time-dependent evolution of such inclusions in solid steel,

although the corresponding relationship between Ti-bearing oxides and the formation of IAF has been verified.^[1–3,9] Moreover, fundamental information on this evolution is important since it is the basis of new oxide metallurgy, which proposes modifying Ti-bearing oxides to those capable of forming IAF by conducting a suitable heat treatment to make full use of oxide inclusions. In another sense, it is necessary to study the variation of the composition of Ti-bearing oxide inclusions during isothermal holding because the chemistry of inclusions is a decisive factor in the initiation of corrosion pits in pipeline steel.^[10]

The evolution of oxide inclusions except for Ti-bearing oxides in solid steel during isothermal holding has been studied by many researchers.^[11–19] The current study differs from the previous ones in the following aspects. (1) The purpose of the previous studies was to prevent the growth of austenite grains by oxides such as MnO-SiO₂ in solid steel that formed during isothermal holding.^[11,12] MnO-SiO₂ inclusions are unrelated to oxide metallurgy. There have been few reports on the variation of Ti-bearing oxides in solid steel, although it has been verified that they act as effective cores to form IAF in the traditional oxide metallurgy. The present study focuses on the time-dependent evolution of Ti-bearing oxide inclusions to serve as the basis of a

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'new oxide metallurgy.' (2) In the current study, the evolution of Ti-bearing oxide inclusions in a fundamental Fe-Al-Ti alloy is investigated, because other alloying elements may affect the evolution of inclusions and because Al and Ti complex deoxidation is frequently adopted in the steelmaking process.

Compared with the limited research on Ti-bearing oxide inclusions in solid steel, research on the thermodynamic description of the Fe-Al-Ti-O system in molten steel has been conducted extensively.^[20–23] Nevertheless, differences of opinion in the types of Ti-bearing oxide phase appearing as stable phases in such a system remain. Recently, Jung *et al.*^[22] calculated the phase diagram for the case that Al_2O_3 , Ti_2O_3 , Ti_3O_5 , and a liquid oxide equilibrate with a metal using the FactSage database. The transient behavior of Ti-bearing oxides in liquid iron has also been investigated by many researchers.^[24–28] Wang *et al.*^[28] pointed out that a liquid Al-Ti oxide phase with nonstoichiometry is probably a stable phase.

In our previous research, the change in Al-Ti oxide from a homogeneous phase to a heterogeneous phase in Fe-Al-Ti alloy heated at 1573 K (1300 °C) for 3 hours was reported.^[29] However, the effect of the isothermal holding time on the evolution of Al-Ti oxide and Al+Ti oxide inclusions as heterogeneous phases was not investigated. Different from our previous paper, the effect of the isothermal holding time on the evolution of Al-Ti oxide inclusions on the composition, morphology, and size distribution is studied in the present study. Also, the evolution of heterogeneous Al+Ti oxide inclusions during isothermal holding, which was not studied in the previous paper, is revealed. Since industrial steels are reheated between 1273 K and 1573 K (1000 °C and 1300 °C) in most cases to contrast and in order to contrast the variation of the Ti-bearing oxide over time from that in our previous paper, which was carried out at the same temperature,^[29] the isothermal holding temperature of 1573 K (1300 °C) was employed in the experiments in the current study.

The aim of the current study is to clarify the effect of the isothermal holding time on the evolution of two types of Ti-bearing oxide inclusions, Al+Ti oxide and Al-Ti oxide inclusions, in Fe-Al-Ti alloy during isothermal holding at 1573 K (1300 °C). The variation of the composition, morphology, and size distribution of the inclusions was investigated systematically to serve as the basis of a new oxide metallurgy. A different characterization method was adopted for each type of oxide inclusion.

II. EXPERIMENTAL

A. Preparation of As-Cast Alloys

The compositions of as-cast alloy1 and alloy2 are shown in Table I.^[29] They were prepared in an induction furnace. Al and Ti were added to molten iron contained in MgO crucible with an interval of 2 minutes at 1873 K (1600 °C) before water quenching. The details of the

experimental procedure and chemical analyses were the same as in our previous study.^[29]

B. Isothermal Holding Experiment

A piece of alloy sample including a part from the interior to the edge of the alloy adjacent to the crucible was cut from the as-cast alloy. The dimensions of the cut sample were 5 mm in length, 14 mm in width, and 4 mm in height. In order to prevent oxidation during isothermal holding, it was sealed in a quartz tube (ID: 8 mm, OD: 9 mm, L: 30 to 40 mm) under vacuum atmosphere. Sealed alloy samples were heated in an electric resistance furnace for 0.5, 1, 3, 6, and 12 hours at 1573 K (1300 °C). The isothermal holding time refers to the holding time from when the sample was placed in the furnace to the water quenching. Details of the experimental setup are given in our previous paper.^[29] After the prescribed isothermal holding time, the quartz tube was removed from the furnace and broken up to quench the alloy in water for 10 seconds.

C. Inclusion Characterization Method

Both as-cast and heated samples were ground by SiC papers after embedding in resin; then, they were polished by diamond suspensions with grain sizes of 3, 1, and 0.25 μm before inclusion characterization.

In this paper, "X+Y oxide" denotes two phases in one inclusion, whereas "X-Y oxide" denotes a single phase composed of two components in as-cast alloys. Note that the term "X-Y oxide" is used even for the heterogeneous phase after isothermal holding to distinguish it from X+Y oxide in the present study.

Two types of Ti-bearing oxide inclusion, Al+Ti oxide and Al-Ti oxide, were observed in as-cast alloy1 and alloy2, as reported in our previous paper.^[29] Secondary electron images and the results of mapping analysis of Al+Ti oxide and Al-Ti oxide inclusions are shown in Figure 1. The Al+Ti oxide inclusions were a heterogeneous phase consisting of Al_2O_3 and TiO_x and had an irregular shape. The Al-Ti oxide inclusions were a homogeneous phase consisting of Al, Ti, and O and had a spherical shape. Similar results were obtained for both as-cast alloys. These two types of inclusion were distributed in different areas of the as-cast alloys. The distribution area of each type of inclusion was maintained during isothermal holding, which enabled the same type of oxide in the heated alloys to be analyzed.

