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Fabrication of $Y_3Al_5O_{12}$-Al_2O_3 eutectic materials having ultra fine microstructure

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Abstract

A mixture of Y_2O_3 and Al_2O_3 with a eutectic composition was melted and quenched rapidly to form an amorphous phase. A eutectic microstructure, which was formed from the amorphous phase, was investigated. A heat-treatment of the amorphous phase at 1000 °C and 1300 °C for 30 min formed an $Y_3Al_5O_{12}$ (YAG: Yttrium Aluminium Garnet)-Al_2O_3 eutectic microstructure. The eutectic microstructure, which was formed from the amorphous phase at 1300 °C for 30 min, was ultra fine. The amorphous film was pulverized and sintered both by conventional sintering and Spark Plasma Sintering (SPS). Following conventional sintering the eutectic microstructures of the conventionally sintered specimens became coarse. By using the conventional sintering method, a high sintering temperature (1600 °C) and long sintering time (24 h) was required to form dense specimens. This resulted in grain growth. On the contrary, the SPS sintered body had an ultra fine eutectic microstructure with a high bulk density. SPS was successful in suppressing grain growth.

Keywords: Grain growth; Sintering; Al_2O_3; $Y_3Al_5O_{12}$

1. Introduction

Several eutectic ceramics have been attracting a great deal of attention because of many superior properties such as flexural strength and creep resistance.[1,2] These room temperature properties are also preserved at high temperature.[3–10] Eutectic ceramics are a promising candidate for structural applications such as a turbine blades used at elevated temperatures.[11,12]

Recently, fabrication methods of the eutectic ceramics have been well researched. Eutectic ceramics are generally fabricated by cooling a melt with a eutectic composition.[1,3,13–15] In a eutectic system, the mixture of eutectic components dissolves in each other while in the liquid state and does not dissolve with each other in the solid state. When the melt with the eutectic composition is cooled from a liquid phase, each component crystallizes individually at the eutectic point. Such eutectic ceramics have characteristic microstructures consisting of fine crystals entangled with each other. The various properties of the eutectic ceramics may depend on the eutectic microstructure size.[16,17] If these materials have an ultra fine eutectic microstructure, superior properties such as higher strength and super plasticity are expected. However, there is little research focused on making much finer eutectic microstructures.

When a melt of eutectic system is cooled, precipitation of each component occurs due to the change in composition of the melt near the precipitating crystal by consuming its neighboring liquid component. This results in the characteristic eutectic microstructure. Such a change in the composition near the precipitating crystal tends to be diluted by convection in liquid phase (melt). In this study an amorphous substance was used instead of a melt. By this method convection was suppressed and an ultra fine eutectic microstructure was obtained.

2. Experimental procedures

2.1. Specimen preparation

Raw materials were Al_2O_3 (Kanto Chemical Co., Inc., Japan, 99.0%) and Y_2O_3 (Wako Pure Chemical Industries, Ltd., Japan, 99.9%) powders. The powders were mixed using an alumina mortar and pestle at a eutectic composition (81.6 mol% of Al_2O_3 and 18.4 mol% of Y_2O_3).[18] The mixed powder was pressed into

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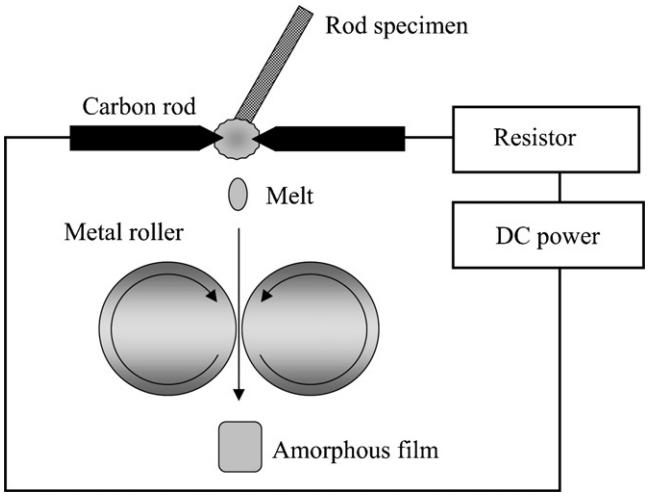

Fig. 1. Diagram of the rapid quenching apparatus.

