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HR-TEM and FIB-SEM characterization of formation of eutectic-like structure from amorphous $GdAlO_3$–Al_2O_3 system

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Abstract: The crystallization process of the eutectic composition of $GdAlO_3$−Al_2O_3 from the amorphous phase prepared by rapid-quenching of melt that leads to the formation of a cantaloupe skin-like microstructure was investigated using focused ion-beam scanning electron microscopy (FIB-SEM) and high-resolution transmission electron microscopy (HR-TEM). The amorphous films were heat-treated at temperatures between 1000 °C and 1500 °C for up to 30 min to form the eutectic phases of $GdAlO_3$ and Al_2O_3. The $GdAlO_3$ and Al_2O_3 crystal phases that formed from the amorphous phase were identified by FIB-SEM and HR-TEM. Both components began to crystallize and grow from the amorphous phase separately at different temperatures. The formation process of these crystal phases was different from that of the ordinary eutectic microstructure solidified from the $GdAlO_3$−Al_2O_3 system. Therefore, the observed structure is termed "eutectic-like" for distinction. The microstructures formed from the amorphous phases at sufficiently high temperatures consisted of ultra-fine microstructures of individually crystallized components and were similar to ordinary eutectic microstructures. By heat-treating the amorphous films at 1500 °C for either 2 min, 8 min or 30 min, the ultra-fine components of $GdAlO_3$ and Al_2O_3 were found to crystallize following a eutectic-like stage after 8 min of heat treatment.
Key words: eutectic; amorphous; $GdAlO_3$−Al_2O_3; eutectic-like; HR-TEM; FIB-SEM; Crystallization

1 Introduction

One solution for realizing the higher operating temperatures of the next-generation turbo-blades operating at gas temperatures as high as 1600 °C is by way of an in-situ development of oxide-based ceramic composites by directed solidification of melt having a eutectic composition. The resulting structure is a single-crystal, three-dimensional lattice with no grain boundary, i.e., a material with coherent interfaces and no vitreous phase.

This material is known to exhibit a mechanical strength that is nearly constant up to the melting temperature unlike polycrystalline ceramics that gradually looses strength with temperature. It is also known that the rupture stress in this material can be increased by reducing the size of the constituent phases without reducing the creep strength. This is the case of perovskite-structured oxides having a high temperature plasticity in a eutectic system (melting at 1700−1900 °C) that combines alumina with a rare earth oxide having either a perovskite ($XAlO_3$; X: Gd, Eu) or a garnet ($Y_3Al_5O_{12}$; Y: Er, Dy, Yb) structure. Recently, eutectic ceramics have been considered to be a candidate not only as a heat-resistant material but also as a functional material in various other applications, such as thermophotovoltaic (TPV) generation [1−3] and porous materials technology [4−6].

Although the formation process of the ordinary eutectic microstructures by cooling the eutectic melts has been well-known, the formation process of the eutectic-like microstructures from an amorphous phase has not so far been elucidated in our previous work [7,8].

The current study focuses on the focused ion-beam scanning electron microscopy (FIB-SEM) and high-resolution transmission electron microscopy (HR-TEM) characterization of the crystallization process of the $GdAlO_3$−Al_2O_3 binary eutectic system [9−12]. We characterized the ultra-fine eutectic microstructure processed both from the eutectic melt and from the amorphous phase.

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2 Experimental

2.1 Sample preparation

The raw materials were the powders of Al_2O_3 (99%, Kanto Chemical, Japan) and Gd_2O_3 (99.95%, Kanto Chemical, Japan). The powders in the eutectic composition 23% (mole fraction) of Gd_2O_3 and 77% (mole fraction) Al_2O_3 were processed using a mortar and pestle in a 3% (mass fraction) polyvinyl alcohol (Waco Pure Chemical Industries, Japan; degree of polymerization: ~500) solution. The mixture was pressed into a rod-shaped compact and was calcined at 1300 °C for 1 h.

The top of the sintered rod was melted by arc discharge; the slow-cooled samples of solid eutectic composite were produced after turning off the discharge. The sample was rapidly cooled by quenching the droplet between rotating aluminum rollers to form an amorphous film. The amorphous films were obtained from heating between 1000 °C and 1600 °C for 30 min to form a eutectic phase of $GdAlO_3$ and Al_2O_3. The films were heated at 1500 °C for various periods ranging from 30 s to 30 min for the investigation of the crystallization process of the ultra-fine microstructures in the eutectic-like composite of $GdAlO_3$ and Al_2O_3.