Because the Al+Ti oxide maintained a heterogeneous phase during isothermal holding, manual SEM-EDS failed to characterize its changes. Automatic SEM-EDS was used to characterize the variation in the composition and size distribution during isothermal holding from a statistical viewpoint. A SEM (ZEISS, EVO 18) in combination with an EDS (Oxford Instruments, INCA) was employed. The characterization of inclusions by automated SEM-EDS is based on the principle that inclusions exhibit a contrasting color from the alloy matrix in backscattered electron images: heavy elements

Table I. Composition of As-Cast Alloys

| Alloy | Soluble Al (Mass Pct) | Soluble Ti (Mass Pct) | Total O (Mass Pct) | Total N (Mass Pct) |
|-------|-----------------------|-----------------------|--------------------|--------------------|
| 1 | 0.0497 | 0.0636 | 0.0020 | 0.0032 |
| 2 | 0.0123 | 0.0586 | 0.0069 | 0.0110 |

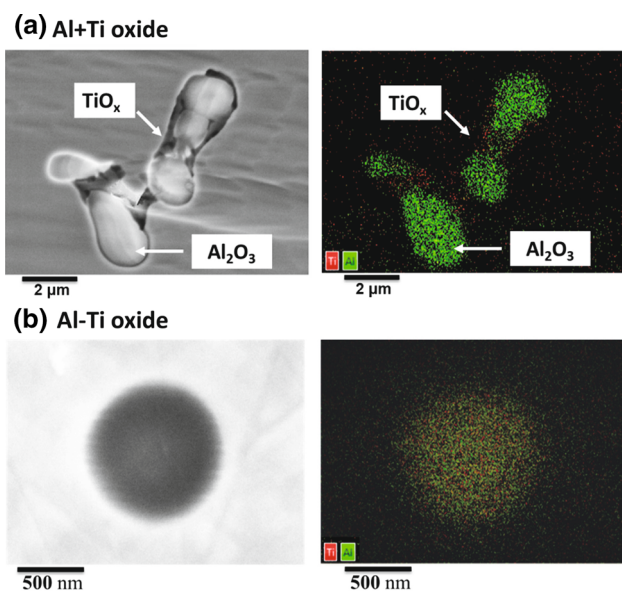


Fig. 1—Secondary electron image and mapping analysis results of (a) Al+Ti oxide inclusions and (b) Al-Ti oxide inclusions in as-cast alloy1 and alloy2.

Table II. Settings in Automated SEM-EDS Measurement

| | |
|-----------------------------------|------------------------|
| Accelerating Voltage | 20 kV |
| Working Distance | 8 mm |
| Resolution | 2048 × 1664 pixels |
| Magnification | 226 |
| Minimum Detectable Particle Size | 0.5 μm |
| EDS Measurement Time per Particle | 0.2 s |
| EDS Measurement Area | whole area of particle |

with large atomic numbers appear brighter because the backscattering of electrons is stronger than that from light elements with small atomic numbers. During the analysis, the stage was automatically adjusted to ensure the optimum working distance; thus, the precise composition of the inclusions was obtained.

The settings applied in the automated SEM-EDS analysis are presented in Table II. Note that the inclusion size was described by a diameter of the circle having the area equivalent to the observed inclusion.

The Al-Ti oxide changed from a homogeneous phase to a heterogeneous oxide consisting of an Al-rich part and a Ti-rich part during isothermal holding as shown in Figure 2. Homogeneous Al-Ti oxide inclusions were also found in the heated alloy, although their numbers were small. After isothermal holding, the changes in the composition, morphology, and size distribution of the

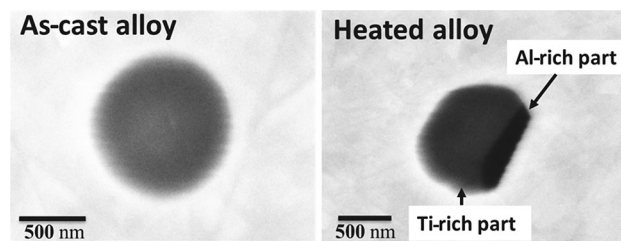


Fig. 2—Change in Al-Ti oxide from homogeneous to heterogeneous phase during isothermal holding at 1573 K (1300 °C).

Al-Ti oxide were manually characterized using a field-emission SEM, where the settings were the same as those employed in our previous study.^[29] The size of inclusions is given as the maximum diameter of the particle.

The structure of the Al-Ti oxide before isothermal holding was analyzed by electron backscattered diffraction (EBSD). The surface of the alloy sample subjected to EBSD was etched by an argon beam at 6.0 kV for 7 hours under a pressure of 2.0×10^{-3} Pa to prevent any contamination during sample preparation.

III. RESULTS AND DISCUSSION

A. Evolution of Al+Ti Oxide During Isothermal Holding

The compositional changes in the Al+Ti oxide inclusions for size ranges of 0.5 to 2, 2 to 4, and over 4 μm for the as-cast and 12 hours-heated alloy are presented in Figure 3 for alloy1 and in Figure 4 for alloy2. The number of inclusions analyzed in each alloy was more than 60.

It was found that Al+Ti oxide inclusions that have a higher Ti concentration tend to be smaller in both the as-cast alloy and the 12 hours-heated alloy. This is considered to be because the Ti in the oxide decreased the interfacial energy between the oxide and the liquid alloy at 1873 K (1600 °C), which will be discussed in the following section. The size and compositional distribution of the inclusions were found to be maintained in both alloys during isothermal holding.

