Eutectic Al_2O_3–$GdAlO_3$ composite consolidated by combined rapid quenching and spark plasma sintering technique

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A mixture of Al_2O_3 and $GdAlO_3$ was melted and rapid quenched to produce an amorphous film. Dense eutectic composites were consolidated from ground amorphous powder using both conventional and spark plasma sintering (SPS). Conventional sintering at temperatures above 1600°C for 24 h was required for complete sintering. However, using SPS complete sintering could be obtained at temperatures between 1300 and 1500°C with no soaking. The SPS technique could consolidate ultrafine eutectic structure from rapid quenched amorphous material, whilst conventional sintering was not successful owing to grain growth. A combination of rapid quenching and SPS resulted in an ultrafine eutectic Al_2O_3–$GdAlO_3$ structure. *BCT/0444*

Keywords: Amorphous phase, Eutectic structure, Rapid quenching, Spark plasma sintering.

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INTRODUCTION

Directionally solidified oxide materials have drawn strong research interest because of their electrical, magnetic and mechanical properties.[1] The microstructures of eutectic materials are quite different from those of ordinary materials.[2] The binary Al_2O_3–Gd_2O_3 system has a characteristic microstructure and superior mechanical properties. Its most remarkable property is its high strength at 1575°C.[3] The properties of the binary system may depend on the scale of the eutectic structure. The eutectic structure is expected to transform from a molten phase with the eutectic composition.

Precipitation from a molten phase can occur from the composition shift near the precipitate. Such composition shifts near the precipitate are diluted by diffusion in the molten phase. Thus the diffusion process in the molten phase might be increased, slowing the transition transformation process, and hindering the process of microstructural refinement.

The focus of the present study is on characterising the processing of the fine eutectic structure, which is transformed from the solid phase of the binary system. Assuming that eutectic composition in the amorphous phase is heated, a precipitate with similar microstructural evolution is expected with a very fine eutectic microstructure. In this case, the diffusion rate in the solid amorphous phase is decreased as a result of the composition shift in the amorphous phase, which impairs the dilution process. A very fine eutectic structure could therefore be expected and was successfully produced from a binary Al_2O_3–Gd_2O_3 system.

EXPERIMENTAL PROCEDURES

The raw materials were powders of Al_2O_3 (99·99%, Sumitomo Chemical, Japan) and Gd_2O_3 (99·99%, Santoku Metal Industry, Japan) with unknown particle sizes. The mixture was melted, so particle sizes were not measured.

In the binary Gd_2O_3–Al_2O_3 system (Fig. 1), grey lines indicate equilibrium. When the liquid of the eutectic composition was cooled, a product of $GdAlO_3$ and Al_2O_3 was crystallised with the eutectic structure of $Gd_3Al_5O_{12}$.[4] Thus the actual behaviour of the system is described by the solid line.

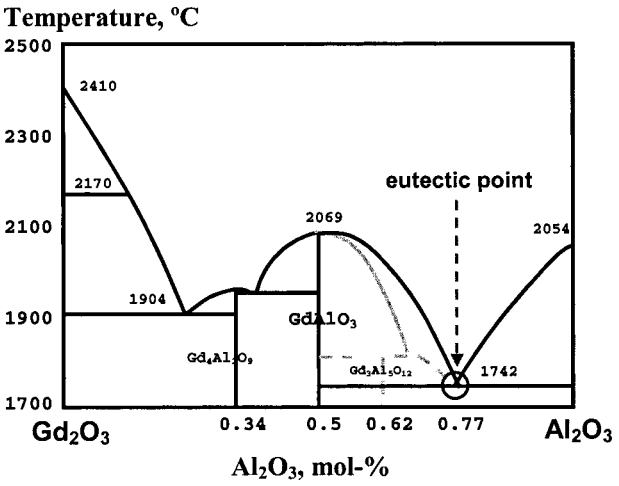
For traditional eutectoid formation, a rod shaped powder compact formed from a mixture of Gd_2O_3 and Al_2O_3 was calcined at 1000°C for 60 min, and melted by arc discharge to produce a solid eutectic composite. The top of the rod was melted by arc discharge, and the discharge was turned off to produce 'slow cooled' samples. 'Rapid cooling' was performed by quenching the droplet between rotating aluminium rollers to form an amorphous film. This rapid quenching technique[5] is shown schematically in Fig. 2.

Microstructures of cross-sections of slow cooled and rapid cooled samples are shown in Fig. 3. The rapid cooled microstructure has much smaller crystal size than after slow cooling. The translucent amorphous film formed in the rapid quenching technique was ground before sintering.

