研 究

Microstructure of $\text{Al}_2\text{O}_3\text{-Y}_3\text{Al}_5\text{O}_{12}$ (YAG) Eutectic Composite Prepared by Melting and SPSToshinori Isobe^{★1}, Mamoru Omori^{★2} and Toshio Hirai^{★2}^{★1}Department of Materials Science, Graduate School of Engineering, Tohoku University, 02 Aoba Aramaki Aoba-ku, Sendai 980-8579.^{★2}Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577.

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SYNOPSIS

Eutectic composites of $\text{Al}_2\text{O}_3\text{-Y}_3\text{Al}_5\text{O}_{12}$ (YAG) were prepared from solids melted by arc discharge and induction heating. Unidirectional solidification was carried out by the floating zone (FZ) method. The melt of the arc discharge was cooled rapidly and resulted in medium crystals. Coupled crystals (Al_2O_3 and $\text{Y}_3\text{Al}_5\text{O}_{12}$) resulting from induction heating and the FZ method were 20–30 μm in width. The eutectic powder, which was prepared by grinding eutectic solids melted by arc discharge and induction heating, was consolidated by the spark plasma system (SPS). The structure of the consolidated was similar to that of a eutectic composite, and was coarsened by the growth of coupled crystals around original particles.

KEY WORDS

eutectic composite, induction heating, floating zone method, spark plasma system, coupled crystals, SPS

1 Introduction

Eutectic composites are invariably formed from the melt with their compositions, and their properties are not same as those of ordinary composites¹⁻³⁾. The structure of the eutectic consists of coupled crystals.

$\text{Al}_2\text{O}_3\text{-Y}_3\text{Al}_5\text{O}_{12}$ (YAG) and $\text{Al}_2\text{O}_3\text{-GdAlO}_3$ eutectic composites have received attention as heat-resistant materials for turbine blades. The composite elaborately prepared by unidirectional solidification of the Bridgman technique results in large coupled single crystals. Each large crystal is a barrier preventing diffusion of materials and vacancies of the other crystal, and its strength is not decreased until 1700 °C⁴⁻⁶⁾. Eutectic composites are melted in Mo and W crucibles near 2200 °C. Considerable times and advanced techniques are required to form unidirectional solids without defects at such a high temperature. The biggest achievable size of such a unidirectional solid is only 50 mm in diameter and 70 mm in length.

Recently, a simple method for fabrication of eutectic bulks has been developed using a powder metallurgy method^{7,8)}. A eutectic powder, which is prepared by grinding eutectic solids melted by arc discharge, can be consolidated by the spark plasma system (SPS). The consolidation results in duplication of the eutectic structure. The size of the crystal depends on the eutectic crystal structure of the powder. Such arc melting yields only

composites of fine and medium structures, because the melt is rapidly cooled. High-temperature properties are affected by crystal size, the strength of fine crystal composites being deteriorated at high temperature. It is necessary to know relationship between the structure and formation technique of eutectic composites to obtain large crystal composites.

In this work, eutectic composites were prepared by induction heating, floating zone (FZ) and arc discharge. The powder prepared from the composite was consolidated by SPS. The structure of these eutectic composites was investigated to clarify its dependence on the solidification and the relationship between the initial and consolidated structures.

2 Experimental procedures

Materials were Al_2O_3 (Sumitomo Chemical Co. Ltd, 99.99 %) and Y_2O_3 (Santoku Metal Co., 99.99 %) powders. The powder with the eutectic composition (18 mol% of Y_2O_3 and 82 mol% of Al_2O_3) was blended in an ethanol slurry using a polyethylene pot and iron balls coated with polyethylene for 24 h. The blend was dried, molded and fired at 1000 °C for 2 h. The fired compact was melted three times by arc discharge, the top and bottom being reversed.

Cylindrical rods 8 mm in diameter and 100 mm in length were shaped by a cold isostatic press, and then fired at 1400

$^{\circ}\text{C}$ for 1 h. The rods were solidified using a commercial FZ equipment (ULVAC, FZ-SS35WV). The growth rates were 2 and 10 mm/h.

Pellets melted by the arc discharge were loaded into a Mo crucible with a diameter of 41 mm and a length of 50 mm. Melting was conducted in a commercial induction heating furnace (KE, DP-100 MP). Mo crucibles were heated to 2200°C by induction heating, and cooled slowly at $1^{\circ}\text{C}/\text{min}$ to a temperature below the melting temperature. Temperatures were measured at the top of the melt.

The solid melted by arc discharge and induction heating was ground using a ball mill consisting of a container and balls made of hard alloy (WC). The obtained powder was rinsed with a mixture of distilled water, H_2NO_3 and H_3PO_4 (3:1:1 in volume) to remove WC. Crystal growth of the pure powder was carried out in a graphite die using spark plasma system (SPS) (Izumi Technology Co. Ltd., SPS1050). The temperature was raised from room temperature to 1620°C over a period of 20 min in a vacuum. The temperature of 1620°C was maintained for 5 min.

The surfaces of the samples were polished using a diamond grinding wheel and diamond slurry for a final relief polish, and observed by a scanning electron microscope (Hitachi Ltd., S-3100H).