B. Evolution of Al-Ti Oxide During Isothermal Holding

1. Phase of Al-Ti oxide in as-cast alloy

Kikuchi patterns of the matrix (point 1) and Al-Ti oxide (point 3) in as-cast alloy1 analyzed by EBSD are shown in Figure 5. The Kikuchi pattern of the ferrite phase of iron was observed for the matrix, whereas it was not observed for the Al-Ti oxide. The Kikuchi

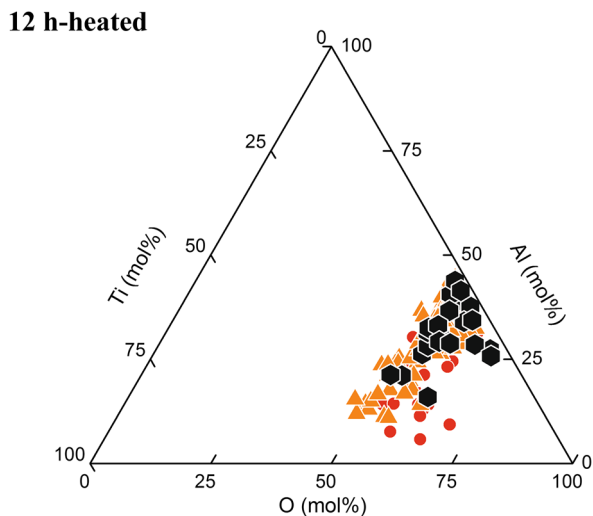
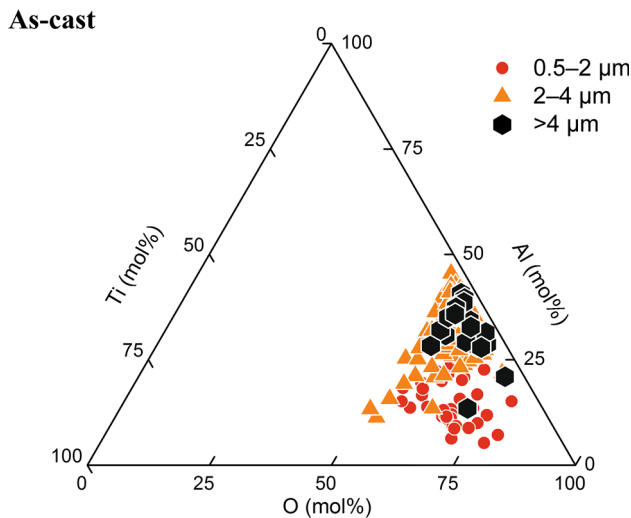


Fig. 3—Size and compositional distribution of Al+Ti oxide inclusions in as-cast alloy1 and after isothermal holding for 12 h at 1573 K (1300 °C).

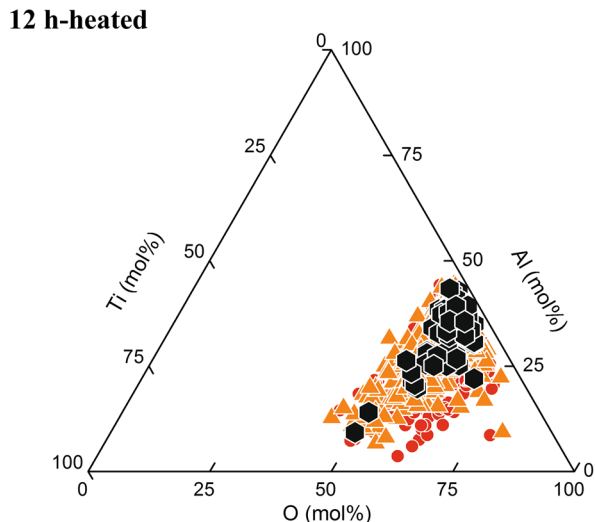
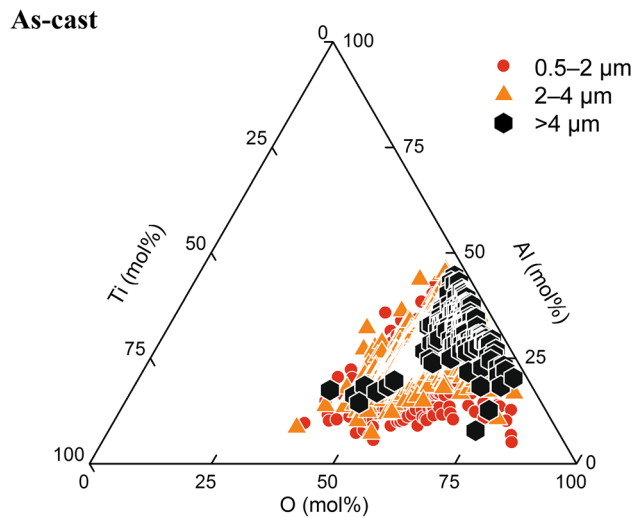


Fig. 4—Size and compositional distribution of Al+Ti oxide inclusions in as-cast alloy2 and after isothermal holding for 12 h at 1573 K (1300 °C).

pattern of point 5 for the alloy matrix and those of points 2 and 4 for the oxide indicate that the Al-Ti oxide was liquid in the molten Fe-Al-Ti-O alloy at 1873 K before water quenching after the combination with the experimental facts in which the Al-Ti oxide inclusions were in spherical shape and in aligned distributions presented in the previous paper.^[29]

2. Change in composition of Al-Ti oxide inclusions during isothermal holding

Most Al-Ti oxide inclusions changed from homogeneous to heterogeneous during isothermal holding. The heterogeneous oxide was composed of two parts: an Al-rich part in which Al and O coexisted, and a Ti-rich part in which Al, Ti and O coexisted. A homogeneous Al-Ti oxide, *i.e.*, oxide inclusions of whose shape changed from spherical to irregular but its composition remained homogeneous, was also found in the heated alloys.

The compositions of the Al-rich part, Ti-rich part, and homogeneous oxide in the heated alloys are shown in Figure 6 for alloy1 and in Figure 7 for alloy2. Since the overall trend of the variation was the same for both alloys, from 30 to 40 Al-Ti oxide inclusions in each heated alloy were selected randomly and analyzed by EDS. The number of homogeneous oxide inclusions observed was zero in alloy1 heated for 12 hours.

