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Technical note

Fabrication of dense material having homogeneous $GdAlO_3$–Al_2O_3 eutectic-like microstructure with off-eutectic composition by consolidation of the amorphous

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Abstract

Off-eutectic microstructures generally have both coarse crystals of rich component and ordinary eutectic microstructures. This paper shows a new method to form a dense bulk material having homogeneous eutectic-like microstructure with off-eutectic compositions. Mixture of Gd_2O_3 and Al_2O_3 powders with the off-eutectic composition was melted and quenched rapidly to form the amorphous phase. The amorphous film was pulverized. The dense bulk material could be fabricated by the consolidation of the amorphous powder using spark plasma sintering method. Field emission scanning electron microscope (FE-SEM) observation of the material showed homogeneous fine eutectic-like microstructure without coarse crystals. This is the first case that such material was successfully prepared.

Keywords: Sintering; Al_2O_3; Consolidation

1. Introduction

Several eutectic ceramics have been attracting a great deal of attention, because of superior properties such as flexural strength and creep resistance.[1–3] The eutectic ceramics are generally produced by cooling a melt with a eutectic composition.[4–6] Various formation processes of the eutectic microstructure from the melt have been studied.[7,8] When the melt with the eutectic composition is cooled, to the eutectic temperature, the repeating cycle of the simultaneous crystallization and growth of each component occurs throughout the melt. Such eutectic ceramics, which are formed through the simultaneous growth in a coupled process, have a characteristic microstructure consisting of fine single crystals entangled with each other. The interfaces formed between the crystals are relatively compatible and an amorphous phase does not exist at the interfaces.[1] Thus, the mechanical properties such as a flexural strength at room temperature are also preserved at high temperature.[9–17] The eutectic ceramics have been a promising candidate for heat-resistible materials.[18] Recently, the eutectic ceramics are considered to be a candidate not only for the heat-resistible materials but also for other various functional applications, such as thermophotovoltaic (TPV) generation systems and porous materials.[19,20] The various properties of the eutectic ceramics may depend on the eutectic microstructure size.[21,22] If these materials have an ultra fine eutectic microstructure, superior properties such as higher strength and superplasticity are expected.

Generally, homogeneous eutectic microstructure can be obtained only at restricted composition in the vicinity of the eutectic composition. The off-eutectic microstructure generally consists of both coarse crystals of the rich component and an ordinary eutectic microstructure.[23] In a binary eutectic system (for example: component X and component Y), a formation process of off-eutectic microstructure has been considered as follows. When the rich component (for example: X) in the liquid phase crystallizes first and grows as primary crystals, the crystal X consumes the component X from the liquid phase. Because of the high diffusion rate and convection of liquid, component to be consumed can be supplied from far place in liquid phase. Accordingly, the growth of crystal X continues until the composition of the liquid phase becomes equal to the eutectic composition. Thus, the crystal X is generally very coarse. Once the composition of the liquid phase reaches the eutectic composition, the normal formation of eutectic microstructure

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occurs. Because of this formation process, the bulk material of the off-eutectic composition having homogeneous eutectic microstructure could have not been fabricated.

If the component to be consumed were not supplied from far place in liquid phase, the crystals of the rich component would not grow to form the coarse primary crystals. Furthermore, the eutectic-like microstructure may be much finer according to the previous studies.[24,25] The specimens obtained previously in the off-eutectic composition were film shape. For practical use, the film shaped specimen should be consolidated into bulk shape. A bulk material of $GdAlO_3/Al_2O_3$ composite with off-eutectic composition was fabricated previously using $GdAlO_3$ and Al_2O_3 powders pulverized as a pseudo-eutectic material.[26] However, the eutectic-like microstructure formed from the amorphous film with the off-eutectic composition[25] was much finer as compared with the pseudo-eutectic microstructure. Therefore, we attempted to form a bulk material having fine and homogeneous eutectic-like microstructure without primary crystals also in the off-eutectic composition by consolidation of the amorphous powder, in which the diffusion rate is very low. Such a material may have a variety of useful properties, because the material has various volume ratios of each component in the various compositions. In the absence of the restriction of ordinary eutectic composition, the materials could be designed freely with the unique eutectic-like microstructure, which consists of the fine crystals entangled with each other. If such a unique material could be obtained, the applications for superior functional materials are possible. For example, the mechanical properties of composites would be improved because the materials could have the best volume ratio of each component. The improvement of the emission properties in emitters of TPV generation systems and the control of the pore volume in porous materials formed by removing one phase in the microstructure would be also possible.