2.2 Specimen preparation and characterization by FIB-SEM and HR-TEM

For the FIB-SEM analysis, a SEIKO FIB/SEM Hybrid System SMI 3050SE was operated with the acceleration voltage of 30 kV, the beam current of 90 pA, and the beam size of 22 nm. An H-bar and lift-out technique was employed to prepare the TEM specimens by FIB milling. For all the specimens, the acceleration voltage of 30 kV and the beam current of 90 pA were applied. The TEM was a JEOL JEM−2100F and was operated at 200 kV at a point resolution 0.19 nm for the high resolution characterization.

3 Results and discussion

Figure 1 shows the HR-TEM analysis of a rapidly quenched specimen and heat-treated specimens of the Gd_2O_3−Al_2O_3 eutectic composition, sintered at 1000 °C for 30 min. The rapidly quenched specimen was found to be mostly amorphous, as shown in Fig. 1, establishing that an amorphous film can be successfully prepared by rapidly quenching the Gd_2O_3−Al_2O_3 eutectic melt.

The HR-TEM analysis of the lattice image of the eutectic 23%Gd_2O_3−77%Al_2O_3 after being sintered at 1000 °C for 30 min reveals a mixed phase of a crystalline region (dark) and a noncrystalline region (bright), as shown in Fig. 1. The dark, crystalline regions exhibit lattices, as indicated by *A*. The bright, noncrystalline regions have no order in atomic arrangement, as indicated by *B*.

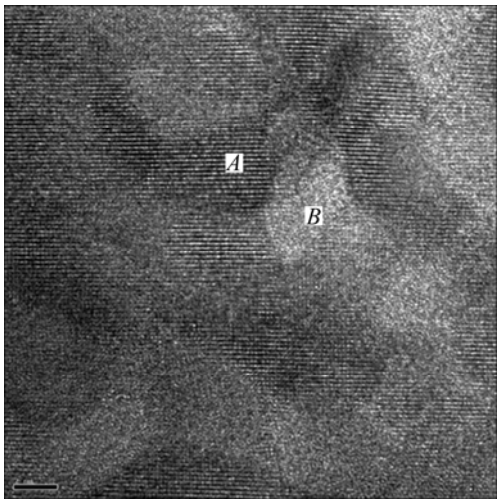

Fig. 1 HR-TEM analysis of lattice image of eutectic 23%Gd_2O_3−77%Al_2O_3 sintered at 1000 °C for 30 min

A low magnification image of the region analyzed by EDS is shown in Fig. 2(a) and the qualitative data for the region are shown in Fig. 2(b) with the peaks for $GdAlO_3$ identified.

For the specimen sintered at 1300 °C for 30 s, dark and bright regions coexist in the TEM image at a low magnification, as shown in Fig. 3(a), in which the dark region is the crystalline Al_2O_3 and the bright region is the crystalline $GdAlO_3$. A high magnification image of $GdAlO_3$ from a bright area is shown in Fig. 3(b), and a high magnification image of Al_2O_3 from a dark area is shown in Fig. 3(c).

The dark areas (Al_2O_3) and the bright areas ($GdAlO_3$) appear to be in an initial or intermediate stage of crystallization, which is confirmed by the TEM analysis of the sample sintered at 1300 °C for 30 s, as shown Fig. 4.

In Figs. 5−7, the eutectic composites sintered at 1500 °C for 2 min, 8 min, or 30 min are compared with the crystalline Al_2O_3 appearing dark and the crystalline $GdAlO_3$ appearing bright, analyzed earlier by FIB-SEM and HR-TEM.

