Application of an Optical DTA for Morphological Transition in the Al$_2$O$_3$–YAP–ZrO$_2$ Metastable Eutectic System

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This paper presents an optical DTA apparatus which is capable to examine the solidification behavior of the Al$_2$O$_3$-based materials. A direct current through the two Mo crucibles effectively heats specimen and reference up to 2400 K. The small heat capacity of the crucible and the specimen enabled a cooling rate up to the order of 10$^2$ K/s. Since accuracy of temperature measurement by two two-color pyrometers was not affected by emissivity change to phase transformation, exothermic and endothermic heats in the specimen was efficiently detected at high temperatures. The developed apparatus was used to examine DTA for $\alpha$-Al$_2$O$_3$ and the Al$_2$O$_3$–YAP–ZrO$_2$ metastable eutectic system. The morphological transition from the entangled eutectic structure to the lamellar eutectic structure was observed at a cooling rate around 10 K/s. At a cooling rate more than 70 K/s, $\alpha$-Al$_2$O$_3$ phase started to solidify as a primary phase. Furthermore, the divorced eutectic solidification was recognized at a cooling rate of 360 K/s.

KEY WORDS: differential thermal analysis (DTA); solidification; ceramics; phase transformation; morphological transition.

1. Introduction

Differential thermal analysis (DTA) has been widely used to detect endothermic or exothermic heats due to phase transformation. In conventional DTA apparatus, specimen and reference material in crucibles are indirectly heated in a furnace. Temperature difference between the specimen and the reference is recorded as a signal of exothermic and endothermic heats in the specimen. Typical heating and cooling rates (i.e. the order of 10$^{-3}$ K/s) is sufficient to measure the phase transformation temperatures such as melting point, which are well defined in thermodynamic equilibrium. On the other hand, the transformation temperatures to be measured are often determined by kinetics of the phase transformation. For example, the phase transformations related to solidification generally depend on temperature profile. It is major subjects to study relationship between the solidified structure and the solidification condition such as nucleation temperature and growth velocity. Thus, the DTA at various temperature profiles are required to measure the solidification behavior quantitatively. However, there are some limitations for the conventional DTA apparatus.

An example for the DTA measurements is solidification behavior of mold slags. The mold slags are well known to be lubricant in the continuous casting of steel, since fraction and distribution of the constituent phases in the film significantly affect the heat transfer between the mold and the molten steel. Thus, it is required to understand the solidification behavior of the mold slag as a function of the cooling rate. The possible heating and cooling rates of the conventional DTA apparatus is not sufficiently high to simulate the temperature profiles of the mold slag film, since the specimen is located in the furnace with large heat capacity. To overcome the limitation, a single hot thermocouple technique has been developed to investigate phase separation in a slag, glass formation and the crystallization of continuous casting mold slag. A double hot thermocouple technique has been also developed to examine the phase transformation under a certain temperature gradient. In the methods, the specimen was melted on the hot junction of the thermocouple by the Joule heat. Thus, it is possible to adjust temperature profiles of the specimen to that in the continuous casting. It should be pointed out that these methods enabled direct observation of the specimen. Growth of the crystals in the molten slag was clearly observed, providing useful information on the crystallization of the mold slag. On the other hand, sensitivity to detect the heat release from the specimen is not high in comparison with the conventional DTA apparatus, since the heat release has to be detected from the heating and cooling curve of the specimen. Maximum temperature for the measurement is restricted by a thermocouple used in the hot thermocouple
techniques. Recently, eutectic ceramic composites produced by unidirectional solidification have been taken into attention as a candidate for high temperature materials, since the Al$_2$O$_3$–Y AG (Y$_3$Al$_5$O$_{12}$, yttrium–aluminum–garnet) eutectic structure that consists of Al$_2$O$_3$ single crystal and Y AG single crystal exhibits desirable for high temperature materials. Besides the high temperature properties, the Al$_2$O$_3$–Y$_2$O$_3$ system has unique properties in solidification. According to a phase diagram reported by Caslavsky and Viechnicki, there are two eutectic reactions in the Al$_2$O$_3$–Y$_2$O$_3$ portion. One is the equilibrium eutectic reaction of Al$_2$O$_3$–Y AG at 2099 K and the other is the metastable eutectic reaction of Al$_2$O$_3$–Y AP (Y AlO$_3$, yttrium–aluminum–perovskite) at 1975 K. Solidification in the metastable eutectic path normally occurs when the melt is once heated up to temperatures above 2273 K. Heating the melt above 2273 K seemed to inhibit Y AG nucleation in the liquid. The experimental results suggested the existence of an irreversible change at temperatures above melting point. However, there is still ambiguity regarding the irreversibility of the change because of the difficulties of thermodynamic measurement. Thus, it is expected that the DTA is used for understanding the unique solidification behavior. In addition, it has been found that heating the metastable eutectic up to temperatures above the metastable eutectic temperature but the equilibrium eutectic temperature produced the undercooled melt for the Al$_2$O$_3$–Y$_2$O$_3$ system and the Al$_2$O$_3$–Y$_2$O$_3$–ZrO$_2$ system. The undercooled melt produced from the metastable eutectic structure in the heating procedure is attractive for developing a novel solidification processing called the undercooled net shaping. In the proposed processing, it is required to produce the fine and uniform metastable eutectic structure in the green particles. Since primary phase is often observed even the eutectic composition, it is important to obtain quantitative cooling conditions in which the fine and uniform metastable eutectic structure was produced. The requirement is another motivation to develop a DTA technique.