2. Experimental procedure

2.1. Sample preparation

Raw materials were Gd_2O_3 (Kanto Chemical Co., Inc., Japan, 99.95%) and Al_2O_3 (Kanto Chemical Co., Inc., Japan, 99.0%) powders. Eutectic composition of $GdAlO_3$–Al_2O_3 system is 23 mol% of Gd_2O_3 and 77 mol% of Al_2O_3. The powders were mixed using an alumina mortar and pestle at an off-eutectic composition (18.4 mol% of Gd_2O_3 and 81.6 mol% of Al_2O_3). The mixed powder (about 3 g in weight) was pressed into a rod. The rod shaped specimen (3 mm × 7 mm × 70 mm) was sintered at 1000 °C for 1 h. One end of the rod shaped specimen was put into an arc flame generated by an arc discharge apparatus.[24] When one end of the rod was melted, a melting droplet was rapid quenched by being dropped into rotating twin stainless rollers. The material obtained was an amorphous film, about 65 μm in thickness. The film was ground, and sieved under 45 μm in particle size. The powder (about 1 g in weight) was sintered by spark plasma sintering (SPS) method (SPS-511S, SPS SYNTEX, Inc., Japan) in a graphite mold (about 15 mm inner diameter).[27] The sintering was carried out under vacuum. The heating rate was 200 °C/min from room temperature to 600 °C, 100 °C/min to 1300 °C and 33 °C/min to 1400 °C. During the sintering, a pressure of 29 MPa was loaded on the specimen. At 1400 °C, the pulse current of SPS was turned off and the pressure was released.

2.2. Characterization

Phases in the specimen were identified by an X-ray diffractometer (XRD, MXP-18, MAC Science Co., Ltd., Japan) with Cu Kα radiation. The accelerating voltage was 40 kV with a filament current of 100 mA. The measurement was performed with angle range from 20° to 80° (2θ), sampling step of 0.02°, and scan speed of $4° \min^{-1}$. The bulk density of the sintered body was measured by the Archimedes method using water. Slow cooled specimen was embedded in an epoxy resin. The embedded specimen and sintered specimen were ground with waterproof abrasive paper sheets (up to #1500) and polished using diamond pastes (up to 1/4 μm). The polished surface of the specimen was coated with a thin layer of Os. The microstructures of specimens were observed by FE-SEM (JSM-6330F, JEOL, Inc., Japan). The accelerating voltage was 5 kV with an emission current of 12 μA.

3. Results and discussion

Fig. 1 shows an XRD pattern of the rapid quenched specimen. In XRD measurement, the rapid quenched specimen was found to be amorphous. This means that an amorphous phase can be successfully fabricated by rapid quenching of the melt with off-eutectic composition (Gd_2O_3/Al_2O_3 = 18.4/81.6 mol/mol).

Fig. 2 shows a bulk material, which was fabricated by the consolidation of the amorphous powder of the off-eutectic composition using SPS technique at 1400 °C with no holding time. The specimen was about 15 mm in diameter and 1 mm in thickness. The relative density of the sintered specimen, whose theoretical density is 5.42 g/cm^3, was 98.7%. The dense bulk material of off-eutectic composition was obtained.

Fig. 3 shows XRD pattern of the bulk material. The XRD pattern of the specimen sintered at 1400 °C showed only $GdAlO_3$ phase with an orthorhombic crystal system (a = 5.25, b = 5.30, c = 7.45) and Al_2O_3 phase with a hexagonal crystal

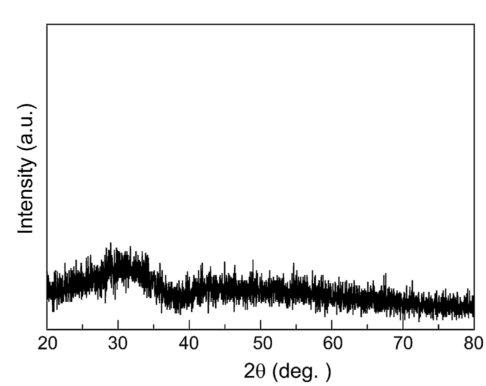

Fig. 1. XRD pattern of the rapid quenched specimen.