In Fig. 5, the bright area is $GdAlO_3$ and the dark area is Al_2O_3. Most of the Al_2O_3 component is crystallized from the amorphous phase along with $GdAlO_3$ after a heat treatment at 1500 °C for 2 min, as shown in Fig. 5, which can be explained well, based on the previous results by KAKEGAWA et al [13]. The completely crystallized components appeared after a heat treatment of 8 min, as shown in Fig. 6. A similar crystallized microstructure is present in the sample sintered for 30 min according to the FIB-SEM micrographs that

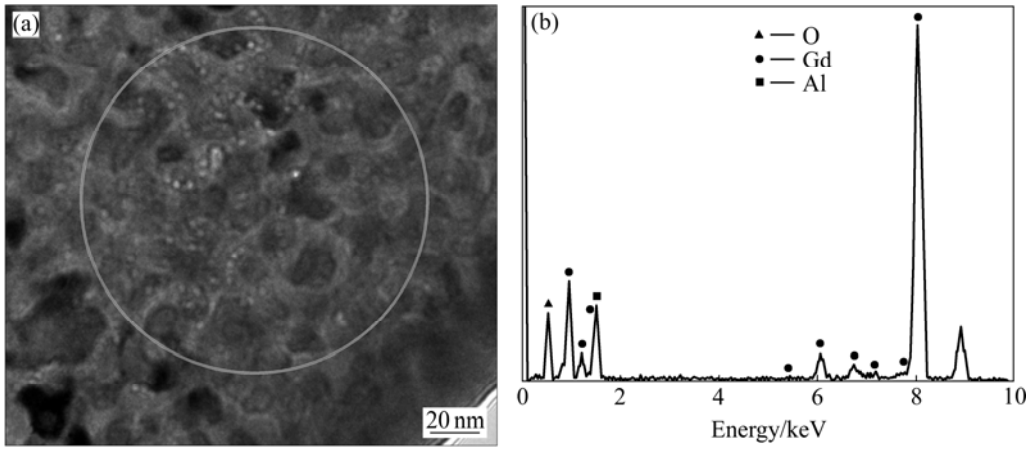

Fig. 2 Region analyzed by EDS (a) and qualitative data with peaks for $GdAlO_3$ identified (b)

