1. Introduction

In the solidification process of steel, most of the nucleation sites are either molten or solid oxides. It is known that a certain amount of lattice misfit between the molten steel and nucleation site is necessary for heterogeneous nucleation. The effects of catalysts on the heterogeneous nucleation of iron alloys have been reported. The contact angle between the molten steel and nucleation site plays an important role in determining the frequency of nucleation events. Recently, experiments using the sessile drop method showed that the contact angle of a molten iron drop on the FeAl$_2$O$_4$ layer formed between the Al$_2$O$_3$ substrate and drop was about 100°; a similar contact angle was obtained on MgAl$_2$O$_4$. The contact angle on MgO changed during observation due to the evaporation of Mg.

KEY WORDS: undercooling; contact angle; oxygen partial pressure; oxides; nucleation.

2. Experimental Method

Electrolytic iron was melted using a hydrogen plasma arc furnace. The use of hydrogen plasma arc melting ensured that the purity of the obtained sample was high. The oxygen content of this sample was 17 ppm, and other impurities were also present only in low concentrations, as listed in Table 1. The obtained sample was machined into a cylindrical shape with a diameter of 3 mm and height of 4 mm. The weight of the cylinder was approximately 0.22 g.

The sample was placed on a single-crystal oxide substrate, which was placed on a platinum plate on an alumina tube pedestal, as shown in Fig. 1. The temperature was measured using a thermocouple that was welded to the rear surface of the platinum plate. The halogen lamps were separated from the sample chamber by quartz plates. Then, the sample was heated at 100 K min$^{-1}$ through the quartz plates by the two halogen lamps, as shown in Fig. 1, under an Ar gas atmosphere. The sample was maintained at desired temperature for 15 min and then cooled at 20 K per min. The oxygen partial pressure of the Ar gas was maintained between 10$^{-15}$ and 10$^{-19}$ atm at 923 K using an oxygen pump.

### Table 1. Chemical composition of iron sample.

| Composition | O | N | C | S | Cl | Cu | H | Si |
|-------------|---|---|---|---|----|----|---|----|
| [mass ppm]  | 17| 4 | 8 | 2 | 40 | 14 | 5 | 5  |
which was also maintained at 923 K. The oxygen pump was supplied a voltage $E$ across the yttria-stabilized zirconia (YSZ) solid electrolyte in order to control the oxygen partial pressure in the Ar gas. The Ar gas flowrate into the furnace was 200 cc/min. The oxygen partial pressure of the Ar gas coming in and out of the chamber was measured simultaneously. The oxygen pump and oxygen sensor were operated using the Nernst equations in Eq. (1). In this work, the reference oxygen partial pressure was air atmosphere, $P_{O_2}^{\text{air}}$.

$$E = \frac{RT}{4F} \ln \frac{P_{O_2}'}{P_{O_2}''} \quad \text{(1)}$$

$$P_{O_2}'' < P_{O_2}' \quad \text{(2)}$$

Single-crystal oxide substrates $Al_2O_3$, MgO and $FeAl_2O_4$ with different crystal orientations were used. The properties of each substrate are summarized in Table 2. As listed in the table, all the substrates were very smooth, uniform, transparent, and disk shaped (diameter, 10 mm; thickness, 1 mm).

![Schematic diagram of experimental apparatus.](image1.png)

Fig. 1. Schematic diagram of experimental apparatus.

Table 2. Properties of single crystal oxide substrates.