a rod. The rod shaped specimen 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. When one end of the rod was melted, the arc discharge was turned off and cooled slowly. This corresponds to the conventional fabrication method of the eutectic microstructure by crystallization from a melt. On the other hand, a melting droplet was rapid quenched by being dropped into rotating twin metal rollers. The materials obtained were amorphous films. The rapid quenching apparatus is shown in Fig. 1. The rapid quenched films were heated at various temperatures for 30 min in order to form a eutectic microstructure. This corresponds to the new fabrication method of the eutectic microstructure. Samples were abbreviated as SC or RQ-xxxx, where SC indicates "Slow Cooled specimen", RQ indicates "Rapid Quenched specimen", and xxxx indicates heating temperature. The abbreviations are listed in Table 1. The amorphous film was ground, and sieved. The powder with particle size of <45 μm was pressed into a disc. It was sintered by the conventional sintering method in atmosphere at 1550 °C, 1580 °C and 1600 °C for 24 h at a heating rate of 10 °C/min. The specimens were about 16 mm in diameter and 1 mm in thickness. The powder was also sintered by the Spark Plasma Sintering (SPS) method.[19] The heating rate was 100 °C/min from room temperature to $T_m - 100$ °C and 33 °C/min to T_m, where T_m is a maximum temperature. The sintering was carried out under vacuum. During the sintering, a pressure of 29 MPa was loaded on the specimen. At T_m, 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. The abbreviations of the sintered specimens are listed in Table 2, where C and S mean "Conventional sintering" and "SPS", respectively.

Table 1
Abbreviations of slow cooled specimen and its heat-treated specimens

Specimen name	Slow cooling	Rapid quenching and heat treatment Heating temperature (°C)
SC	O	–
RQ-0	–	0
RQ-700	–	700
RQ-1000	–	1000
RQ-1300	–	1300

Table 2
Abbreviations of sintered specimens

Specimen name	Conventional sintering		SPS	
	Temperature (°C)	Time (h)	Temperature (°C)	Time (min)
C-1550	1550	24	–	–
C-1580	1580	24	–	–
C-1600	1600	24	–	–
S-1200	–	–	1200	0
S-1300	–	–	1300	0
S-1400	–	–	1400	0

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). The bulk density of the sintered bodies was measured by the Archimedes method using water. Slow cooled specimen (SC) and film shaped specimens (RQ series) were embedded in an epoxy resin. The embedded specimens and sintered specimens (C and S series) were polished using a diamond paste. The microstructures of those specimens were observed by a field emission scanning electron microscopy (FE-SEM, JSM-6330F, JEOL, Inc., Japan).

3. Results and discussion

In a binary eutectic system (for example: component A and component B), a formation process of eutectic microstructure has been considered as follows.[20] When component A in the melt crystallizes and grows, the crystal of A consumes the component A from the melt. Thus, during the crystallization of A, the concentration of component B in the melt around the crystal increases. When the concentration of B around the crystal runs up to a certain value, a nucleation of component B occurs on the crystal A. This causes a switching of the crystallization process. The same phenomenon occurs during the crystallization of B. This switching of crystallization is what forms the eutectic microstructure. The increasing concentration in the liquid phase (melt) around the crystal tends to be diluted by convection and high diffusion rates through the liquid phase, resulting in slow switching. Even in such a situation, generally, the eutectic microstructure formed from the liquid phase is still small. If convection does not occur and the diffusion rate is low, the eutectic microstructure may be much finer. Therefore, we studied a formation of eutectic microstructure from an amorphous phase in which convection does not occur.

Fig. 2 shows an XRD pattern of the eutectic specimen (SC), which was formed by the slow cooling of a melt with the eutectic composition. Only $Y_3Al_5O_{12}$ (YAG: Yttrium Aluminum Garnet) and Al_2O_3 phases, which are the end members of this eutectic system, were observed. Fig. 3 shows XRD patterns of

