Production of Undercooled Melt by Heating the Metastable Al$_2$O$_3$-YAP Eutectic Structure

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This paper demonstrates the undercooled melt formation from the metastable eutectic structure by heating procedures in the Al$_2$O$_3$-YAG system. Phase transformation during heating/cooling procedures is detected by optical DTA equipment. Firstly, the Al$_2$O$_3$-YAP metastable eutectic structure is obtained by solidification after heating the melt above 2273 K. The undercooled melt formation is confirmed when the Al$_2$O$_3$-YAP metastable eutectic structure composed of crystalline phases is heated up to temperatures above the metastable eutectic temperature for the equilibrium eutectic composition (18.5 mol% Y$_2$O$_3$) and the metastable eutectic composition (23.5 mol% Y$_2$O$_3$). The undercooled melt formation is immediately followed by the solidification in the Al$_2$O$_3$-YAG equilibrium path for the 18.5 mol% Y$_2$O$_3$ specimens. For the 23.5 mol% Y$_2$O$_3$ specimens, the obtained undercooled melt is kept even for as long as 3600 s without solidification. Furthermore, the fine and uniform Al$_2$O$_3$-YAG eutectic structure is obtained when the melting and the solidification simultaneously occur. The solidification with the exothermic heat beside the melting with the endothermic heat has a great advantage for heat release of the latent heat. Consequently, the high growth rate leads to the fine eutectic structure in the off-eutectic composition.

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1. Introduction

Recently, melt growth ceramics (MGC) have been taken into account as a candidate of high temperature materials. Especially, the eutectic composites consisting of single crystal Al$_2$O$_3$ and single crystal YAG (Y$_3$Al$_5$O$_{12}$, yttrium-aluminum-garnet) with neither colonies nor grain boundaries exhibits excellent properties. The composite exhibits a flexural strength of 360–500 MPa from room temperature to 2073 K in an air atmosphere. The compression creep strength at 1873 K is about 13 times higher than that of sintered composites with the same chemical composition. The Al$_2$O$_3$–GAP (GdAlO$_3$, gadolinium-aluminum-perovskite) eutectic composites produced by the melt growth have a flexural yield stress of about 700 MPa, and display some plastic deformation rather than brittle fracture at 1873 K. Furthermore, single crystals of YAG are well known to be a laser host material. Melt growth of YAG single crystal has been also taken into attention to obtain high quality YAG.

There are some problems related to solidification in the Al$_2$O$_3$–YAG system. One of the problems is difficulty of YAG nucleation. The melt with YAG composition normally solidifies as the Al$_2$O$_3$–YAP (YAlO$_3$, yttrium-aluminum-perovskite) metastable system, if the melt is cooled without seeding. Rapid solidification in the Al$_2$O$_3$–Y$_2$O$_3$ system (20–32 mol% Y$_2$O$_3$) leads to the unique solidified structure that comprised of two glass phases with different densities but essentially identical composition. For the levitation experiments, glass spheroids distributed in matrix glass phase is obtained from highly undercooled YAG melt. Furthermore, the cellular morphology of YAG is obtained by seeding SiO$_2$ trigger needle even beyond the hypercooling limit by using an aero-acoustic levitator. The liquid-liquid separation in YAG melt was suggested by the Hem technique. The liquid-liquid separation can occur in the undercooled YAG melt at 2263 K. In the experimental condition, YAP crystals nucleated at the crucible bottom and covered lower part of the specimen, suggesting that occurrence of the separation. They reported that there are only indirect evidence for the liquid-liquid separation in spite of the positive results.