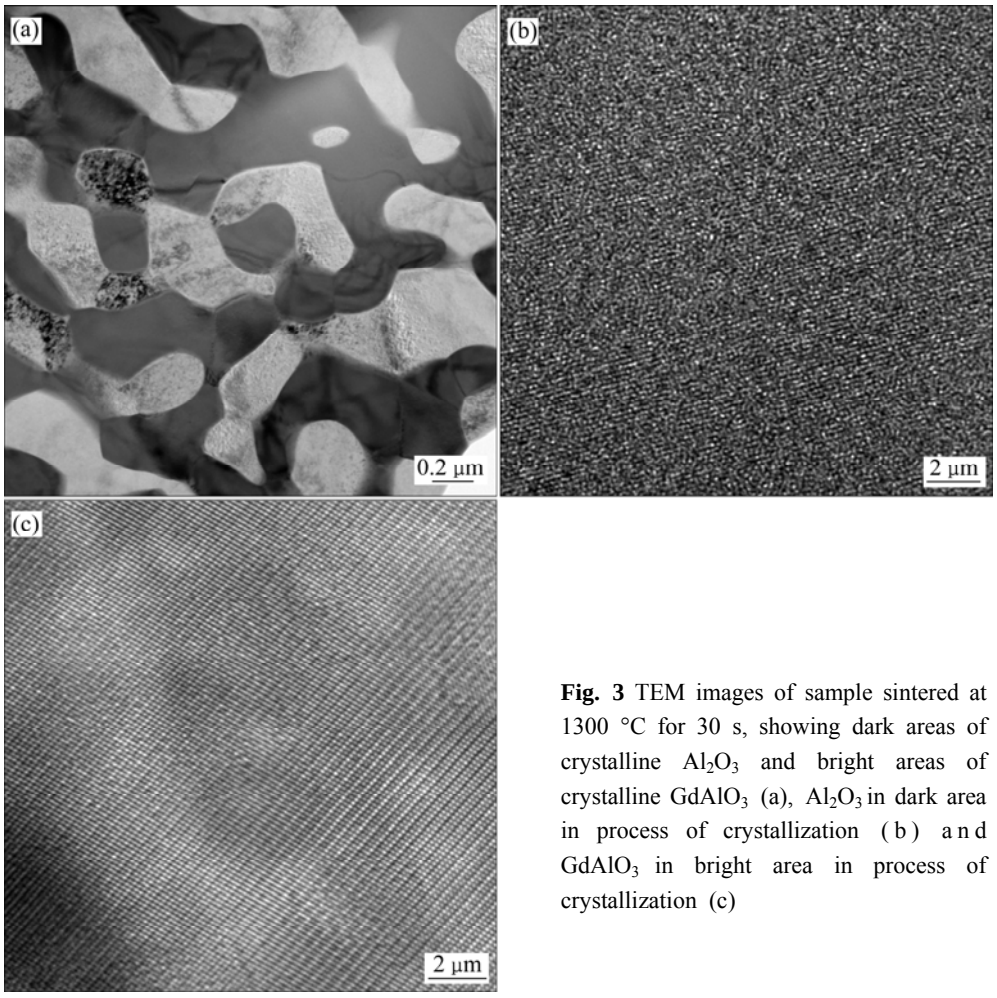

Fig. 3 TEM images of sample sintered at 1300 °C for 30 s, showing dark areas of crystalline Al_2O_3 and bright areas of crystalline $GdAlO_3$ (a), Al_2O_3 in dark area in process of crystallization (b) and $GdAlO_3$ in bright area in process of crystallization (c)

show apparently fine, eutectic-like microstructures. These microstructures having an appearance of a cantaloupe skin are intertwined $GdAlO_3$ and Al_2O_3 crystals, as confirmed by the TEM analysis presented in Fig. 7. It is confirmed that the crystallization process of Gd_2O_3−Al_2O_3 completes after being sintered at 1500 °C for 8 min.

The formation process of eutectic-like microstructures from the amorphous phase is presumably different from that of an ordinary eutectic microstructure, as mentioned in Refs. [7,8]. In general, an ordinary eutectic microstructure is formed by simultaneously crystallizing individual components at a eutectic temperature. In contrast, the crystallization and the growth of the $GdAlO_3$ and Al_2O_3 components from the amorphous phase begin separately at different heating temperatures. In the case of

Fig. 4 TEM analysis of sample sintered at 1300 °C for 30 s

low temperatures, in which the Al_2O_3 component cannot crystallize, the microstructure consists of round-shaped $GdAlO_3$ crystals and the amorphous Al_2O_3 phase, as proved by KAKEGAWA et al [13].

When one component nucleates and grows, the component is consumed during the crystallization and its concentration is lowered. As a result, the crystal growth slows down. However, there is a directional fluctuation in the crystal growth [14,15]. If the growth occurs on a convex part of the crystal, the concentration of its component in the surrounding region increases and the crystal can grow further. In addition, the crystal grows while releasing the latent heat and enhancing the growth. In this mechanism, the crystal will not grow into a sphere but into a long and thin shape. There is also a directional fluctuation of the component in the amorphous phase that

