Solidification and shape casting of Al₂O₃–YAG eutectic ceramics from the undercooled melt produced by melting Al₂O₃–YAP eutectics

Hideyuki Yasuda, Itsuo Ohnaka, Yoshiki Mizutani, Akira Sugiyama, Takashi Morikawa, Satoshi Takeshima, Takumi Sakimura, Yoshiharu Waku

Abstract

There are two eutectic systems in the Al₂O₃-rich portion of the Al₂O₃–Y₂O₃ system: one is the Al₂O₃–YAG equilibrium eutectic system and the other is the Al₂O₃–YAP metastable eutectic system. Heating the Al₂O₃–YAP metastable eutectic structure up to temperatures above the metastable eutectic temperature but below the equilibrium eutectic temperature produced the undercooled melt. Solidification in the equilibrium path immediately followed the undercooled melt formation. The solidification in the equilibrium path along with the melting of the metastable eutectic structure resulted in a fine and uniform equilibrium eutectic structure with lamellar spacing of less than 1 μm. The equilibrium eutectic structure was not affected by the metastable eutectic structure used for the undercooled melt formation. Shape casting and joining of alumina rods were demonstrated using the undercooled melt produced by the melting of the Al₂O₃–YAP metastable eutectic structure. The fine eutectic structure was obtained throughout the castings. Coupling of the solidification and the melting achieved a higher growth rate than conventional solidification from the undercooled melt. The skewed coupled growth zone due to the kinetic effect contributed to formation of the fine eutectic structure at the metastable eutectic composition.

Keywords: Eutectic solidification; Precision casting; Ceramic composites; Undercooling; Coupled growth

1. Introduction

Unidirectionally solidified Al₂O₃-based eutectic composites have been recognized as having excellent mechanical properties at high temperatures [1–9]. The Al₂O₃–YAG eutectic composites consist of single crystals of Al₂O₃ and YAG (YAG: Y₃Al₅O₁₂, yttrium–aluminum–garnet). They exhibit flexural strengths of 360–500 MPa from room temperature to 2073 K in an air atmosphere [5]. Their compression creep strengths at 1873 K are about 13 times higher than those of sintered composites with the same chemical compositions [6]. Therefore, because of their mechanical properties, eutectic ceramics such as the Al₂O₃–YAG system have received much attention in relation to high temperature use.

Besides the development of the eutectic composites for high temperature use, some interesting phenomena related to solidification have been reported in the Al₂O₃–YAG system. There are two eutectic systems [10], one is the Al₂O₃–YAG equilibrium eutectic system and the other is the Al₂O₃–YAP metastable eutectic system (YAP: YAlO₃, yttrium–aluminum–perovskite). The melt with the YAG composition normally solidifies along the Al₂O₃–YAP (YAlO₃, yttrium–aluminum–perovskite) metastable solidification path, if the melt is cooled without seeding [11]. Difficulty with YAG nucleation has been found in the melt growth of YAG crystals.

The hypercooling limit (769 K) has been achieved using an aero-acoustic levitator for the YAG composition specimens, because of the nucleation difficulty [12]. The cellular
The morphology of YAG was obtained, even beyond the hypercooling limit, since the large kinetic effect deviated the thermal saturation from unity. The melt that has undercooling beyond the hypercooling limit can be solidified adiabatically. The adiabatic solidification is very attractive from various aspects. The solidification rate is apparently independent of the heat extraction rate from castings. This means that uniform solidified structures are obtained over castings. However, the highly undercooled melt is generally formed during rapid cooling procedures. Adiabatic solidification has not been used in practical solidification processing.

The YAG nucleation difficulty gives rise to the selection of eutectic systems in the Al2O3–Y2O3 system. Caslavsky and Viechnicki reported a phase diagram for the Al2O3-rich portion of the Al2O3–Y2O3 system obtained by using optical differential thermal analysis [10]. Two eutectic reactions exist; one is the equilibrium eutectic reaction of Al2O3–YAG at 2099 K, the other is the metastable one of Al2O3–YAP at 1975 K. Selection of the solidified system between the two eutectic systems is determined by nucleation of YAG in the composition range of 13.5–28.5 mol% Y2O3 [10,13–15]. Heating the melt above 2273 K completely inhibits YAG nucleation, and consequently the Al2O3–YAP metastable system is selected. It should be emphasized that the heating and cooling procedures completely control the solidification path in the Al2O3–Y2O3 system.

Our previous papers [16,17] showed that the Al2O3–YAP metastable eutectic structure generated a new way to produce an undercooled melt below the equilibrium eutectic temperature. Heating of the Al2O3–YAP metastable eutectic structure to temperatures above the metastable eutectic temperature (1975 K) produced the undercooled melt [15]. In accordance with the previous work [15], the DTA analysis was performed as follows: The Al2O3–23.5 mol% Y2O3 powder was heated to 2300 K and then kept at this temperature for 150 s. The melt was cooled at cooling rates of 1, 10, 70 or 300 K/s in order to vary the lamellar spacing of the Al2O3–YAP metastable eutectic structure. The Al2O3–YAP metastable eutectic structure obtained was heated at a heating rate of 10 K/s. The melting of the Al2O3–YAP metastable eutectic structure and the solidification in the Al2O3–YAG equilibrium path were observed by DTA. The growth velocity was estimated from the solidification time and the sample size.