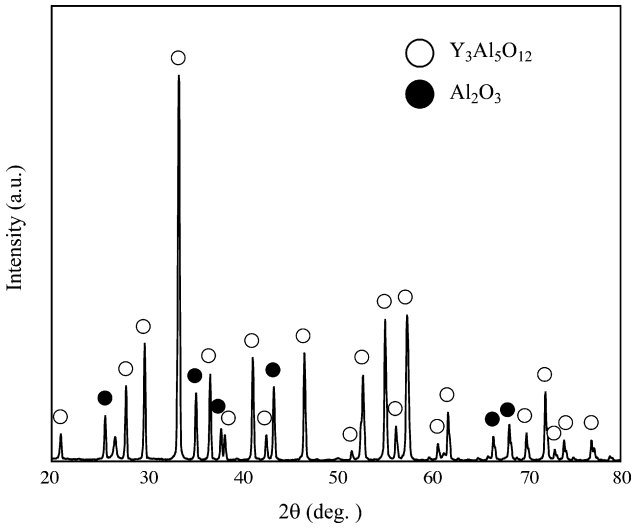

Fig. 2. XRD pattern of SC.

a rapid quenched specimen (RQ-0) and heat-treated specimens (RQ-700, RQ-1000 and RQ-1300). RQ-0 (Fig. 3(a)) was amorphous. This illustrates that an amorphous film can be fabricated by the rapid quenching of a melt with a eutectic composition. RQ-700, which had been heat-treated at 700 °C, was nearly amorphous (Fig. 3(b)). The XRD patterns of RQ-1000 and RQ-1300, which had been heat-treated at 1000 °C (Fig. 3(c)) and 1300 °C (Fig. 3(d)), showed YAG and Al_2O_3 phases. The diffraction peaks of Al_2O_3 were weak. This is because the scattering factor of aluminum is lower than that of yttrium. As the heating temperature was increased, the crystal phases of binary eutectic components (YAG and Al_2O_3) increased.

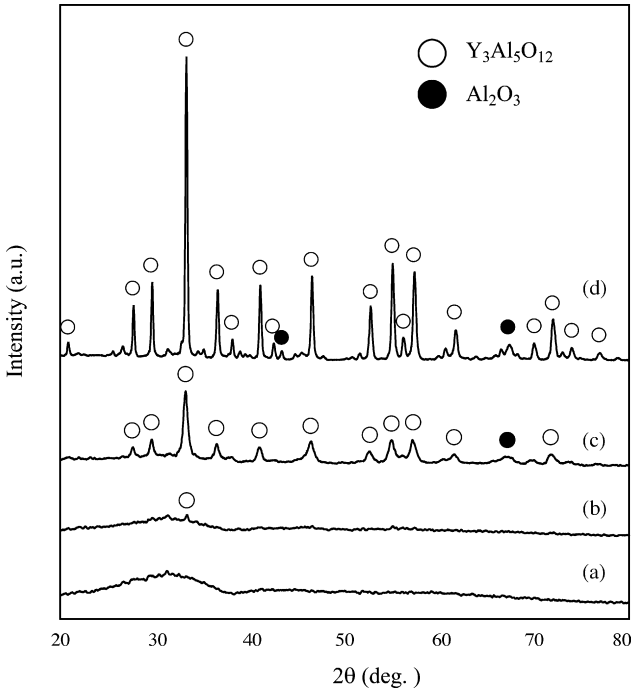

Fig. 3. XRD patterns of (a) RQ-0 (b) RQ-700 (c) RQ-1000 and (d) RQ-1300.