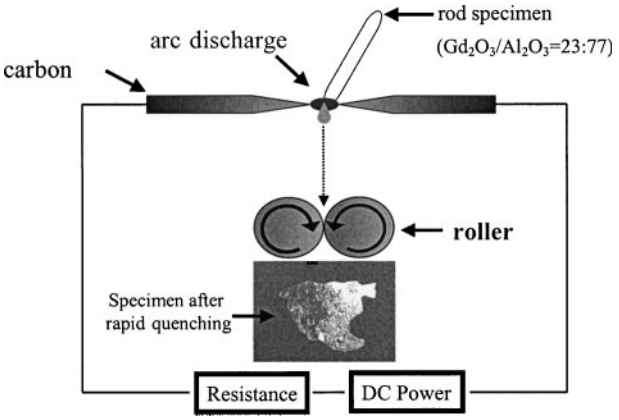
For complete sintering, conventional isostatic sintering was performed above 1600°C for 24 h. Using SPS, however, sintering conditions ranged from 1300 to 1500°C with no soaking time, i.e. sintering was much quicker and at a lower temperature than with conventional sintering. Using the SPS technique (Fig. 4), with its advantages of low sintering temperature and short sintering time, the production of a sintered body with a very fine eutectic structure was expected from the rapid quenched amorphous material.[6]

RESULTS AND DISCUSSION

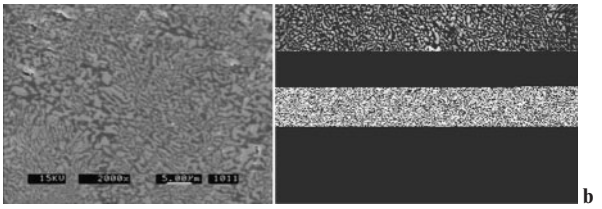
Cross-sectional micrographs showed microstructures with features several micrometres in size in both slow and rapid cooled samples. The XRD pattern of the film formed by rapid quenching was amorphous (Fig. 5). SEM observation of film cross-sections, indicated by the line, which was moulded with epoxy resin, revealed no eutectic structure.



1 Phase diagram of binary Gd_2O_3–Al_2O_3 system



2 Schematic diagram of combined arc discharge and rapid quenching technique



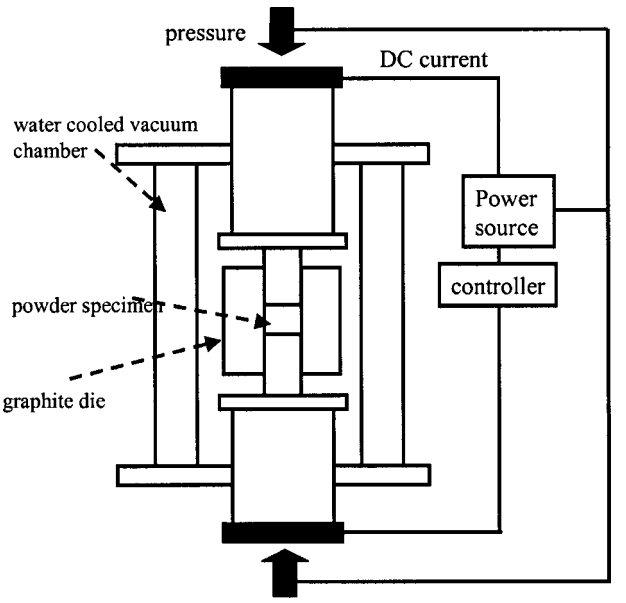
3 SEM micrographs showing microstructures after *a* slow cooling and *b* rapid cooling

Further heat treatment might result in eutectic precipitation.

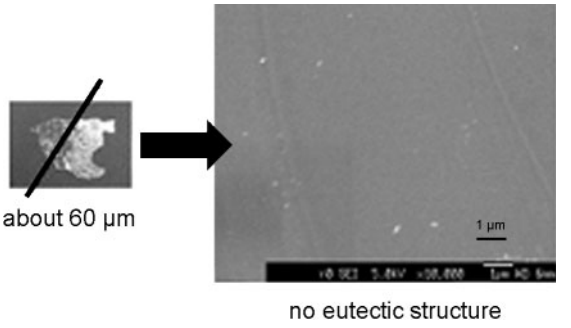
XRD patterns of rapid quenched materials after heating at 1200 and 1300°C for 30 min are shown in Fig. 6. The heat treated materials showed crystalline phase peaks. At 1200°C, Al_2O_3 phase was not detected probably because the peak strength of Al_2O_3 is weak. The diffraction peak for Al_2O_3 is so weak in the sample at 1300°C that the atomic scattering factor of Al is much smaller than that of Gd.