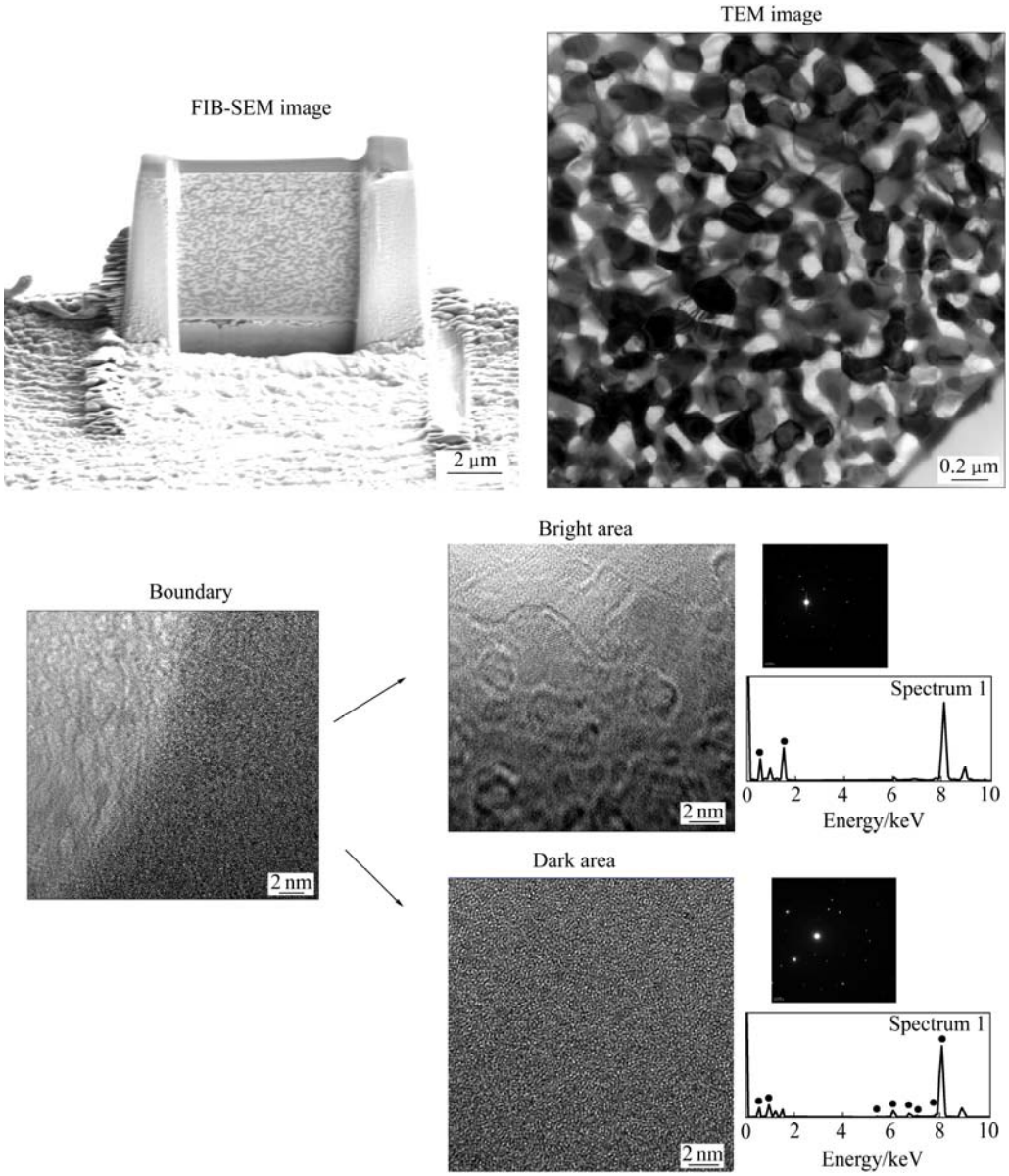

Fig. 5 FIB-SEM and HR-TEM microstructures of eutectic composites sintered at 1500 °C for 2 min (Crystalline Al_2O_3 appears dark and crystalline $GdAlO_3$ appears bright)

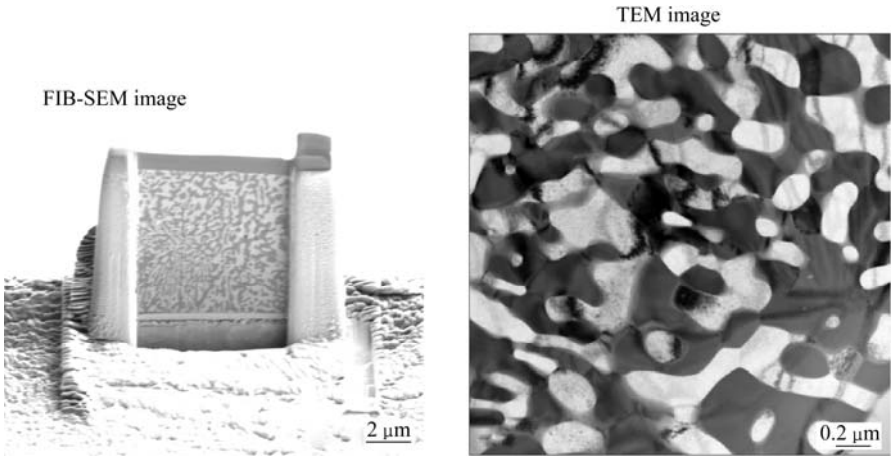

Fig. 6 FIB-SEM and HR-TEM microstructures of eutectic composites sintered at 1500 °C for 8 min (Crystalline Al_2O_3 appears dark and crystalline $GdAlO_3$ appears bright)