Fig. 1 shows the phase diagram of the Al2O3–Y2O3 system [10]. The metastable eutectic structure without any primary phase was obtained not at the equilibrium eutectic composition, but at the metastable eutectic composition [16]. Thus, the metastable eutectic composition was selected in order to investigate the eutectic solidification and to perform shaping using the undercooled melt. The Al2O3–Y2O3 powder with Al2O3–23.5 mol% Y2O3 composition was prepared by using 99.99% purity α-Al2O3 (2–3 μm diameter) and 99.9% purity Y2O3 (2–3 μm diameter). Powder was wet ball milled with ethanol to obtain a homogeneous slurry and was then dried under vacuum.

The solidification behavior in the undercooled melt produced by heating the metastable eutectic structure was investigated with optical differential thermal analysis apparatus [15]. The weight of the powder for the DTA measurement was approximately 20 mg. The Al2O3–YAP metastable eutectic structure was obtained when the melt was heated once to a temperature above 2273 K [15]. In accordance with the previous work [15], the DTA analysis was performed as follows: The Al2O3–23.5 mol% Y2O3 powder was heated to 2300 K and then kept at this temperature for 150 s. The melt was cooled at cooling rates of 1, 10, 70 or 300 K/s in order to vary the lamellar spacing of the Al2O3–YAP metastable eutectic structure. The Al2O3–YAP metastable eutectic structure obtained was heated at a heating rate of 10 K/s. The melting of the Al2O3–YAP metastable eutectic structure and the solidification in the Al2O3–YAG equilibrium eutectic path were observed by DTA. The growth velocity was estimated from the solidification time and the sample size.

It is of interest to understand the eutectic solidification accompanied by the melting of the metastable eutectic structure, in order to develop novel solidification processing. This paper shows the eutectic solidification of the Al2O3–YAG eutectic accompanied by the melting of the Al2O3–YAP metastable eutectic structure. The effect of the Al2O3–YAP metastable eutectic structure on the solidification of the Al2O3–YAG eutectic system is presented. Undercooled melt shaping is also demonstrated in order to examine the feasibility of this process. This paper then discusses the mechanism of the eutectic solidification accompanied by melting.
2.2. Undercooled melt shaping

The Al₂O₃–23.5 mol% Y₂O₃ powder was melted in a Mo crucible (10 mm in diameter) by an induction furnace. After keeping the melt temperature above 2300 K, the Al₂O₃–YAP metastable eutectic structure was obtained by solidifying the melt. The solidified specimens were crushed into particles with diameters of 50–100 μm in an Alumina mortar. The constituent phases were identified by X-ray diffraction.

Molds used for the undercooled melt shaping consisted of two Mo parts. One was the upper columnar mold and the other was the bottom mold, which was like a mortar. To investigate the shaping potential of the undercooled melt, an upper columnar mold with grooves was used, which produced castings with a honeycomb shape. The thickness of the honeycomb wall was 300 μm. The dimensions of the bottom mold were 6 mm inner diameter and 8 mm depth.

The crushed particles were inserted into the bottom Mo mold, and then the upper Mo mold was set. Ta foil was put in the carbon dies to avoid any reaction between the Mo molds and the carbon dies. The carbon dies had the following dimensions: outer diameter 30 mm, inner diameter 12 mm and height 50 mm. The carbon dies were heated by direct current under a vacuum. The temperature of the dies was measured by a two-color pyrometer.

Joining of sintered Al₂O₃ rods was also examined using the Al₂O₃–YAP metastable eutectic particles as solder. The Al₂O₃ rods were polished so that they had smooth surfaces. Al₂O₃–YAP metastable eutectic particles were put between the two sintered Al₂O₃ rods in the Mo molds, and then the Al₂O₃ rods and Al₂O₃–YAP metastable eutectic particles were pressed into the Mo molds. The heating and cooling procedures were the same as those used for producing the column-shaped castings. The pressure used for the joining was 8 MPa.

3. Results and discussion

3.1. Undercooled melt formation and the eutectic solidification

Fig. 2(a) shows typical DTA curves at a heating rate of 10 K/s for the Al₂O₃–23.5 mol% Y₂O₃ specimens with the Al₂O₃–YAP metastable eutectic structure. Since the DTA measurements have been reported in previous works [16, 17], the typical DTA curves are explained briefly in order to characterize the undercooled melt formation and the solidification from the undercooled melt.