The compositional deviation of Al-Ti oxide to higher Al and higher Ti contents from those of the as-cast alloy during isothermal holding was observed for alloy1 but not for alloy2. The depth of the spatial analysis of EDS for the Ti-rich part was calculated to be 0.4 μm under the present experimental conditions using Castaing's formula. The calculation was done by assuming the Ti-rich part in the heterogeneous oxide to be Al₂TiO₅ with a density of 3.702 g/cm³.^[30] Because the size of the oxide was around 1 μm in alloy1 and even smaller in alloy2, as shown later, the X-ray signal of Al from the

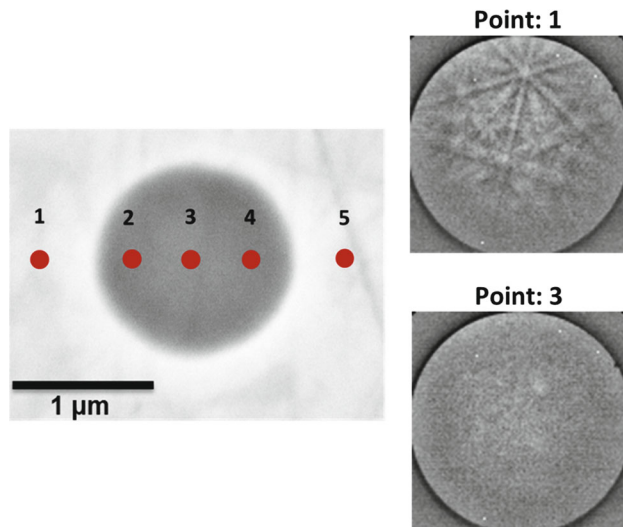


Fig. 5—Kikuchi patterns of matrix (point 1) and Al-Ti oxide (point 3) in as-cast alloy1 analyzed by EBSD.

Ti-rich part may have been strongly affected by the adjacent Al-rich part during the EDS analysis, especially for alloy2. Therefore, the actual Al/Ti molar ratio of the Ti-rich part is considered to be lower than the measured results in both alloys. Therefore, it is considered that the same phase separation may have proceeded in alloy2 during isothermal holding.

The composition of the homogeneous oxide was near that of the Ti-rich part in both alloys regardless of the isothermal holding time. The scattered data for the oxygen content are due to the limited accuracy of EDS analysis for light elements.

The composition changed after isothermal holding for 0.5 hour for both alloys, which became more apparent with increasing isothermal holding time. It is considered that phase separation between the Al-rich part and Ti-rich part increasingly occurred with time during isothermal holding. The composition of the Al-rich part approached that of pure alumina during isothermal holding.

3. Change in ratio of heterogeneous Al-Ti oxide during isothermal holding

The change in the ratio of the heterogeneous oxide in alloy1 and alloy2 during isothermal holding is presented in Figure 8. Number of observed Al-Ti oxide inclusions in each alloy was 80 to 100.

The ratio of the heterogeneous oxide increased in each alloy during isothermal holding, and it was over 90 pct in both alloys after 1 hour. The ratio of the heterogeneous oxide was larger in alloy1 than in alloy2 after isothermal holding for 0.5 hour, which indicates the earlier transformation from the homogeneous phase to heterogeneous phase in alloy1 during isothermal holding. The reason for this will be explained later.

4. Change in morphology of Al-Ti oxide during isothermal holding

The change in the morphology of the Al-Ti oxide during isothermal holding is shown in Figure 9. Similar results were obtained for both alloys.

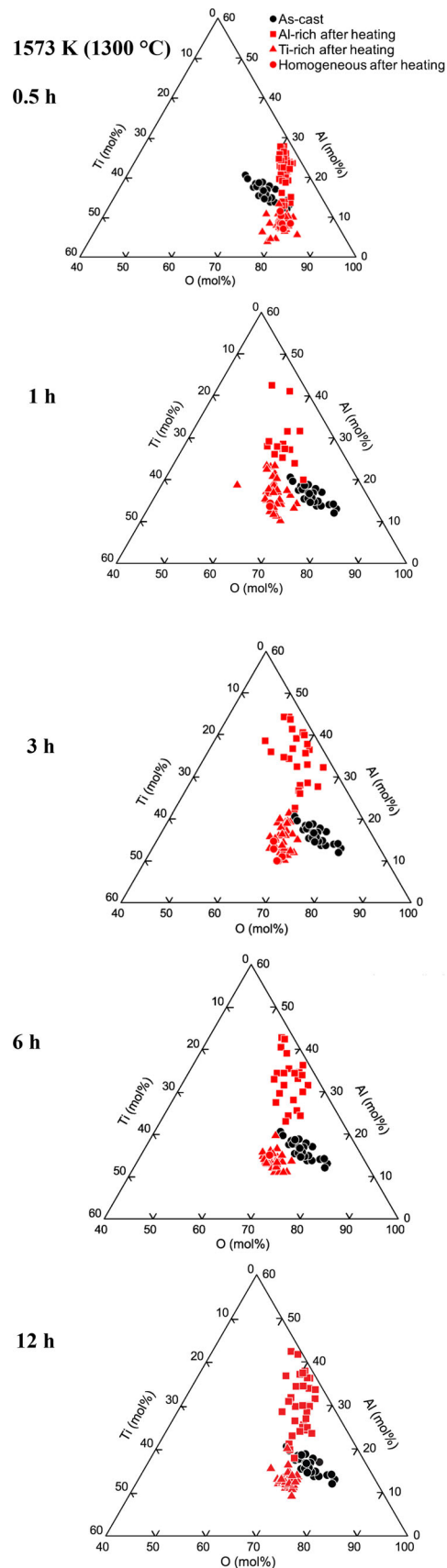


Fig. 6—Composition in Al-rich part, Ti-rich part, and homogeneous part in alloy1 heated for 0.5, 1, 3, 6, and 12 h at 1573 K (1300 °C).

