Selection of eutectic systems in Al$_2$O$_3$–Y$_2$O$_3$ ceramics

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Abstract

There are two eutectic reactions in the Al$_2$O$_3$-rich portion of the Al$_2$O$_3$–Y$_2$O$_3$ pseudo-binary system; one is the equilibrium Al$_2$O$_3$–YAG eutectic reaction at 1826°C, and the other is the metastable Al$_2$O$_3$–YAP eutectic reaction at 1702°C. Selection of the Al$_2$O$_3$–YAG and the Al$_2$O$_3$–YAP eutectics was examined in terms of cooling rate, nucleation temperature and maximum melt temperature. When the melt was cooled from 2100°C at any cooling rate, it always nucleated below the Al$_2$O$_3$–YAP eutectic temperature, therefore the Al$_2$O$_3$–YAP eutectic was selected. The Al$_2$O$_3$–YAG eutectic was selected when the melt was cooled from 1900°C at a cooling rate of less than 1 K s$^{-1}$. The selection of the two eutectic systems was determined by the nucleation temperature, although the maximum holding temperature of the melt and the cooling rate significantly affected the nucleation temperature. The structure of the melt, such as coordination of oxygen and chemical order when being heated to 2100°C may affect the nucleation behavior. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Composites which consist of a ceramics matrix and strong ceramic fibers are known to exhibit improved toughness and strength, because the brittleness is reduced by the fiber/matrix interface. Recently, unidirectional solidification of Al$_2$O$_3$–YAG [1] and Al$_2$O$_3$–GdAlO$_3$ [2] was employed to produce ceramics composites by eutectic growth. The unidirectionally solidified Al$_2$O$_3$/YAG eutectic composites exhibited high strength, thermal stability and creep resistance at high temperatures [2–4]. Waku et al. have demonstrated that eutectic composites consisting of a single crystal Al$_2$O$_3$ and a single crystal YAG without colonies had high thermal stability and high strength at temperatures of up to 1800°C [1,5,6]. The compression creep strength at a strain rate of $10^{-4}$ s$^{-1}$ and a temperature of 1600°C was much higher than that of the sintered composites [6]. Al$_2$O$_3$/GdAlO$_3$ eutectic composite has also been produced by unidirectional solidification [2]. The composites displayed plastic deformation rather than brittle fracture at 1600°C and maximum operating temperature was expected to be 1700°C. These ceramic composites produced by solidification processing have taken into account as high-temperature materials. It is important to understand the behavior of the solidification in order to control the fine eutectic structure. However, there is still some ambiguity in understanding solidification behavior.

The Al$_2$O$_3$–Y$_2$O$_3$ pseudo-binary system is composed of Y$_2$Al$_2$O$_5$ (YAG), YAI$_3$O$_5$ (YAP), Y$_3$Al$_2$O$_5$ compounds. One of the compounds, YAG, has been taken into account as a laser device. Several kinds of the phase diagram have been reported for this system [7–13]. Phase stability and phase diagram have been examined in comparison with the previous studies by Cockayne [13]. Caslavsky et al. [12] performed optical differential thermal analysis and obtained melting points of the YAG and YAP compounds and the phase diagram. Fig. 1 shows the phase diagram of the Al$_2$O$_3$-rich portion of the Al$_2$O$_3$–Y$_2$O$_3$ system [12]. In the phase diagram, the equilibrium eutectic reaction (α-Al$_2$O$_3$–YAG at 1826°C) and the metastable eutectic reaction (α-Al$_2$O$_3$–YAP at 1702 ± 7°C) were indicated. Melt heated to temperatures by 1990°C obeyed solidification path in accordance with the equilibrium phase diagram, while melt cooled down from temperatures above 1900°C followed the metastable solidification path. It was suggested that the selection of metastable eutectic system arose from the difficulty of the aluminum atoms to attain four-fold coordination in the YAG structure.

In general, it is not the melt temperature before cooling but the nucleation and/or growth velocity of the interface
that results in the selection of the solidified structure. It is valuable to examine the eutectic selection in terms of cooling rate, nucleation temperature and maximum holding temperature of the melt. Nucleation behavior and selection of the eutectic systems for the Al₂O₃–18.5 mol%Y₂O₃ melt is presented. Correlation between nucleation temperature and selection of the eutectic systems will be discussed.

2. Experiments

Specimens were prepared from 99.99% α-Al₂O₃ powder and 99.9% Y₂O₃ powder. A wet ball milling with addition of ethanol was used in order to obtain a homogeneously mixed slurry. The composition of the slurry was Al₂O₃–18.5 mol%Y₂O₃, which corresponded to the eutectic composition of α-Al₂O₃–YAG. The slurry was dried in a vacuum. A Mo crucible was used to melt the specimen and to measure the cooling curves. The dimensions of the specimen were 8 mm diameter and 5 mm height. The Mo crucible was heated by rf-induction under a vacuum of 10⁻² Torr. Temperature measurement was carried out by a two-colors pyrometer. A schematic picture of the furnace is presented in Fig. 2.

