Consolidation of Al$_2$O$_3$–GdAlO$_3$ eutectic powder prepared from induction-melted solid and strength at high temperatures

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Abstract

A eutectic powder of Al$_2$O$_3$–GdAlO$_3$ was melted using a Mo crucible by induction heating. The melt was slowly solidified, resulting in a eutectic solid with coarse Al$_2$O$_3$ and GdAlO$_3$ phases. The eutectic solid was ground and sieved into 3–44 μm and 64–124 μm particles. The powders were consolidated to produce a eutectic composite by spark plasma sintering. Mechanical properties of the consolidated eutectic composite were measured at room temperature. High temperature strength was obtained at temperatures up to 1673 K. Superplastic deformation of the eutectic composite was not observed on stress–strain curves at 1673 K, but did occur in the case of a conventional composite at 1573 K. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Oxide eutectic composites are promising engineering materials for use at high temperatures, and there have been many studies on such composites. The strength of an Al$_2$O$_3$–ZrO$_2$(8.8Y$_2$O$_3$) eutectic composite fabricated by a floating zone method is maintained at temperatures near 1600 °C [1]. This eutectic composite is composed of a single crystal, which is responsible for the improved high temperature strength. Al$_2$O$_3$–Y$_2$Al$_2$O$_7$ (YAG) and Al$_2$O$_3$–GdAlO$_3$ eutectic composites have received attention as heat-resistant materials for turbine blades [2,3] because of their high strength at temperatures above 1773 K. These composites must be carefully prepared using a Mo crucible by a modified Bridgman technique and are composed of large crystals of the constituent phases of 10–30 μm in width; no grain boundaries are contained in the composites. On the other hand, an Al$_2$O$_3$–YAG eutectic composite fabricated by the modified Bridgman technique loses 30% of its room temperature strength at 1648 K [4]. Strength reduction of 25% results at 1653 K in an Al$_2$O$_3$–ZrO$_2$(3.5Y$_2$O$_3$) eutectic composite prepared by a floating zone method, such composite having a texture consisting of colony structures [5]. The internal friction of the Al$_2$O$_3$–YAG eutectic composite starts to increase at 1523–1573 K [6], while the specimen to be measured is cut out from the eutectic composite maintaining its strength above 1773 K [2]. The increase of the internal friction depends on the migration of dislocations, such migration causing plastic deformation and, therefore, a decrease of strength. From these cited reports, it is appropriate to consider that the strength of certain eutectic composites is reduced at around 1673 K to some extent. However, eutectic composites can be used at high temperatures, since the reduction of strength is not large. Eutectic composites are fabricated by unidirectional solidification methods, which are not adequate to produce large or near-net-shape materials. Therefore, solidified composites are not candidates for high temperature materials such as turbine blades.

The powder of an Al$_2$O$_3$–GdAlO$_3$ eutectic composite is consolidated by spark plasma sintering (SPS) [7–9], and the consolidation of an Al$_2$O$_3$–YAG composite is carried out by hot pressing [10]. The eutectic powders used in the above-cited studies were prepared by arc discharge, which is a simple technique resulting in the formation of fine crystals due to the rapid cooling during solidification of the melt. On the other hand, the eutectic structure grown by unidirectional solidification is coarse and does not change when held at 1873 K [11]. The fine crystal structure of a eutectic Al$_2$O$_3$–YAG fiber (Saphikon fiber) is coarsened at 1773 K [12]. The high temperature stability of a eutectic composite is achieved due to the coarse crystal structure such as 10–30 μm. Consolidation may be better carried out using eutectic powders having large constituent crystals.

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In this paper, a eutectic composite of Al₂O₃–GdAlO₃ was melted in a Mo crucible by induction heating and was slowly cooled there to obtain a coarse structure. The cooled solid was crushed and sieved into two kinds of powders, one with a particle size ranging from 3 to 44 μm and the other with a particle size of 64–124 μm. These powder particles were consolidated by SPS. The density of the consolidated eutectic was measured at room temperature, and the strength was measured at temperatures up to 1673 K.