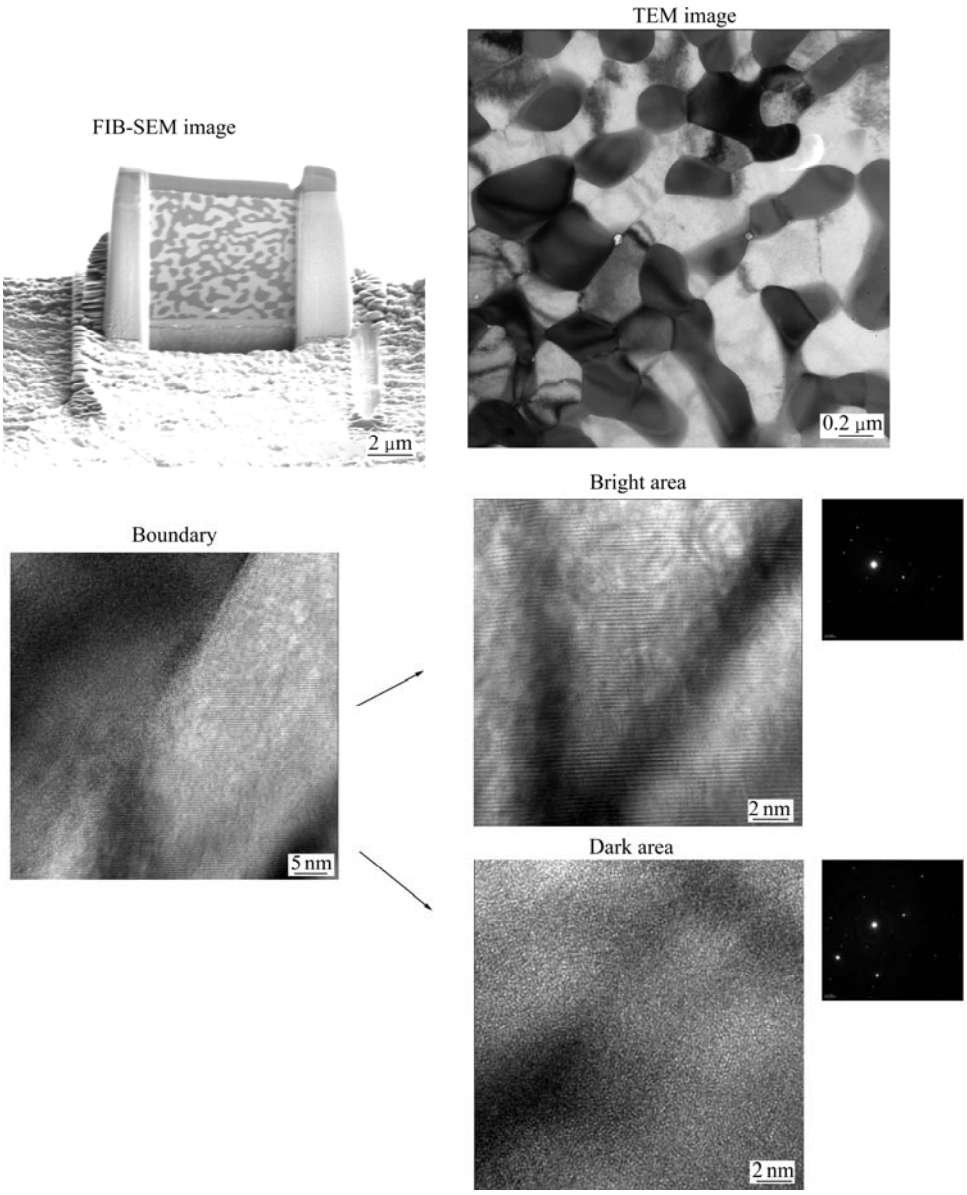

Fig. 7 FIB-SEM and HR-TEM microstructures of eutectic composites sintered at 1500 °C for 30 min (Crystalline Al_2O_3 appears dark and crystalline $GdAlO_3$ appears bright)

makes the long thin crystals to intertwine when they meet. GAP crystallizes in this way first and then Al_2O_3 crystallizes later.

The above explains why the observed microstructure is different from an ordinary eutectic microstructure. The fine, eutectic-like microstructure cannot materialize from the crystallization of a single component. As the heating temperature reaches an appropriate temperature, the Al_2O_3 component can crystallize along with the remaining amorphous Al_2O_3 phase. When heat treated at 1500 °C, the Al_2O_3 component begins to crystallize immediately along with the $GdAlO_3$ component and forms a fine eutectic-like microstructure with a cantaloupe skin appearance, as shown in Fig. 5.