Another problem is the eutectic selection in the Al$_2$O$_3$–Y$_2$O$_3$ system. The confusing phase selection resulted in different phase diagrams by different researchers. Csáslavský and Viechnicki precisely performed optical differential thermal analysis and proposed a phase diagram for the Al$_2$O$_3$–rich portion of the Al$_2$O$_3$–Y$_2$O$_3$ system. Two eutectic reactions exist in the phase diagram; one is the equilibrium eutectic reaction of Al$_2$O$_3$–Y$_2$O$_3$ at 2099 K, the other is the metastable one of Al$_2$O$_3$–YAP at 1975 K. Selection of the two eutectic systems is determined by nucleation of YAG in the composition range of 13.5–28.5 mol% Y$_2$O$_3$. Heating the melt above 2273 K inhibits YAG nucleation and consequently the Al$_2$O$_3$–YAP metastable system is selected. Although the inhabitation of YAG nucleation suggested some change occurred in the melt, there is still uncertainty. Control of the YAG nucleation is one of the important factors for the microstructure development.

From a viewpoint of melt growth for YAG single crystal and the eutectic composites, the difficulty of YAG nucleation and the selection of the eutectic systems were often troublesome. However, it might be interesting to consider use of the nucleation difficulty and the eutectic selection in another solidification processing. This paper demonstrates undercooled melt formation in the Al$_2$O$_3$–Y$_2$O$_3$ system by using the difficulty of YAG nucleation and the eutectic selection. Criterion for the undercooled melt formation and a novel solidification processing by using the undercooled melt are discussed.

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2. Experiments

Al₂O₃–Y₂O₃ powders with Al₂O₃–18.5 and 23.5 mol% Y₂O₃ compositions are prepared by using 99.99% α-Al₂O₃ (2–3 μm diameter) and 99.9% Y₂O₃ (2–3 μm diameter). 18.5 mol% Y₂O₃ is the Al₂O₃–YAG eutectic composition and 23.5 mol% Y₂O₃ is the Al₂O₃–YAG metastable eutectic composition. Powder is wet ball milled with ethanol to obtain homogeneous slurry. After the slurry is dried in a vacuum at 373 K, the dried powder is used for DTA experiments. An optical DTA apparatus, as shown in Fig. 1, performed differential thermal analysis. Specimens are put in one of two dimples (5 mm diameter, 1.5 mm depth) on Mo plates (7 mm in width, 100 mm in length, 0.1 mm in thickness). The Mo plate with the specimen is covered with another Mo plate with the same dimension. DC current directly heats the specimen between two Mo plates. Ar atmosphere (about 50 Pa) is kept during the measurements to avoid deposition of Mo on the SiO₂ glass. Dimples of the Mo plate are measures by two two-color pyrometers. One of the pyrometer measures the dimple on the specimen and the other the dimple on the standard. In the present work, nothing was inserted in the dimple for the standard. Emissivity change of the specimen due to phase transformation did not affect the accuracy in temperature, since the pyrometers always measure the surface of Mo plate. The temperature difference between the two dimples gives DTA curves. Calibration of the pyrometer was performed so that beginning of the endothermic heat due to melting of the Al₂O₃–YAG eutectic structure was equal to be 2099 K.

Heating and cooling procedures for the DTA measurement are as follows. Firstly, the mixed powder is heated up to temperatures above 2173 K below 2273 K to obtain uniform melt. Al₂O₃–YAG eutectic structure is obtained by cooling the melt in accordance with the previous studies. For every measurement of DTA curves, the specimens composed of the Al₂O₃–YAG eutectic structure are used as an initial structure. In order to obtain the Al₂O₃–YAP eutectic structure, the specimens with the initial Al₂O₃–YAG eutectic structure are heated up to temperatures above 2273 K at a heating rate of 1 K/s and the melt is cooled in the Al₂O₃–YAP eutectic solidification path. Then, the specimens with the Al₂O₃–YAP eutectic structure are heated up to temperatures above the Al₂O₃–YAP metastable eutectic temperature (1973 K) and below the Al₂O₃–YAG eutectic temperature (2099 K) at a heating rate of 1 or 10 K/s. After holding at the temperature, the specimens are cooled at a cooling rate of 10 K/s.

The specimens with the Al₂O₃–YAP eutectic structure are also heated up to a given temperature and are held for a given time. After holding the specimens, the specimens are quenched to examine temperature-time dependence of the phase transformation from the Al₂O₃–YAP structure to the Al₂O₃–YAG structure. X-ray diffraction and EPMA were performed to identify the constituent phases α-Al₂O₃, YAG and YAP. Conventional SEM observed microstructure.