This paper presents an optical DTA technique in which temperatures of specimen and reference material are measured by pyrometers. The technique enables the DTA in temperature range up to 2400 K at a cooling rate up to 10$^2$ K/s. The basic design is capable for other materials by choosing materials for crucible, although the DTA apparatus is initially designed for the Al$_2$O$_3$-based materials. Firstly, the design of the optical DTA is presented. Second, DTA of α-Al$_2$O$_3$ is presented to study feasibility of the technique. Finally, the DTA technique is used to determine critical cooling rates for the ternary eutectic structure formation in the Al$_2$O$_3$–Y$_2$O$_3$–ZrO$_2$ system.

2. Design of the Optical DTA Technique

2.1. Arrangement of the Differential Thermal Analysis Apparatus

The optical DTA apparatus was designed for measurement of phase transformation temperatures at high temperatures and high cooling rates, and thus, needed to satisfy the following conditions. Firstly, DTA had to be carried out at temperatures up to 2500 K, since the DTA can be applied for Al$_2$O$_3$-based oxides (i.e. melting point of α-Al$_2$O$_3$ is 2318 K). Next, the maximum cooling rate had to be of the order of 10$^2$ K/s, since the cooling rate is an important parameter to determine phase/morphological selections.

Figure 1 shows a schematic illustration of the optical DTA apparatus. The Mo crucible connected with water-cooled Cu electrodes was placed at the center of a vacuum chamber. A direct current through the Mo crucible directly heated the specimen and the reference material by the Joule heat. Two-color pyrometers (temperature range: 1673–3273 K, wavelengths: 0.85 and 1.00 μm) were inclined and were placed above the chamber, measured temperatures of the specimen and reference through SiO$_2$ glass. Ar gas introduced from outlets near the SiO$_2$ glass window was evacuated by a vacuum pump during the DTA.

A block diagram of the optical DTA apparatus is shown in Figure 2.
in Fig. 2. A direct current ranging from 4 to 20 mA was obtained from the pyrometers. The signals were converted into temperatures by amperemeters connected with a PC controller. The signal of a reference temperature was connected with a programmable temperature controller through the amperemeter. The programmable controller controls output of a DC power source in accordance with a programmed temperature profile. A function generator triggers synchronous measurements of signals from the pyrometers.

