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Formation of $GdAlO_3$–Al_2O_3 composite having fine pseudo-eutectic microstructure

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Abstract

$GdAlO_3$ and Al_2O_3 powders were mixed and pulverized using ball mills. The prepared powder was sintered by SPS at 1450 °C without holding time. SEM observation of the sintered specimen showed a eutectic-like microstructure. This is called 'pseudo-eutectic' in this research. The microstructure formed from a powder pulverized by a tumbling ball mill for one week was much finer than that by a planetary ball mill for 5 and 10 h. The fine homogeneous eutectic-like (pseudo-eutectic) microstructures could be formed at both eutectic and off-eutectic compositions. In case of crystallization from a melt of eutectic components, homogeneous eutectic microstructures can be formed only at restricted compositions very close to the eutectic one. Coarse primary crystals generally exist in the eutectic microstructure at off-eutectic compositions. The pseudo-eutectic microstructures can be formed at any compositions because a mixing ratio of the starting powders can be varied.

Keywords: Milling; Al_2O_3; Pseudo-eutectic; $GdALO_3$; Composites; Microstructure

1. Introduction

Several eutectic ceramics have high flexural strength and creep resistance not only at a room temperature but also at elevated temperatures.[1–12] Thus, the eutectic ceramics are a promising candidate for high temperature structural applications such as the turbine blades. Moreover, the eutectic ceramics are expected recently for not only the heat resisted materials but also other various applications, such as thermophotovoltaic (TPV) generation systems[13] and porous materials.[14] The eutectic ceramics are generally produced by crystallization from a liquid phase (melt) with a eutectic composition.[15–17] When the melt with the eutectic composition is cooled, each component crystallizes and grows simultaneously at the eutectic temperature. Such eutectic ceramics have characteristic microstructures consisting of fine crystals entangled with each other. Various formation processes of the eutectic microstructure have been considered.[18,19] Glass formation and devitrification in Al_2O_3–rare earth oxide systems were also researched.[20,21] Generally, homogeneous eutectic microstructures can be obtained only at eutectic composition and its vicinity in one eutectic system; *i.e.* near the eutectic composition. If the eutectic microstructure having any volume ratio of each component could be obtained, a variety of different useful properties might be obtained. However, there is little research for eutectic materials having off-eutectic compositions.

When a melt of an off-eutectic composition is cooled, a rich component initially crystallizes and grows, consuming the component. This continues until the composition of the liquid phase reached the eutectic composition. Thus, the off-eutectic microstructure generally consists of both coarse primary crystals and an ordinary eutectic microstructure.[22] If a homogeneous eutectic microstructure without primary crystals could be obtained at off-eutectic compositions, unique microstructures having any volume ratio of each component is expected. We developed a fabrication method of a eutectic-like microstructure different from crystallization of the eutectic melt. In a eutectic system, the mixture of components dissolves with each other while in the liquid state yet remains immiscible in the solid state. When a particle mixture of eutectic components (Fig. 1(a))

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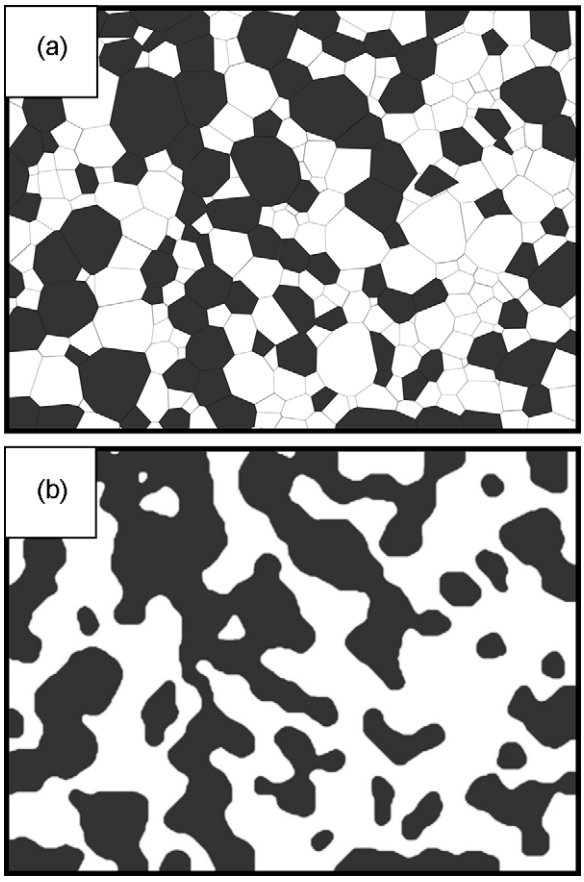

