Effect of Oxide Catalyst on Heterogeneous Nucleation in Fe–10mass%Ni Alloys

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In order to elucidate the nature of heterogeneous nucleation, a differential scanning calorimetry (DSC) thermal analysis of Fe–10mass%Ni alloys containing oxide catalysts was conducted. For all oxide catalysts, the maximum frequency in the particle-size distributions diminishes and the modal value increases with a decrease in the amount of deoxidizers or with an increase in the elapsed time after deoxidizer addition. That is, the number of smaller particles decreases, while the number of larger particles increases. In proportion to this change of the particle-size distribution, the critical undercooling (ΔT) increases. For the same amount of deoxidizers and the same elapsed time, the value of ΔT for the primary crystal of the γ phase is smaller in the order of MgO, ZrO2, Al2O3, and CaO–Al2O3. Oxide catalysts grow by Ostwald ripening, therefore the growth can be controlled by the diffusion of oxygen. Thus, the decrease of the soluble oxygen content by strong deoxidizers results in the inhibition of particle growth.

KEY WORDS: Fe–Ni alloy; heterogeneous nucleation; critical undercooling; oxide catalyst; particle-size distribution; Ostwald ripening.

1. Introduction

Various phenomena of solidification-structure formation caused by heterogeneous nucleation have been encountered in material production processes and have been studied extensively. Studies on heterogeneous nucleation have been performed from the viewpoint of controlling these phenomena. However, the heterogeneous nucleation mechanism is not yet understood sufficiently, owing to the experimental difficulty and the complexity of the phenomena.

Therefore, in order to elucidate the nature of heterogeneous nucleation, an experimental approach different from others was taken in our previous studies1,2) in which we used a differential scanning calorimetry (DSC) apparatus. The DSC apparatus has the advantage that various transformation phenomena are examined based on both temperature-time profiles and DSC thermograms. The undercoolings of pure Fe, Fe–Ni alloys (Ni content: 1.0 to 29.3 mass%), and Fe–Ni–Cr alloys (Ni+Cr content=30 mass% (constant); Ni content: 7.5 to 29.3 mass%) containing TiN and Al2O3 were measured systematically. Then, some important features of heterogeneous nucleation, such as the relationship between catalysts (nucleation agents), chemical compositions, and nucleated primary crystals, were synthetically elucidated. The effect of the crystallized content of catalyst (that is, the number of catalyst nuclei) on the critical undercooling was also discussed, and consequently, the importance of the dispersion of ultrafine catalyst nuclei, including the inhibition of ripening, coarsening, and float-out, to heterogeneous nucleation was suggested.

In the present study, the measurement of undercooling using a DSC apparatus is applied to Fe–10mass%Ni alloys deoxidized with Mg, Zr, Ca, and Al. In view of the importance of the number of catalyst nuclei to the critical undercooling, the particle-size distribution of deoxidation products, that is, oxide catalysts, and their characteristics were measured by potentiostatic electrolysis3,4) using nonaqueous solutions as electrolytes. Some important features of the heterogeneous nucleation caused by oxide catalysts, such as the relationship between the kind of catalyst, the particle-size distributions (related to the amount of deoxidizers and the elapsed time after deoxidizer addition), and nucleated primary crystals were elucidated.

2. Experiment

2.1. Preparation of Samples

In order to exclude the strong turbulent motion of the melt, 70g samples of Fe–10mass%Ni mother alloy were melted, and then kept at 1600°C for 30 min in an alumina crucible under an ultrahigh-purity Ar gas atmosphere in a high frequency induction furnace (frequency: 100kHz), with a graphite susceptor. At this point, the initial oxygen content in the melt of the mother alloy was from 100 to
Various kinds of deoxidizer (Ni–10mass%Mg, Fe–10mass%Zr, Ni–7mass%Ca, and Fe–10mass%Al) were added into the melt of the mother alloy, and then the melt was stirred for 10 s with an alumina rod for uniform dispersion of deoxidation products. The amount of deoxidizer corresponding to 0.05 mass% or 0.1 mass% was selected, respectively. Then, the melt was kept at 1600°C for different durations (60, 180, 600, or 1800 s). Then, it was finally quenched in a water bath after it was taken from the furnace. In this manner, 18 kinds of samples were made. The chemical composition was adjusted to the desired contents of Mg, Zr, Ca, Al, and O. Table 1 shows the chemical compositions of the samples. These samples are classified into group A (Mg- and O-rich), group B (Zr- and O-rich), group C (Ca-, Al- and O-rich), and group D (Al- and O-rich) corresponding to the deoxidation products, that is, the desired oxide catalysts.