2.2. Configuration of Crucibles and Specimen

Phase transformation temperatures are often measured from the curing curves, since exothermic and endothermic heats change slope of the cooling curves. However, sensitivity of the detection is generally lower than that of the DTA. Thus, configuration of the crucibles and the specimen was designed to enable the DTA measurements. Mo plates (0.1 mm in thickness) with two dimples were used as a crucible. Dimensions of the Mo crucible are shown in Fig. 3(a). The two dimples, 3 or 5 mm in diameter and 1 or 1.5 mm high, were placed at 15 or 20 mm from the top of the crucible.
mm in depth were placed at the center of the Mo plate. Configuration of specimen, reference and crucible are shown in Fig. 3(b). The specimen was put in one of the two dimples on the lower Mo crucible, while nothing was put in the other dimple for the reference. The lower Mo crucible was covered with the upper Mo plate of the same dimensions. The two crucibles were joined at several points by spot welding so that the specimen touched both of the crucibles during the heating and cooling procedures. Thicknesses of specimen between the crucibles were typically 0.1–0.5 mm in thickness for specimen 5–50 mg in weight.

Joule heat due to the direct current through the Mo crucible sufficiently heated the specimen and reference between the two Mo crucibles at temperatures up to 2500 K, since melting point of Mo is 2896 K. The Mo crucibles and the specimen of 10–20 mg have a rather small heat capacity in comparison with the crucibles. Reduction of the heat capacity contributed to the achievement of high cooling rates. In the present configuration, the maximum cooling rate was approximately 500 K/s when the direct current was suspended.

### 2.3. Temperature Distribution in the Mo Crucible and the Specimen

It is important to evaluate temperature distribution in the specimen at the high cooling rates, since temperature distribution in the cooling specimen may give seriously unreliable data. Figure 4 shows the schematic illustration of the Mo crucibles and the specimen. Since the radius of the specimen was roughly 10 times larger than the thickness, the heat transport in z direction becomes dominant. For simplicity, the heat transfer in the crucibles and the specimen is treated as one-dimensional heat transfer; Mo crucible/specimen/Mo crucible as shown in Fig. 4(b).

At the surface of Mo crucibles, the heat flux by the radiation is approximately given by

\[ q_{\text{radiation}} = \varepsilon \sigma (T_{\text{surface}}^4 - T_0^4) \]

Here, \( \varepsilon \) and \( \sigma \) are emissivity and the Stefan-Boltzmann constant, respectively. If one strictly considers the heat transport by the radiation, a factor determined by the geometrical configuration should be included in Eq. (1). However, temperatures of the Mo crucible, typically 1400–2400 K, are much higher than that of the surrounding wall and the reflection from the chamber wall is negligible in the present apparatus. Furthermore, the temperature distribution in the specimen depends on not the expression of Eq. (1) but the amount of \( q_{\text{radiation}} \). In fact, the emissivity is a fitting parameter to simulate the experimentally obtained cooling curves. Therefore, Eq. (1) gives an adequate estimation for the heat transport by the radiation from the Mo surface.

At the surface of Mo crucibles, the heat flux by the conduction is given by

\[ q_{\text{conduction}} = h(T_{\text{surface}} - T_0) \]

The \( h \) is a heat transfer coefficient between the surface and the Ar gas in the chamber. The contribution of Eq. (2) can be small in comparison with that of Eq. (1) because of the high temperatures and the Ar pressure, 200 Pa at most. Therefore, only the heat transport by the radiation, Eq. (1), is included in the calculation.

The energy conservation equation in the Mo crucible and the specimen are given by the following equation,

\[ \rho C_v \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial z^2} + q_{\text{radiation}} \]

Fig. 4. (a) Schematic illustration of the Mo crucibles and the specimen, (b) configuration of the Mo crucibles and the specimen for the one-dimensional numerical calculation and (c) example of the temperature distribution during cooling.
The \( \rho C_p \) is the heat capacity and \( \lambda \) is the thermal conductivity. The \( nj^2 \) means the Joule heat (\( \rho \): specific resistivity, \( j \): current density). The temperature distribution in the Mo crucible and the specimen during the cooling stage was numerically evaluated by using Eqs. (1) and (3). Physical parameters used in the calculation are listed in Table 1. In the calculation, the current density was adjusted at every time step so that temperature change of the upper Mo surface coincided with a given cooling rate. The typical cooling rate was 500 K/s when the direct current was stopped. So, the emissivity of the Mo crucibles, 0.22, was determined so that the initial cooling rate of 500 K/s is achieved in the calculation when the direct current was suspended. The temperature distribution in the Mo crucibles and the specimen was examined at various cooling rates. Figure 5(a) shows the calculated temperature profiles of the top Mo surface. The calculated temperature profile obtained by stopping the current denotes “free”. The measured temperature profile obtained by stopping the current was also plotted in Fig. 5(a). The temperature profile denoted by “free” approximately simulated the experimental one, indicating that the amount of heat transport from the Mo surface is adequately estimated.

