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Formation of $Y_3Al_5O_{12}$–Al_2O_3 eutectic microstructure with off-eutectic composition

Yohei Harada, Naofumi Uekawa, Takashi Kojima, Kazuyuki Kakegawa *

Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

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Abstract

Homogeneous-eutectic microstructure of $Y_3Al_5O_{12}$–Al_2O_3 system without coarse primary crystals was formed at an off-eutectic composition. This method utilizes a low migration rate in an amorphous phase. A mixture of Y_2O_3 and Al_2O_3 having the off-eutectic composition was melted and quenched rapidly to form an amorphous phase. A heat-treatment of the amorphous phase at 1000 °C and 1300 °C for 30 min formed $Y_3Al_5O_{12}$ and Al_2O_3 phases. SEM observation of this material, which was formed from the amorphous phase at 1300 °C for 30 min, showed homogeneous eutectic-like microstructure. The formation of the primary crystals (coarse Al_2O_3), which are always observed in the off-eutectic compositions by ordinary method, was completely suppressed.

Keywords: Al_2O_3; $Y_3Al_5O_{12}$; Eutectic microstructures; Crystallization

1. Introduction

From the point of view of global environmental protection, a development of high-efficient gas turbines for a power generation, a jet engine, etc., is required. For that purpose, turbine blades used at higher temperatures are necessary to improve a thermal efficiency. They are needed both of high strength and creep resistance at elevated temperatures.

Several eutectic ceramics are widely noticeable materials, because they have many superior properties such as flexural strength and creep resistance.[1–3] These room temperature properties are also preserved at high temperature.[4–12] Eutectic ceramics are a promising candidate for structural applications such as a turbine blade.

Recently, the fabrication of eutectic ceramics has been well researched. Eutectic ceramics are generally produced by cooling a liquid phase (melt) with a eutectic composition.[13–15] In a eutectic system, the mixture of eutectic components dissolves with each other while in the liquid state yet remains immiscible in the solid state. Various formation processes of the eutectic microstructure have been considered.[16,17] When the melt with the eutectic composition is cooled, each component crystallizes and grows simultaneously under the eutectic point. Such eutectic ceramics, which are formed through the simultaneous growth in a coupled process, have a characteristic microstructure consisting of fine crystals entangled with each other. The various properties of the eutectic ceramics may depend on the eutectic microstructure size.[18,19] If these materials have an ultrafine eutectic microstructure, superior properties such as higher strength and superplasticity are expected. Based on an idea that the suppression of convection in a parent phase of eutectic materials would result in much finer microstructure, $GdAlO_3/Al_2O_3$ and $Y_3Al_5O_{12}/Al_2O_3$ eutectic ceramics were prepared from an amorphous phase.[20,21] The microstructure obtained was much finer than that of materials generally prepared from a melt. We assumed that the mechanism of the crystallization from amorphous phase is almost the same as that from melt of traditional eutectic. In our previous research, we confirmed that the microstructure formed from an amorphous was similar to that formed from a melt. Glass formation and devitrification in Al_2O_3–rare earth oxide system were also researched.[22,23] However, there is little research for eutectic materials having an off-eutectic composition.

Generally, homogeneous-eutectic microstructure can only be obtained at restricted composition in one eutectic system. When a melt of off-eutectic composition is cooled, rich component

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* Corresponding author. Tel.: +81 43 290 3371.
E-mail address: kake@faculty.chiba-u.jp (K. Kakegawa).

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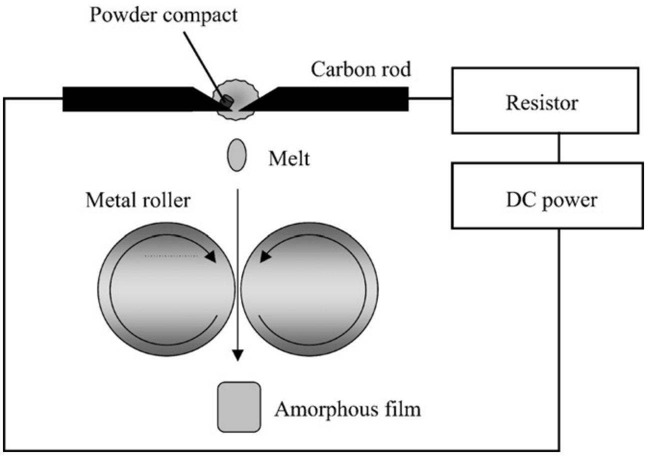