| Material   | Plane index | Contour [mm] | Roughness $[R_s \, \text{nm}]$ | Roughness $[R_m \, \text{nm}]$ | Thickness [mm] |
|------------|-------------|--------------|-------------------------------|-------------------------------|----------------|
| $Al_2O_3$  | (0001)      | $\phi 10 \pm 0.1$ | -                             | -                             | 1.0 $\pm$ 0.05 |
| $Al_2O_3$  | (1012)      | $\phi 10 \pm 0.071$ | 0.712                         | 8.860                         | 1.0 $\pm$ 0.029 |
| $Al_2O_3$  | (1120)      | $\phi 10 \pm 0.051$ | 0.197                         | 2.220                         | 1.0 $\pm$ 0.037 |
| MgO        | (100)       | $\phi 10 \pm 0.031$ | 0.606                         | 4.055                         | 1.0 $\pm$ 0.023 |
| MgAl$_2$O$_4$ | (100)   | $\phi 10 \pm 0.041$ | 1.179                         | 4.895                         | 1.0 $\pm$ 0.038 |
| MgAl$_2$O$_4$ | (110)  | $\phi 10 \pm 0.036$ | 0.086                         | 1.404                         | 1.0 $\pm$ 0.027 |
| MgAl$_2$O$_4$ | (111)  | $\phi 10 \pm 0.043$ | 0.312                         | 6.343                         | 1.0 $\pm$ 0.019 |

The contact angle of the molten iron alloy on the substrate was measured while maintaining the desired temperature, 1 873 K at the platinum plate. The sample was monitored through a top window with a video camera. The measured temperatures was superimposed on the video and recorded on VHS tape during the course of the experimental work. The temperature and oxygen partial pressures were also recorded by a digital data logger. After the sample was melted, it was irradiated with ultraviolet light from the left side (Fig. 1, and the shape of the sample was observed though a visible light cut filter with a digital camera. After the temperature of 1 873 K was reached, the image of the sample was captured once every minute. The degree of undercooling of the iron alloy was measured during cooling. After the experiment was conducted, a cross section of the sample was observed using EPMA with EDS and WDS.
3. Results

3.1. Undercooling of Molten Pure Iron on the Oxide Substrate

The sample chamber was vacuumed under $6 \times 10^{-5}$ Torr using an oil rotary pump and an oil diffusion pump in order to check for any leakage in the chamber and to remove gaseous impurities from the sample and the chamber. Then argon gas was introduced into the chamber. The oxygen partial pressure was set to $10^{-15}$ or $10^{-19}$ atm. The oxygen partial pressures and the temperature of the platinum plate under the substrate were recorded as shown in Fig. 2. During heating, when the sample was melted, the measured temperature was defined as the melting point of the sample. Since the impurity content of the sample was very low, the mushy zone was quite small. The errors in the measured temperatures originating from the configuration of the samples and thermal properties of the substrate were corrected for on the basis of the melting point of the sample. An actual temperature of the sample was 60±30 K higher than that of the platinum plate. The sample was actually heated to 1933±30 K with 100 K/min. The oxygen partial pressure in the inlet gas was well stabilized by using the oxygen pump. The reproducibility of the oxygen partial pressure in the inlet gas was very high during course of the experiments. The oxygen partial pressure in the outlet gas decreased and reached about $10^{-21}$ atm after about 16 min under all experimental conditions. The temperature was stable at 1933 K. During cooling, the recalescence of the sample was detected as shown in Fig. 2(b), and then the solidifying point was obtained at the temperature arrowed by A. The undercooling was obtained from the difference between the measured melting and solidifying points. The results of the measured undercooling of pure iron on various substrates are summarized in Table 3. In the case of the Al$_2$O$_3$ and MgAl$_2$O$_4$ substrates, the effects of the oxygen partial pressure in the inlet gas and the orientation of the substrate on the degree of undercooling were observed. The obtained values of the undercooling under $10^{-15}$ atm were higher than that under $10^{-19}$ atm in the inlet argon gas.

3.2. Contact Angle between Molten Iron and Oxide Substrate

The contact angle was measured at both left and right sides of the sample at the triple point among gas, substrate, and molten iron from the photographs obtained at 1933 K. The average value of the measured contact angles was plotted in Figs. 3 and 4 as a function of the time at 1933 K. $P_{O_2}$ has a minimal effect on the contact angle. The contact angle decreased gradually after melting the sample on the substrate. Six minutes after the temperature reached 1933 K, the contact angle showed a constant value around 100° for

Table 3. Undercooling of pure-iron on the various substrates under $P_{O_2}=10^{-15}$ atm and $P_{O_2}=10^{-19}$ atm in the inlet argon gas.