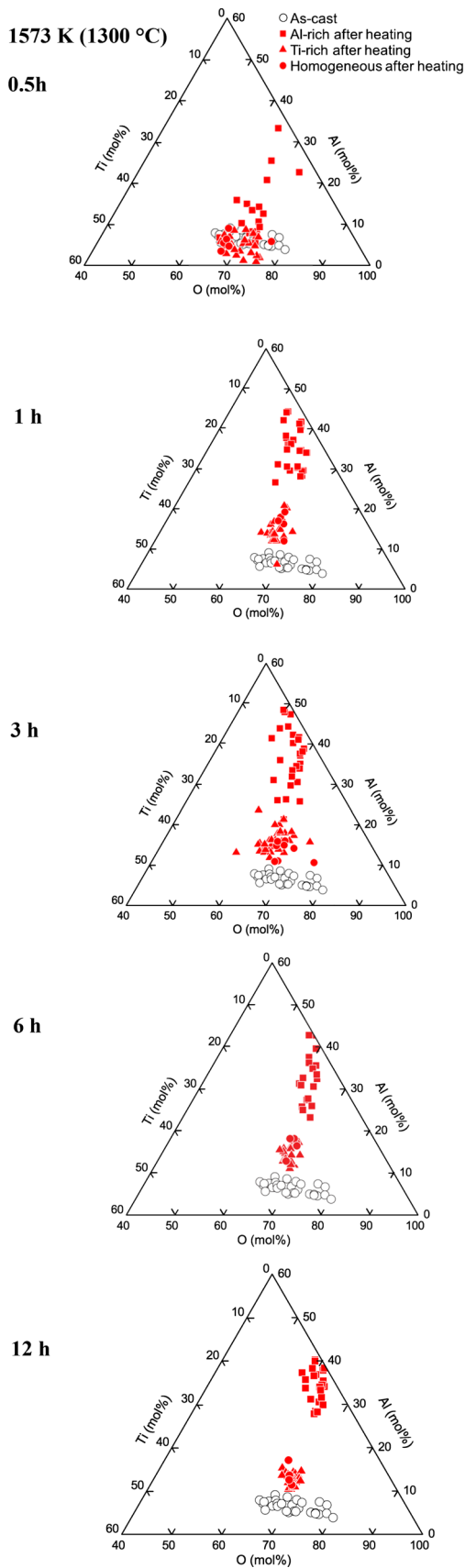


Fig. 7—Composition in Al-rich part, Ti-rich part, and homogeneous part in alloy2 heated for 0.5, 1, 3, 6, and 12 h at 1573 K (1300 °C).

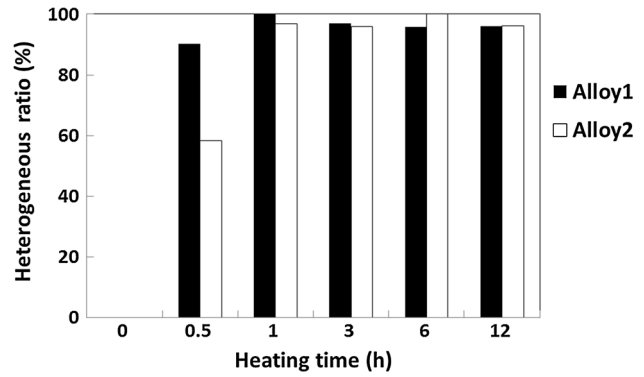


Fig. 8—Change in ratio of heterogeneous oxide in alloy1 and alloy2 during isothermal holding at 1573 K (1300 °C).

It was found that the shape of the oxide after isothermal holding was irregular and random. The Al-rich part mostly existed on the surface of the oxide; however, the specific location and its shape were random. The Al-rich part was also found in the inner part of the oxide. With increasing isothermal holding time, the morphology of the oxide became increasingly irregular as shown in Figure 9(c).

5. Change in size distribution of Al-Ti oxide during isothermal holding

The size distributions of the Al-Ti oxide after isothermal holding for different times are shown in Figure 10 for alloy1 and in Figure 11 for alloy2. Most of the Al-Ti oxide is around 1 μm in both alloys, while it is smaller in alloy2, in which the Ti content of the Al-Ti oxide is larger. The agglomeration rate of inclusions was found to be smaller in Fe-10mass pctNi alloy deoxidized by Ti/Al than in the same alloy deoxidized by Al at 1873 K (1600 °C).^[31,32] The agglomeration of inclusions was attributed to the decrease in interfacial tension between the inclusions and molten alloy. Although experimental data of the interfacial tension between Al-Ti oxide and molten alloy at 1873 K (1600 °C) are lacking, it is reasonable to deduce that the interfacial energy of Al-Ti oxide between molten Fe-Al-Ti-O alloy decreases with increasing Ti content of the oxide at 1873 K (1600 °C) on the basis of the value of the interfacial tension between Al_2O_3 with liquid iron^[33] of 2.29 J m^{-2} and those of Ti_2O_3 and TiO_2 with liquid iron^[34] of 1.2 and 0.51 J m^{-2} , respectively. Because the Ti content in alloy2 is larger than that in alloy1, the Al-Ti oxide is smaller in alloy2.

During isothermal holding, the distribution characteristics in size were maintained in both alloys. The range of the size distribution of inclusions in both alloys increased with the isothermal holding time. The morphology of the oxide changed from spherical to irregular during isothermal holding and the degree of irregularity increased over time as shown in Figure 9. Because the sizes shown in Figures 10 and 11 refer to the maximum particle diameter, the range of the size distribution increased during isothermal holding.

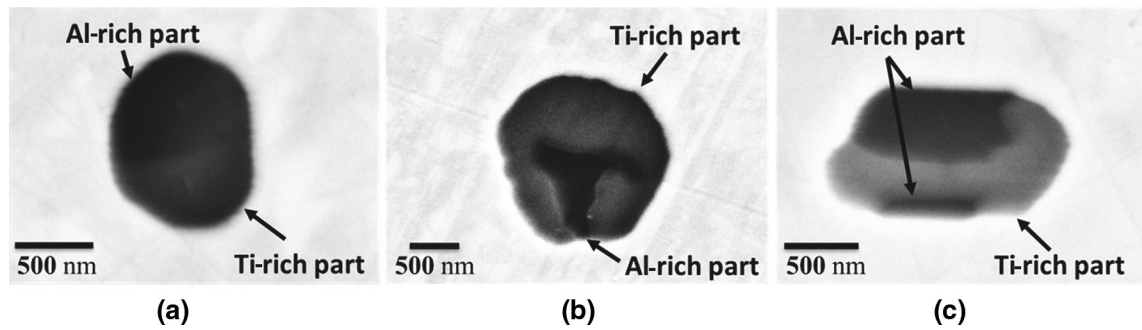


Fig. 9—Change in morphology of Al-Ti oxide during isothermal holding at 1573 K (1300 °C). (a) Alloy heated for 1 h; (b) alloy heated for 6 h; (c) alloy heated for 12 h.