2. Experimental procedures

Starting materials were Al₂O₃ (Sumitomo Chemical Co. Ltd., 99.99%) and Y₂O₃ (Santoku Metal Co., 99.99%) powders. The powders were placed in a polyethylene pot together with iron balls coated with polyethylene and ethano1 and were blended for 86.4 ks. The molar ratio of Al₂O₃ to Y₂O₃ was 77:23, which corresponded to the eutectic composition. The blend was dried, molded and then fired at 1273 K for 7.2 ks. The fired compact was melted four times by arc discharge, the top and bottom being reversed.

Ingots produced by the arc discharge were loaded into a M0 crucible with a diameter of 41 mm and a length of 50 mm. Melting of the ingots was conducted in a commercial induction heating furnace (Kokusai Electric Co. Ltd, DP-100MP). The Mo crucible was heated up to 2473 K on the surface of the melt, and cooled slowly at a cooling rate of 0.05–0.083 K/s. The direction of solidification was not controlled. The temperature of the melt surface was measured by an optical pyrometer.

The solidified ingot was ground using a ball milling apparatus made of a WC-Co hard metal. The powder obtained was sieved into two types of powders, one with rather fine particles, 3–44 μm in diameter, and the other with coarse particles, 64–124 μm in diameter. The powders were rinsed with a mixture of distilled water, HNO₃ and H₃PO₄ (3:1:1 in volume) to remove the WC impurities which came from the hard metal. The consolidation of the pure powders was carried out in a graphite die using SPS (Sumitomo Coal Mining Co. Ltd, SPS1050) in a vacuum. The powder in the die was heated from room temperature to 1893 K at a rate of 1.33 K/s and held at 1893 K for 300 s. Conventional composites consisting of polycrystals of Al₂O₃ and YAG were fabricated from the eutectic composition powders of Al₂O₃ and Y₂O₃ by the same heating condition as that for the eutectic powder.

The density of the consolidated eutectic composite was determined based on Archimedes’ principle using water. The elastic modulus of the composites, from 5 to 10 mm in thickness and 20 mm in diameter, was measured by the pulse-echo overlap ultrasonic technique using an ultrasonic detector (Hitachi Kenki Co. Ltd, Japan, ATS-100) and a storage oscilloscope (Iwasaki Tsushinki Co. Ltd, Japan, DS6411). The polished surface and the surface thermally etched in air for 1.2 ks at 1673 K were observed with a scanning electron microscope (Hitachi Ltd, Japan, S-3100H). Flexural strength was determined at room temperature and at temperatures from 1273 to 1673 K using the three-point bending test machine (Shimazu Co. Ltd, Japan, Autograph DSS-500). Sample dimensions were 3 mm × 4 mm × 15 mm. The span of the lower knife edge was 10 mm. All testing was done at a crosshead speed of 8.3 × 10⁻⁵ mm/s. A Vickers hardness tester (Akashi Co. Ltd, Japan, AVK) was used for hardness and toughness measurements of the eutectic composite under a load of 98 N. Fracture toughness was calculated from Vickers hardness, Young’s modulus, and crack length at indents [13].

3. Results and discussion

The structure of the induction melted and solidified ingot is shown in Fig. 1. The light-colored phase is alumina and the dark-colored one is YAG. The arrangement of the two phases was irregular on the colony boundaries, which made

![Fig. 1. SEM image of eutectic composite melted by induction melting.](image-url)
Fig. 2. SEM image of the eutectic consolidated from 3 to 44 μm particles.

the colony structure clear. The crystal sizes of alumina and YAG were larger than those in the arc-melted button [9]. There were two textures in the colony. One consisted of columnar structures finely and regularly controlled from 0.5 to 2 μm in width (1 area). The other was composed of random columnar structures from 5 to 10 μm in width (2 area), the sizes of which were similar to those of unidirectionally solidified crystals (5–10 μm in width) [3]. The colony was formed due to constitutional supercooling of the melt close to the solidification front. This supercooling is realized when impurity atoms exist or two crystal components are separated in the small area of melt [14]. Elaborate techniques are required to fabricate a eutectic composite without colonies. There is a relationship between the crystal size in the colony and at its boundary. The growth rate of constituent phases decreases at the colony boundary, resulting in the formation of coarsened crystals [14]. Waku et al. obtained large column-like eutectic composites using a unique technique at a high temperature [2,3]. In the present work, the solidification rate and the solidification direction were not controlled, thus resulting in the formation of colonies. However, it was not important to grow a eutectic composite without colonies in this study because the eutectic composite was ground into powders.