Fig. 1. Diagram of the rapid-quenching apparatus.

crystallizes and grows. The off-eutectic microstructure generally consists of both coarse primary crystals and an ordinary eutectic microstructure.[24] If a eutectic microstructure without primary crystals could be obtained at off-eutectic composition, a variety of different useful properties might be obtained. Furthermore, the fine homogeneous-eutectic microstructure having various volume ratios of each component may be possible at various compositions.

In this study, homogeneous-eutectic microstructure without coarse primary crystals was formed from an amorphous phase at an off-eutectic composition in $Y_3Al_5O_{12}$–Al_2O_3 system (eutectic composition[25]: $Y_2O_3/Al_2O_3 = 18.4/81.6$ mol%).

2. Experimental procedure

2.1. Sample preparation

Al_2O_3 (Kanto Chemical Co. Inc., Japan, 99.0%) and Y_2O_3 (Wako Pure Chemical Industries Ltd., Japan, 99.9%) powders were mixed at an off-eutectic (Al_2O_3 rich) composition (85.3 mol% of Al_2O_3 and 14.7 mol% of Y_2O_3). The mixture was kneaded with poly vinyl alcohol solution (10 wt%). This was ejected from a small hole and dried to form a small powder compact. The compact was put into an arc flame generated by an arc discharge apparatus. When the piece was melted, the discharge was turned off and cooled slowly. This corresponds to the conventional fabrication method of the off-eutectic microstructure by crystallization from melt. Alternatively, the melt was quenched rapidly by dropping it into rotating twin metal rollers. The material obtained was an amorphous film. The rapid-quenching apparatus is shown in Fig. 1. The amorphous films were then heated at 700 °C, 1000 °C and 1300 °C for 30 min to form an off-eutectic microstructure. This corresponds to the new fabrication method using crystallization from amorphous phase.

2.2. Characterization

Phases in the specimens were identified by an X-ray diffractometer (XRD, Cu Kα, 40 kV, 100 mA, MXP-18, MAC Science Co. Ltd., Japan). Slow-cooled specimen and film shaped specimens were embedded in an epoxy resin. The embedded specimens were polished using a diamond paste. The microstructures of specimens were observed by a field emission scanning electron microscopy (FE-SEM, JSM-6330F, JEOL Inc., Japan).

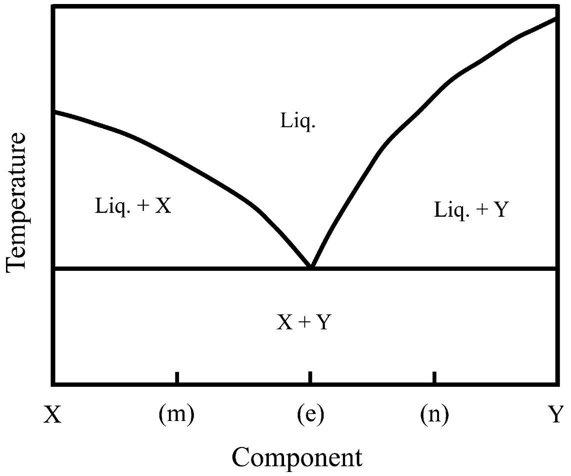

Fig. 2. Schematic phase diagram of typical binary eutectic system, indicating (m) off-eutectic composition (X rich), (e) eutectic composition and (n) off-eutectic composition (Y rich).