C. Evolution Mechanism of Al-Ti Oxide During Isothermal Holding

The evolution mechanism of Al-Ti oxide during isothermal holding at 1573 K (1300 °C) is considered to involve the precipitation of Al_2O_3 from the oxide owing to crystallization of glassy oxide. This consideration is based on the following experimental results:

- (1) In the case that the matrix reacts with the Al-Ti oxide during isothermal holding, it will probably follow the unreacted core model, in which the Al in the matrix reduces the TiO_x in the oxide to form an Al-rich part, with some unreacted parts remaining. However, this contradicts the compositional change in the oxide during isothermal holding shown in Figure 6. It is concluded that the composition of the oxide also changed in alloy2, despite the limited accuracy of the EDS analysis.
- (2) On the assumption that the variation in the composition is caused by the reaction between the oxide inclusions and the alloy matrix during isothermal holding, a ring-shaped reaction layer is expected to form, which contradicts the morphology of the heterogeneous oxide inclusions after isothermal holding shown in Figure 9. Moreover, the Al-rich part found in the inner part of the oxide shown in Figure 9(b) also contradicts this assumption.
- (3) The ratio of the heterogeneous Al-Ti oxide was larger in alloy1 than in alloy2 after isothermal holding for 0.5 hour as shown in Figure 10. This is attributed to two reasons. First, the phase separation of the oxide proceeds more rapidly in alloy1 because the Al/Ti molar ratio in the oxide in alloy1 is larger. Second, the Al in the matrix reduces the Al-Ti oxide to form alumina during isothermal holding since the Al concentration in the matrix of alloy1 is larger than that in alloy2. However, it is difficult to distinguish these two reasons from the present experimental results. Furthermore, the ratio of the heterogeneous oxide was larger in the alloy heated at 1273 K than in the alloy heated at 1573 K (1300 °C) for the same isothermal holding time, which will be reported in our next paper. This suggests that

the change in the oxide during isothermal holding corresponds to the composition of the Al-Ti oxide, indicating that the mechanism involves the crystallization of the glassy oxide. Owing to the higher Al content in the Al-Ti oxide in alloy1 than that in alloy2, the precipitation of Al_2O_3 during crystallization occurs earlier in alloy1.

It is proposed that the evolution mechanism of Al-Ti oxide during isothermal holding involves the crystallization of the oxide from the glassy state. During isothermal holding, Al and O diffuse from the inside of the oxide to the surface to precipitate alumina, which is the Al-rich part, while the remaining part is the Ti-rich part found in the heterogeneous oxide. Owing to the limitation of the two-dimensional inclusion characterization, both heterogeneous and homogeneous oxides were observed in the heated alloys. In the case that the exposed section includes both Al-rich and Ti-rich parts of the heterogeneous oxide, the heterogeneous oxide is observed and in the case that the exposed section only includes the Ti-rich part in the heterogeneous oxide, the homogeneous oxide is observed. It is considered that all Al-Ti oxides changed from the homogeneous phase to the heterogeneous phase on the basis of our three-dimensional observation. This also explains the low probability of occurrence of the homogeneous oxide in the heated alloys.

Another issue is whether a reaction occurs between the Al-Ti oxide and the matrix alloy during isothermal holding. If such a reaction occurs, there should be an Al concentration gradient in the area adjacent to the Al-rich part of the Al-Ti oxide in the heated alloy. The width of this area is probably of nanometer order. However, EDS cannot detect such a gradient owing to the low concentration of Al in the alloy, even after erasing the Al signal from the Al-rich part of the Al-Ti oxide. An Auger microscope (PHI-650SAM) was employed to detect the Al gradient; however, no gradient was detected since the Al concentration in the alloy was lower than 0.1 mol pct, which is the detection limit of this Auger microscope.

It is supposed that Al and Ti exist as Al_2O_3 and Ti_2O_3 in the Al-Ti oxide, respectively. The reaction during isothermal holding is considered to be