| Substrate | Plane index | Undercooling (K) |
|-----------|-------------|-----------------|
| Al$_2$O$_3$ | (0001) | 213 | 160 |
| Al$_2$O$_3$ | (1012) | 225 | 211 |
| Al$_2$O$_3$ | (1120) | 195 | 145 |
| MgO | (100) | 46 | 53 |
| MgAl$_2$O$_4$ | (100) | 169 | 121 |
| MgAl$_2$O$_4$ | (111) | - | 171 |
| MgAl$_2$O$_4$ | (111) | - | 149 |

Fig. 2. (a) Change in $P_{O_2}$ in the inlet outlet argon gas under $P_{O_2}$ enter the furnace controlled $10^{-15}$ atm and temperature of the sample. (b) Increase in temperature change indicated by circle in upper figure (a). Recalescence was observed.

Fig. 3. Change in contact angle between pure iron and oxide substrate as a function of elapsed time at the holding temperature. Data obtained for $P_{O_2}=10^{-15}$ atm in the inlet argon gas.
both Al$_2$O$_3$ and MgAl$_2$O$_4$ under $P_{O_2}/P_{H_2} = 10^{-15}$ atm in the inlet argon gas. When $P_{O_2} = 10^{-19}$ atm in the inlet argon gas, the contact angle showed almost same phenomena as the $10^{-15}$ atm case. With the MgO substrate, the measured contact angle was scattered and decreased with time. No significant effects of the oxygen partial pressure were observed for all substrates.

### 3.3. Observation of Interface between Solidified Iron and the Oxide Substrate

The thickness of the reaction layer varied according to the different oxygen partial pressure and orientation of the substrate as summarized in Table 4.

#### 3.3.1. Al$_2$O$_3$ Substrate

Figures 5 and 6 show an SEM image of a cross section of the interface between solidified iron and the substrates. The reaction layer formed on the (1120) plane was thicker than that formed on the (1012) plane. The reaction layer was identified as FeAl$_2$O$_4$ using EPMA. Inside the solidified iron, small FeO particles marked by circles were observed as shown in Fig. 7 under all experimental conditions.

#### 3.3.2. MgAl$_2$O$_4$ Substrate

Figure 8 shows the interface between the solidified iron and MgAl$_2$O$_4$ substrate obtained under $P_{O_2} = 10^{-19}$ atm in the inlet argon gas. The observed reaction layer was discontinuous and thin. As listed in Table 4, the thickness of the reaction layer for MgAl$_2$O$_4$ (100) was larger than for the others. The reaction layer contained Mg, Al, O, but with several atomic percent Fe.
3.3.3. MgO Substrate

In the case of MgO substrate, no reaction layer was observed under both low and high oxygen partial pressure cases as shown in Fig. 9. However, small particles of FeO were detected in the sample.

4. Discussion

4.1. Oxygen Partial Pressure in the Chamber at 1933 K

The measured contact angle was not affected by the oxygen partial pressure or surface orientation of the substrates. The measured values were almost same as the values obtained by Kapilashrami and Seetharaman\(^\text{10}\) in the case of iron melts on refractory metal substrates. They also found a reactive layer at the interface between the molten iron and the oxide substrate, and the thickness of the reactive layer to be approximately 30 to 80 \(\mu \text{m}\). Several other researchers\(^\text{5,6,11,12}\) have reported on the effects of the oxygen partial pressure on the wettability of molten iron on an alumina substrate. Ogino et al.\(^\text{11}\) reported that the reaction layer was found at the interface between the molten iron and the oxide substrate, and the thickness of the reaction layer was about 200 \(\mu \text{m}\) when the oxygen concentration of the solidified iron droplet was 285 ppm. This result was obtained under \(P_{O_2}=10^{-3}\) atm. Furthermore, the measured contact angle in this study was almost 100\(^\circ\) after 16 min at 1933 K; this value is consistent with the values obtained by Ogino et al. under \(P_{O_2}=10^{-3}\) atm. The thickness of the reaction layer on alumina substrate in this study was less than 6 \(\mu \text{m}\). From these comparisons, oxygen partial pressure in the chamber at 1933 K is estimated to be about 10\(^{-7}\) atm.