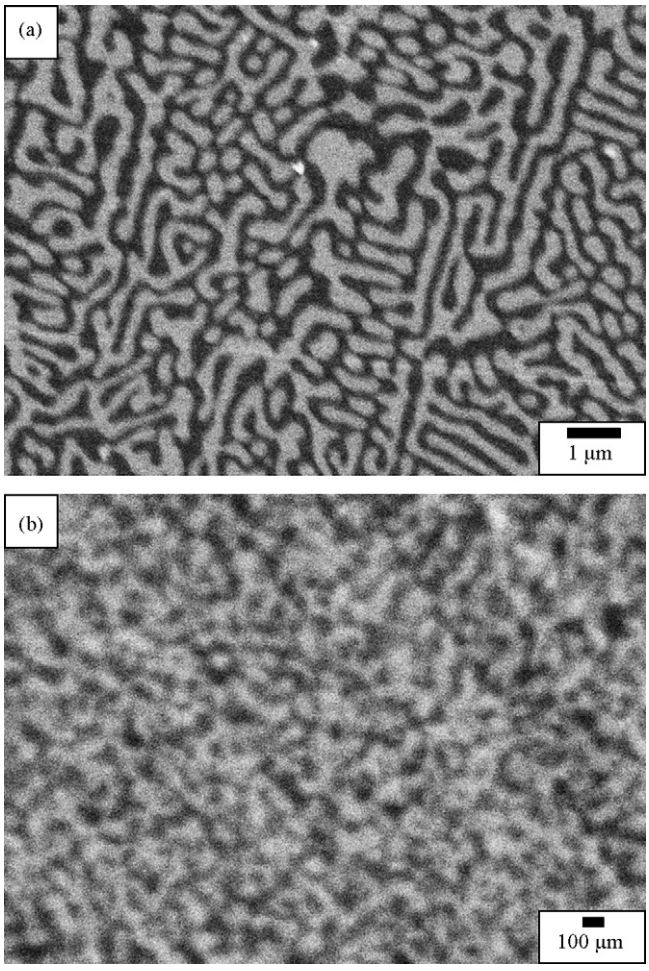

Fig. 4. SEM micrograph of SC and RQ-1300.

Fig. 4(a) shows a SEM micrograph of SC illustrating a eutectic microstructure. This microstructure is similar to the one found in Waku's report.[4,5] Fig. 4(b) shows a SEM micrograph of RQ-1300, which was formed by heat-treatment from the rapid

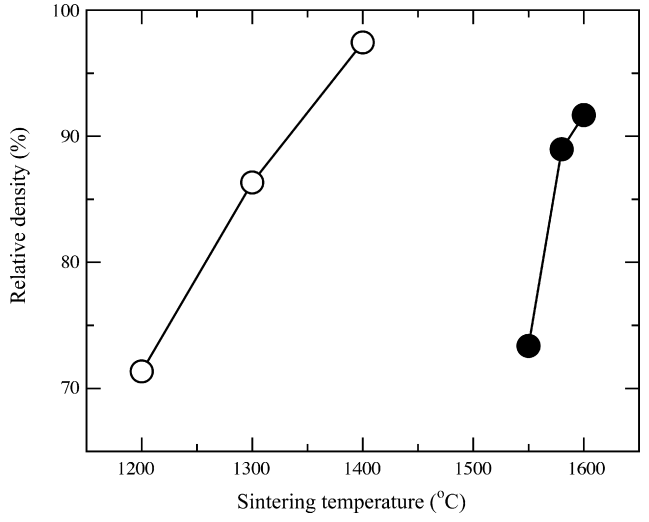

Fig. 5. Relationship between relative density and sintering temperature: (●) by conventional sintering method; (◯) by SPS.

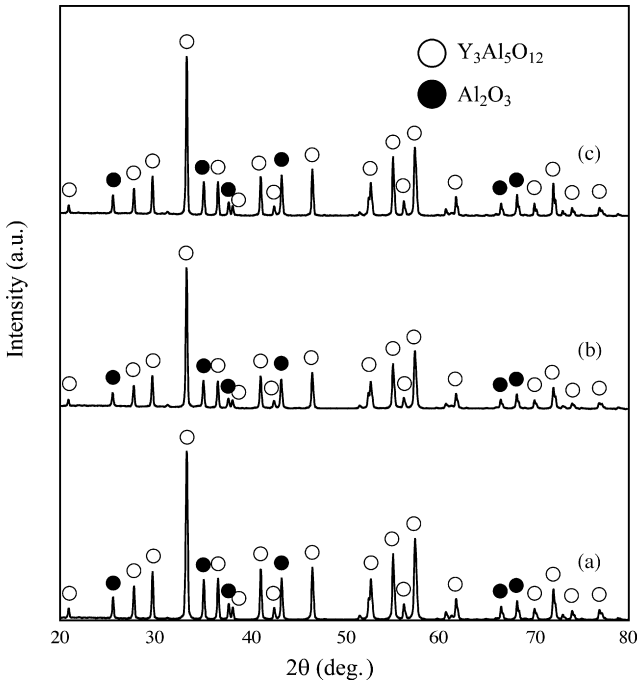

Fig. 6. XRD patterns of sintered materials by the conventional sintering method: (a) C-1550; (b) C-1580; (c) C-1600. Sintering period: 24 h.

