Formation and microstructure of Al$_2$O$_3$-YAG eutectic ceramics by phase transformation from metastable system to equilibrium system

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Abstract. Unidirectionally solidified Al$_2$O$_3$-YAG(Y$_3$Al$_5$O$_{12}$: yttrium-aluminum-garnet) eutectic ceramic composites have been recognized as encouraging heat-resistance materials because of the superior mechanical properties at high temperatures. In addition to the excellent mechanical properties at high temperatures, some interesting solidification phenomena have been reported in the Al$_2$O$_3$-Y$_2$O$_3$ system. The Al$_2$O$_3$-YAG equilibrium eutectic at 2099 K and the Al$_2$O$_3$-YAP metastable eutectic at 1975 K exist in the Al$_2$O$_3$-Y$_2$O$_3$ system. The heating the metastable eutectic up to temperatures above the metastable eutectic temperature produced the undercooled melt. Solidification in the equilibrium path accompanied the melting of the metastable eutectic. The solidification process using undercooled melt resulted in the fine and uniform eutectic structure. In this study, the effect of the initial Al$_2$O$_3$-YAP particles size on the undercooled melt formation was examined. The Al$_2$O$_3$-YAP particles with diameters more than several µm resulted in the transformation through the undercooled melt. EBSD analysis showed that the domains of Al$_2$O$_3$ grains with same crystallographic orientation were observed and that their domain size depended on the Al$_2$O$_3$-YAP particles size. On the other hand, for the Al$_2$O$_3$-YAP particles with a diameter of 500 nm, the each Al$_2$O$_3$ grain with diameter of about 1 µm had the different crystallographic orientations, which suggested that the transformation from metastable eutectic to equilibrium eutectic occurred in the solid state. The increase in the Al$_2$O$_3$-YAP free surface area suppressed the undercooled melt formation.

1. Introduction
The melt growth composite (MGC) of ceramics are of considerate practical concern due to the excellent mechanical properties at high temperatures. Especially, unidirectionally solidified Al$_2$O$_3$-YAG eutectic ceramics consisting of single crystal Al$_2$O$_3$ and single crystal YAG is attractive for high-temperature materials [1-2]. The composites showed the flexural strength of 360-400 MPa from room temperature to 2073 K [2]. In addition to the excellent mechanical properties at high temperatures, some interesting solidification phenomena have been reported in the Al$_2$O$_3$-Y$_2$O$_3$ system [3-4]. There are two eutectic systems in the phase diagram of Al$_2$O$_3$-Y$_2$O$_3$ system in the Al$_2$O$_3$ rich part, one is Al$_2$O$_3$-YAG equilibrium eutectic system and the other is Al$_2$O$_3$-YAP(YAlO$_3$: yttrium aluminum-perovskite) metastable eutectic system. In the composition range of 13.5-28.5 mol%Y$_2$O$_3$, the selection of the two eutectic metastable systems is determined because of the suppression in the nucleation of
YAG [5-6]. When heating the melt with the metastable eutectic composition above 2273K, Al₂O₃-YAP metastable system is indispensably selected.

Our previous papers [7] showed that heating the Al₂O₃-YAP metastable eutectic particles with diameters 20-45 µm up to temperatures above the metastable eutectic temperature of 1975 K but below equilibrium eutectic temperature of 2099 K produced the undercooled melt. Solidification in the equilibrium path accompanied melting of the metastable eutectic system. The coupling of the melting and the solidification enabled a nearly adiabatic transformation, resulting in the fine and uniform eutectic structure. This unique solidification process is attractive for fabricating the dense Al₂O₃-YAG composites with a fine microstructure.