On the other hand, the oxygen partial pressure in the outlet Ar gas was reduced to about 10\(^{-7}\) atm under both cases \(P_{O_2}=10^{-15}\) and 10\(^{-19}\) atm in inlet argon gas. The oxygen partial pressure was set to 10\(^{-15}\) atm and 10\(^{-19}\) atm at 923 K by using an oxygen pump. The oxygen partial pressure in outlet gas probably achieved the equilibrium condition between molten iron and oxide substrate under both experimental conditions since the oxygen partial pressure in the outlet argon gas was almost 10\(^{-21}\) atm under all experimental conditions. The argon gas used was of ultra high purity but contained small amount of oxygen and water, and other impurities. Naito et al.\(^\text{13}\) and Tomioka et al.\(^\text{14}\) have already pointed out that oxygen partial pressure is controlled under \(\text{H}_2–\text{O}_2–\text{H}_2\text{O}\) equilibrium under high hydrogen content buffer gas. The formation of water is shown by following equations.

\[
2\text{H}_2(\text{g})+\text{O}_2(\text{g})=2\text{H}_2\text{O}(\text{g}) \quad \Delta G^0=-493\,070+109.887\,T \quad (\text{J/mol})
\]

The oxygen partial pressure in argon gas is assumed to be controlled by the above reaction. The oxygen sensor and oxygen pump were operated at 923 K. A ratio of \(P_{\text{H}_2\text{O}}/P_{\text{H}_2}\) at 923 K is assumed to be maintained at 1933 K and was obtained from the measured oxygen partial pressure. Then the oxygen partial pressure at 1933 K is calculated by following Eq. (5).

\[
P_{O_2} = \frac{1}{K_{1933\,K}} \left( \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \right)_{923\,K}^{2}
\]

where \(P_{O_2}=10^{-15}\) and 10\(^{-19}\) atm in the inlet argon gas at 923 K were calculated as 0.38 and 3.8\(\times\)10\(^{-5}\) atm, respectively. Therefore, under this experimental condition, the inlet argon gas probably has a high oxygen partial pressure. The oxygen partial pressure becomes 4\(\times\)10\(^{-7}\) atm at 1933 K. The oxygen partial pressure of 4\(\times\)10\(^{-7}\) atm is probably the highest among the value of oxygen partial pressure which can be achieved in the chamber at 1933 K. The equilibrium among \(\text{H}_2–\text{O}_2–\text{H}_2\text{O}\) system partially explains the high oxygen partial pressure in the chamber at 1933 K.

Therefore, from these discussions, the equilibrium oxygen partial pressure in the chamber at 1933 K is estimated to be in the range between 10\(^{-7}\) and 10\(^{-9}\) atm. If the actual oxygen partial pressure is close to these values at 1933 K, and then the formation of FeO and FeAl\(_2\)O\(_4\) could take place following discussion.

4.2. Undercooling and Contact Angle

4.2.1. \(\text{Al}_2\text{O}_3\)

Under these experimental conditions, the following reactions may take place.

\[
4/3\text{Al}(\text{l})+\text{O}_2(\text{g})=2/3\,\text{Al}_2\text{O}_3(\text{s}) \quad \Delta G^0=-1\,126\,890+218.81\,T \quad (\text{J/mol})
\]

\[
\text{Fe}(\text{l})+1/2\text{O}_2(\text{g})=\text{FeO}(\text{l}) \quad \Delta G^0=-232\,700+45.31\,T \quad (\text{J/mol})
\]
The stability of each oxide is shown in Fig. 10 as a function of the oxygen partial pressure and the temperature. Under $P_{O_2} = 10^{-3}$ atm and at 1933 K, $Al_2O_3$, $FeAl_2O_4$ is stable, and $FeO$ can form. These results closely match the observation of the reaction layer at the interface and FeO particles in the solidified iron drop. The contact angle was probably measured between the reaction layer and the molten iron. The surface tension of molten iron is strongly affected by any impurities, especially oxygen.\(^{11,12}\) The equilibrium oxygen partial pressure is almost same despite any difference in the oxygen partial pressure in the inlet argon gas. The amount of dissolved oxygen may be almost the same as the value of the contact angle.