Endothermic heat was always detected during the heating stage at the metastable eutectic temperature (1975 K), indicating the melting of the metastable eutectic structure. In the case of curve A, the exothermic heat immediately followed the endothermic heat. The exothermic heat corresponded to the solidification in the Al₂O₃–YAG equilibrium eutectic path, resulting in the fine and uniform Al₂O₃–YAG equilibrium eutectic structure. The fine eutectic structure without any primary phase at the off-eutectic composition, 23.5 mol% Y₂O₃, is not obtained when the melt is cooled from temperatures above the equilibrium eutectic temperature.

In the case of curve B, exothermic heat was detected when the endothermic heating was nearly completed. The primary YAG crystals and the Al₂O₃–YAG equilibrium eutectic structure were obtained in the solidified structure. Curve B was observed in the DTA measurement in which a small amount of the sample is used. However, this solidification mode was never observed in the casting. The exothermic heat in curve B is much larger than that in curve A.

As seen in Fig. 2(b), the transformation from the metastable system to the equilibrium system was completed in less than 4 s in curve A, whereas the transformation required 8 s in curve B. The solidification following the melting significantly reduced the solidification time.

The coupling of the solidification in the equilibrium eutectic path and the melting of the metastable eutectic structure resulted in the evolution of the fine eutectic structure which was not obtained by conventional
solidification of the melt. In previous work [17], the enthalpy change from the metastable system to the equilibrium system was roughly estimated to be $-5 \text{ kJ/mol}$ for $\text{Al}_2\text{O}_3 - 23.5 \text{ mol\% Y}_2\text{O}_3$ from the enthalpy change ($-32 \text{ kJ/mol at 298 K}$) of $3\text{YAlO}_3 + \text{Al}_2\text{O}_3 = \text{Y}_3\text{Al}_5\text{O}_{12}$ [18]. The value of $5 \text{ kJ/mol}$ is much smaller than the latent heats (111 kJ/mol for $\text{Al}_2\text{O}_3$ and 516 kJ/mol for YAG [18]). The solidification accompanied by the melting can be completed even in nearly adiabatic conditions. Thus, the solidification rate was not controlled by heat extraction from the sample. It is of interest to understand how the growth velocity is determined, and how the fine eutectic structure is formed even at the off-eutectic composition.

3.2. Effect of the $\text{Al}_2\text{O}_3 - \text{YAP}$ eutectic structure on the undercooled melt formation

The following two steps are candidates for the rate-determining step in the nearly adiabatic solidification due to the coupling of the solidification and the melting: one is the solidification of the $\text{Al}_2\text{O}_3 - \text{YAG}$ equilibrium eutectic structure, and the other is the melting of the $\text{Al}_2\text{O}_3 - \text{YAP}$ metastable eutectic structure.

Since the melting points of the constituent phases are higher than the eutectic temperature, solute diffusion between the two phases controls melting of the metastable eutectic structure. Thus, the melting rate may depend on the lamellar spacing. Namely, the solidification of the equilibrium eutectic structure accompanied by the melting of the metastable eutectic structure can be affected by the lamellar spacing of the $\text{Al}_2\text{O}_3 - \text{YAP}$ metastable eutectic structure.

Fig. 3 shows the $\text{Al}_2\text{O}_3 - \text{YAP}$ metastable eutectic structures obtained at different cooling rates. The lamellar spacing obtained by the cooling procedures (1–300 K/s) ranged from 50 nm to 0.45 μm. The $\text{Al}_2\text{O}_3 - \text{YAG}$ equilibrium eutectic structures obtained by heating the $\text{Al}_2\text{O}_3 - \text{YAP}$ metastable eutectic structures with different lamellar spacings are shown in Fig. 4. A fine and uniform eutectic structure was obtained in every sample.

Fig. 5 shows the relationship between the $\text{Al}_2\text{O}_3 - \text{YAP}$ metastable eutectic spacing and the $\text{Al}_2\text{O}_3 - \text{YAG}$ equilibrium eutectic spacing. The $\text{Al}_2\text{O}_3 - \text{YAG}$ equilibrium eutectic spacing is almost independent of the $\text{Al}_2\text{O}_3 - \text{YAP}$ metastable eutectic spacing. This result shows that the melting of the $\text{Al}_2\text{O}_3 - \text{YAP}$ metastable eutectic structure does not contribute to selection of the solidification rate. The $\text{Al}_2\text{O}_3 - \text{YAP}$ metastable eutectic structure obtained by cooling at a rather low cooling rate such as 1 K/s is sufficient to produce the fine and uniform eutectic structure through the solidification accompanied by the melting.

Fig. 6 shows the lamellar spacing of the $\text{Al}_2\text{O}_3 - \text{YAG}$ equilibrium eutectic structure obtained by the solidification accompanied by the melting. The experimental results obtained by the unidirectional solidification [19,20] and by the solidification from the undercooled melt [21] are also presented. The experimental results roughly obey the Jackson–Hunt relationship [22]. The growth velocities of the solidification accompanied by the melting range from $0.8 \times 10^{-3}$ to $2 \times 10^{-3}$ m/s; these are almost 10 times higher than those measured in the solidification in the undercooled melt. The solidification accompanied by the melting of the metastable eutectic structure is accomplished in nearly adiabatic conditions [17]. The coupling of the exothermic reaction and the endothermic reaction achieved the high growth velocity. However, the growth velocity of $10^{-3} \text{ m/s}$ is not as high as the growth velocity in the rapid solidification of metallic alloys.