Figure 5(b) shows the temperature differences between the top Mo surface and the center, \( \Delta T_{SC} \), and the maximum temperature in the specimen, \( \Delta T_{specimen} \). In the case of cooling rates less than 100 K/s, the temperature differences are always less than 1 K. Even for the “free” cooling condition, the maximum temperature difference between the Mo surface and the specimen is less than 3 K. Accuracy of the pyrometers that was estimated to be approximately 10 K even if the calibration was performed (as mentioned in the next section) is larger than the temperature difference, 3 K. Therefore, the measurement of the Mo surface temperature sufficiently provides in the specimen temperature.

In the apparatus, two Mo crucibles are used for the DTA measurement. The dispersion of the physical properties in the Mo crucibles may affect the temperature distribution in the specimen. Especially, the dispersion in the specific electrical resistivity should be examined, since the Joule heat is proportional to the electrical resistivity. Figure 6 shows the temperature difference between the top surface and the bottom surface for two different conditions. One is that the electrical resistivity of the bottom crucible is 95 % of the top crucible, and the other is 90 %. The values of 5 and 10 % is actually much larger than that measured in the Mo crucibles used in the experiments. As shown in Fig. 6, the estimated temperature difference is less than 1 K even when resistivity of the bottom crucible is 90 % of the top crucible. Furthermore, the difference tends to decrease with increasing the cooling rate. The numerical calculation indicates that the present configuration of the Mo crucibles and the specimen enabled the DTA at cooling rates up to \( 10^2 \) K/s.

### 2.4. Temperature Measurement

Calibration of the two-color pyrometers is often troublesome because most materials are far from being a blackbody, and emissivity depending on temperature, phase and
surface condition are unknown in most cases. In measurement of the Al$_2$O$_3$-based ceramic materials, calibration for the Mo crucible was done so that the endothermic heats detected at a low heating rate due to the melting of $\alpha$-Al$_2$O$_3$ and Al$_2$O$_3$–YAG eutectic structures coincided with 2318 K and 2099 K, respectively. The error of the two-color pyrometers was approximately 10 K in the temperature range of 1800–2500 K after the calibration.

The present configuration of the two Mo crucibles and the specimen gave an advantage for temperature measurement by the pyrometers. It is usually difficult to distinguish endothermic/exothermic heats from emissivity changes due to isothermal phase transformation when pyrometer measures the specimen surface. In this apparatus, the two pyrometers always measured the surfaces of the Mo crucible of which the back touched the specimen. Once calibration of the pyrometers for the Mo crucible surface was done, the accuracy of the measured temperature was independent from any emissivity change due to phase transformation in the specimen.

In the case of the Mo crucible, suppression of vapor deposition on the SiO$_2$ glass was also important in keeping of temperature measurements accurate, since deposition on the SiO$_2$ glass changed the light transmission through the SiO$_2$ glass which consequently affected the accuracy of the pyrometer measurement of temperature. In this apparatus, an Ar pressure of 50–200 Pa avoided such deposition and kept of temperature measurements accurate during the DTA.

For the present DTA measurement at high cooling rates, the horizontal axis represented the specimen temperature. Power inputs by the Joule heat to specimen and reference were essentially the same, since the dimples for specimen and reference were symmetrically placed. However, the heat capacity of the specimen invariably differed from that of the reference. As the cooling rate increased, deviation of the specimen temperature from the reference temperature becomes large because of the heat capacity difference. Thus, the specimen temperature should be used as the horizontal axis when the high cooling rates were performed.