3 Results and discussion

3.1 Melt by arc discharge

The cooling rate of the melt obtained by arc discharge was not regulated, and differed from place to place in the solid. The crystal size was nonuniform throughout the solid. Fig. 1 shows that medium (about $1\text{--}5\text{ }\mu\text{m}$ in width) crystals were precipitated by the arc discharge and formed in most of the solid. The white phase was YAG, and the black phase was alumina, being confirmed by EPMA. The medium-sized crystals were slightly oriented from the

Fig.1 SEM image of medium structure melted by arc discharge.

bottom to the top of the melt, even though the cooling was not unidirectional solidification. The size of the crystals was similar to that of a eutectic fiber fabricated at a slow cooling rate of 5.08 cm/h by the EGF technique⁹). A few fine crystals (about $0.3\text{ }\mu\text{m}$ in width) shown by arrows were scattered in the matrix of the medium-sized crystals, as shown in Fig. 2. Such fine crystals are formed at a greater growth rate of 4 cm/h in a crucible 1.9 cm in diameter by the Bridgman technique and indicate a section perpendicular to the direction of growth¹⁰). The formation of fine and medium-sized crystals depends on cooling conditions. Fine crystals are grown when cooling is rather rapid and when there is a loose temperature gradient between the melt and the solid. When the arc melting was stopped, conditions at some of places were adequate for the formation of fine crystals, but conditions at most places led to the precipitation of medium-sized crystals.

3.2 Melt by induction heating

The solidification in the Mo crucible was not unidirectional growth. The crucible was embedded in zirconia bubble insulators and not cooled unidirectionally. The cooled bulk contained large pores and cracks. It was hard to obtain solids without defects.

Colonies of large, homogeneous crystals (about $20\text{ }\mu\text{m}$ in width) were bonded with huge coupled crystals (more than $30\text{ }\mu\text{m}$ in width), as shown in Fig. 3. However, the directions of growth of all colonies were different. Nucleation occurred at many places in the melt, resulting in colonies. Regular crystal growth was stopped at boundaries where huge irregular crystals connected each colony. A high magnification of the SEM image of the colony is shown in Fig. 4. The crystal growth was controlled unidirectionally in some places. The crystal size and shape were the same as those of the bulk solidified unidirectionally⁶.

Fig.2 SEM image of fine structure melted by arc discharge.

Thermal expansion was different between parallel and perpendicular directions of the colony growth. Cracks in the cooled solid may have been caused by the uncontrolled cooling. These results indicate that sound bulk crystals cannot be grown under conditions of the cooling.

3.3 Melt by the floating zone technique

There were cracks in the coupled crystals grown by the floating zone (FG) method, changing the growth rate from 10 to 2 mm/h. When coupled crystal growth was perfectly achieved, each crystal becomes a long single crystal. Thermal expansion was increased with extension of the crystal length and was responsible for the crack formation. It was hard to prepare good solids by FZ, because the growth of coupled crystals was very sensitive to the large temperature gradient of the melt prepared by FZ.

The crystal structure perpendicular to the growth direction is shown in Fig. 5. The coupled crystals were lined up in the direction of growth. The maximum crystal size was about 30 μm in width, nearly the same as that of the solid reported by Waku et al⁹. The large crystal prepared

by the Bridgman method was achieved at a growth rate of 10 mm/h of FZ.

Unidirectional solidification by FZ did not yield fine crystals. FZ solidification is similar to that of the fabrication of eutectic fibers. The temperature gradient of both techniques is steep, and inadequate for the produce of fine crystals.

3.4 Consolidation by SPS

Fig. 6 shows the structure of the eutectic composites consolidated by SPS from the powder melted by arc discharge. The crystal size was larger than that of the arc melt. The growth of coupled crystals was promoted around the eutectic powder during the consolidation. However, the crystals of the solid consolidated by SPS were of medium size and not grown as large as stable crystals of 20–30 μm . The growth period was regulated, due to the consolidation time being as short as 5 min. It is not clear how crystal size and shape are affected by the heating time of SPS. Long consolidation time may be effective for increasing the crystal size.

Fig.3 SEM image of colony structure melted by induction heating.

Fig.5 SEM image of large structure melted by floating zone method.

Fig.4 SEM image of large structure melted by induction heating.

Fig.6 SEM image of solid from arc-discharge powder consolidated by SPS.

The SEM image of Fig. 7 indicates the structure of the eutectic composite consolidated from the powder prepared from the solid melted by induction heating. There were homogeneous crystals as particles and huge crystals which were larger than those of the powder. Such huge crystals were precipitated at the bottom of the solid melted by induction heating, but were scarcely observed in the solid consolidated from the arc-melt powder. When the cooling condition was deviated from unidirectional solidification, many coupled crystals were grown greatly. The consolidation by SPS can reproduce eutectic structure, but cannot be regarded as unidirectional solidification. It is not clear whether the huge crystals are stable at high temperature.

4 Summary

The coupled crystals grown in the condition of unidirectional solidification were large and homogeneous with a width of 20–30 μm , the same as crystals grown by the Bridgman growth method. The crystals precipitated by arc discharge consisted of small amounts of fine crystals (about 0.3 μm in width) and a large portion of medium-sized crystals. The solid melted by induction heating and cooled in a Mo crucible resulted in colonies of large homogeneous crystals bonded with huge crystals. Powders of solids prepared by arc discharge and induction heating were consolidated by SPS. The consolidation made it possible to reproduce the eutectic structure and fabricate large near-net-shaped composites.

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Fig. 7 SEM image of solid from induction-heating powder consolidated by SPS.

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