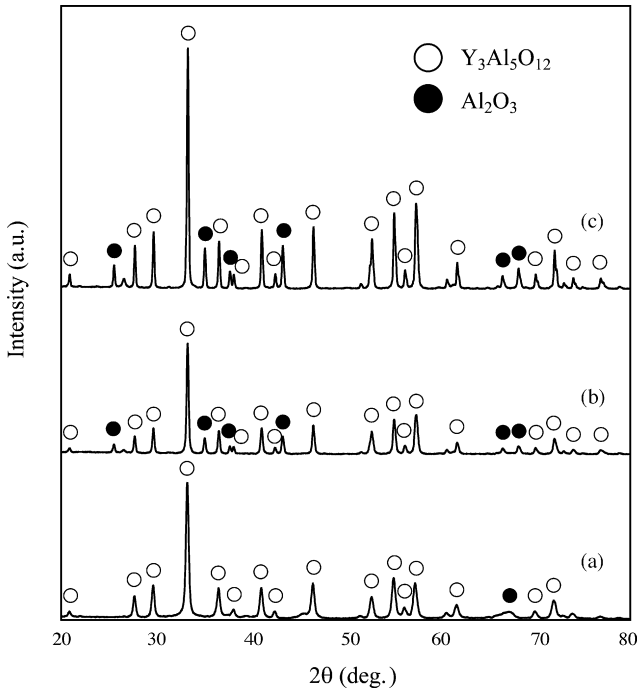

Fig. 7. XRD patterns of sintered materials by SPS: (a) S-1200; (b) S-1300; (c) S-1400.