Fig. 3. Microstructure solidified in the $\text{Al}_2\text{O}_3 - \text{YAP}$ metastable eutectic structure. Cooling rate: (a) 1 K/s, (b) 10 K/s and (c) 70 K/s.

Fig. 4. Microstructure solidified in the $\text{Al}_2\text{O}_3 - \text{YAG}$ equilibrium eutectic structure through the melting of the $\text{Al}_2\text{O}_3 - \text{YAP}$ metastable eutectic structures (Fig. 3). Initial structure: $\text{Al}_2\text{O}_3 - \text{YAP}$ metastable eutectic structures obtained at (a) 1 K/s, (b) 10 K/s and (c) 70 K/s.
### 3.3. Feasibility of precision casting and joining

The solidification of the Al₂O₃–YAG equilibrium eutectic structure accompanied by the melting of the Al₂O₃–YAP metastable eutectic structure has some advantages for precision casting [17]. The nearly adiabatic transformation means that the solidification rate is independent of the casting size. Consequently, the fine and uniform eutectic structures are expected throughout the castings. The volume expansion of 11% in the transformation from Al₂O₃ and YAP to YAG [23] contributes to reduction of the porosities in the castings. Furthermore, the fine eutectic structure with the lamellar spacing less than 1 μm is beneficial for the precision casting of fine parts, since the isotropic mechanical properties are maintained even in casting sizes in the order of 10 μm. A simple shape casting was preliminary demonstrated in the previous work [17]. Thus, this paper examines the uniformity of the eutectic structure in the casting, the honeycomb-type casting and joining alumina rods.

Fig. 7(a) shows the dimensions of the Al₂O₃–YAG casting (compact) produced by using the Al₂O₃–YAP metastable eutectic particles. As seen in Fig. 7(b), the fine and uniform eutectic structure is obtained in the casting. The microstructures at the edge and at the center are shown in Fig. 7(c) and (d), respectively. Boundaries between the initial Al₂O₃–YAP metastable eutectic particles are not recognizable. No remarkable change in lamellar spacing of the Al₂O₃–YAG equilibrium eutectic structure is observed throughout the casting. This result shows that the nearly adiabatic solidification achieves a fine and uniform eutectic structure with a lamellar spacing of 1 μm or less throughout the casting.

Fig. 8(a) shows the Mo molds used for the honeycomb-type casting. The mold was 2 mm in height and the grooves were 300 μm thick. Fig. 8(b) shows the casting with the honeycomb shape. The honeycomb shape of the Mo mold was well reproduced in the Al₂O₃–YAG casting. This shows that the undercooled melt produced by melting the Al₂O₃–YAP metastable eutectic structure can be used for shaping. It has been known that metallic amorphous alloys with a large undercooled liquid region have many advantages for superplastic micro/nano-formability [24–27]. Thus, the undercooled melt formation in the Al₂O₃–Y₂O₃ system could be an alternative micro-shaping technique for the ceramics.

The ability to reduce the temperature at which the process needs to be carried out is also an advantage with undercooled melt shaping. The undercooled melt processing can be used for joining ceramic materials. The Al₂O₃–YAP metastable eutectic particles were used as solder to join the sintered Al₂O₃ rods. The configurations of the Al₂O₃ rods and the Al₂O₃–YAP particles are shown in Fig. 9(a). Fig. 9(b) shows a cross section of the Al₂O₃ rods after joining. The initial Al₂O₃–YAP grains were not seen in the Al₂O₃–YAG equilibrium eutectic structure between the rods. Although some pores were observed in the sintered Al₂O₃ rods, hardly any pores were observed in the Al₂O₃–YAG equilibrium eutectic structure. The Al₂O₃–YAG equilibrium eutectic layer was uniformly covered with the fine Al₂O₃–YAG equilibrium eutectic structure. Some Al₂O₃ crystals in the Al₂O₃–YAG equilibrium eutectic structure grew continuously from the Al₂O₃ rod. The sintered Al₂O₃ rods were joined to each other well by the undercooled melt processing that produced the Al₂O₃–YAG equilibrium eutectic layer.

The precision casting and the joining successfully demonstrate that the undercooled melt shaping using the Al₂O₃–YAP metastable eutectic particles produces...
the expected advantages such as the fine and uniform eutectic structure throughout the casting, less porosity and a lower processing temperature.

3.4. Mechanism of the eutectic growth

3.4.1. Kinetic undercooling

Fig. 10 shows a schematic illustration of the solidification of the Al2O3–YAG equilibrium eutectic structure accompanied by the melting of the Al2O3–YAP metastable eutectic structure. Undercooling at the solidifying interface consists of the kinetic undercooling and the undercooling due to the coupled growth, which includes the undercooling due to curvature and solute-build-up. The present study shows that the melting of the Al2O3–YAP metastable eutectic structure does not affect the solidification rate. Thus, the melting of the Al2O3–YAP metastable eutectic structure occurs at the metastable eutectic temperature.