Fig. 1. Schematic image of the pseudo-eutectic formation. (a) Particle mixture of eutectic components, (b) expected microstructure after sintering of (a).

is sintered, connection of the same component results in formation of the eutectic-like microstructure as shown in Fig. 1(b). We call this microstructure "pseudo-eutectic". In order to form the fine pseudo-eutectic microstructure, following points should be considered. (1) Sufficient pulverization. (2) Homogeneous dispersion of the each component. The sufficient pulverization of the starting powder is required because a sintered microstructure grows coarser than the starting particles. If the particles of one component are localized, such particles form a large grain after sintering. Thus, homogeneous dispersion of the each component is also required. The particles of the component were pulverized and dispersed by use of ball mills. The pseudo-eutectic microstructures were fabricated by sintering this.

2. Experimental procedure

2.1. Sample preparation

Fig. 2 shows a schematic phase diagram of the Gd_2O_3–Al_2O_3 system. There are two eutectic systems. The $GdAlO_3$–Al_2O_3 eutectic system was used in this study. Thus, $GdAlO_3$ should be prepared as the starting material. Gd_2O_3 (Kanto Chemical Co., Inc., Japan, 99.95%) and Al_2O_3 (Kanto Chemical Co., Inc., Japan, 99.0%) powders were mixed in a molar ratio of 50 mol% Gd_2O_3 and 50 mol% Al_2O_3. The mixture was pressed into a rod. The rod shaped specimen was sintered at 1000 °C for 1 h.

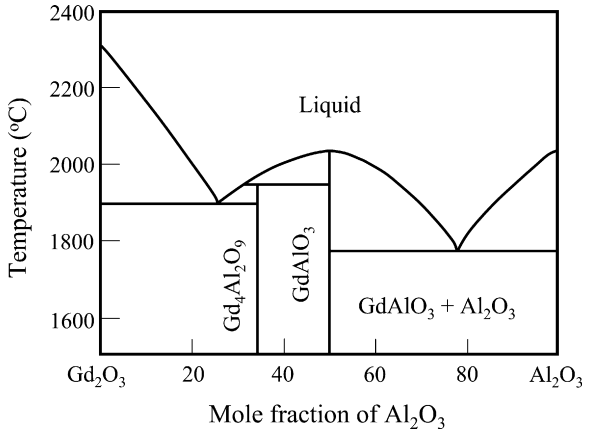

Fig. 2. Schematic phase diagram of Gd_2O_3–Al_2O_3 system.

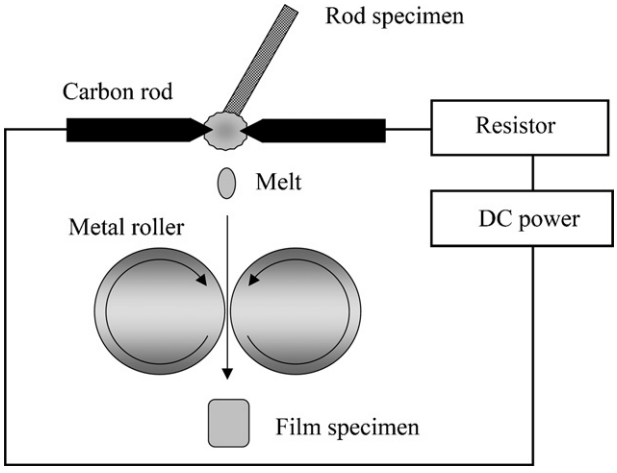

Fig. 3. Diagram of the rapid quenching apparatus.