### 2.2. Measurement of Particle-size Distribution of Oxide Catalysts and Their Identification

The particle-size distribution was measured for deoxidation products extracted as residues on a filter after electrolysis for each sample. This method has the advantage that the size distribution of ultrafine particles, which act as nucleation agents, is exactly examined. The detailed procedure is as follows.

The sample was dissolved by potentiostatic electrolysis (voltage: 150 mV, electric current: 50 mA), until the total amount of electric charge reached 150 coulombs. The amount of dissolved sample was about 0.05 g. The 10% AA electrolyte was used for samples of group B (Zr- and O-rich) and group D (Al- and O-rich), and the 2% TEA electrolyte was used for samples of group A (Mg- and O-rich) and group C (Ca-, Al- and O-rich). For the preparation of the 10% AA electrolyte, 10 g of tetramethylammonium chloride was dissolved into 100 mL of acetylacetone, followed by the addition of methanol to the total volume of 1000 mL. For the preparation of the 2% TEA electrolyte, 10 g of tetramethylammonium chloride was dissolved into 20 mL of triethanolamine, followed by the addition of methanol to the total volume of 1000 mL. Then, the electrolyte was filtered using a polycarbonate membrane filter with open pore size of 0.05 μm (10 mm in diameter). The particles on the filter were carefully observed at a magnification of 10,000 times by scanning electron microscopy (SEM). About 10⁴ μm², corresponding to about 0.01% of the filter area, was taken as the observed area, because the particles were dispersed uniformly over the whole filter. The size distribution of the particles was measured on the micrograph of the SEM projection image. Furthermore, their compositions were analyzed on several points of a particle using an electron probe microanalyzer (EPMA). The deoxidation products with Mg, Zr, and Al were detected as pure MgO, ZrO₂, and Al₂O₃, respectively. Those with Ca were detected as 40mass%CaO–60mass%Al₂O₃ owing to the reaction with the alumina crucible, and were in the form of liquid globules.

Thus, the size distributions and the compositions of the
particles obtained on a filter were determined by SEM and using EPMA, respectively. It is possible to assume that oxides such as MgO, ZrO$_2$, Al$_2$O$_3$ (solid), and CaO–Al$_2$O$_3$ (liquid) were first crystallized and then suspended in the melts. They then act as catalysts during solidification because their sizes are very small.

2.3. DSC Experiment

A small piece of each sample was machined into a disc (3 mm in diameter, 2 mm in height), melted, and then solidified in an alumina crucible under an ultrahigh-purity Ar gas atmosphere in the DSC apparatus. The heating rate ($R_h$) was kept constant at 20°C/min up to 1 600°C. Then, undercooling was measured at a cooling rate ($R_c$) of 20°C/min. The temperature was recorded at 0.4-second intervals, for the increase in detection accuracy.

In thermal analysis during heating, the equilibrium temperatures of the melting point, and the latent heat of fusion are obtained. On the other hand, in thermal analysis during cooling, the nonequilibrium temperatures are obtained for the crystallization of the primary crystal of either δ phase or γ phase (starting point of nucleation), $T_\delta$ nucleation and $T_\gamma$ nucleation, respectively. Here, the difference between the melting point during heating and the starting point of nucleation during cooling is defined as the extent of undercooling for heterogeneous nucleation ($\Delta T$). The melting points were reproduced exactly in accordance with the equilibrium-phase diagram calculated by Thermo Calce$^{15}$ (database: TC-FE2). In addition, the values of the latent heat of fusion were almost the same as the calculated values. It was judged from these results that the present DSC thermal analysis is reliable.