Here, we consider the kinetic undercooling of the eutectic growth. In the case of the regular eutectic growth, the similar undercooling of the two constituent phases causes the symmetrical growth zone. It was, however, reported that the linear kinetic coefficient, \( \mu_{YAG} \), of YAG was \( 3.5 \times 10^{-5} \) m/sK, around 10 times lower than that of Al2O3 [12]. The skewed coupled growth zone must be considered because of the large difference between the linear kinetic coefficients.

For Al2O3 and YAG, the growth velocity (V) is considered to be proportional to the undercooling (\( \Delta T \)).

\[
V_{Alumina} = \mu_{Alumina}\Delta T_{Alumina} \tag{1}
\]

\[
V_{YAG} = \mu_{YAG}\Delta T_{YAG} \tag{2}
\]

Assuming the above equations are valid even at the off-stoichiometric compositions, the relationships between the interface temperature (\( T^* \)) and composition (\( C^* \)) are given by

\[
T^*_{Alumina} = T_e + m_{Alumina}(C^*_{Alumina} - C_e) - \Delta T_{Alumina} \tag{3}
\]

\[
T^*_{YAG} = T_e + m_{YAG}(C^*_{YAG} - C_e) - \Delta T_{YAG} \tag{4}
\]

Here, \( T_e \) and \( C_e \) are the equilibrium eutectic temperature and the equilibrium eutectic composition, respectively. Slopes of the liquidus lines for Al2O3 and YAG are \( m_{Alumina} \) and \( m_{YAG} \), respectively.

In the coupled growth, the growth velocities of the two constituent phases must be the same. Thus, the kinetic undercoolings of the two phases are given by

\[
\Delta T_{Alumina} = \frac{V_{eutectic}}{\mu_{Alumina}}, \tag{5}
\]
where \( V_{\text{eutectic}} \) is the growth velocity of the eutectic interface.

Since the interface temperatures of the two constituent phases are also the same during the coupled growth, Eqs. (3) and (4) give

\[
T^* = T_e = \frac{\Delta T_{\text{YAG}}}{m_{\text{YAG}}} - \frac{\Delta T_{\text{Alumina}}}{m_{\text{Alumina}}} \left( \frac{1}{m_{\text{YAG}}} - \frac{1}{m_{\text{Alumina}}} \right)^{-1} \tag{7}
\]

By using Eqs. (5) and (6),

\[
T^* = V_{\text{eutectic}} \frac{1}{m_{\text{YAG}}} - \frac{1}{m_{\text{Alumina}}} \mu_{\text{Alumina}} \left( \frac{1}{m_{\text{YAG}}} - \frac{1}{m_{\text{Alumina}}} \right)^{-1} \tag{8}
\]

Therefore, the undercooling of the eutectic growth can be estimated by the following equation:

\[
\Delta T_k = V_{\text{eutectic}} \left( \frac{1}{m_{\text{YAG}}} - \frac{1}{m_{\text{Alumina}}} \right) \mu_{\text{Alumina}} \left( \frac{1}{m_{\text{YAG}}} - \frac{1}{m_{\text{Alumina}}} \right)^{-1} \tag{9}
\]

Here, \( m_{\text{Alumina}} \) and \( m_{\text{YAG}} \) are \(-18.5\) and \(9.5\) K/mol\% [10], respectively. If the \( m_{\text{Alumina}} \) is assumed to be \(3.5 \times 10^{-4}\) m/s\( \cdot \)K and it is 10 times larger than \( m_{\text{YAG}} \), the kinetic undercooling, \( \Delta T_k \), obeys the following relationship:

\[
\left( \frac{\Delta T_k}{K} \right) = 1.9 \times 10^4 \left( V_{\text{eutectic}}/(\text{ms}^{-1}) \right) \tag{10}
\]

The interface temperatures and the interface compositions for \( V = 1 \times 10^{-3} \) and \( 2 \times 10^{-3} \) m/s are also plotted in Fig. 11. The apparent eutectic point shifts in the \( Y_2O_3 \)-rich direction as a function of the growth velocity. For example, the apparent eutectic point is at a composition of 20 mol\% \( Y_2O_3 \) (1.5 mol\% \( Y_2O_3 \) higher than the equilibrium eutectic composition) and a temperature of 2059 K (38 K lower than the equilibrium eutectic temperature) at a growth velocity of \( 2 \times 10^{-3} \) m/s. As shown in Fig. 11, the growth velocities for the solidification of the Al\(_2\)O\(_3\)–YAG system accompanied by the melting of the Al\(_2\)O\(_3\)–YAP metastable eutectic structure ranged from \(0.8 \times 10^{-3}\) to \(2 \times 10^{-3}\) m/s. Thus, the kinetic undercooling is expected to be in the order of \(10^4\) K.
respectively.