One end of the rod shaped specimen was put into an arc flame generated by an arc discharge apparatus. When one end of the rod was melted, the melted droplet was quenched rapidly by being dropped into rotating twin metal rollers. The melt was quenched into a film shape because the film could be ground easily. The rapid quenching apparatus is shown in Fig. 3. The specimen

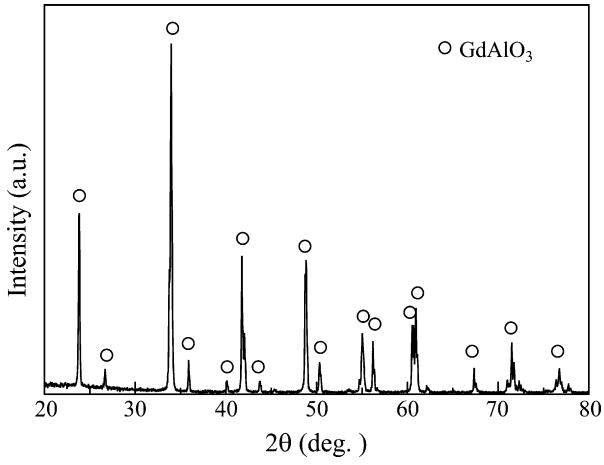

Fig. 4. XRD pattern of the quenched specimen. Gd_2O_3: 50 mol%, Al_2O_3: 50 mol%.

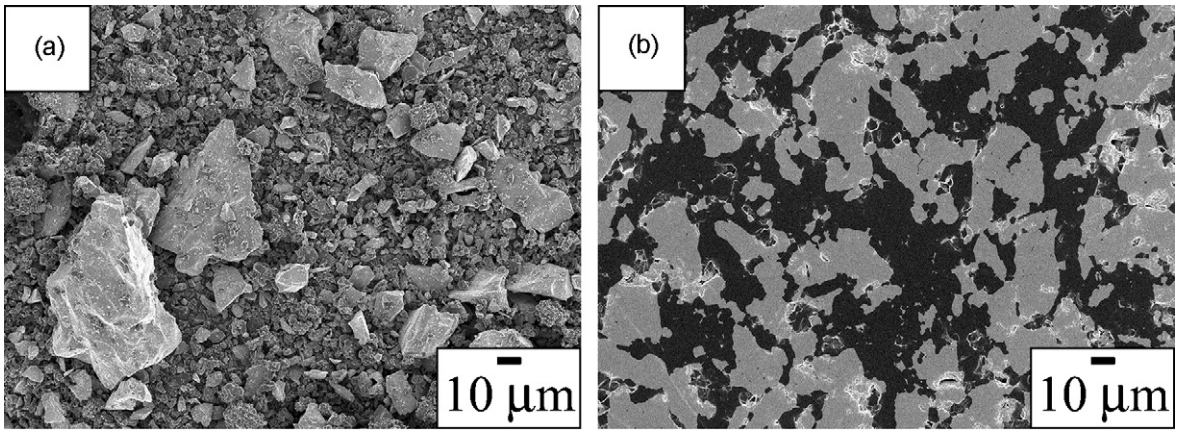

Fig. 5. SEM micrographs of (a) powder mixed using an alumina mortar and pestle for 30 min, and (b) the sintered specimen.