3. Differential Thermal Analysis for $\alpha$-Al$_2$O$_3$

Figure 7 shows a DTA curve of $\alpha$-Al$_2$O$_3$ (7 mg in weight). The horizontal axis represents the reference temperature. The specimen was heated and then cooled at 1 K/s. Endothermic heat due to the melting of $\alpha$-Al$_2$O$_3$ was used for the calibration of the pyrometers. The exothermic heat due to nucleation and growth of $\alpha$-Al$_2$O$_3$ was clearly detected at 2140 K in the cooling stage. The result indicated that the configuration in which the specimen was placed between the two Mo crucibles provided the sensitivity for exothermic and endothermic heats. The capability of the DTA apparatus for high cooling rates was also examined by using $\alpha$-Al$_2$O$_3$ specimens (about 30 mg in weight). Figure 8 shows DTA curves at several cooling rates. Cooling rates of 1, 10 and 50 K/s were controlled by the temperature controller described in Fig. 2, while a cooling rate of 500 K/s was obtained by stopping the supply of the direct current. Here, the horizontal axis represents the specimen temperature. The exothermic heats due to nucleation and growth of $\alpha$-Al$_2$O$_3$ were clearly detected at every cooling rate. No significant difference was recognized in the DTA curves at
cooling rates up to 50 K/s. The exothermic heat was clearly detected even at a cooling rate of 500 K/s, although the obtained data were uneven because of the high sampling rate. The obtained DTA curves of α-Al2O3 indicated that this DTA apparatus enabled the detect of exothermic and endothermic heats at the high temperatures up to 2 400 K and at high cooling rates up to the order of 103 K/s.

It is difficult to design general-purpose DTA apparatus usable at high temperatures, since most materials are reactive at high temperatures and the choice of crucible material strongly depends on the specimen to be analyzed. Since this paper focuses on solidification behaviors such as phase/morphological selections of Al2O3-based oxides, the Mo crucible was used. The crucible material depends on the objective specimen. Therefore, the basic design of the optical DTA apparatus will also be applicable for other materials at high temperatures by choosing the adequate material for the crucible.

4. Morphological Transition in the Al2O3–Y2O3–ZrO2 Eutectic System

Figure 9 shows the phase diagram of the Al2O3–Y2O3–ZrO2 pseudo-ternary system.24) For the Al2O3–Y2O3 pseudo-binary system, the Al2O3–YAG equilibrium eutectic composition and the Al2O3–YAP metastable eutectic composition are abbreviated to E5 and E5*, respectively. The eutectic points in the pseudo-binary system fall to the pseudoternary eutectic points. The Al2O3–YAG–ZrO2 equilibrium eutectic composition and the Al2O3–YAP–ZrO2 metastable eutectic composition are abbreviated to E4 and E4*, respectively. ZrO2 that precipitates in the Al2O3–YAG–ZrO2 equilibrium eutectic reaction is indicated by F1, while ZrO2 in the Al2O3–YAP–ZrO2 metastable eutectic reaction by F2.

Composition of the specimen used for the DTA measurement was the metastable eutectic composition (Al2O3–21mol%Y2O3–12mol%ZrO2), since the fine and uniform metastable eutectic structure was desired for the undercooled melt formation.21) The powder with the metastable eutectic composition were prepared by using 99.99% α-Al2O3 (2–3 μm diameter), 99.9% Y2O3 (2–3 μm diameter) and 98% ZrO2 (1 μm diameter). Powder was wet ball milled with ethanol to obtain homogeneous slurry. After the slurry was dried in a vacuum at 373 K, the dried powder was used for DTA measurements.

Heating and cooling procedures for the DTA measurement were as follows. Firstly, the mixed powder was heated up to temperature above 2 100 K and below 2 200 K and then was cooled at a cooling rate of 1 K/s. The heating and cooling procedure resulted in the Al2O3–YAG–ZrO2 equilibrium eutectic path.21) The specimens solidified in the equilibrium eutectic system were heated up to temperatures above 2 400 K at a heating rate of 1 K/s, and after holding the melt for 150 s, the specimens were cooled at a given cooling rate. Consequently, the specimen solidified in the Al2O3–YAP–ZrO2 metastable eutectic path.21) The obtained morphology was classified in terms of the cooling rate. The cooling rate was not constant when the power supply was suspended as shown in Fig. 5(a). In the cases, the cooling rate just before the nucleation was adopted as the cooling rate to classify the morphological transition.