3. Results and Discussion

3.1 DTA curves and microstructure for the 18.5 mol% Y₂O₃ specimens

Figure 2 shows the phase diagram of the Al₂O₃–Y₂O₃ system and DTA curves when the Al₂O₃–YAP metastable eutectic structure was obtained by heating the melt above 2273 K. The phase diagram clearly indicates the two eutectic reactions, although an ambiguity remains in the liquidus line of YAP at a composition range of 40–50 mol% Y₂O₃. The endothermic heats at about 2099 K on the heating curves correspond to the Al₂O₃–YAG equilibrium eutectic temperature, while the exothermic heat due to nucleation and growth of the metastable eutectic system is detected below the metastable eutectic temperature. The Al₂O₃–YAP eutectic structure is always obtained by heating the specimen up to 2273 K as shown in Fig. 2. Selection of the eutectic systems in the present work is consistent with the previous works. It should be emphasized that selection of the eutectic systems is completely controlled by the heating/cooling procedure.

Figure 3 shows DTA curves for the Al₂O₃–18.5 mol% Y₂O₃ specimens when the specimen with the Al₂O₃–YAP eutectic structure are heated at a heating rate of 10 K/s and then are cooled at a cooling rate of 10 K/s. Fluctuation of the DTA curves originates from noise of the two-colors pyrometer, i.e. fluctuation at 1900 K on curve “A”. For all the specimens, endothermic heat is detected at around 1975 K, suggesting the melting of the Al₂O₃–YAP metastable eutectic structure. The DTA curves are roughly classified into two groups, although it is somewhat difficult to define the precise criterion for the two groups. One is that rather large exothermic heat is detected after the clear endothermic heat, indicated by curve “A” in Fig. 3. The other is that the exothermic heat immediately follows the endothermic heat, indicated by curve “B” in Fig. 3.
Fig. 2 (a) Phase diagram of the \( \text{Al}_2\text{O}_3 \)-rich portion of \( \text{Al}_2\text{O}_3 \)-\( \text{Y}_2\text{O}_3 \) system.\(^{11}\) \( \text{Al}_2\text{O}_3 \)-\( \text{YAG} \) equilibrium eutectic temperature: 2099 K, \( \text{Al}_2\text{O}_3 \)-\( \text{YAP} \) metastable eutectic temperature: 1975 K. (b) DTA curves when the \( \text{Al}_2\text{O}_3 \)-\( \text{YAP} \) eutectic structure is obtained by heating the melt above 2273 K. The temperature calibration is done by coinciding beginning of the endothermic heat the \( \text{Al}_2\text{O}_3 \)-\( \text{YAG} \) eutectic temperature in the heating stage.

The exothermic heat of curve “B” is smaller than that of curve “A”. For both cases, no other endothermic or exothermic heat is detected below the metastable eutectic temperature. The DTA curves indicate that solidification or reaction completes above the metastable eutectic temperature.

Figure 4(a) shows the \( \text{Al}_2\text{O}_3 \)-\( \text{YAP} \) metastable eutectic structure used as the initial microstructure for the DTA measurement in Fig. 3. The specimens are almost covered with rod-like \( \text{Al}_2\text{O}_3 \)-\( \text{YAP} \) eutectic structure with lamellar spacing of less than 1 \( \mu \)m, although some coarse \( \text{Al}_2\text{O}_3 \) crystals are identified. Figure 4(b) shows the microstructure obtained by curve “A” of Fig. 3. The specimen consists of \( \text{Al}_2\text{O}_3 \) and YAG phase. YAG dendrites and coarse \( \text{Al}_2\text{O}_3 \) crystals are observed in the \( \text{Al}_2\text{O}_3 \)-\( \text{YAG} \) eutectic region. The microstructure of curve “B” of Fig. 3 is shown in Fig. 4(c). X-ray diffraction indicates that the constituent phases are \( \text{Al}_2\text{O}_3 \) and YAG. The rather fine \( \text{Al}_2\text{O}_3 \)-\( \text{YAG} \) eutectic structure is observed, although the primary \( \text{Al}_2\text{O}_3 \) is distributed in the specimen.
3.2 DTA curves and microstructure for the 23.5 mol% Y$_2$O$_3$ specimens