It was pointed out that the lamellar spacing in the irregular eutectic system was larger than that estimated from the coupled growth model [22,28,30]. The Al2O3–YAP system exhibits the entangled eutectic structure, which is more complex than the irregular eutectic structure. The estimation of the undercooling must have uncertainty even if the value of $K_r$ is precisely estimated from the physical properties. Here, the $K_r$ is roughly estimated by using the capillary effect [30]. The equilibrium temperature change due to the effect of curvature is given by $\Delta T_c = \frac{2\Gamma}{\kappa}$. (13)

When the Gibbs-Thomson coefficient is $1 \times 10^{-7}$ mK, the undercooling $(\Delta T_c)$ is $0.25$ K. The undercooling due to the coupled growth will be much smaller than the kinetic undercooling in the nearly adiabatic solidification condition.

3.4.3. Heat transfer between the Al2O3–YAG interface and the Al2O3–YAP interface

The coupled growth of Al2O3–YAG equilibrium eutectic system occurred at the Al2O3–YAP metastable eutectic composition in the undercooled melt produced by melting the Al2O3–YAP metastable eutectic structure. In contrast, the dendritic YAG crystals as a primary phase were observed in the specimens solidified from the undercooled melt when the undercooled melt was achieved by cooling the melt from temperatures above the liquidus temperature [21]. The growth rates observed in the solidification from the undercooled melt are approximately 10 times smaller than those observed in the solidification accompanied by the melting. This means that the occurrence of the coupled growth at the metastable eutectic composition is attributed to the melting accompanying with the solidification. The experimental results suggest that a thin liquid layer exists between the Al2O3–YAG equilibrium eutectic interface and the Al2O3–YAP metastable eutectic interface so that the latent heat due to the solidification is absorbed by the melting (Fig. 10). Thus, it is desired to evaluate the thickness of the undercooled melt between the solidifying interface and the melting interface.

For simplicity, the one dimensional heat transfer from the solidifying interface to the melting interface is considered here. It is also assumed that the latent heat of...
the Al₂O₃–YAG equilibrium eutectic solidification is completely absorbed by the melting of the Al₂O₃–YAP metastable eutectic solidification, in order to consider the steady state growth in the adiabatic condition.

The steady state of the planar interface growth is achieved only when the undercooling reaches the hypercooling limit. The growth rate is determined by the growth kinetics, and temperature profile in the liquid phase is passively given by

\[ T = T_{\text{interface}}^* - \Delta T_{\text{hyper}} \{1 - \exp[-(V/\alpha)z]\}, \]  

(15)

where \(\alpha\) is the thermal diffusivity, \(T_{\text{interface}}^*\) and \(\Delta T_{\text{hyper}}\) are the solidifying interface temperature and the hypercooling limit, respectively. The thermal diffusion length is expressed by \(\alpha/V\). It is helpful to exploit the steady state growth at the hypercooling limit, in order to consider the heat transfer in the solidification accompanied by the melting.

In the case of the solidification accompanied by the melting, the steady state temperature profile between the solidifying interface (\(z = 0, T = T_{\text{equ}}^*\)) and the melting interface (\(z = \delta, T = T_{\text{meta}}^*\)) is derived with the same manner of Eq. (15).

\[ T = T_{\text{equ}}^* - \Delta T_{\text{hyper}} \{1 - \exp[-(V_{\text{eutectic}}/\alpha)z]\} \]
\[ \Delta T_{\text{hyper}} = T_{\text{equ}}^* - T_{\text{meta}}^* \]

Here, \(\delta\) is the thickness of the liquid phase. At the steady state, the heat release due to the solidification has to balance with the heat transfer from the solidifying interface. Thus,

\[ -\lambda \frac{\partial T}{\partial z} \bigg|_{z=0} = \Delta H \cdot V_{\text{eutectic}}. \]  

(17)

By using Eqs. (16) and (17), the heat balance gives the following relationship:

\[ \frac{\delta}{(\alpha/V_{\text{eutectic}})} = -\ln \left[1 - \frac{\Delta T^*}{\Delta H/pC_p}\right] \]
\[ = -\ln \left[1 - \frac{\Delta T^*}{\Delta T_{\text{hyper}}}\right] \]  

(18)

Eq. (18) indicates that the thickness of the liquid phase depends on the growth velocity of the eutectic interface. Substituting Eq. (18) to Eq. (16) gives Eq. (15). This means that the temperature profile in the solidification accompanied by the melting agrees with the temperature profile in the solidification at the hypercooling limit.