obtained was $GdAlO_3$ film. $GdAlO_3$ is one component of the Gd_2O_3–Al_2O_3 eutectic system as shown in Fig. 2. The $GdAlO_3$ films were ground, and sieved under 45 μm. The $GdAlO_3$ powder obtained and Al_2O_3 powder were blended in a ratio of 46 mol% $GdAlO_3$ and 54 mol% Al_2O_3. This composition corresponds to the eutectic one (Gd_2O_3/Al_2O_3 = 23/77 mol/mol).[23] The volume ratio of $GdAlO_3/Al_2O_3$ is about 51/49. The powder blended was mixed with an alumina mortar and pestle for 30 min. The powder was also milled by a planetary ball mill (Al_2O_3 pot, Ø 5 mm Al_2O_3 balls, PULVERSITTE 6, Fritsch DE, Germany) at 20.94396 rad/s (200 rpm) for 5 or 10 h, and a tumbling ball mill (polypropylene pot, Ø 2 mm Al_2O_3 balls, V-1 ML, Irie Shokai Co., Ltd., Japan) at 25.13275 rad/s (240 rpm) for one week, respectively. Each powder mixed was named as "P-mortar", "P-planetary (5 h)", "P-planetary (10 h)", or "P-tumbling", respectively, where "P" means powder. The powder was sintered by the SPS (Spark Plasma Sintering) method. The heating rate was 100 °C/min from a room temperature to 1350 °C and 33 °C/min to 1450 °C. The sintering was carried out under vacuum. During the sintering, a pressure of 29 MPa was applied