In the experiments for the cooling curve measurement, the mixed powders were heated to temperatures below 2000°C. The melt was cooled at a cooling rate of about 0.5 K s⁻¹. A specimen which nucleated above 1700°C was used for the cooling curve measurement. Then, heating and cooling curves were measured at a given rate. The pyrometers were calibrated so that the temperature at which the specimen was completely melted coincided with the equilibrium eutectic temperature (1826°C). The crystal structures of the specimens were identified by X-ray diffraction at room temperature, whilst the microstructure was observed by SEM (back electron image).

3. Results and discussion

Fig. 3(a) shows the cooling curves of Al₂O₃–18.5 mol%Y₂O₃ cooled from about 1900°C. In the case of a cooling rate of 0.1 K s⁻¹, exothermic heat due to nucleation and growth was detected at 1775°C. For the specimens cooled at a cooling rate of 20 K s⁻¹, exothermic heat was detected at 1620°C, which is below the eutectic temperature of Al₂O₃–YAP. Nucleation occurred above 1700°C when the specimens were cooled at a cooling rate of less than 1 K s⁻¹, while it occurred below 1700°C when the specimens were cooled at a cooling rate of more than 2 K s⁻¹. The cooling curves of the specimen cooled from 2100°C are shown in Fig. 3(b). When the cooling rate was 30 K s⁻¹, nucleation occurred at about 1625°C. Even at a cooling rate of 0.3 K s⁻¹, nucleation did not occur above the eutectic temperature of Al₂O₃–YAP, 1700°C. Solidification did not start when the specimen was cooled from 2100°C and kept at 1720°C for 1.8 ks.

In order to examine the effect of initial structure before melting, the specimen which once solidified below 1700°C was heated again up to 1900°C. Nucleation temperatures of the once solidified specimens depended on cooling rate as well as the specimens shown in Fig. 3(a). Thus, effect of the
Fig. 3. Cooling curves of the \( \text{Al}_2\text{O}_3-18.5 \text{ mol}\% \text{Y}_2\text{O}_3 \): (a) cooling from temperature below 2000°C; (b) cooling curves from temperatures above 2000°C.

maximum melt temperature on the nucleation was diminished and initial structure before melting did not affect the selection of the eutectic systems.

Fig. 4 shows examples of X-ray diffraction patterns for the \( \text{Al}_2\text{O}_3-18.5 \text{ mol}\% \text{Y}_2\text{O}_3 \). The diffraction peaks of \( \alpha-\text{Al}_2\text{O}_3 \) and \( \text{YAG} \) were observed for the specimen which nucleated above 1700°C, while the diffraction peaks of \( \alpha-\text{Al}_2\text{O}_3 \) and \( \text{YAP} \) were observed for the specimen nucleated below 1700°C. X-ray diffraction indicated that the \( \alpha-\text{Al}_2\text{O}_3-\text{YAG} \) eutectic system was selected when the specimens nucleated above 1700°C. The \( \alpha-\text{Al}_2\text{O}_3-\text{YAP} \) eutectic system was always selected when the specimen nucleated and solidified below 1700°C. According to the phase diagram presented by Caslavsky [12], the metastable \( \alpha-\text{Al}_2\text{O}_3-\text{YAP} \) eutectic temperature was 1702 ± 7°C. Undercooling of melt below the metastable eutectic temperature permits the metastable eutectic system to be thermodynamically selected. The fact that nucleation above 1700°C led to the equilibrium eutectic system while nucleation below 1700°C led to the metastable eutectic system was explained by the proposed phase diagram [12].

Fig. 5 shows SEM observation of solidified structures of the \( \text{Al}_2\text{O}_3-18.5 \text{ mol}\% \text{Y}_2\text{O}_3 \). As shown in Fig. 5(a), faceted–faceted eutectic structure was clearly observed in the speci-

men, which was cooled at 0.1 K s\(^{-1}\) and nucleated at 1803°C. The black phase is \( \alpha-\text{Al}_2\text{O}_3 \), while the white phase is the \( \text{YAG} \). The lamellar spacing was about 10 μm. The specimen which was cooled at 1.5 K s\(^{-1}\) and nucleated at 1745°C exhibited finer faceted–faceted eutectic structure,

Fig. 4. X-ray diffraction patterns of the solidified \( \text{Al}_2\text{O}_3-18.5 \text{ mol}\% \text{Y}_2\text{O}_3 \) Upper: nucleation below 1700°C and lower: nucleation above 1700°C. The diffraction peaks of Mo correspond to the Mo crucible.