In the present study, \(T_{\text{meta}}^*\) should be equal to the metastable eutectic temperature (1975 K), since the melting does not affect the solidification rate as seen in Figs. 4 and 5. Thus, the undercooling and the temperature difference between the interfaces satisfy the following relationship:

\[ \Delta T_{\text{h}} + \Delta T_c + \Delta T^* = T_{\text{equ}}^* - T_{\text{meta}} \]  

(19)

As mentioned in Section 3.4.2, the undercooling due to the coupled growth is negligible in the present case, so

\[ \Delta T_{\text{h}} + \Delta T_c = T_{\text{equ}}^* - T_{\text{meta}} \]  

(19a)

In the solidification of the Al₂O₃–YAG equilibrium eutectic structure accompanied by the melting of the Al₂O₃–YAP metastable eutectic structure, the growth velocity and the thickness of the liquid phase are determined so as to satisfy Eqs. (9), (18) and (19a). The observed growth velocity ranged from \(0.8 \times 10^{-3}\) to \(2 \times 10^{-3}\) m/s. For example, at a growth velocity of \(2 \times 10^{-3}\) m/s, \(\Delta T_{\text{h}}\) and \(\Delta T^*\) are 38 and 86 K, respectively.

Since the hypercooling limit \(\Delta T_{\text{hyper}}\) of YAG is reported to be 769 K [12], the hypercooling limit of the Al₂O₃–YAG equilibrium eutectic system will be of the same order. Assuming \(\alpha = 1 \times 10^{-6}\) m²/s, the thickness of the liquid phase is roughly evaluated to be in the order of \(10^{-5}\) m. The thermal diffusion length \(\alpha/V_{\text{eutectic}}\) is also estimated to be of the order of \(10^{-3}\) m at the growth rate of \(2 \times 10^{-3}\) m/s. Thus, the thickness of the liquid phase is much smaller than the thermal diffusion length. On the other hand, the thickness is sufficiently thick to develop the solute diffusion layer ahead of the eutectic growth interface.

As mentioned Section 2, the enthalpy change of 5 kJ/mol from the Al₂O₃–YAG system to the Al₂O₃–YAP system is much smaller than the latent heats (111 kJ/mol for Al₂O₃ and 516 kJ/mol for YAG [18]). As seen in Fig. 2(b), the average temperature increase of the sample in the solidification accompanied by the melting is roughly 15 K. Thus, the assumption used here does not cause a serious error for discussing the undercooled melt layer. The simple consideration of the one-dimensional heat transfer suggests that the solidification interface and the melting interface are close to each other, with respect to the thermal diffusion length.

3.4.4. Coupled growth at the off-eutectic composition

Fig. 12 shows a morphological map of the Al₂O₃–YAG eutectic system as a function of the growth velocity and the composition. The Al₂O₃–YAG equilibrium eutectic system has a narrow coupled growth zone for unidirectional solidification [19] and solidification from the undercooled melt [21]. The composition range of the coupled growth for the solidification in the undercooled melt was approximately 2–4 mol%, even at the lowest growth velocity of \(1.4 \times 10^{-7}\) m/s, and became narrower at higher growth velocities.

In the solidification of the Al₂O₃–YAG equilibrium eutectic structure accompanied by the melting of the Al₂O₃–YAP metastable eutectic structure, a higher growth velocity was achieved compared to that observed in the conventional solidification in the undercooled melt. At higher growth velocities, the skewed coupled growth zone due to the kinetics effect should be considered. By using Eqs. (3), (4) and (9), the relationship between the growth
velocity and the apparent eutectic composition was calculated and is plotted by a bold dashed line in Fig. 12. The apparent eutectic composition clearly tends to shift to the $Y_2O_3$-rich side when the growth velocity exceeds $10^2 \text{m/s}$. Although there is a slight discrepancy between the coupled growth at $23.5 \text{mol}\%$ $Y_2O_3$ and the dashed line, the coupled growth at the metastable eutectic composition of $23.5 \text{mol}\%$ $Y_2O_3$ is primarily explained by considering the skewed coupled growth zone due to the kinetic effect. This implies that the growth velocities ranging from $0.8 \times 10^{-3}$ to $2 \times 10^{-3} \text{m/s}$ are selected so that the coupled growth occurs at the metastable eutectic composition. The thickness of the liquid phase is passively determined to achieve the growth velocity for the coupled growth.

### 4. Conclusions

The solidification of the $Al_2O_3$–$YAG$ equilibrium eutectic structure accompanied by the melting of the $Al_2O_3$–$YAP$ metastable eutectic structure was investigated. Shape casting using the undercooled melt formation was also demonstrated.

1. The solidification of the $Al_2O_3$–$YAG$ equilibrium eutectic structure accompanied by the melting of the $Al_2O_3$–$YAP$ metastable eutectic structure significantly reduced the solidification time. The $Al_2O_3$–$YAG$ equilibrium eutectic structure obtained by the solidification accompanied by the melting did not depend on the $Al_2O_3$–$YAP$ metastable eutectic structure, which had lamellar spacing ranging from 50 nm to 0.5 µm.

2. Precision casting and joining were successfully demonstrated by the undercooled melt shaping using the $Al_2O_3$–$YAP$ metastable eutectic particles. The nearly adiabatic solidification achieved a fine and uniform eutectic structure with lamellar spacing of less than 1 µm throughout the castings.