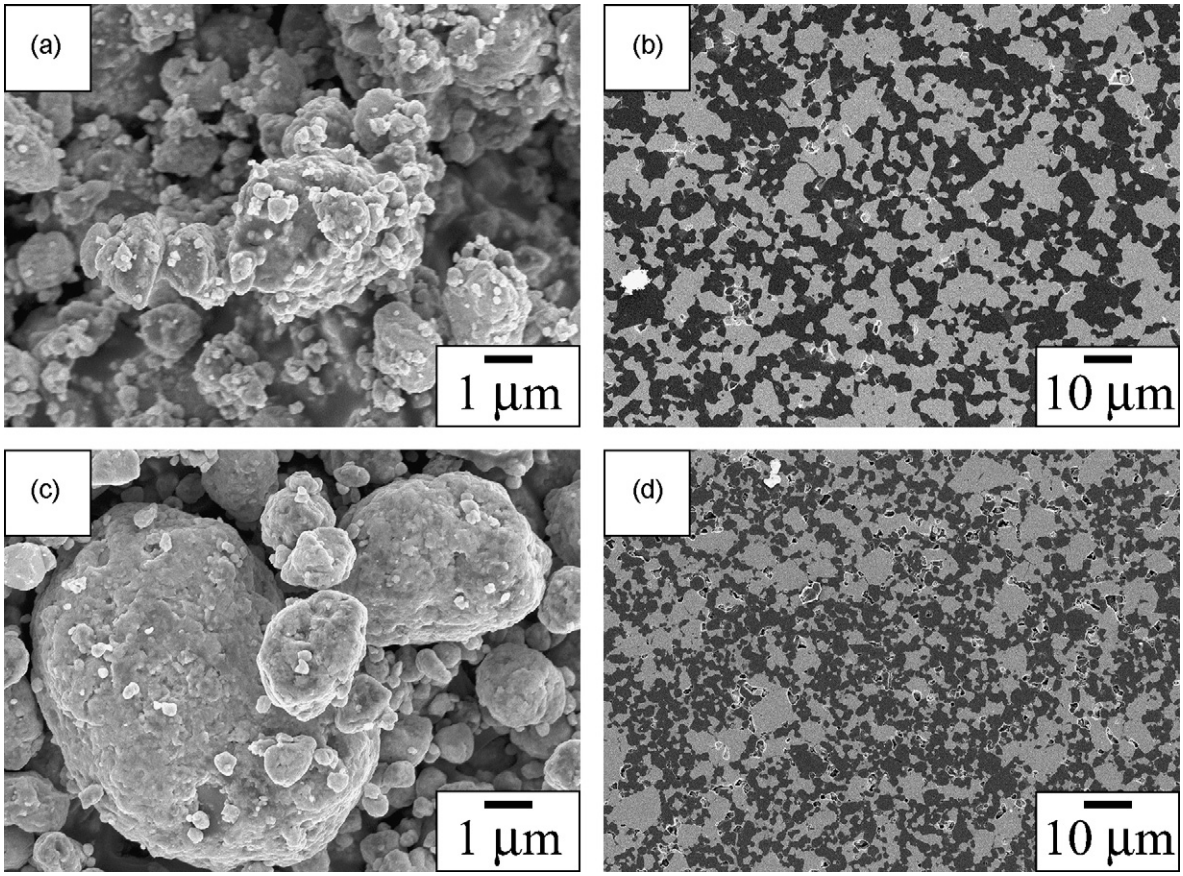

Fig. 6. SEM micrographs of (a) powder mixed using the planetary ball mill for 5 h, (b) the sintered specimen, (c) powder mixed using the planetary ball mill for 10 h, and (d) the sintered specimen.

on the specimen. At 1450 °C, the pulse current of SPS was turned off and the pressure was released. The specimens were about 15 mm in diameter and 1 mm in thickness. Each sintered specimen was named as "S-mortar", "S-planetary (5 h)", "S-planetary (10 h)", or "S-tumbling", respectively, where "S" means sintered body.

2.2. Characterization

Phases in the powder were identified by an X-ray diffractometer (XRD, Cu Kα, 40 kV, 100 mA, MXP-18, MAC Science Co., Ltd., Japan). The bulk density of the sintered specimens was measured by the Archimedes method using water. The specimens were ground with diamond disks and polished using diamond pastes (up to 1/4 μm). The pulverized powders and the sintered specimens were observed using a field emission scanning electron microscope (FE-SEM, JSM-6330F, JEOL, Inc., Japan).

3. Results and discussion

Fig. 4 shows an XRD pattern of the quenched specimen from an equimolar mixture of Gd_2O_3 and Al_2O_3. Only $GdAlO_3$ phase was observed. Single phase of $GdAlO_3$ was successfully obtained. Fig. 5(a) shows a SEM micrograph of "P-mortar", which was mixed using an alumina mortar and pestle for 30 min. Coarse particles were observed among fine particles. By the use of the mortar and pestle, sufficient pulverization of particles was not attained. Fig. 5(b) shows a SEM micrograph of "S-mortar". Relative density (ρ_r) of "S-mortar" was 97.3%. In the SEM micrograph, the blight area is $GdAlO_3$ while the dark area represents Al_2O_3. This contrast is due to the difference of the atomic numbers of gadolinium and aluminum. The microstructure was very coarse.

Fig. 6(a and c) shows SEM micrographs of "P-planetary (5 h)" and "P-planetary (10 h)", which were milled using the planetary ball mill for 5 or 10 h, respectively. The planetary ball mill can mix and pulverize the powder with high energy by both rotation and revolution of the pot containing the powder and balls.[24] The particle size of "P-planetary (5 h)" and "P-planetary (10 h)" was finer than that of "P-mortar". However, many coarse particles also existed. The particles once crushed during the milling seem to be agglomerated again by a high energy generated from the planetary ball mill. Especially, coarse agglomerated particles were observed remarkably in "P-planetary (10 h)". Fig. 6(b and d) shows SEM micrographs of "S-planetary (5 h)" ($\rho_r = 98.4\%$) and "S-planetary (10 h)" ($\rho_r = 91.0\%$). Although the eutectic-like microstructure consisting of $GdAlO_3$ and Al_2O_3 phases entangled with each other was observed, each phase was coarse due to agglomeration of the particles. The fine pseudo-eutectic microstructure could not be formed by use of the planetary ball mill.