Some of the particles smaller than 44 μm in diameter contained only alumina or YAG due to the coarse eutectic structure in the solidified ingot. SPS is used to sinter metal and ceramics in the plasma and in the electric field [15,16]. SPS has five factors for material synthesis: spark plasma, plasma impact, electric field, electric current and rapid heating [17]. It has not been clarified how these factors affect the consolidation of the eutectic powders. The shrinkage of the powder compact and its cessation are monitored in the SPS process. This shrinkage monitoring is very useful for determining the accurate temperature of sintering and for achieving full densification.

The SEM images of the consolidated eutectic composite are shown in Figs. 2 and 3. The eutectic structures of the ground powder were observed in the eutectic composite consolidated from 3 to 44 μm particles, as shown in Fig. 2.

Fig. 3. SEM image of the eutectic consolidated from 64 to 124 μm particles.
The spaces between the eutectic particles were filled with a two-phase region consisting of alumina and YAG, which was formed during the SPS process and which had a rather coarse structure. Such a two-phase region similar to that observed in Fig. 2 exists in the eutectic composite consolidated from 64 to 124 μm particles as shown in Fig. 3, although the structure in the two-phase region is coarser in Fig. 3. The coarseness of the structure in the two-region can be correlated with the particle size of the initial ground powder, and the coarser structure appeared around the larger powder particles. The thermal-etched surface of the consolidated eutectic composite is shown in Fig. 4. Grain boundaries were recognized in the two-phase region between the eutectic structures of the ground powder particles. The number of the grain boundaries was smaller compared with that of a conventional composite which was fabricated from the eutectic composition powders of Al₂O₃ and Y₂O₃ and resulted in a polycrystal composite. It is concluded from these results that a eutectic structure can be obtained by the consolidation of ground eutectic particles using SPS.

The properties of the consolidated eutectic are shown in Table 1. A density higher than 99.5% was achieved for both compacts prepared from 3 to 44 μm and 64–124 μm powders, indicating that SPS is useful for the production of dense materials. The consolidation of large powder particles seems to be accompanied by plastic deformation. The consolidation temperature of 1620 °C is near the melting point of the eutectic composite [9]. The plastic deformation of the particles accelerates the consolidation and results in high density. Furthermore, the growth of crystals is another important factor in the pulsed electric field. It has been shown that the growth of CoSb₃ crystals is accelerated by the skin current and the pulsed electric field in the SPS process [17]. If the pulsed electric field facilitates the growth of alumina and YAG, the number of grain boundaries is surely decreased. The growth of large alumina and YAG crystals consumes the small ones and results in the reduction of the number of grains. These two factors are advantageous for the production of a eutectic composite with fewer grain boundaries and lower porosities. Young’s modulus, fracture toughness and Poisson’s ratio were almost the same for all samples listed in Table 1. Vickers hardness is higher for the composite with higher relative density. In the measurement of the flexural strength by the three-point bending test, the span was 10 mm. This narrow span was adopted since the space available in the furnace to measure the high temperature strength was small. The strength measured for a 30-mm span was found to be about 20% lower than that for a 10-mm span at room temperature. The finest grain of 1–5 μm of the conventional composite resulted in the highest strength of 706 MPa as shown in Table 1. The eutectic composite consolidated from 3 to 44 μm particles had a strength of 605 MPa. In the work of Omori et al. [9], however, the strength of the

![Fig. 4. SEM image of thermal-etched surface of the eutectic consolidated from 3 to 44 μm particles.](image)

| Powder (μm) | Relative density (%) | Vickers hardness (GPa) | Fracture toughness (MPa m³/²) | Young’s modulus (GPa) | Poisson’s ratio | Flexural strength (MPa) |
|------------|----------------------|------------------------|-----------------------------|----------------------|----------------|------------------------|
| 3–44       | 99.9                 | 19.0 ± 0.1             | 4.6 ± 0.5                   | 342                  | 0.26           | 605 ± 65               |
| 64–124     | 99.8                 | 18.9 ± 0.7             | 4.3 ± 0.8                   | 344                  | 0.26           | 402 ± 48               |
| Composite¹ | 99.5                 | 17.6 ± 0.7             | 4.3 ± 0.3                   | 347                  | 0.25           | 706 ± 94               |