Figure 10 shows the DTA curves of the specimens solidified in the Al2O3–YAG–ZrO2 equilibrium eutectic system. In the heating step (heating rate of 1 K/s), the endothermic heat due to melting of the Al2O3–YAG–ZrO2 equilibrium eutectic structure was detected. In the present work, calibration of the pyrometer was performed so that the beginning of the endothermic heat was equal to be the eutectic temperature (1 988 K) reported by Lakiza and Lopato.24) In the cooling step after holding at temperatures above 2 300 K, the exothermic heat was detected below the metastable eu-

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**Fig. 9.** Projection of the solidification paths on the phase diagram of the Al2O3–Y2O3–ZrO2 system.24) e5: equilibrium eutectic point in the Al2O3–Y2O3 pseudo-binary system (2 099 K), e5*: metastable eutectic point in the Al2O3–Y2O3 pseudo-binary system (1 975 K), E4: equilibrium eutectic point in the Al2O3–Y2O3–ZrO2 pseudo-ternary system (1 988 K) and E4*: metastable eutectic point in the Al2O3–Y2O3–ZrO2 pseudo-ternary system (1 923 K).

**Fig. 10.** Differential thermal analysis of the Al2O3–21mol%Y2O3–12mol%ZrO2 (metastable eutectic composition). The specimens were heated at 1 K/s and were cooled at a given rate.
tectic temperature. X-ray diffraction patterns of the solidified specimens indicated that the specimens consisted of the metastable eutectic system. According to the previous work,\textsuperscript{21)heating the melt up to 2 300 K inhibited the YAG nucleation and the melt was undercooled below the metastable eutectic temperature. The solidification below the metastable eutectic temperature obeyed the metastable eutectic path. The selection of the eutectic systems in the present study was consistent with the previous work.\textsuperscript{21)}

Nucleation temperature tended to decrease with increasing cooling rate. As the cooling rate increases, the rate of the heat release increased. As a result, the exothermic heat due to the solidification in the metastable eutectic system increased with increasing the cooling rate.

Figure 11 shows the solidified structure in the DTA specimens. In the case of 0.8 K/s (Fig. 11(a)), the ternary eutectic structure was observed. The constituent phases tended to exhibit the faceted interface. The eutectic structure in which the two phases entangled each other composed of Al$_2$O$_3$ (black) and YAP (gray). The ZrO$_2$ particles (white) of which size was less than 0.5 \( \mu \text{m} \) was recognized in the between the Al$_2$O$_3$ phase and the YAP phase. The lamellar eutectic structure in which the two phases tended to regularly align in the growth direction was observed at a cooling rate more than 10 K/s (Fig. 11(b)). The lamellar spacing is approximately 0.2–0.4 \( \mu \text{m} \) in the case of 17 K/s. In the lamellar eutectic structure, ZrO$_2$ phase was not recognized within the resolution of the SEM. At a cooling rate of 72 K/s, the Al$_2$O$_3$ crystals (black) were observed as a primary phase. The primary Al$_2$O$_3$ crystals exhibited the dendritic shape, indicating that the Al$_2$O$_3$ crystals grew in advance. The lamellar eutectic structure was produced behind the growth of the primary Al$_2$O$_3$ crystals. The lamellar eutectic structure observed at 72 K/s is the same as that observed at 17 K/s. At higher cooling rate such as 360 K/s, the lamellar eutectic structure was observed only in the restricted area surrounded by the coarse Al$_2$O$_3$ and YAP crystals.

In the specimen cooled at 360 K/s, the divorced eutectic solidification occurred, in which the two constituent phases independently grew without any cooperation through the solute exchange. In general, the lamellar spacing produced in the eutectic growth is much smaller than the primary dendrite arm spacing in the same solidification condition. The suppression of the eutectic growth resulted in the coarse solidified structure consisting of the primary phases even at the higher cooling rate. The present result showed that the transition from the entangled eutectic to the lamellar eutectic, and the transition to the divorced eutectic occurred in the Al$_2$O$_3$–YAP–ZrO$_2$ metastable eutectic system.