3. Results

By paying special attention to the relationship between the kind of catalyst and the kind of primary crystal, the effects of deoxidation operational factors on the extent of critical undercooling ($\Delta T$) at the cooling rate of $R_c=20$°C/min are clarified, as summarized in Fig. 1. The amount of deoxidizers and the elapsed time after deoxidizer addition will lead directly to the particle-size distributions. The primary crystal was of the δ phase or the γ phase in the case of Al$_2$O$_3$ catalyst, though the primary crystal was only of the γ phase in the case of other catalysts. It seems that in the case of Al$_2$O$_3$ catalyst, the transition from FA mode to A mode takes place near 10 mass% Ni, in accordance with the result obtained in our previous study.$^{11}$ That is, the appearance of nonequilibrium phases during cooling in these alloys is classified into two cases. (1) FA mode: After crystallization of the primary crystal of the δ phase, the triple-phase state consisting of the L + δ + γ phases is formed through a peritectic reaction. Then, after solidification is completed, it transforms to the γ phase. (2) A mode: Solidification is completed in the single-phase state of the γ phase. In any case, it is clear that for all oxide catalysts, the maximum frequency in the particle-size distributions diminishes and the modal value increases with a decrease in the amount of deoxidizers or with an increase in the elapsed time. This result means that the number of smaller particles decreases, while the number of larger particles increases. It is notable that the critical undercooling surely increases in proportion to this change of the particle-size distribution.

3.1. MgO Catalyst and ZrO$_2$ Catalyst

Temperature–time profiles and DSC thermograms for samples of group A and group B are shown in Figs. 2 and 4, respectively. Only A mode appeared. The correlations between $\Delta T$ and the particle-size distributions are summarized in Figs. 3 and 5. With the same amount of deoxidizers and the same elapsed time, ZrO$_2$ catalyst has a lower maximum frequency and a larger modal value as compared with MgO catalyst. Consequently, the value of $\Delta T$ for the primary crystal of the γ phase is smaller in the order of MgO and ZrO$_2$.

3.2. CaO–Al$_2$O$_3$ Catalyst

In group C again, only A mode appeared. The correlations between $\Delta T$ and the particle-size distributions are summarized in Fig. 6. With the same amount of deoxidizers and the same elapsed time, CaO–Al$_2$O$_3$ catalyst has a higher maximum frequency and a larger modal value as compared with ZrO$_2$ catalyst and MgO catalyst. Consequently, the value of $\Delta T$ for the primary crystal of the γ phase is smaller in the order of MgO and CaO–Al$_2$O$_3$.

3.3. Al$_2$O$_3$ Catalyst

Temperature–time profiles and DSC thermograms for samples of group D are shown in Fig. 7. Both FA mode and A mode appeared. The correlations between $\Delta T$ and the particle-size distributions are summarized in Fig. 8. With the same amount of deoxidizers and the same elapsed time, Al$_2$O$_3$ catalyst has the lowest maximum frequency and the largest modal value. The value of $\Delta T$ for the primary crystal of the δ phase is always smaller than that for the primary crystal of the γ phase, in accordance with the result obtained in our previous study.$^{11}$ In samples with $[O]=23$ ppm, $\Delta T=154$°C for the primary crystal of the γ phase. Briefly, with the same amount of deoxidizers and the same elapsed time, the value of $\Delta T$ for the primary crystal
Fig. 2. Typical examples of temperature–time profiles and DSC thermograms obtained at a cooling rate of $R_c=20\,^\circ\text{C}/\text{min}$ for samples of group A (Mg- and O-rich).

Fig. 3. Correlations between extent of critical undercooling and particle-size distributions for samples of group A (Mg- and O-rich).

Fig. 4. Typical examples of temperature–time profiles and DSC thermograms obtained at a cooling rate of $R_c=20\,^\circ\text{C}/\text{min}$ for samples of group B (Zr- and O-rich).

Fig. 5. Correlations between extent of critical undercooling and particle-size distributions for samples of group B (Zr- and O-rich).
of the γ phase is smaller in the order of MgO, ZrO₂, Al₂O₃, and CaO–Al₂O₃. Of course, this order includes the effect of the particle-size distribution. Thus, in order to reveal the catalytic potency itself for the primary crystal of the γ phase, ΔT of the MgO catalyst was compared with that of the ZrO₂ catalyst under almost the same particle-size distribution. As shown in Fig. 9, the value of ΔT is smaller in the order of ZrO₂ and MgO. That means that the catalytic potency of ZrO₂ is greater.