3. In the solidification accompanied by the melting, growth velocities ranging from $0.8 \times 10^{-3}$ to $2 \times 10^{-3} \text{m/s}$ were achieved. The kinetic undercooling was estimated to be of the order of $10^1 \text{K}$, whereas the undercooling due to the coupled growth was of the order of $10^{-1} \text{K}$.

4. The simple consideration of the heat transfer suggests that the thickness of the liquid phase between the solidification interface and the melting interface is much smaller than the thermal diffusion length. The coupling of the solidification and the melting resulted in the higher growth velocities. The skewed coupled growth zone due to the kinetic effect at high growth velocities may enable the fine eutectic structure to be formed even at the metastable eutectic composition.

### Acknowledgements

This work was supported by the 21st Century COE Program given by the Ministry of Education, Culture, Sports, Science and Technology, Japan. This work was also supported by a Grant-in-Aid for Scientific Research.

### References

[1] T. Mah, T.A. Parthasarathy, Ceram. Engng Sci. Proc. 11 (1990) 1617–1627.
[2] T.A. Parthasarathy, T. Mah, Ceram. Engng Sci. Proc. 11 (1990) 1628–1638.
[3] T.A. Parthasarathy, T. Mah, J. Am. Ceram. Soc. 76 (1993) 29–32.
[4] Y. Waku, H. Ohtsubo, N. Nakagawa, Y. Kohtoku, J. Mater. Sci. 31 (1996) 4663–4670.
[5] Y. Waku, N. Nakagawa, T. Wakamoto, H. Ohtsubo, K. Shimizu, Y. Kohtoku, J. Mater. Sci. 33 (1998) 4943–4951.
[6] N. Bahlawane, T. Watanabe, Y. Waku, A. Mitani, N. Nakagawa, J. Am. Ceram. Soc. 83 (2000) 3077–3081.
[7] N. Nakagawa, Y. Waku, T. Wakamoto, H. Ohtsubo, K. Shimizu, Y. Kohtoku, J. Jpn. Inst. Met. 64 (2000) 101–107.
[8] Y. Waku, N. Nakagawa, T. Wakamoto, H. Ohtsubo, K. Shimizu, Y. Kohtoku, Nature 389 (1997) 49–52.
[9] J.I. Caslavska, D.J. Viechnicki, J. Mater. Sci. 15 (1980) 1709–1718.
[10] B. Cocks, B. Lent, J. Cryst. Growth 46 (1979) 371–378.
[11] K. Nagashio, K. Kuribayashi, Acta Mater. 49 (2001) 1947–1955.
[12] H. Yasuda, I. Ohnaka, Y. Mizutani, N. Maeda, Y. Waku, Proceedings of M.C. Flemings Symposium, TMS, Boston, 2000, pp. 171–176.
[13] H. Yasuda, I. Ohnaka, Y. Mizutani, Y. Waku, Sci. Tech. Adv. Mater. 2 (2001) 67–71.
[14] Y. Mizutani, H. Yasuda, I. Ohnaka, Y. Waku, Mater. Trans. 42 (2001) 238–244.
[15] H. Yasuda, Y. Mizutani, I. Ohnaka, A. Sugiyama, Y. Waku, Mater. Trans. 42 (2001) 2124–2130.
[16] H. Yasuda, Y. Mizutani, I. Ohnaka, A. Sugiyama, T. Morikawa, Y. Waku, J. Am. Ceram. Soc. 86 (2003) 1818–1820.
[18] I-C. Lin, A. Navrotsky, J.K.R. Weber, P.C. Nordine, J. Non-Cryst. Solids 243 (1999) 273–276.
[19] Y. Mizutani, H. Yasuda, I. Ohnaka, N. Maeda, Y. Waku, J. Cryst. Growth 244 (2002) 384.
[20] A. Yoshikawa, B.M. Epelbaum, K. Hasegawa, S.D. Durbin, T. Fukuda, J. Cryst. Growth 205 (1999) 305–316.
[21] Y. Mizutani, H. Yasuda, I. Ohnaka, N. Maeda, Y. Waku, J. Jpn. Inst. Metals 66 (2002) 9.
[22] K.A. Jackson, J.D. Hunt, Trans. Metall. AIME 236 (1966) 1129–1142.
[23] R.S. Hay, J. Am. Ceram. Soc. 77 (1994) 1473–1485.

[24] A. Inoue, Mater. Sci. Engng A A304-306 (2001) 1–10.
[25] A. Inoue, K. Ohtera, K. Kita, T. Masumoto, Jpn. J. Appl. Phys. 27 (1988) L2248–L2251.
[26] A. Inoue, T. Zhang, T. Masumoto, Mater. Trans. JIM 30 (1989) 965–972.
[27] A. Inoue, T. Zhang, T. Masumoto, Mater. Trans. JIM 1 (1990) 48–151.
[28] W. Kurz, D.J. Fisher, Int. Met. Rev. 24 (1979) 177–204.
[29] R. Trivedi, P. Magnin, W. Kurz, Acta Metall. 35 (1987) 971.
[30] W. Kurz, D.J. Fisher, Fundamentals solidification, Trans. Tech. (1989) 93–115.