Figure 5(a) shows typical DTA curves when the specimens with the Al$_2$O$_3$–YAP metastable eutectic structure are heated at a heating rate of 10 K/s. As shown in curves “B” and “C” of Fig. 5(a), the two groups as mentioned above are obtained for the 23.5 mol% Y$_2$O$_3$ specimens as well as the 18.5 mol% Y$_2$O$_3$ specimens. Furthermore, another type of the DTA curves are observed, indicated by curve “A” of Fig. 5(a). In the case of curve “A” of Fig. 5(a), the exothermic heat does not follow the endothermic heat at temperatures above 1975 K. The specimen in which the endothermic heat completes is kept without any exothermic heat for 30 s. In the cooling stage, an exothermic heat is clearly detected at temperatures below 1975 K. In the case of curve “A,” Al$_2$O$_3$ and YAP must be completely melted and the undercooled melt is kept at temperatures above the metastable eutectic temperature and below the equilibrium eutectic temperature. In the temperature range for the metastable eutectic composition, only YAG can nucleate. Therefore, the YAG nucleation results in the three different DAT curves.

Figure 5(b) shows DTA curves when the specimens are heated at 1 K/s. At the lower heating rate, the obtained DTA curves are also classified into three groups, indicated by curves “D,” “E” and “F.” In the case of curve “D”, the specimen is kept even for 1800 s without any heat release due to phase transformation after the endothermic heat at 1975 K and the exothermic is detected below 1975 K in the cooling stage.

Figure 6(a) shows the Al$_2$O$_3$–YAP metastable eutectic structure before the DTA measurement in Fig. 5. In comparison with the Al$_2$O$_3$–YAP metastable eutectic structure with 18.5 mol% Y$_2$O$_3$ in Fig. 4(a), coarse α-Al$_2$O$_3$ crystals is not observed at the eutectic boundaries. Figure 6(b) shows the microstructure obtained in curve “D” of Fig. 5(b). X-ray diffraction indicated that the specimen consists of the Al$_2$O$_3$–YAP metastable eutectic structure. The microstructure suggests that the endothermic and the exothermic heats in curve “D” of Fig. 5(b) corresponds to melting and solidification of the Al$_2$O$_3$–YAP metastable eutectic system, respectively. It means the undercooled melt is formed from the metastable eutectic structure in the heating stage and exits for 1800 s at temperatures below the Al$_2$O$_3$–YAG eutectic temperature. The melt reversely solidifies in the Al$_2$O$_3$–YAP eutectic solidification path.

Figure 6(c) shows the obtained microstructure in the case of curve “E” of Fig. 5(b). Dendritic YAG crystals are distributed in the Al$_2$O$_3$–YAG eutectic matrix. The microstructure implies dendritic growth of YAG occurs in the undercooled melt produced by heating the metastable eutectic structure above the metastable eutectic point. Microstructure obtained in curve “F” of Fig. 5(b) is shown in Fig. 6(c). The specimen is covered with the fine and uniform Al$_2$O$_3$–YAG eutectic structure. The rounded shape of α-Al$_2$O$_3$ phase in the Al$_2$O$_3$–YAG eutectic structure differs from α-Al$_2$O$_3$ in the typical Al$_2$O$_3$–YAG eutectic structure shown in Fig. 6(c). The lamellar spacing of the uniform Al$_2$O$_3$–YAG eutectic structure is several μm, which is almost equal to the conventional eutectic structure in Fig. 6(c). In this case, the exothermic heat follows the endothermic heat as shown in Fig. 5(b). The solidification in the Al$_2$O$_3$–YAG path and the melting of Al$_2$O$_3$–YAP eutectic system simultaneously occur in the specimen. The advantage of heat release at the solidifying front increases the
growth velocity and can result in the coupled growth from the undercooled melt.