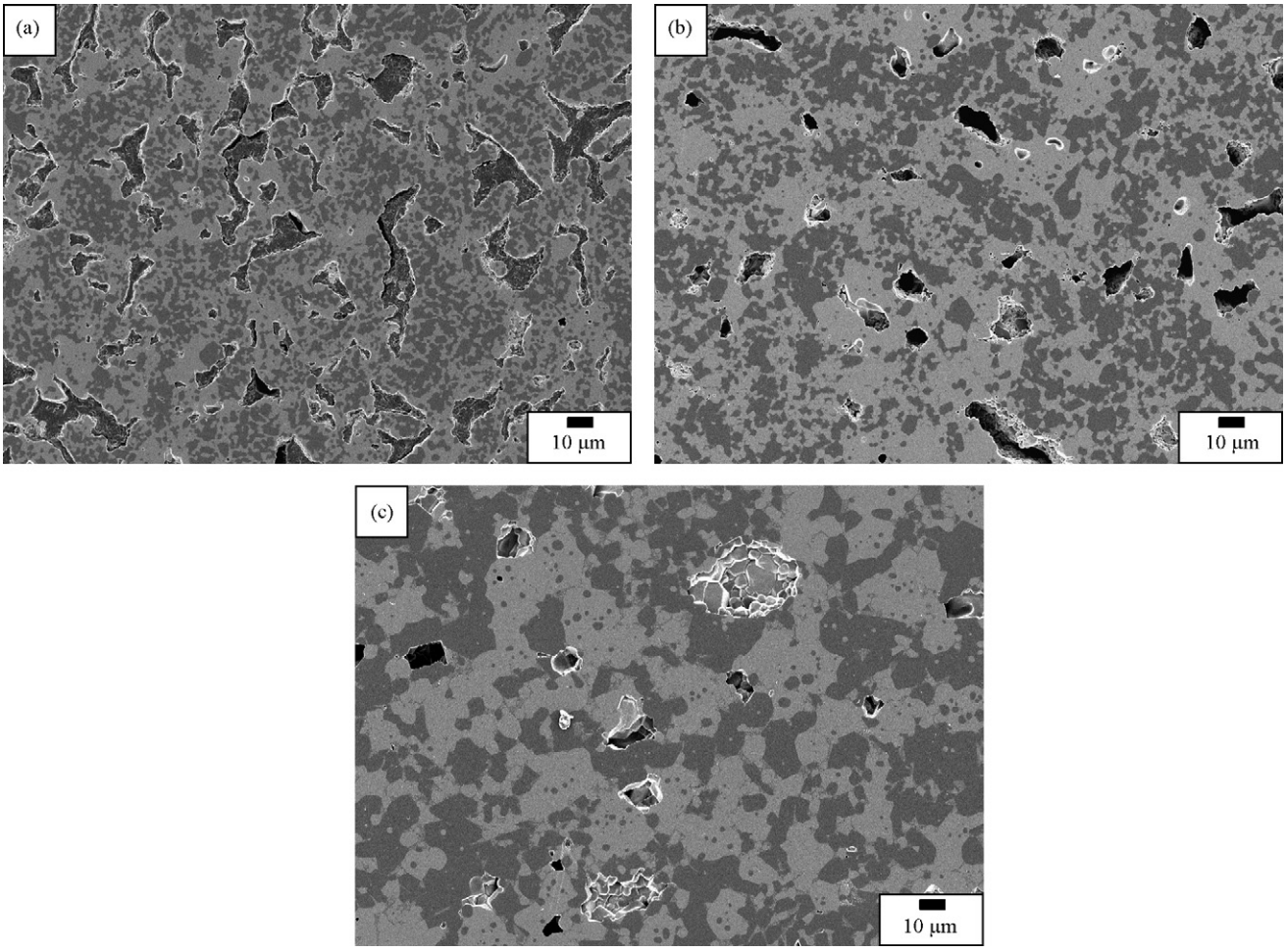

Fig. 8. SEM micrographs of sintered materials by conventional sintering method: (a) C-1550; (b) C-1580; (c) C-1600. Sintering period: 24 h.

quenched film at 1300 °C for 30 min. In the SEM micrograph, the white area is YAG while the black area represents Al_2O_3. This contrast is due to the difference of the atomic numbers of aluminum and yttrium. The SEM micrograph showed YAG and Al_2O_3 crystals entangled with each other. RQ-1300 also exhibited a typical binary eutectic microstructure. It is noteworthy that RQ-1300 has a much finer microstructure than that of SC.

For practical use, the film shaped specimen should be consolidated into a bulk shape. To achieve this the amorphous film formed by rapid quenching was pulverized and sintered both by the conventional sintering and by SPS. Fig. 5 shows the relationship between the relative density and the sintering temperature for sintered specimens. Plots represented by ● are for C-1550, C-1580 and C-1600, which are processed using conventional sintering. Plots represented by ○ are for S-1200, S-1300 and S-1400, which are consolidated by SPS. As the sintering temperature was increased, the relative density increased in both sintering methods. By the conventional sintering method, the relative density was only 90%, even when it was sintered at 1600 °C. On the other hand, densification by SPS was significant, even at lower temperatures.

Fig. 6 shows XRD patterns of specimens by the conventional sintering method. (a)–(c) are for C-1550, C-1580 and C-1600, respectively. All the specimens had YAG and Al_2O_3 phases. This means that the binary eutectic components were crystallized during the sintering process.

Fig. 7 shows XRD patterns of specimens by SPS. (a)–(c) are for S-1200, S-1300 and S-1400, respectively. S-1300 and S-1400 had both YAG and Al_2O_3 peaks. S-1200 is also considered to have both phases. The reason that peak of Al_2O_3 was not observed may be that peak height of Al_2O_3 is much lower than those of YAG.

Fig. 8 shows SEM micrographs of C-1550 (a), C-1580 (b) and C-1600 (c). All the specimens have a large amount of porosity. As the sintering temperature was increased, the boundaries between particles became more inconspicuous. Also, the size of each phase was increased and the shape of each phase became more spherical. Thus, a sufficiently dense sintered body having the characteristic eutectic microstructure cannot be obtained by using the conventional sintering method.

Fig. 9 shows SEM micrographs of S-1200 (a), S-1300 (b) and S-1400 (c). As the maximum temperature of SPS, T_m, was increased, the size of the eutectic microstructure slightly increased. The ultra fine eutectic microstructure was clearly observed in S-1400. Although the SEM image of S-1200 is not clear, it is believed that it has very fine eutectic microstructure,