The growth rate was roughly estimated to be $R/t_s$ ($R$: radius of the melt, $t_s$: solidification time) from the data obtained in the optical DTA.\textsuperscript{25) Figure 12} shows the undercooling, the solidification time, the growth rate and the morphology of the solidified structure. The undercooling increases with increasing the cooling rate, while the solidification time decreases. Thus, the estimated growth rate ranges from $10^{-3}$ m/s to $10^{-7}$ m/s. The estimation of the growth rate suggested that morphological transition from the entangled eutectic structure to the lamellar eutectic structure occurred at $10^{-7}$ m/s. The primary Al$_2$O$_3$ was observed at a growth rate more than $10^{-3}$ m/s and the divorced eutectic solidification occurred at growth rate more than $10^{-7}$ m/s.

The optical DTA apparatus enabled the DTA for the Al$_2$O$_3$–YAP–ZrO$_2$ metastable eutectic system at cooling rates up to $4 \times 10^2$ K/s. The morphological transition in the eutectic structure was clearly recognized by using the DTA apparatus. From a viewpoint of the undercooled melt shap-
The measured DTA for pyrometers always measured at the surface of the Mo crucible. The emissivity change due to phase transformation in the surface and the specimen was less than 1 K. Furthermore, for example, the temperature difference between the Mo crucible and covered by another Mo crucible of the same shape. A direct current through the two crucibles effectively heated the specimen and the reference. The numerical calculation that the Mo surface temperature did not differ from the specimen temperature in the present configuration.

The DTA apparatus was developed to investigate the solidification behavior at the temperatures up to 2,400 K and the cooling rates up to the order of 10^2 K/s. In the apparatus, the specimen and the reference was put in dimples of a Mo crucible and covered by another Mo crucible of the same shape. The measured DTA for α-Al₂O₃ clearly detected endothermic heat due to melting and exothermic heat due to solidification at cooling rates up to 10^3 K/s. The experimental results indicated that the melt with the Al₂O₃-YAP eutectic composition should be cooled at cooling rates of 20–40 K/s to produce the fine and uniform eutectic structure for the undercooled net shaping.

**5. Conclusion**

The DTA apparatus was developed to investigate the solidification behavior at the temperatures up to 2,400 K and the cooling rates up to the order of 10^2 K/s. In the apparatus, the specimen and the reference was put in dimples of a Mo crucible and covered by another Mo crucible of the same shape. A direct current through the two crucibles effectively heated the specimen and the reference. The numerical calculation that the Mo surface temperature did not differ from the specimen temperature in the present configuration. For example, the temperature difference between the Mo surface and the specimen was less than 1 K. Furthermore, the emissivity change due to phase transformation in the specimen did not affect the temperature measurement, since pyrometers always measured at the surface of the Mo crucible. The measured DTA for α-Al₂O₃ clearly detected endothermic heat due to melting and exothermic heat due to solidification at cooling rates up to 10^3 K/s. The experimental results proved that the present DTA apparatus enabled the DTA measurements for the Al₂O₃-based oxides at various cooling rates.

Morphological transition in the Al₂O₃–YAP–ZrO₂ eutectic system was found at the metastable eutectic composition. The DTA provided the nucleation temperature and the solidification time at cooling rates up to 360 K/s. As the cooling rate increased, the nucleation temperature decreased. In the case of 0.8 K/s, the Al₂O₃–YAP–ZrO₂ eutectic structure was observed, in which the constituent phases, Al₂O₃, and YAP entangles each other. The ZrO₂ phase was recognized in between the Al₂O₃ phase and the YAP phase. The morphological transition from the entangled eutectic structure to the lamellar eutectic structure was observed at the cooling rate around 10 K/s. The primary Al₂O₃ crystals were observed in the solidified specimen at the cooling rate of 70 K/s. Furthermore, the solidified structure suggested that the divorced eutectic solidification occurred at 360 K/s. The experimental results indicated that the melt with the Al₂O₃–YAP eutectic composition should be cooled at cooling rates of 20–40 K/s to produce the fine and uniform eutectic structure for the undercooled net shaping.

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