3. Results and discussion

Fig. 2 shows a schematic phase diagram of the typical binary eutectic system, where (e) indicates eutectic composition and (m) and (n) indicate off-eutectic compositions. Fig. 3 is an illustration to show our image of expected microstructures schematically. Fig. 3 (L) shows an image of expected microstructures (upper figure) and the volume ratio (lower figure) of crystals formed from the liquid phase (ordinary method). A uniform eutectic microstructure covering the entirety of the material can normally be formed only at the eutectic composition (L_e in Fig. 3 (L)). In this composition, when the component X in the liquid phase crystallizes and grows, the crystal of X consumes the component X from the liquid phase. Thus, during the crystallization of X, the concentration of component Y around the crystal increases. When the concentration of Y around the crystal X runs up to a certain value, a nucleation of component Y occurs on the crystal X. This causes a switching of the crystallization process. The same phenomenon occurs during the crystallization of Y. This repeating cycle occurs at both of X phase and Y phase throughout the melt. The simultaneous crystallization and growth of components X and Y are what forms the characteristic eutectic microstructure (E_X and E_Y), in which binary crystals entangle with each other. The increasing concentration of one component in the liquid phase around the growing crystal tends to be diluted by convection and high diffusion rates through the liquid phase, resulting in slow compositional switching. Even in such a situation, the eutectic microstructure formed from the liquid phase is still quite fine.

In the case of an off-eutectic composition (L_m, L_n in Fig. 3 (L)), coarse crystals of the rich component generally exist as primary crystals (P_X, P_Y) embedded in an ordinary eutec-