Fig. 7(a) shows a SEM micrograph of "P-tumbling", which was milled by the tumbling ball mill for one week. The particle size of "P-tumbling" was finer than that of "P-planetary (5 h)" or "P-planetary (10 h)". Agglomerated particles were not existed. The pulverizing energies of the planetary ball mills are generally higher than that of the tumbling ball mills. On the other hand,

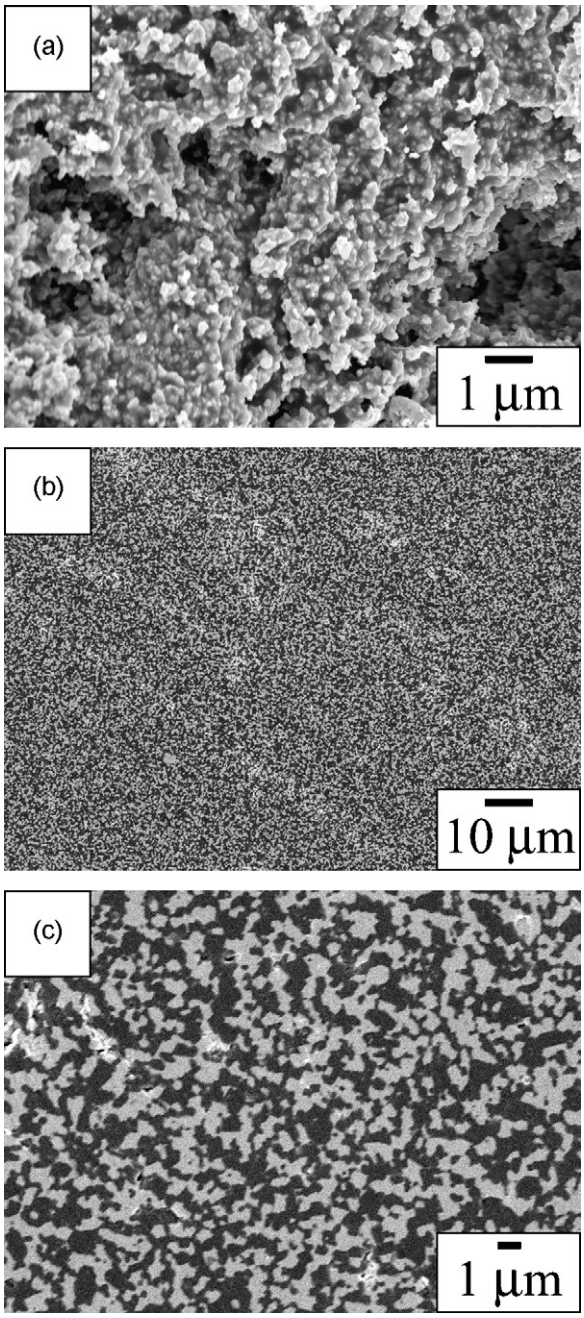

Fig. 7. SEM micrographs of (a) powder mixed using the tumbling ball mill for one week, (b and c) the sintered specimen.

the tumbling ball mill generates lower energy than the planetary ball mill. Although the tumbling ball mill needed a long time until the particles became fine, the agglomeration of particles did not occur and the particles were very fine. Fig. 7(b) shows SEM micrograph of "S-tumbling" ($\rho_r = 95.2\%$). Compared with Fig. 6(b and d) at the same magnification, the microstructure was very fine. The magnified SEM micrograph (Fig. 7(c)) showed a eutectic-like microstructure, in which binary phases entangle with each other. The fine pseudo-eutectic microstructure could be formed by use of the tumbling ball mill.