3.3 Phase transformation from the Al$_2$O$_3$–YAP system to Al$_2$O$_3$–YAG system

The DTA curves and the obtained microstructures evidently indicate that the heating procedure of the metastable eutectic structure above the metastable eutectic point leads to melting of the metastable eutectic structure and consequently to the undercooled melt formation below the equilibrium eutectic point. However, it is better to deny another possibility about the transformation, since the melting and the undercooled melt formation is not commonly recognized for various systems. Another possibility is solid phase transformation controlled by diffusion.

The melting behavior is well known to occur just at the melting point, while the diffusion-controlled transformation is the thermally activated reaction. In the later case, reaction rate depends on temperature. Thus, estimation of the activation energy provides useful information to evaluate the transformation. In order to estimate the activation energy, the specimens with the Al$_2$O$_3$–YAP metastable eutectic structure are heated up to a given temperature and are quenched after holding for a given time. The constituent system in the quenched specimen (the Al$_2$O$_3$–YAP system or the Al$_2$O$_3$–YAG system) was classified in terms of holding time and holding temperature, as shown in Fig. 7.

Activation energy for the transformation is estimated from the slope in the time-temperature plot. The dash slope in Fig. 7, which is drawn as possible as the activation energy becomes small, gives activation energy of about 2.3 MJ/mol. The value of 2.3 MJ/mol is too high to accept as the activation energy of diffusion in oxides, since the activation energy is generally several 100 kJ/mol at most. The estimated activation energy is
tion energy indicates that the phase transformation is not consistently understood if only assumes the diffusion-controlled transformation. Therefore, it is obvious that melting of the metastable $\text{Al}_2\text{O}_3$–YAP eutectic structure by the heating procedure results in the undercooled melt formation and consequently leads to the transformation to the $\text{Al}_2\text{O}_3$–YAG system. The observed endothermic and exothermic heats are related to the undercooled melt formation and solidification from the undercooled melt formation.

3.4 Undercooled melt formation and fine eutectic structure

In the present study, it is worth emphasizing that not the amorphous phase but the crystalline phases produce the undercooled melt at temperatures below the equilibrium eutectic temperature in the heating stage. The undercooled melt with 23.5 mol% $\text{Y}_2\text{O}_3$ is kept even for 1800 s, while the solidification in the $\text{Al}_2\text{O}_3$–YAG system immediately follows the undercooled melt formation for 18.5 mol% $\text{Y}_2\text{O}_3$. According to the phase diagram in Fig. 2(a), the melt must be obtained at the metastable eutectic composition, if nucleation of YAG is still inhibited during the heating procedure. The fact that the undercooled melt is kept without any solidification indicates that nucleation of YAG tends to be inhibited in the solid state and in the undercooled melt. In the case of 18.5 mol% $\text{Y}_2\text{O}_3$, $\alpha$-$\text{Al}_2\text{O}_3$ remains even if YAP and a part of $\alpha$-$\text{Al}_2\text{O}_3$ are melted at the metastable eutectic temperature. The remained $\alpha$-$\text{Al}_2\text{O}_3$ may act as a catalyst for nucleation of YAG. Thus, the undercooled melt formation is followed by solidification in the $\text{Al}_2\text{O}_3$–YAP system.

For 23.5 mol% $\text{Y}_2\text{O}_3$ specimens, the fine and uniform $\text{Al}_2\text{O}_3$–YAG eutectic structure is obtained when the $\text{Al}_2\text{O}_3$–YAG eutectic solidification simultaneously occurs with melting of the $\text{Al}_2\text{O}_3$–YAG eutectic structure. The simultaneous reactions provide a unique thermal condition for the solidification. Lin et al. reported thermodynamic data on solidification of molten YAG. Enthalpy changes at 298 K for 3YAlO$_3$(YAP) + $\text{Al}_2\text{O}_3$ = $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) and $\text{Y}_3\text{Al}_5\text{O}_{12}$ (glass) = $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) are estimated to be $-32$ and $-276 \text{kJ/mol}$, respectively. The heat of fusion of YAG at 2240 K is estimated to be 516 kJ/mol. The heat of fusion for $\text{Al}_2\text{O}_3$ or YAG must be much larger than the enthalpy change of the transformation from YAP and $\text{Al}_2\text{O}_3$ to YAG, although data at the metastable eutectic temperature are not available.