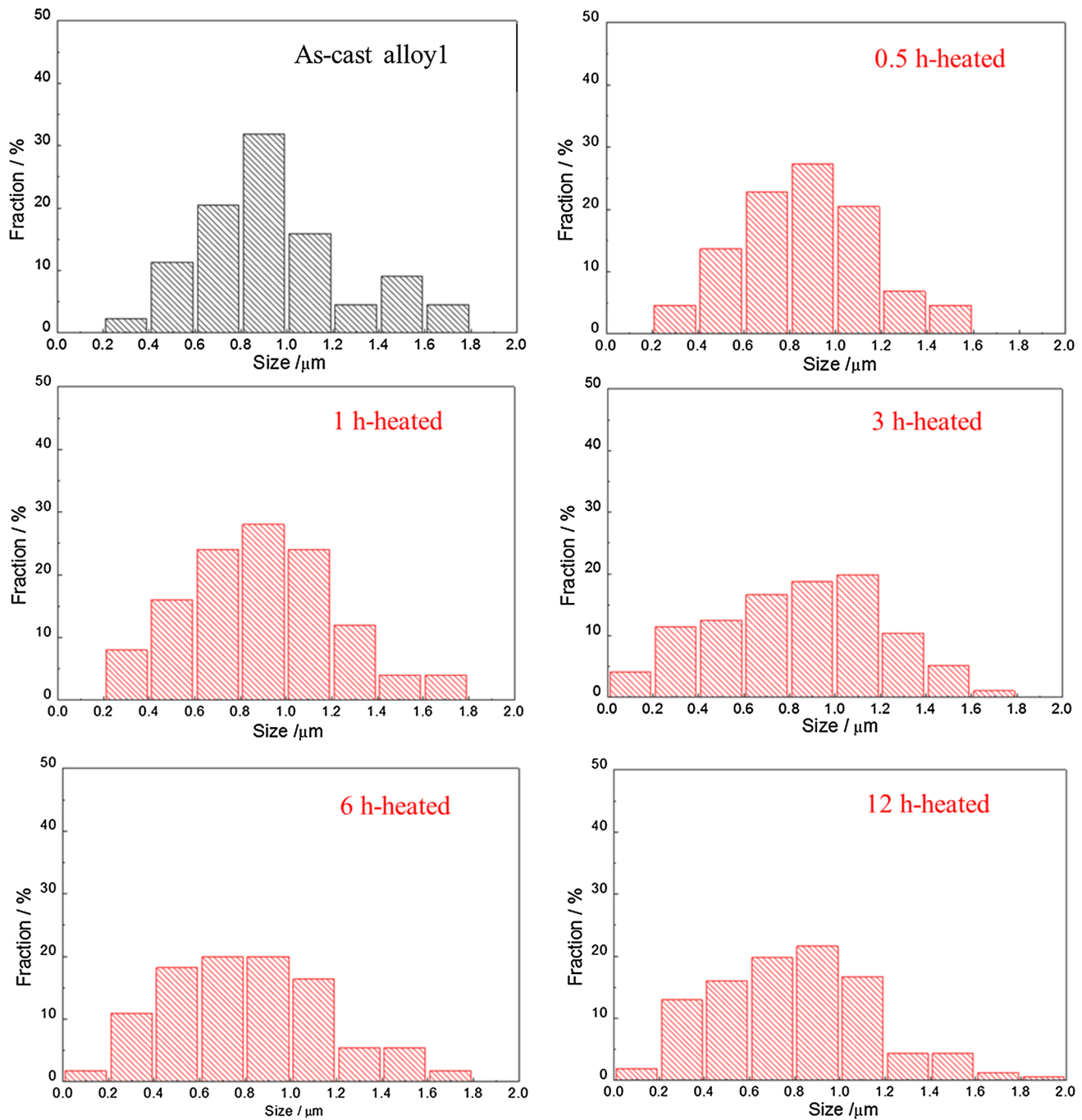
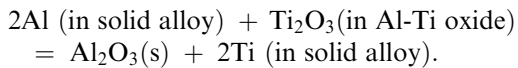
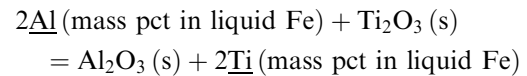


Fig. 10—Change in size distribution of Al-Ti oxide during isothermal holding at 1573 K (1300 °C) for alloy1.



As the thermodynamic data of this reaction in the solid alloy at 1573 K (1300 °C) are unavailable, the thermodynamic calculation of this reaction is assumed to be equivalent to that in liquid Fe as follows^[35,36]:



$$\Delta G^\circ = -45200 - 25.3 T \text{ J/mol}$$

$$K = \frac{a_{\text{Al}_2\text{O}_3} \cdot a_{\text{Ti}}^2}{a_{\text{Ti}_2\text{O}_3} \cdot a_{\text{Al}}^2} \quad [1]$$

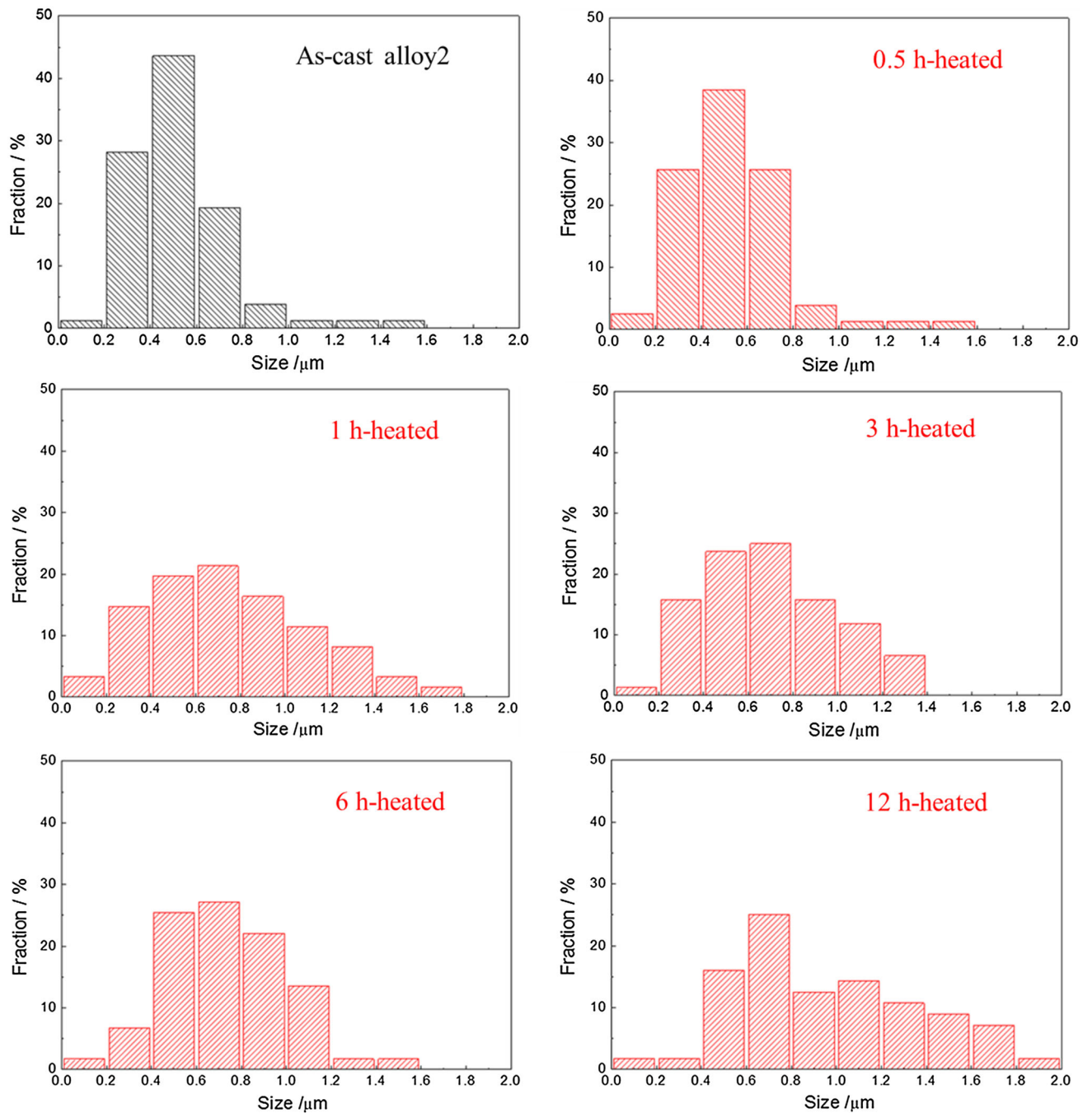


Fig. 11—Change in size distribution of Al-Ti oxide during isothermal holding at 1573 K (1300 °C) for alloy2.