Figure 7 compares slow cooled material and material precipitated from the amorphous phase. The two SEM images on the right show structures from amorphous phase produced by rapid quenching. With the same magnification as the slow cooled material, eutectic structure was not observed, but higher magnification revealed ultrafine eutectic structure.

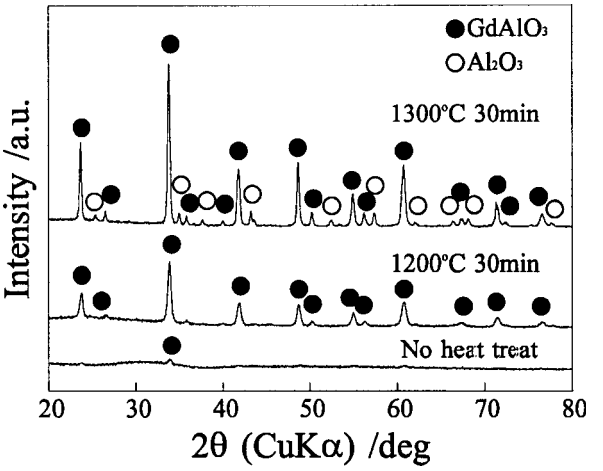
An amorphous powder with a particle size of 2–20 μm, ground from the rapid quenched material, was used to fabricate a bulk specimen by conventional sintering for 24 h at a heating rate of 10 K min^{-1}. The specimen was 12 mm in diameter and 1·5–2·0 mm thick. Below 1500°C, a



4 Spark plasma sintering apparatus



5 SEM micrograph showing microstructure of film formed by rapid quenching

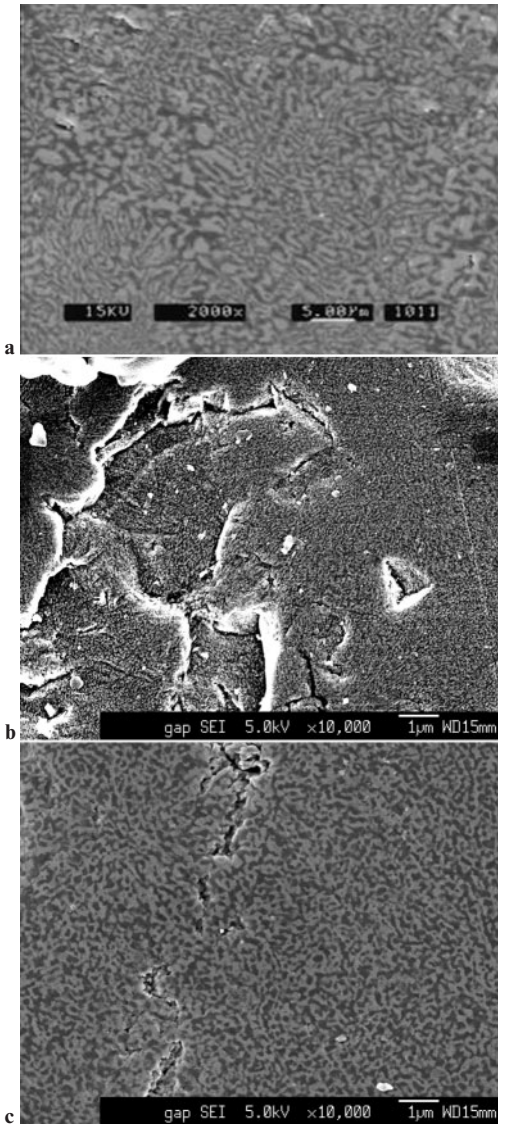


6 XRD patterns of rapid quenched materials sintered at 1200 and 1300°C for 30 min

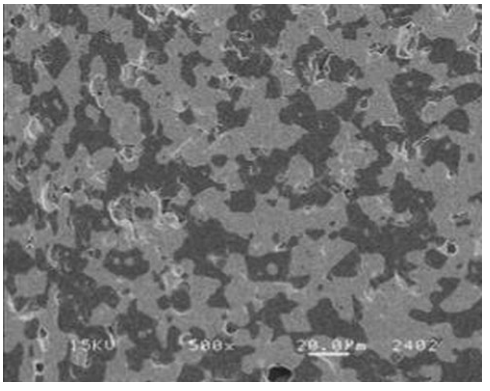
sintered body was not available for measurement of sintered density.