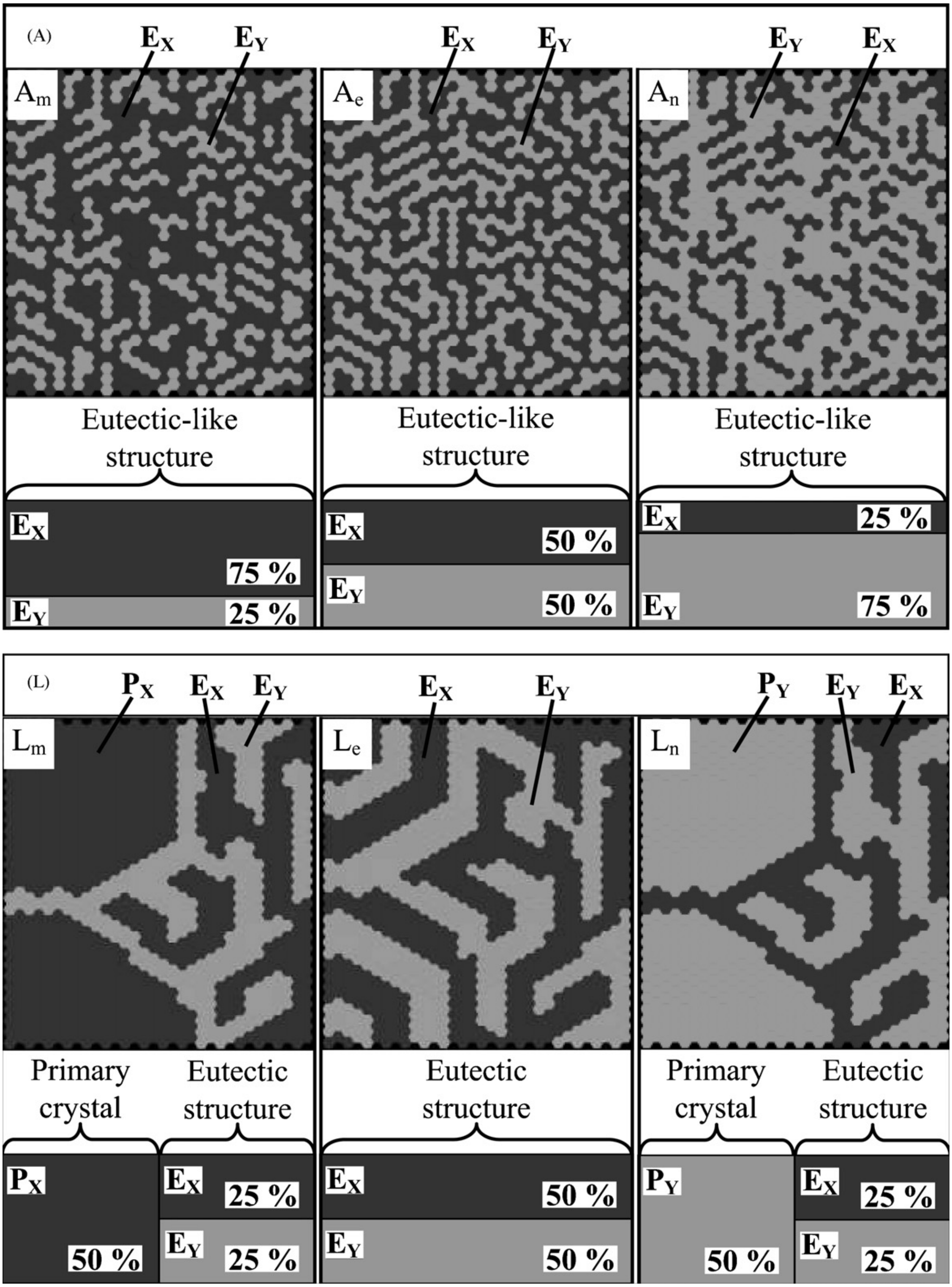

Fig. 3. Schematic image of expected microstructures and volume ratio of crystals. (L) Ordinary method: from liquid phase. Coarse primary crystals are expected for L_m and L_n. (A) New method: from amorphous phase. Homogeneous eutectic-like microstructure without primary crystals is expected for all compositions. Subscripts m, n and e: composition indicated in Fig. 2. P_X: primary crystal of X; P_Y: primary crystal of Y; E_X: crystal of X as a part of eutectic; E_Y: crystal of Y as a part of eutectic.

tic microstructure.[24] We now consider a case of L_m. When the rich component (X) in the liquid phase crystallizes first and grows, the crystal X consumes the component X from the liquid phase. Thus, during the crystallization of X, the concentration of component Y around the crystal increases. However, the concentration of component Y around the crystal is diluted by convection and high diffusion rates through the liquid phase. Accordingly, the growth of crystal X contin-

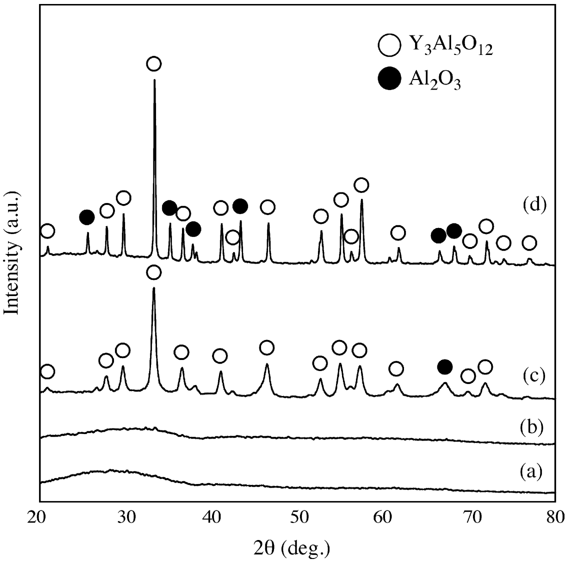

Fig. 4. XRD patterns of (a) a specimen fabricated by rapid quenching a liquid phase with an off-eutectic composition, and specimens heat-treated at (b) 700 °C, (c) 1000 °C and (d) 1300 °C.

ues until the composition of the liquid phase becomes equal to the eutectic composition. Thus, the primary crystal X is generally very coarse. Once the composition of the liquid phase reaches the eutectic composition, the normal formation of eutectic microstructure mentioned above follows. Consequently, the off-eutectic microstructure generally consists of coarse primary crystals (P_X) and an ordinary eutectic microstructure (E_X and E_Y). The same phenomenon also occurs in the Y-rich composition (L_n), forming a microstructure that consists of primary crystals (P_Y) and the ordinary eutectic microstructure.