The amount of undercooling of the iron on $Al_2O_3 (1012)$ was 14 K less under $P_{O_2} = 10^{-10}$ atm than that under $P_{O_2} = 10^{-15}$ atm in the inlet argon gas. The amount of undercooling of the iron on $Al_2O_3 (0001)$ and $Al_2O_3 (1120)$ was also about 50 K less. The effect of the oxygen partial pressure on the contact angle was not significant. A thin layer of hercynite ($FeAl_2O_4$) was observed at the interface in all cases. That means the undercooling of iron occurred on the same material, hercynite, under different oxygen partial pressure conditions. The degree of undercooling was often related to the lattice misfit between the solidified iron and the substrates using the planar disregistry proposed by Bramfit.\(^{11}\) However, in this case the planar disregistry between $\delta$-iron and hercynite could not explain the difference in undercooling. The difference in undercooling is related to the thickness of the reactive layer, $FeAl_2O_4$, observed at the interface between the solidified steel and the substrates as shown in Fig. 11. In the case of the $Al_2O_3 (0001)$ and $Al_2O_3 (1120)$, the thickness of the reactive layer increased from 3.5 to 6 $\mu$m and from 3 to 6 $\mu$m with the decrease in the oxygen partial pressure from $10^{-15}$ to $10^{-19}$ atm in the inlet argon gas, respectively. When hercynite is formed at the interface, the O and Al from $Al_2O_3$ should dissolve into the molten iron, and Fe moves to the reactive layer. As the thickness of the reactive layer increases, the amount of those impurities in the molten iron increases. Therefore, the amount of undercooling decreases. Kudoh \textit{et al.}\(^{15}\) reported that the degree of undercooling of iron decreased with the increasing of Al content in the iron drop. The results of this study are consistent with the results of Kudoh \textit{et al.}, which implies that the number of nucleation sites increases as the amount of impurity in the molten iron increases. When the number nucleation sites increases, then the nucleation frequency in the molten iron may also increase, resulting in a decrease in the degree of undercooling.

The effect of the crystal orientation of the substrates on the thickness of the reaction layer was observed. The thickness of the reaction layer for $10^{-19}$ atm in the inlet argon gas was thicker than that for $10^{-15}$ atm case for all substrates. However, the reactivity of the each crystal layer under different oxygen partial pressure conditions has not been clarified yet. Further investigations are required.

4.2.2. $MgAl_2O_4$

$MgAl_2O_4$ may react with iron as follows.\(^{16}\)

$$MgAl_2O_4 = Mg + 2Al + 4O$$

Since a small particle of FeO was observed in the solidified iron, the oxygen partial pressure was probably high during the observation. The oxygen content may have been high enough to form $MgAl_2O_4$ during the experiment. The amount of undercooling increased as the thickness of the reaction layer increased as listed in Table 4. The effect of impurities in the molten iron on undercooling is probably significant as well as $Al_2O_3$ cases. In contrast, the reaction layer was discontinuous, allowing the molten iron to come into direct contact with the $MgAl_2O_4$ substrate. Both the impurities and the crystal orientation of the substrates may have a coupled effect on the undercooling of iron. The change in the contact angle in the $MgAl_2O_4$ case is also explained as well as $Al_2O_3$ case. The value of the contact angle of $MgAl_2O_4$ is close to that of $FeAl_2O_4$. This result indicates that the interfacial energy between molten iron and $MgAl_2O_4$ is quite similar to that of $FeAl_2O_4$. Since the surface tension of molten iron had the same value in both cases.