¹ Conventional composite.
consolidated eutectic composite was not high, being 290 MPa, because the ground eutectic powders contained particles as coarse as 124 μm and the strength was measured by the three-point bending test using a 30-mm span. There is a clear relationship between the strength and the powder particle size. The improvement in strength can be achieved by the appropriate selection of particle size and consolidation techniques regarding heating rate, sintering temperature and duration. The strength (402 MPa) of the eutectic prepared from 64 to 124 μm particles was the lowest of all the samples in Table 1. These results indicate that large defects are included along large particles inside the consolidated materials. The strength of 402 MPa is not bad considering the use of the powder with large particles. Conventional composites are not prepared from powders containing particles as large as 124 μm. Excellent ceramic powders for sintering are usually less than 1 μm in diameter. The strength, σ, is correlated with fracture toughness (KIC) and crack length (Cc), as follows:

\[
KIC^2 = \pi \sigma^2 Cc
\]

In this paper the fracture toughness was obtained by an indentation fracture method [13], and the strength was measured by the three-point bending test. The calculated crack length was 36 μm for the eutectic prepared from 64 to 124 μm particles and 12 μm for the conventional composite. The consolidated eutectic composite contained smaller defects such as cracks than those expected from the particle size of the initial powder. It remains unclarified as to whether the crack length is decreased using eutectic powder instead of polycrystal powders or whether such reduction is enhanced by the effect of SPS.

The strength at high temperatures was measured for the eutectic composite consolidated from 3 to 44 μm particles at temperatures from 1273 to 1673 K in a vacuum, as shown in Fig. 5. Fig. 6 shows the nominal stress–displacement curves measured at these temperatures. The conventional composite was superplastically deformed at 1573 and 1673 K. The strength of the consolidated eutectic and the conventional composite decreased at 1273 K. The conventional composite steeply lost its strength at the temperatures above 1273 K. The consolidated eutectic fractured at 1673 K while it was still being elastically deformed, and

![Graph showing flexural strength vs. temperature for eutectic and conventional composites.]

![Graph showing nominal stress vs. displacement for conventional and eutectic composites.]

Fig. 5. Flexural strength of consolidated eutectic and conventional composites at room and high temperatures.

Fig. 6. Nominal stress–displacement curves of conventional composite and the eutectic consolidated from 3 to 44 μm particles.
the fracture strength decreased to about 60% of that at room temperature. The eutectic structure is responsible for the strength at high temperatures [1–5]. The coarse two-phase region in the space between the eutectic particles contained grain boundaries and was similar to the conventional composite structure, which can reduce high temperature strength. The reduction of the strength of the consolidated eutectic might decrease with decreasing grain boundaries. The unidirectional eutectic composite gradually loses its strength at temperatures above 1273 K, but it holds 75% of the original strength at 1653 K [5]. The high temperature strength of the consolidated eutectic is not bad for high performance materials for use at high temperatures and can be improved by decreasing the number of the grain boundaries of the consolidated eutectic composite.

4. Summary

An Al₂O₃−GdAlO₃ ingot of the eutectic composition was prepared by induction melting in a Mo crucible. The ingot having a columnar structure composed of regular and random crystals was ground and sieved to two types of powders, one having diameters of 3–44 μm and the other with diameters of 64–124 μm. These particles were consolidated by the SPS. The consolidation of the eutectic particles made the formation of a eutectic structure possible to some extent, but the two-phase region consisting of alumina and YAG in the space between the eutectic particles contained grain boundaries. The strength was measured at room temperature and at high temperatures up to 1673 K. The strength of the consolidated eutectic was 605 MPa for the 3–44 μm powders and 402 MPa for the 64–124 μm particles at room temperature. Superplastic deformation was not observed on the stress–strain curves at 1673 K, but the strength was decreased to less than half of that at room temperature.