In Fig. 8, the microstructure of material conventionally sintered at 1600°C for 24 h from rapid quenched powder is shown. Grain growth was significant, with a final size of about 50 to 100 μm, and the material could not be fully sintered.

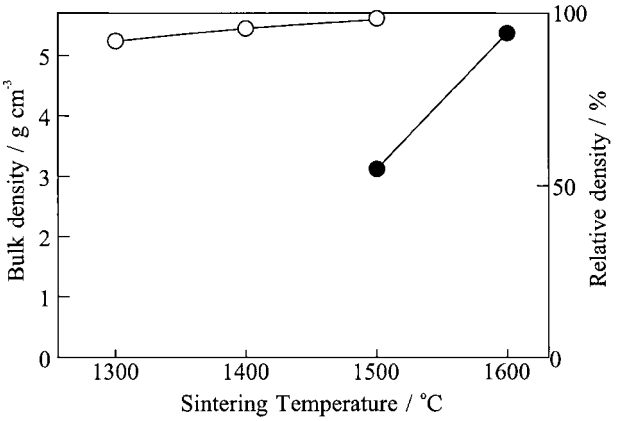
Figure 9 presents the relationship between density and sintering temperature for samples consolidated by SPS at



7 SEM micrographs comparing microstructure of *a* slow cooled sample, and of material precipitated from amorphous phase by rapid quenching after heating at *b* 1200°C and *c* 1300°C for 30 min: ultrafine eutectic structure visible in *b*,*c*



8 SEM micrograph showing microstructure of material conventionally sintered at 1600°C for 24 h: light areas are Gd rich phase ($GdAlO_3$) and dark areas Al rich (Al_2O_3)

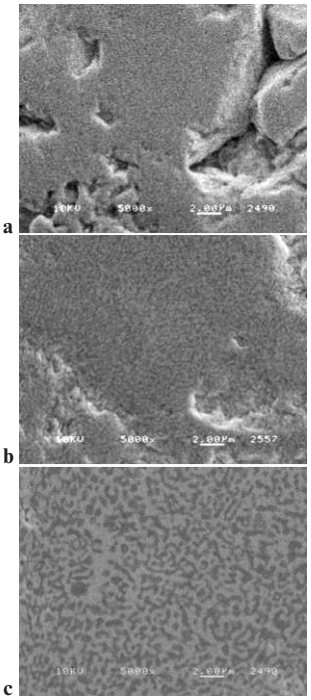


9 Variation of density with sintering temperature for samples sintered at 1300, 1400 and 1500°C by SPS with no soaking time: comparative data shown for conventional sintering at 1500 and 1600°C

1300, 1400 and 1500°C with no soaking time. The specimens were 15 mm in diameter and 1·5–2·0 mm thick. Highly sintered materials with 99% relative density could be obtained at 1500°C, a significantly lower temperature than with the conventional sintering method.

The SEM micrographs in Fig. 10 show significant microstructural change with increasing sintering temperature from 1300 to1500°C. An ultrafine microstructure is established after sintering at 1500°C, which looks like a very typical microstructure of binary Al_2O_3–$GdAlO_3$.[1] Comparing conventional sintering at 1600°C for 24 h (Fig. 8) and SPS at 1500°C with no soaking time (Fig. 10), a typical ultrafine eutectic Al_2O_3–$GdAlO_3$ microstructure may be observed only in the SPS sample.

It is evident that a proper combination of rapid quenching and SPS can synthesise a sintered material with ultrafine and dense eutectic structure. An Al_2O_3–$GdAlO_3$ sintered body with eutectic microstructure can be



10 SEM micrographs of samples sintered at *a* 1300, *b* 1400, *c* 1500°C by SPS

successfully consolidated from amorphous state material by rapid quenching and the SPS technique.

CONCLUSIONS

After melting and rapid quenching a mixture of Al_2O_3–$GdAlO_3$, the result is an amorphous film. Using spark plasma sintering, this ground amorphous powder was consolidated into a dense sintered body with a typical ultrafine Al_2O_3–$GdAlO_3$ eutectic structure. An ultrafine eutectic structure can be obtained by heat treatment of amorphous material produced by rapid quenching. Sintered material with ultrafine and dense eutectic structure was obtained by an appropriate combination of rapid quenching and SPS at lower temperature and more quickly than by conventional sintering.

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