4.2.3. $MgO$

$MgO$ also reacts with iron as follows.\(^{17}\)

$$MgO = Mg + O$$

$MgO$ may dissolve into iron. Since the boiling point of magnesium is 1363 K, the dissolved magnesium evaporates...
as follows:

\[
\text{Mg} = \text{Mg (g)} \]

The dissolved magnesium accumulates near the surface of the molten iron, and then the magnesium may evaporate from the surface. The surface tension of molten iron may change with magnesium content at the surface of the molten iron. The observed contact angle repeats decrease and increase, and gradually decreased with time. This observation implies that this reaction repeated and oxygen content in the sample simultaneously increased with time. In the MgO case, since the molten iron was attached to the MgO substrates, the planar disregistry can explain the low undercooling of the iron because the value of the planar disregistry is 3.3%. According to Bramfitt, when planar disregistry is less than about 12%, the nucleating agent is potent. Therefore, the degree of undercooling is effectively decreased.

4. Conclusion

The reproducibility of the experimental conditions of the sessile drop technique related to the oxygen partial pressure in the atmosphere gas was well established. Then the following results were obtained. In the case of Al₂O₃ and MgAl₂O₄, the change in the degree of undercooling were dependent on the existence of the reaction layer and its thickness under this experimental conditions. The dissolved impurities in the molten iron have shown a significant effect on the degree of undercooling. However, the effects of oxygen partial pressure and orientation of the oxides substrates on the contact angle and the degree of undercooling were not entirely clear since the reaction layer was formed at the interface. In the case of MgO, the reaction layer was not observed. The undercooling was governed by the lattice misfit between the 6-iron and MgO. The change in the contact angle on MgO must be governed by the evaporation of magnesium from the surface of the molten iron.

Further investigation is required in order to understand the nucleation phenomena and the estimation of oxygen partial pressure in argon gas.

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REFERENCES

1) B. Bramfitt: Metall. Trans., 1 (1970), 1987.
2) K. Nakajima, H. Hasegawa, S. Kumkoa and S. Mizoguchi: Metall. Mater Trans. B, 24B (2003), 539
3) K. Nakajima, H. Hasegawa, S. Khunkoa and M. Hayashi: ISIJ Int., 46 (2006), 801.
4) T. Ohashi, T. Hiromoto, H. Fujii, Y. Nuri and K. Asano: Tetsu-to-Hagané, 62 (1976), 614.
5) M. E. Valdez, P. Uranga, K. Fuchigami, H. Shibata and A. Cramb: Metall. Mater. Trans. B, 37B (2006), 811.
6) M. E. Valdez, H. Shibata and A. W. Cramb: Metall. Mater. Trans. B, 37B (2006), 959.
7) T. Suzuki, J. Inoue and T. Koseki: ISIJ Int., 47 (2007), 847.
8) Y. Watanabe, H. Shibata and S. Kitamura: CAMP-ISIJ, 21 (2008), 159, CD-ROM.
9) K. Mimura, K. Saito and M. Ishihara: J. Jpn. Inst. Met., 63 (1999), 1181.
10) E. Kapilashrami and S. Seetharaman: J. Mater. Sci., 40 (2005), 2372.
11) K. Ogino, K. Nogi and Y. Koshida: Tetsu-to-Hagané, 59 (1973), 1380.
12) K. Nakashima, K. Takihira, K. Mori and N. Shinozaki: J. Jpn. Inst. Met., 55 (1991), 1199.
13) K. Naito, T. Tsai and S. Watanabe: Solid State Ionics, 1 (1980), 509.
14) K. Tomioka and H. Suito: Bull. Inst. Adv. Mater. Process., Tohoku Univ., 47 (1991), 10.
15) M. Kudo, J. Tanaka, K. Okuyama and K. Ohsasa: Bull. Faculty Eng., Hokkaido Univ., No. 162, (1992), 191.
16) H. Itoh, M. Hino and S. Ban-ya: Tetsu-to-Hagané, 84 (1998), 85.
17) H. Itoh, K. Fujii, T. Nagasaka and M. Hino: Steel Res., 74 (2003), 86.