(a) 20μm
(b) 10μm
(c) 20μm
(d) 10μm

Fig. 5. SEM observation of the solidified \( \text{Al}_2\text{O}_3-18.5 \text{ mol}\% \text{Y}_2\text{O}_3 \): (a) \( \alpha-\text{Al}_2\text{O}_3-\text{YAG} \) eutectic, cooling from 1990°C, cooling rate: 0.2 K s\(^{-1}\), nucleation temperature 1800°C; (b) \( \alpha-\text{Al}_2\text{O}_3-\text{YAG} \) eutectic, cooling from 1900°C, cooling rate: 1.5 K s\(^{-1}\), nucleation temperature 1745°C; (c) \( \alpha-\text{Al}_2\text{O}_3 \) and \( \alpha-\text{Al}_2\text{O}_3-\text{YAP} \) eutectic, cooling from 1900°C, cooling rate: 20 K s\(^{-1}\), nucleation temperature 1620°C; (d) \( \alpha-\text{Al}_2\text{O}_3 \) and \( \alpha-\text{Al}_2\text{O}_3-\text{YAP} \) eutectic, cooling from 2100°C, cooling rate: 20 K s\(^{-1}\), nucleation temperature 1625°C.
as shown in Fig. 5(b). The lamellar spacing was roughly 5 μm.

On the other hand, primary α-Al2O3 and rod-like eutectic structure were observed when the specimen was cooled from about 1900°C at a cooling rate of 20 K s⁻¹ and nucleated at 1619°C as shown in Fig. 5(c). The α-Al2O3–YAP eutectic structure was observed between the primary α-Al2O3. The primary α-Al2O3 was surrounded with halo of the YAP. Fig. 5(d) shows the α2O3–YAP eutectic structure in the specimen, which was cooled from 2096°C at 20 K s⁻¹ and nucleated below 1700°C. There is no difference in the solidified structure between the specimen which was cooled from 1900°C and the specimen which was cooled from 2100°C, although there was a remarkable difference in nucleation behavior.

In the case of cooling of the melt from temperatures below 2000°C, both the equilibrium and the metastable eutectic systems could be selected by changing the cooling rate. This result suggested that cooling from temperatures above 2000°C is not a required condition for the selection of the metastable eutectic system. The present results also indicated that once the melt was undercooled below the metastable eutectic temperature (1702°C), the metastable Al2O3–YAP eutectic system was always selected. The most dominant factor in the selection of the two eutectic systems was the nucleation. Nucleation of the Al2O3–YAP system is intrinsically easier than that of the Al2O3–YAP eutectic system, even when the melt was heated below 2000°C.

The YAG is known to be a material for laser devices and single crystal growth of the YAG was examined [13–15]. Cockayne reported that the YAG revealed one enigma in the solidification behavior [13]. The melt with the YAG composition (37.5 mol% Y2O3) did not artificially nucleate at its melting point. Difficulty of the YAG nucleation reported in the crystal growth of the YAG affected the eutectic solidification.

The maximum temperature of the melt before cooling significantly affected the nucleation of the Al2O3–YAG eutectic system. Selection of the Al2O3–YAP eutectic system was never observed if the melt was heated to temperatures above 2000°C. Even the melt was kept at 1720°C for 1.8 ks, solidification did not occur. The melt seemed to have irreversibly changed during heating above 2000°C. Because the melt was opaque for the YAG composition, the possibility of two immiscible liquids was reported in Ref. [13]. In the present solidified structure of the Al2O3–Y2O3, evidence of two immiscible liquids was not detected. Equipment for optical differential thermal analysis has been developed and the DTA curves of the Al2O3–18.5 mol% Y2O3 have been measured [16]. No exothermic or endothermic heat was detected during heating to 2200°C, although heat of fusion was clearly detected. Thus, the change of the melt around 2000°C will cause a small enthalpy change in comparison with the heat of fusion, if it exists. Coordination of oxygen around aluminum may have an important role for the melt change [13]. Four-fold coordination exists in the YAG structure, while only Al–O octahedra exists in the α-Al2O3 structure and the YAP structure. Coordination in the melt may change during heating and affect nucleation behavior.

4. Conclusions

Eutectic selection in the Al2O3–18.5 mol% Y2O3 system was examined. The selection of the eutectic systems was clearly classified by the nucleation temperature; the Al2O3–YAG (equilibrium eutectic) system was selected when nucleation occurred above 1700°C, while the Al2O3–YAP (metastable) system was selected when the melt was undercooled below 1700°C. The metastable eutectic system had priority in the selection below 1700°C, due to difficulty of YAG nucleation.

The maximum melt temperature before cooling significantly affected nucleation of the YAG. The melt heated to temperatures above 2000°C never nucleated above 1700°C and consequently the metastable system was selected. The structure of the melt, such as coordination of oxygen and chemical order, may change during heating.

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