In the case of crystallization from a melt with a composition apart from a eutectic one, coarse primary crystals of

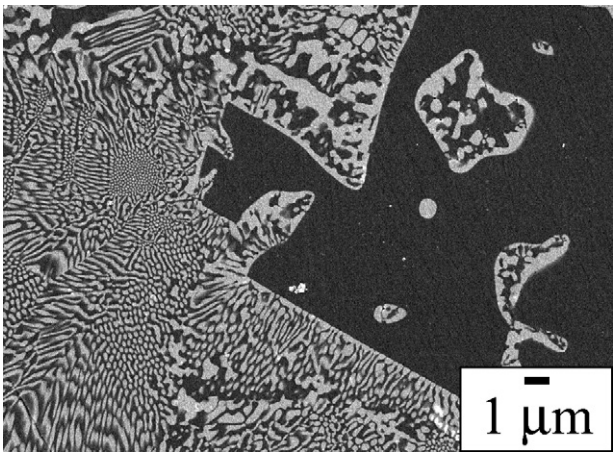

Fig. 8. SEM micrograph of the off-eutectic microstructure crystallized from the melt (Gd_2O_3/Al_2O_3 = 18.4/81.6 mol/mol).

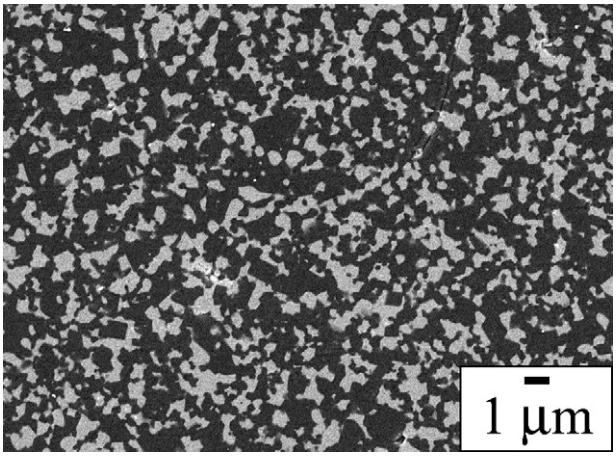

Fig. 9. SEM micrograph of the pseudo-eutectic microstructure (Gd_2O_3/Al_2O_3 = 18.4/81.6 mol/mol).

rich phase are crystallized. Fig. 8 shows a SEM micrograph of an off-eutectic microstructure crystallized from the melt (Gd_2O_3/Al_2O_3 = 18.4/81.6 mol/mol). The coarse Al_2O_3 crystal existed in a eutectic microstructure as a primary crystal. As for the pseudo-eutectic, the homogeneous microstructure can be formed at any composition because a mixing ratio of the powders can be varied. The pseudo-eutectic microstructure with off-eutectic composition was formed by the use of the tumbling ball mill for one week. Fig. 9 shows a SEM micrograph of the pseudo-eutectic microstructure (ρ_r = 96.6%) having the same composition with Fig. 8. The homogeneous pseudo-eutectic microstructure with no coarse primary crystals was observed.

4. Conclusion

This paper focused on a fundamental fabrication method of fine eutectic-like microstructures having various volume ratios. The method is not crystallization from a melt like a traditional fabrication method of the eutectic materials. Components of the Gd_2O_3–Al_2O_3 eutectic system, $GdAlO_3$ and Al_2O_3 powders, were mixed and pulverized using ball mills. By sintering the mixed powders, a eutectic-like (pseudo-eutectic) microstructure was formed. Pulverized particles by the planetary ball mill were agglomerated, and the microstructure of the sintered material was not fine. On the contrary, pulverized particles by the tumbling ball mill were very fine. The microstructure prepared from this powder was also fine and homogeneous. Generally, the homogeneous eutectic microstructure cannot be formed in case of usual crystallization from the melt with the off-eutectic composition: the usual off-eutectic microstructure has coarse crystals of the rich component as primary crystals embedded in the ordinary eutectic microstructure. The homogeneous pseudo-eutectic microstructure with the off-eutectic composition could be formed in this research. By this method, fabrication of materials having the homogeneous eutectic-like microstructure, which can have any volume ratio of each component, became possible. This fabrication method could be applied to various eutectic applications covering wide fields. Variable volume ratio of phases in the structure would realize enhanced thermo mechanical properties, diversified mechanical properties, optimized TPV properties, porous materials having controlled pore volume, *etc*. These examinations are future works.

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