The effect of the Al₂O₃-YAP particle size on the microstructure was also examined [8-9]. The Al₂O₃-YAG compact produced by the Al₂O₃-YAP metastable eutectic particles with diameters 20-45 µm had the fine and uniform eutectic structure with a lamellar spacing of submicron order. In the Al₂O₃-YAG compact produced by the Al₂O₃-YAP particles with diameters less than 20 µm, the Al₂O₃ phase with a diameter of 2.5 µm were dispersed in the YAG matrix. In order to increase the surface area of Al₂O₃-YAP particle, the Al₂O₃ and YAP powder mixtures with a diameter of 500 nm were prepared. Transformation to Al₂O₃-YAG eutectic occurred in the solid state reaction [10]. The microstructure of Al₂O₃-YAG compact showed that the Al₂O₃ phases with the diameter of 1-2 µm were uniformly dispersed in the YAG matrix.

It is reported that YAG phase is likely to nucleate at the Al₂O₃/YAP phase boundaries when the Al₂O₃-YAP compact was heated at low heating rate of 0.16 K/s and that 11% volume expansion in the phase transformation (Al₂O₃+YAP→YAG) suppresses the nucleation of the YAG phase[4]. Thus, the increase in the free surface area of the Al₂O₃-YAP particles for volume expansion can influence on undercooled melt formation. In this study, the effect on the Al₂O₃-YAP particle size on the undercooled melt formation was examined from the viewpoint of the crystallographic orientation. The preferential site for YAG nucleation in the Al₂O₃-YAP bulk was also examined by AFM analysis.

2. Experimental Procedure
The α-Al₂O₃ powder and Y₂O₃ powder were weighed according to the Al₂O₃-23.5mol%Y₂O₃ which is the Al₂O₃-YAP metastable eutectic composition. Their powders were ball milled with ethanol for 24 h to obtain homogeneous slurry and was dried in a vacuum. The mixed powder was melted in a Mo crucible by an induction furnace in an Ar atmosphere. The Al₂O₃-YAP metastable eutectic structure was obtained by solidifying the melt kept the above 2300 K. The solidified specimens were crushed into particles and sieved through a 45-63 µm, 32-45 µm and 20 µm in decreasing order. The Al₂O₃-YAP metastable eutectic particles of 20-45 µm and less than 20 µm in size were prepared.

The polymerized complex method [11], which provides the fine and uniform ceramics particle, was utilized in order to prepare the nano-sized YAP particles. Citric acid and ethylene glycol were added in the proportion of 4 moles and 180 moles, respectively, for each mole of metal cation. Citric acid, Al(NO₃)₃·9H₂O and Y(NO₃)₃·6H₂O, according to the nominal composition of YAlO₃, were dissolved in ethylene glycol at 473 K. The formation of the polymer between ethylene glycol and the metal citrate complexes was promoted at 473-573 K. When the colloidal solution was condensed, it became highly viscous. Viscous polymeric product was decomposed to a fine powder at 723 K. The powder precursor was calcined at 1573 K for 18 ks in air to enhance the crystallization and eliminate the organic contents. The obtained powders and α-Al₂O₃ powders with a diameter of 500 nm were completely mixed with a planetary ball milling apparatus for 72 ks at 300 rpm according to the metastable eutectic composition.

The desired Al₂O₃-YAP metastable eutectic particles were inserted into the Mo mold, which has outer diameter of 10 mm and inner diameter of 6 mm. The Mo mold was inserted into the carbon die and then the Al₂O₃ powder was put into carbon die to avoid the energization of the Mo die. The graphite die was heated to 2023 K at the heating rate of 1.7 K/s under the pressure of 40 MPa. The specimen was kept for 60 s at the desired temperature in vacuum.
3. Results and Discussion

Figure 1. Al$_2$O$_3$ crystallographic orientation mappings of the (a) Al$_2$O$_3$-YAP particles and the Al$_2$O$_3$-YAG compacts produced by metastable eutectic particles with diameters (b) 20-45 µm, (c) less than 20 µm and (d) 500 nm. Each circle in Figure 1(c) shows the domains of Al$_2$O$_3$ grains with the same crystallographic orientations.