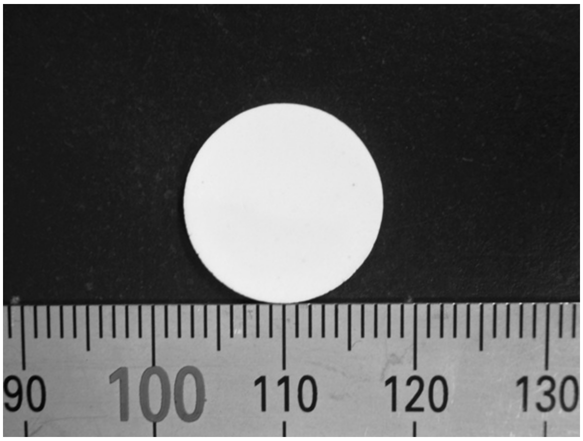

Fig. 2. The shape of the bulk material consolidated by the sintering of the amorphous powder using SPS method.

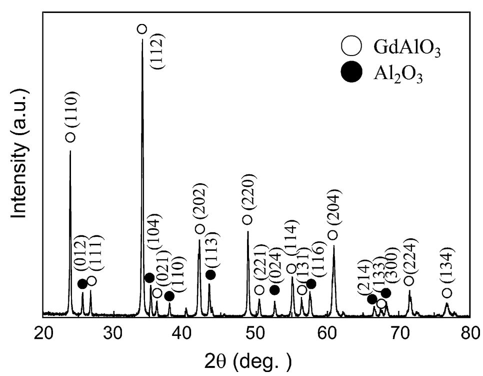

Fig. 3. XRD pattern of the bulk material consolidated by the sintering of the amorphous powder using SPS method. ○: $GdAlO_3$, ●: Al_2O_3.

system ($a = 4.76$, $c = 12.99$). This means that the binary eutectic components ($GdAlO_3$ and Al_2O_3) were crystallized from the amorphous phase during SPS process. In the XRD pattern, the diffraction peaks of Al_2O_3 are weak. This is because the scattering factor of aluminum is much lower than that of gadolinium.

A typical off-eutectic microstructure formed from the melt of the off-eutectic composition has coarse crystals of the rich component surrounded with the ordinary eutectic microstructure.[23,25] Fig. 4 shows a SEM image of the bulk material obtained in this study. In the SEM micrograph, the bright 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 aluminium. The SEM micrograph showed ultra fine and homogeneous $GdAlO_3/Al_2O_3$ eutectic-like microstructure, in which both crystals entangled with each other. The coarse Al_2O_3 crystals, which were observed in the usual off-eutectic microstructures with Al_2O_3 rich composition, did not exist.

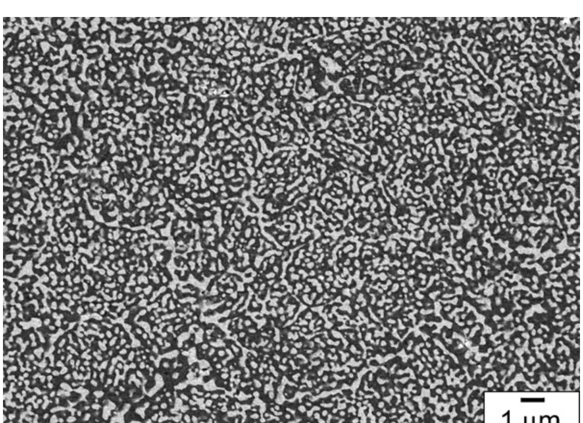

Fig. 4. SEM image of the bulk material consolidated by the sintering of the amorphous powder using SPS method.

4. Conclusion

By the consolidation of the amorphous powder using SPS technique, the dense bulk material having ultra fine eutectic-like microstructure without coarse primary crystals could be obtained regardless of off-eutectic composition. This is the first case that such material was successfully prepared. In this method, the fine homogeneous eutectic-like microstructures having various volume ratios of each component are possible at various compositions. In the absence of the restriction of ordinary eutectic composition, the materials could be designed freely with the unique eutectic-like microstructure, which consists of the fine crystals entangled with each other. The unique materials having such a characteristic microstructure, which have been normally impossible to be formed, can be promising candidate in wide fields, such as the heat-resistible materials, TPV generation systems and porous materials. For example, the mechanical properties of composites would be improved because the materials could have the best volume ratio of each component. The improvement of the emission properties in emitters of TPV generation systems and the control of the pore volume in porous materials formed by removing one phase in the microstructure would be also possible.

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