If the dilution of the increasing component around the growing crystal does not occur, the coarse crystals of the rich component may not form even for off-eutectic compositions. Therefore, we studied the formation of eutectic microstructures from a solid-state amorphous phase, in which the diffusion rate is very low. When the rich component crystallizes in the amorphous phase, the increasing concentration around the crystal is not diluted due to sluggish diffusion through the solid phase. Thus, the nucleation of the opposite component is expected to occur immediately before the rich phase grows as primary crystals. As a result, a uniform microstructure is expected even for off-eutectic compositions. Fig. 3(A) shows an image of expected microstructures (upper figure) and the volume ratio (lower figure) of crystals formed from the amorphous phase for the eutectic composition (A_e) and the off-eutectic compositions (A_m and A_n). In the any composition, a uniform microstructure without coarse primary crystals may be formed by such a formation method. Furthermore, because of the short switching interval of the crystallization, the microstructure may be much finer like $GdAlO_3/Al_2O_3$ and $Y_3Al_5O_{12}/Al_2O_3$ microstructure at a eutectic composition.[20,21]

By XRD measurement, the slow-cooled specimen formed from a liquid phase with an off-eutectic composition was found to have only $Y_3Al_5O_{12}$ and Al_2O_3 phases, which are the end members of this eutectic system. Fig. 4 shows XRD patterns of a rapid-quenched specimen and heat-treated specimens. The rapid-quenched specimen was found to be amorphous as shown in Fig. 4(a). This means that an amorphous film can be successfully fabricated by rapid quenching a liquid phase with an off-eutectic composition. The specimen heat-treated at 700 °C was nearly amorphous (Fig. 4(b)). The XRD patterns of the specimens heat-treated at 1000 °C (Fig. 4(c)) and 1300 °C (Fig. 4(d)) showed $Y_3Al_5O_{12}$ and Al_2O_3 phases. As the heating temperature was increased, the crystal phases of binary eutectic components ($Y_3Al_5O_{12}$ and Al_2O_3) increased.

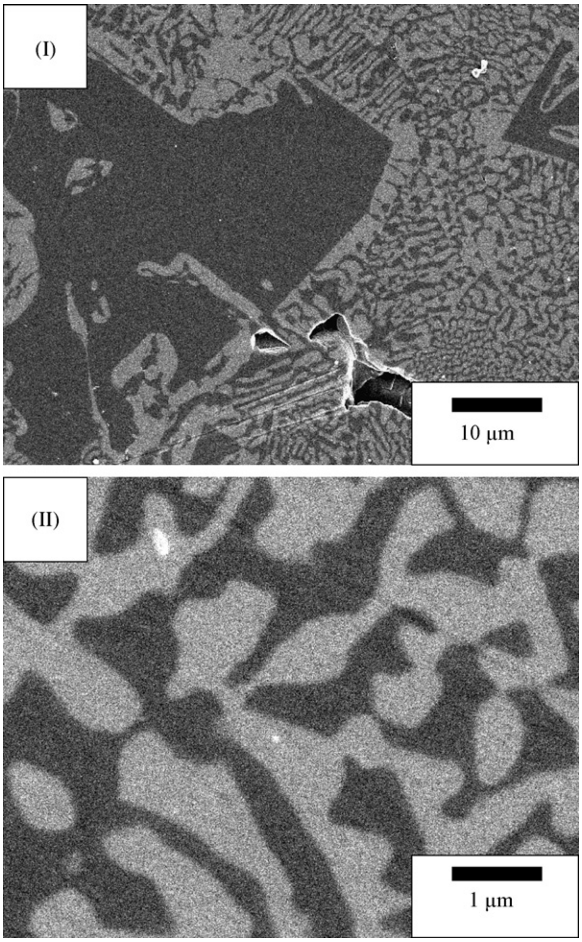

Fig. 5. SEM image of the microstructures formed from a liquid phase by slow cooling. (I) Low magnification and (II) high magnification of eutectic microstructure area. Coarse primary crystals are observed in (I).

Fig. 5(I) shows a SEM image of the microstructure formed from the liquid phase by slow cooling. The typical off-eutectic microstructure in $Y_3Al_5O_{12}/Al_2O_3$ system was observed. In the SEM micrograph, the bright area is $Y_3Al_5O_{12}$, while the dark area represents Al_2O_3. This contrast is due to the difference of the atomic numbers of aluminum and yttrium. The SEM micrograph showed that coarse primary Al_2O_3 crystals with faceted interfaces were dispersed in a typical binary eutectic microstructure. In the area of the eutectic microstructure, $Y_3Al_5O_{12}$ and Al_2O_3 crystals entangled with each other (Fig. 5(II)).