4. Discussion

It is clear that for all oxide catalysts, the maximum frequency in the particle-size distributions diminishes and the modal value increases with a decrease in the amount of deoxidizers or with an increase in the elapsed time after deoxidizer addition. If this change of the particle-size distributions cannot be inhibited, it might be difficult to apply the oxide catalyst in the control of the solidification-structure. Therefore, let us discuss the growth mechanism of oxide catalyst in the Fe–10mass%Ni alloy melt.

In a system where there are dispersed particles of various sizes, which are soluble in the surrounding medium, the smaller particles tend to dissolve and their solute elements crystallize into the larger particles. The driving force of this mechanism is derived from the consequent reduction in interfacial free energy. This is the process referred to as Ostwald ripening. A comprehensive theory of particle coarsening in isothermal systems was first developed by Lifshitz and Slyozov⁶) and Wagner⁷) (LSW). It was found, by LSW, that, in the regime of coarsening (steady state), the cube of an average particle radius (R(t)) increases linearly with time (t):

\[ R(t)^3 = R(0)^3 + 3K_{LSW}t \]  

where \( R(0)^3 \) is the average radius at \( t = 0 \), and \( K_{LSW} \) is the coarsening-rate constant given by

\[ K_{LSW} = \frac{4}{9} \frac{2\sigma \rho^p C_k D_k}{RT(C_p^k - C_k)} \]  

where \( C_k \) is the content of solute element \( k \) (=Mg, Zr, Ca, Al, and O) in the melt, \( C_k^p \) is the content of element \( k \) in the particle, \( R \) is the gas constant, \( T \) is temperature, \( \rho^p \) is the molar volume of the particle, and \( \sigma \) is the interfacial free energy between the particle and the melt. Equations (1) and (2) can be used to predict the particle growth after deoxidizer addition. As shown in Fig. 10, all of MgO, ZrO₂, CaO–Al₂O₃, and Al₂O₃ catalysts satisfied the \( t^{1/3} \) dependence particle growth based on Ostwald ripening. The coarsening-rate constant \( (K_{LSW}) \) can be approximately obtained as the slope of regression line in a plot of \( R(t) \) versus \( t^{1/3} \), because \( R(0) \) is comparably small. For the same amount of deoxidizer, the values of \( K_{LSW} \) are arranged in the order of CaO–Al₂O₃ > MgO > ZrO₂ > Al₂O₃. Since oxide catalyst and each solute element of which the oxide catalyst is composed are in an equilibrium state, the soluble oxygen content \( (C_{O}) \) is approximately estimated. Figure 11 shows the relationship between \( K_{LSW} \) and \( C_{O} \) for each oxide catalyst. \( K_{LSW} \) increases in proportion to \( C_{O} \). This means that the decrease of \( C_{O} \) by strong deoxidizers results in the inhibition of particle growth. In the actual steel-making process, the following measure can be taken to inhibit the
growth of crystallized catalyst particles: the timely addition of some deoxidizers according to the order of deoxidation potency. Suzuki et al. also suggested that MnO–SiO$_2$–Al$_2$O$_3$ particles grow by Ostwald ripening during solidification in continuously cast slabs and test ingots of stainless steel (AISI 304) deoxidized weakly with Mn and Si, and that the particle growth can be controlled by the diffusion of oxygen. However, their average particle sizes are one order of magnitude larger than ours.

5. Conclusions

Some important features of the heterogeneous nucleation caused by oxide catalysts, that is, the relationships between the kinds of catalyst, their particle-size distributions (related to the amount of deoxidizers and the elapsed time after deoxidizer addition), and nucleated primary crystals, were elucidated. The following results were obtained.

(1) For all oxide catalysts, the maximum frequency in the particle-size distributions diminishes and the modal value increases with a decrease in the amount of deoxidizers or with an increase in the elapsed time. That is, the
number of smaller particles decreases while the number of larger particles increases. In proportion to this change of the particle-size distribution, the critical undercooling (ΔT) increases. For the same amount of deoxidizer and the same elapsed time, the values of ΔT for the primary crystal of the γ phase are arranged in the order of MgO<ZrO2<Al2O3<CaO–Al2O3.

(2) Oxide catalysts grow by Ostwald ripening, therefore the growth can be controlled by the diffusion of oxygen. Thus, the decrease of the soluble oxygen content by strong deoxidizers results in the inhibition of particle growth.

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