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References

[1] C.O. Hulse, J.A. Batt, Effect of eutectic microstructures on the mechanical properties of ceramic oxides, Final Technical Report UARL-N910803-10, May 1974; NTIS AD-781995/6GA; 140pp.
[2] Y. Waku, H. Ohtsubo, N. Nakagawa, Y. Kohtoku, Sapphire matrix composites reinforced with single crystal YAG phases, J. Mater. Sci. 31 (1996) 4663–4670.
[3] Y. Waku, N. Nakagawa, T. Wakahuto, H. Ohtsubo, K. Shimizu, Y. Kohtoku, A. Ductile, Ceramics eutectic composite with high strength at 1873 K, Nature 389 (6646) (1997) 49–52.
[4] T. Mah, T.A. Parthasarathy, L.E. Matson, Processing and mechanical properties of Al₂O₃/Y₃Al₂O₆ (YAG) eutectic composite, Ceram. Engng Sci. Proc. 11 (9–10) (1990) 1617.
[5] J.Y. Pastor, P. Poza, J. Llorca, J.I. Pena, R.I. Merino, V.M. Orera, Mechanical properties of directionally solidified Al₂O₃–ZrO₂ (Y₂O₃), Mater. Sci. Engng A308 (2001) 241–249.
[6] S. Takata, S. Ueno, Y. Kawakami, T. Akatsu, Y. Tanabe, E. Yasuda, Y. Waku, Microstructure and high-temperature internal friction of unidirectionally solidified Al₂O₃–Y₂O₃ eutectic composite, J. Ceram. Soc. Jpn 109 (6) (2001) 561–564.
[7] T. Isobe, M. Omori, T. Hirai, The preparation and mechanical properties of eutectic composite by SPS (Spark Plasma System), in: Organizer Committee of the International Japan–Korea Seminar on Ceramics, Okayama, Japan (Ed.), Proceeding of the 16th International Japan–Korea Seminar on Ceramics, 1999, pp. 93–96.
[8] T. Isobe, M. Omori, T. Hirai, Microstructure of Al₂O₃–Y₂Al₂O₇ (YAG) eutectic composite precipitated from melt and the consolidated by SPS, J. Jpn. Soc. Powder Powder Metall. 47 (3) (2000) 298–301.
[9] M. Omori, T. Isobe, T. Hirai, Consolidation of eutectic powder of Al₂O₃–GdAl₂O₃, J. Am. Ceram. Soc. 83 (11) (2000) 2878–2880.
[10] T. Mah, T.A. Parthasarathy, R.J. Kerans, Processing, microstructure, and strength of alumina–YAG eutectic polycrystals, J. Am. Ceram. Soc. 83 (8) (2000) 2088–2090.
[11] Y. Waku, N. Nakagawa, T. Wakahuto, H. Ohtsubo, K. Shimizu, Y. Kohtoku, High-temperature strength and thermal stability of a unidirectionally solidified Al₂O₃/YAG eutectic composite, J. Mater. Sci. 33 (1998) 1217–1225.
[12] W.J. Clegg, A. Kelly, J.E. Pitchford, Composites for use at high temperature, in: K. Niihara, K. Nakano, T. Seino, E. Yasuda (Eds.), High Temperature Ceramic Matrix Composites III, Trans Tech Publishers, Switzerland, 1998, pp. 315–320.
[13] G.R. Antis, P. Chantikul, B.R. Lawn, D.B. Marshal, A. Critical, Evaluation of indentation techniques for measuring fracture toughness. I. Direct crack measurements, J. Am. Ceram. Soc. 64 (9) (1981) 533–538.
[14] H.W. Weart, D.J. Mack, Eutectic solidification structures, Trans. AIME 212 (10) (1958) 664–670.
[15] K. Inoue, Electric-discharge sintering, US Patent No. 3,241,956, 1966.
[16] K. Inoue, Apparatus for electrically sintering discrete bodies, US Patent No. 3,250,892, 1966.
[17] M. Omori, Sintering, consolidation, reaction and crystal growth by the spark plasma system (SPS), Mater. Sci. Engng A287 (2) (2000) 183–188.