When the solidification and the melting simultaneously occur in a restricted area, most of the latent heat released by the solidification is consumed for the melting of the metastable eutectic structure. Only the much smaller heat release is required to complete the solidification in comparison with the solidification in melt. The advantage on the heat release leads to high growth rate of the eutectic solidification in the specimens. The high growth rate can result in the coupled growth even at the off-eutectic composition (23.5 mol% $\text{Y}_2\text{O}_3$) with respect to the $\text{Al}_2\text{O}_3$–YAG eutectic reaction.

3.5 Application of the undercooled melt formation

The eutectic solidification in the $\text{Al}_2\text{O}_3$–YAG system and the melting of the $\text{Al}_2\text{O}_3$–YAP system simultaneously occur when the metastable eutectic structure with the 23.5 mol% $\text{Y}_2\text{O}_3$ specimens are heated above the metastable eutectic temperature. In a sense, the simultaneous reactions produce the non-equilibrium semisolid state followed by the solidification to the fine and uniform eutectic structure. The undercooled melt and the semisolid state have been generally recognized to have many advantage, i.e., the undercooled state formation by using amorphous alloys with a large supercooled liquid region. One of the examples is shape forming by using superplastic micro/nano-formability of the supercooled liquid state produced from amorphous La–Al–Ni–Co–Cu alloys.

The undercooled melt formation and the solidification presented in the study have advantages for the novel shape casting in which solidification plays an important role for shape forming. Shape casting by using the undercooled melt can be performed at lower temperatures. In the case of ceramics, the lower process temperatures are preferable, since difficulty for casting comes from their high melting temperatures. The $\text{Al}_2\text{O}_3$–YAG eutectic structure (23.5 mol% $\text{Y}_2\text{O}_3$) produced from the undercooled melt is uniform and fine in comparison with that produced in the equilibrium solidification path. Therefore, it is interesting to develop a novel solidification processing using the undercooled melt for this system.

4. Conclusions

The undercooled melt formation and the solidification from the undercooled melt are examined by using the optical DTA apparatus for $\text{Al}_2\text{O}_3$–18.5 mol% $\text{Y}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$–23.5 mol% $\text{Y}_2\text{O}_3$. The former composition corresponds to the equilibrium eutectic composition and the later the metastable eutectic composition.

(1) The $\text{Al}_2\text{O}_3$–YAP metastable eutectic structure is always obtained by heating the melt up to temperatures above 2273 K. The eutectic selection is consistent with the previous studies.

(2) Formation of the undercooled melt is confirmed for both compositions, when the specimens with the obtained metastable eutectic structure are heated up to temperatures above the metastable eutectic temperature.

(3) For the 18.5 mol% $\text{Y}_2\text{O}_3$ specimens, the solidification in the equilibrium path ($\text{Al}_2\text{O}_3$–YAG) follows the melting of the metastable eutectic structure. Coarse $\text{Al}_2\text{O}_3$ crystals and YAG crystals are observed in the solidified specimens.

(4) For the 23.5 mol% $\text{Y}_2\text{O}_3$ specimens, the undercooled melt produced in the heating procedure is kept for as long as 1800 s. Furthermore, the fine and uniform $\text{Al}_2\text{O}_3$–YAG eutectic structure is formed when the melting of the metastable eutectic structure and the solidification in the equilibrium path simultaneously occur.

(5) The simultaneous melting and solidification reduces process temperature for the shape casting and produces the uniform and fine eutectic structure.

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