4 Conclusions

An ultra-fine microstructure of $GdAlO_3$ and Al_2O_3 is formed from the amorphous phase following an eutectic-like stage by simultaneously crystallizing both the components at a sufficiently high temperature of 1500 °C for 8 min. The eutectic-like microstructure formed from the amorphous phase is very fine in texture compared with an ordinary eutectic microstructure.

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REFERENCES

[1] AMANO T, YAMAGUCHI M. Analysis of energy balance of electricity and heat generated by TPV generators [J]. Solar Energy Mater Solar Cells, 2001, 66: 579−583.

[2] SAI H, YUGAMI H, NAKAMURA K, NAKAGAWA N, OHTSUBO H, MARUYAMA S. Selective emission of $Al_2O_3/Er_3Al_5O_{12}$ eutectic composite for thermophotovoltaic generation of electricity [J]. Jpn J Appl Phys, 2000, 39: 1957−1961.

[3] NAKAGAWA N, OHTSUBO H, WAKU Y, YUGAMI H. Thermal emission properties of $Al_2O_3/Er_3Al_5O_{12}$ eutectic ceramics [J]. J Eur Ceram Soc, 2005, 25: 1285−1291.

[4] LEE J H, YOSHIKAWA A, FUKUDA T. Growth of $MgAl_2O_4$/MgO eutectic crystals by the micro-pulling-down method and its characterization [J]. J Eur Ceram Soc, 2005, 25: 1351−1354.

[5] DYNYS F W, SAYIR A. Self assemble silicide architectures by directional solidification [J]. J Eur Ceram Soc, 2005, 25: 1293−1299.

[6] LARREA A, ORERA V M. Porous crystal structures obtained from directionally solidified eutectic precursors [J]. J Cryst Growth, 2007, 300: 387−393.

[7] HARADA Y, UEKAWA N, KOJIMA T, KAKEGAWA K. Fabrication of $Y_3Al_5O_{12}$−Al_2O_3 eutectic materials having ultra fine microstructure [J]. J Eur Ceram Soc, 2008, 28: 235−240.

[8] HARADA Y, UEKAWA N, KOJIMA T, KAKEGAWA K. Formation of ultrafine eutectic-like microstructures of various rare earth oxide-Al_2O_3 systems by use of amorphous phases [J]. J Mater Res, 2008, 23: 3396−3402.

[9] WAKU Y, NAKAGAWA N, WAKAMOTO T, OHTSUBO H, SHIMIZU K, KOHTOKU Y. A ductile ceramic eutectic composite with high strength at 1873 K [J]. Nature, 1997, 389: 49−52.

[10] WAKU Y, OHTSUBO H, NAKAGAWA N, KOHTOKU Y. Sapphire matrix composites reinforced with single crystal YAG phases [J]. J Mater Sci, 1996, 31: 4663−4670.

[11] WAKU Y, NAKAGAWA N, WAKAMOTO T, OHTSUBO H, SHIMIZU K, KOHTOKU Y. High-temperature strength and thermal stability of a unidirectionally solidified Al_2O_3/YAG eutectic composite [J]. J Mater Sci, 1998, 33: 1217−1225.

[12] WAKU Y, NAKAGAWA N, WAKAMOTO T, OHTSUBO H, SHIMIZU K, KOHTOKU Y. Fabrication of $Y_3Al_5O_{12}$−Al_2O_3 eutectic materials having ultra fine microstructure [J]. J Mater Sci, 1998, 33: 4943−4951.

[13] HAN Y H, NAGATA M, UEKAWA N, KAKEGAWA K. Eutectic Al_2O_3–$GdAlO_3$ composite consolidated by combined rapid quenching and spark plasma sintering technique [J]. Brit Ceram Trans, 2004, 103: 219−222.

[14] LEE J H, YOSHIKAWA A, DURBIN S D, YOON D H, FUKUDA T, WAKU Y. Microstructure of Al_2O_3/ZrO_2 eutectic fibers grown by the micro-pulling down method [J]. J Cryst Growth, 2001, 222: 791−796.

[15] LEE J H, YOSHIKAWA A, KAIDEN H, LEBBOU K, FUKUDA T, YOON D H, WAKU Y. Microstructure of Y_2O_3 doped Al_2O_3/ZrO_2 eutectic fibers grown by the micro-pulling-down method [J]. J Cryst Growth, 2001, 231: 179−185.

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