Fig. 6(I) shows a SEM image of the microstructure formed from an amorphous film by a heat-treatment at 1300 °C for 30 min. In the same magnification of Fig. 5(I), the coarse

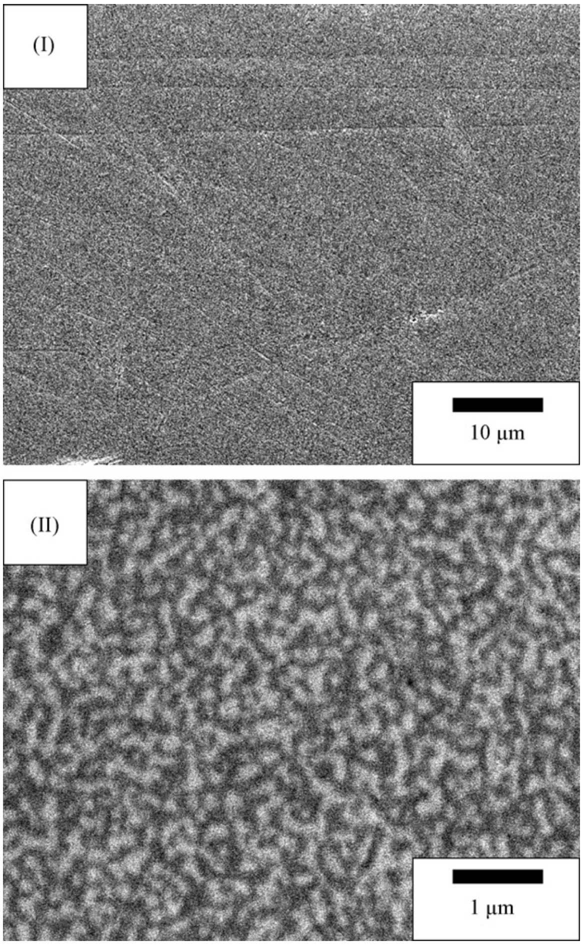

Fig. 6. SEM image of the microstructures formed from an amorphous film by heat-treatment at 1300 °C for 30 min. (I) Low magnification and (II) high magnification. Homogeneous eutectic-like microstructure without primary crystals was obtained.

primary Al_2O_3 crystals were not observed. The magnified SEM micrograph (Fig. 6(II)) shows only an $Y_3Al_5O_{12}/Al_2O_3$ eutectic-like microstructure, which $Y_3Al_5O_{12}$ and Al_2O_3 crystals entangled with each other. Furthermore, it is noteworthy that the heat-treated specimen at 1300 °C had a much finer microstructure than that of the slow-cooled specimen. Despite the off-eutectic composition, the fine $Y_3Al_5O_{12}/Al_2O_3$ eutectic-like microstructure without coarse primary crystals can be formed by the crystallization from the amorphous phase. The specimen obtained in this research was about only 65 µm in thickness. For practical use, the film shaped specimen should be consolidated into a bulk shape. We have obtained bulk specimens having fine eutectic-like microstructure from amorphous films using SPS technique.[20,21] A consolidation of the off-eutectic material developed in this study will also be possible. It will be a future work.

4. Conclusion

By crystallizing the liquid phase, uniform eutectic microstructure can be obtained only at restricted composition in one eutectic system. In the off-eutectic composition, the eutectic microstructure is generally formed around coarse primary crystals of the rich component. By traditional fabrication eutectic microstructure having various volume ratios of the components is difficult.

By using an alternate approach the formation of coarse primary crystals was suppressed by the crystallization from the amorphous phase. Despite the off-eutectic composition, a fine eutectic-like microstructure without coarse primary crystals could be formed. In this research, the fine homogeneous eutectic-like microstructure having various volume ratios of each component may be possible at various compositions. This fabrication method can be applied to any eutectic system. Eutectic ceramics are a promising candidate for superior heat-resistant materials. These off-eutectic materials have a possibility to exhibit superior properties to traditional eutectic or polycrystalline materials, depending on the interfaces.

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