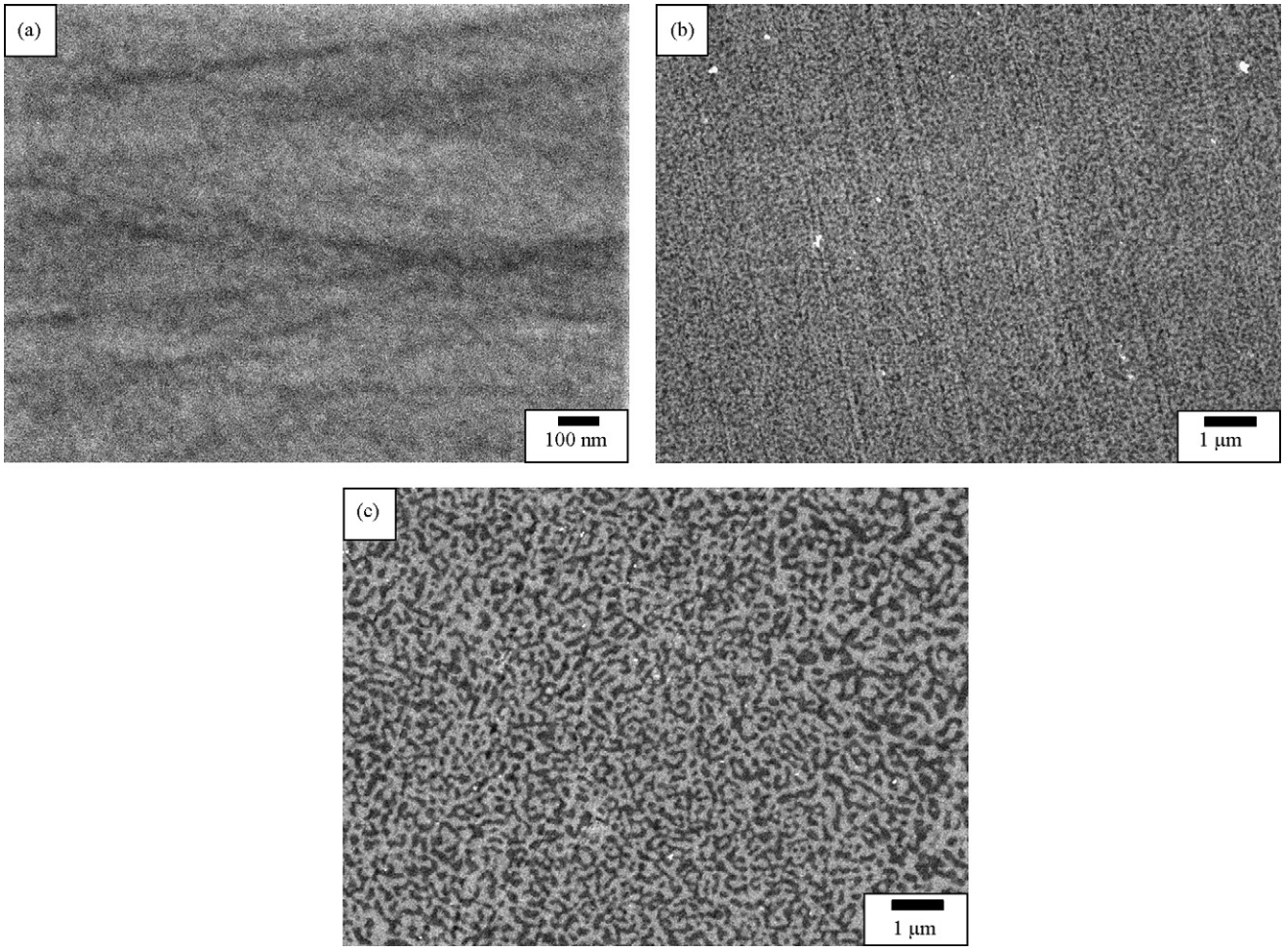

Fig. 9. SEM micrographs of sintered materials by SPS: (a) S-1200; (b) S-1300; (c) S-1400.

considering the results of XRD observation (Fig. 7(a)) and the other SEM images (Fig. 9(b) and (c)). Using SPS a sintered body having an ultra fine eutectic microstructure with a high bulk density (97.4% for S-1400) was obtained.

4. Conclusion

An amorphous film of $Y_3Al_5O_{12}$-Al_2O_3 system was fabricated by rapid quenching of a melt with the eutectic composition. A post-quench heat-treatment of the amorphous film formed the desired eutectic microstructure. The eutectic microstructure, which was formed from the amorphous phase at 1300 °C for 30 min, was ultra fine in nature. By processing these materials in the amorphous phase, convection can be suppressed, resulting in an ultra fine eutectic microstructure. Following quenching and heat-treatment the amorphous film was pulverized and sintered both by conventional sintering and via the SPS technique. By using the conventional sintering method, sufficiently dense sintered bodies having an ultra fine eutectic microstructure could not be obtained. Conversely, the sintered bodies having an ultra fine eutectic microstructure with high bulk density could be fabricated by using SPS.

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