The standard states of Al and Ti refer to those at a concentration of 1 mass pct in liquid Fe. The standard states of Ti_2O_3 and Al_2O_3 refer to those of the pure solid compounds. The temperature T is in Kelvin.

The thermodynamic calculation is done on the basis of the following assumptions:

1. The value of standard Gibbs energy change of the reaction at 1573 K (1300 °C) can be derived from the data measured in liquid Fe.

2. The activity coefficient of Al and Ti in liquid Fe is unity, and the effects of O and N are neglected.

The reaction can occur when the activity of Ti_2O_3 in Al-Ti oxide exceeds 0.0025 in alloy1 and 0.034 in alloy2 during isothermal holding at 1573 K (1300 °C). However, experimental thermodynamic data are unavailable. Therefore, the possibility of a reaction between the Al-Ti oxide and the matrix during isothermal holding in the present study cannot be ruled out.

Because the compositions of both the Al-rich part and the Ti-rich part in the Al-Ti oxide were almost maintained after isothermal holding for more than 1 hour, as shown in Figures 6 and 7, it is considered that the crystallization had been completed after isothermal holding for 1 hour. The equilibrium phases of the Al-Ti oxide at 1573 K (1300 °C) were found to be alumina and $Al_xTi_nO_z$. Since experimental thermodynamic data of the Fe-Al-Ti-O system at 1573 K (1300 °C) are missing, the obtained result was compared with the Al_2O_3 - Ti_2O_3 phase diagram calculated by FactSage, as introduced in our previous paper.^[29] Our results differ from the calculated results showing that Al_2TiO_5 and Magneli Ti_nO_{2n-1} are the equilibrium phases. This indicates that the thermodynamic data of this system still need to be optimized.

Ti-bearing oxide inclusions can serve as preferential nucleation sites to form the IAF microstructure during solidification and improve the strength and toughness of steel. Although the mechanism has not been fully clarified, it was found that the Mn depletion zone in the vicinity of the oxide greatly affects IAF formation through the mechanism by which Mn is absorbed into the cation vacancies of the Ti-bearing oxide.^[37] The existence of a Mn depletion zone at the interface between the Ti_2O_3 in steel and the matrix was first experimentally verified using nanoprobe TEM-EDS, as reported by Byun *et al.*^[5] It was also pointed out that the nucleation potency of different Ti-bearing oxides has a significant effect on IAF formation.^[1-5] Recently, thermodynamic analysis of the formation of the Mn depletion zone near a Ti-bearing oxide was conducted by Kang *et al.*^[38] These results indicate that IAF formation is strongly determined by the composition and structure of the Ti-bearing oxide. Among the various Ti-bearing oxides, oxides containing Al and Ti are frequently observed in practical steel, which have been proved to effectively form the IAF microstructure through the formation of the Mn depletion zone.^[39-41] Therefore, fundamental data on the changes in Ti-bearing oxide inclusions during isothermal holding are needed.

The results of the current study challenge the traditional view in oxide metallurgy that Ti-bearing oxides are stable in solid steel during isothermal holding. They reveal that changes in Ti-bearing oxide inclusions can occur in solid steel during isothermal holding.

As an extension of “traditional oxide metallurgy”, the authors propose that it is possible to modify Ti-bearing oxide inclusions that cannot form IAF to those capable of forming IAF by the following two steps: (1) the formation of a certain type of oxide, and (2) a suitable heat treatment. For this purpose, obtaining fundamental information on the evolution of different types of Ti-bearing oxide inclusions in solid alloys during isothermal holding is the first step.

Different from our previous report,^[29] the evolution of Al+Ti oxide as a heterogeneous phase is investigated and the time-dependent evolution of both Al+Ti oxide and Al-Ti oxide inclusions during isothermal holding at 1573 K (1300 °C) is reported.

The results of the present study suggest that the Al-Ti oxide hardly changes, whereas heat treatment at 1573 K (1300 °C) for 0.5 hour is sufficient to change the Al-Ti oxide. The changes in the composition, morphology, and size distribution of the Al-Ti oxide with the isothermal holding time were clarified. In a sense of its application, the inclusion change may occur in reheating process in steelmaking, joint part subjected to high temperature in welding, or Al- and Ti-killed steels heated for sufficient temperature and time.

IV. CONCLUSIONS

The effect of the isothermal holding time which was varied from 0.5 to 12 hours on the evolution of two types of Ti-bearing oxide inclusions, Al+Ti oxide, and Al-Ti oxide, in solid Fe-Al-Ti alloy in terms of their composition, shape, and size distribution during isothermal holding at 1573 K (1300 °C) was investigated systematically. The following results were obtained.

- (1) The size and compositional distribution of Al+Ti oxide were maintained during isothermal holding.
- (2) Most of the Al-Ti oxide changed from homogeneous to heterogeneous during isothermal holding. Little homogeneous Al-Ti oxide was found in the heated alloys.
- (3) The composition of Al-Ti oxide changed within 0.5 hour, and it changed earlier in the Al-Ti oxide with the higher Al content. The composition of the Al-rich part approached that of pure alumina upon isothermal holding, the morphology of the inclusions changed from spherical to irregular, and their size distribution became broader. The mechanism of their changes was considered to involve the precipitation of alumina from the oxide owing to crystallization of glassy oxide during isothermal holding.
- (4) The results suggest that it is possible to change Ti-bearing oxide inclusions by isothermal holding. This is the first step toward modifying Ti-bearing oxide inclusions in solid steel by heat treatment as a new concept in oxide metallurgy.

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