The Al$_2$O$_3$ crystallographic orientation mappings of Al$_2$O$_3$-YAG compacts produced by the Al$_2$O$_3$-YAP particles with diameters 20-45 µm, less than 20 µm and 500 nm are shown in Figure 1(b), (c) and (d) respectively. For comparison, the Al$_2$O$_3$ crystallographic orientation mapping of Al$_2$O$_3$-YAP particles is shown in Figure 1(a). Al$_2$O$_3$-YAP particles had the lamellar structure with a lamellar spacing of about 0.5 µm. The Al$_2$O$_3$ grains with same crystallographic orientation in the range of at least 50 µm were observed. For Al$_2$O$_3$-YAG compacts produced by the Al$_2$O$_3$-YAP grains with diameters 20-45 µm and less than 20 µm, the domains of the Al$_2$O$_3$ grains with the same crystallographic orientation were observed, and their domains size were approximately 20 µm and 4-15 µm, respectively. These results suggested that the Al$_2$O$_3$ grains in each domain connected with each other. The volume of undercooled melt during the transformation from the metastable system to equilibrium system depended on initial Al$_2$O$_3$-YAP particle size. As to YAG phase, the domains of YAG grain with a same crystallographic orientation were not observed regardless of the Al$_2$O$_3$-YAP particles size, which indicated that the eutectic structure formed through undercooled melt was composed of discontinuously grown YAG grains with continuously grown Al$_2$O$_3$ grains[10]. On the other hand, for the Al$_2$O$_3$-YAG compact formed by the Al$_2$O$_3$-YAP particles with a diameter of 500 nm, the most of Al$_2$O$_3$ grains with 1-2 µm had the different crystallographic orientation, which suggests that the transformation from the metastable system to the equilibrium system occurred in the solid state.

YAG nucleation in the free surface area of the Al$_2$O$_3$-YAP bulk with diameter of 10 mm was observed by AFM analysis. Since the Al$_2$O$_3$ and YAP phases were distinguished by using the difference in their hardness, final polishing was performed with Al$_2$O$_3$ suspension. The concave and convex portions indicate YAP and Al$_2$O$_3$, as shown in Figure 2(a). After polishing, the Al$_2$O$_3$-YAP bulk was heated at the heating rate of 1.7 K/s up to 1773 K which is under metastable eutectic temperature and was then quenched. AFM observation showed that the prominent parts were observed in the free surface area of Al$_2$O$_3$-YAP bulk as shown in Figure 2(b). The prominent areas were formed by the volume expansion of 11 % when YAG phase was formed in the solid state. Thus, YAG can be preferentially formed at the free surface area of Al$_2$O$_3$-YAP bulk even under the condition of the lower temperature than metastable eutectic temperature and the high heating rate. Based on these results, the increase in the free surface area of Al$_2$O$_3$-YAP particle promoted the YAG nucleation.
4. Conclusions
The effect on the initial Al₂O₃-YAP particle size on the undercooled melt formation and the preferential site for YAG nucleation in the Al₂O₃-YAP bulk were examined. EBSD analysis showed that the domain size of the Al₂O₃ grains with the same crystallographic orientation for the Al₂O₃-YAP particles with diameters 20-45 µm and less than 20 µm was approximately 20 µm and 4-15 µm, respectively. The volume of undercooled melt during the transformation from the Al₂O₃-YAP metastable system to Al₂O₃-YAG equilibrium system depended on Al₂O₃-YAP particle size. On the other hand, for the Al₂O₃-YAP particle with a diameter of 500 nm, Al₂O₃ grains had the different crystallographic orientation, which indicate the solid-state transformation from metastable eutectic to equilibrium eutectic. AFM analysis showed that YAG nucleation preferably occurred on the free surface area of the Al₂O₃-YAP bulk. Based on these results, the increase in the Al₂O₃-YAP free surface area promoted YAG nucleation and suppressed the undercooled melt formation.

Acknowledgements
This study was supported by Priority Assistance for the Formation of Worldwide Renowned Centers of Research - The Global COE Program (Project: Center of Excellence for Advanced Structural and Functional Materials Design) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. This works was also supported by a Giant-in-Aid for Young Scientists (B)(No.20760506) and Nippon Sheet Glass Foundation For Materials Science and Engineering.

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