LASER REMELTED $AL_2O_3/ER_3AL_5O_{12}$ EUTECTIC *IN SITU* COMPOSTE CERAMICS FOR HIGH TEMPERATURE THERMAL EMISSION APPLICATIONS

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1 Introduction

The strong demand for high temperature structural materials is the major motivation for the continuous development of new materials based on muti-compoment compounds, since some of these compounds exhibit an interesting combination of high-temperature strength and good oxidation resistance. *In situ* composite material systems combine two or more phases homogeneously grown from melt to well optimize the overall material properties and performance, and consequently, attracting much more attention in the past few years [1-2]. Directional solidification and single crystal growth technique can obtain directional and single crystal solidification microstructure, extremely improving the properties of materials. Thus, many efforts have been devoted to controlling and optimizing the microstructure by directional solidification methods [3-4].

In the field of composite ceramics, recent developmental directionally solidified Al_2O_3-based eutectic *in situ* composite presents superior creep resistance, oxidation resistance and attractive high temperature strength retention [5,6], considering as the promising candidate for high-temperature applications above 1650℃. As a result, various preparation methods of oxide ceramics based on directional solidification have been developed [7-9]. However, most of previous researches were aimed only to structural materials for high temperature application [10-12]. Because the directionally solidified eutectics generally present refined microstructure aligned along the growth direction, they also possess great potential to the functional applications. In the application field for these materials, a specific feature of interest with the rare-earth oxides, for example, Er_2O_3, Yb_2O_3 and Ho_2O_3 have strong band emission, which ranges from the visible to the nearinfrared wavelength region. The bands permit strong thermal excitation at high temperatures, allowing their use as selective emitters applied in thermophotovoltaic (TPV) generation systems [13]. As compared with conventional generation systems, TPV generation systems have advantageous of no moving parts, high power density, wide-ranging heat source and low costs, which have been studied as one of the new generation systems of electricity. Therefore, development of high temperature thermal emission materials for thermophoto-voltaic generation appilications is of current interest for a number of technology sectors.

In the present study, we focus on the directionally solidified $Al_2O_3/Er_3Al_5O_{12}$(EAG) eutectic *in situ* composite ceramic to investigate it as potential selective emitter for TPV systems. The Al_2O_3/EAG eutectic ceramic is rapidly prepared by laser zone remelting technique which allows no need of crucible, very high melting temperature, large thermal temperature gradient (>10^4 K/cm) and high growth rates [14]. The processing method and the main appearance of this eutectic ceramic are investigated. The effects of rapid solidification on the microstructure characteristic, the solidification behavior and the emission properties are analyzed.

2 Experimental

2.1 Materials and Specimen Preparation

Starting materials are commercially available Al_2O_3 (99.99%) and Er_2O_3 (99.99%) powders with diameter of 1-2 μm. The powders with eutectic composition (81mol% Al_2O_3 and 19 mol% Er_2O_3) [15] are uniformly mixed by wet ball milling with an aqueous solution of polyvinyl alcohol. The mixed powder is dried at 473K and then pressed into plate (40mm×5mm ×5mm) by uniaxial die pressing for 10 minutes at 25 MPa. The precursor rods are sintered at 1500℃ for 2 hours to increase the density and handle strength. The laser zone remelting method and a5 kW ROFIN-SINAR850 CO_2 laser were used to directionally solidify the eutectic rods in a vacuum chamber, as shown in Fig.1. The sample is moved by the numerically-controlled worktable with 5-axis and 4-direction coupled motion to realize the laser beam scanning along the sample axis. The laser power is 200 W and the stage traveling speed (traverse rate) is established at 800 μm/s.

2.2 Characterization

The laser remelted samples are cut from the transverse and longitudinal cross-section, and prepared by diamond polishing in order to be observed in a field emission scanning electron microscope (FSEM, Supra 55). The phase and composition of the composite are determined by energy disperse spectroscopy (EDS, Oxford) and X-ray diffraction (XRD, Rigakumsg-158) techniques. The emission property is tested by the UV-Vis spectrometer (UV-3150).

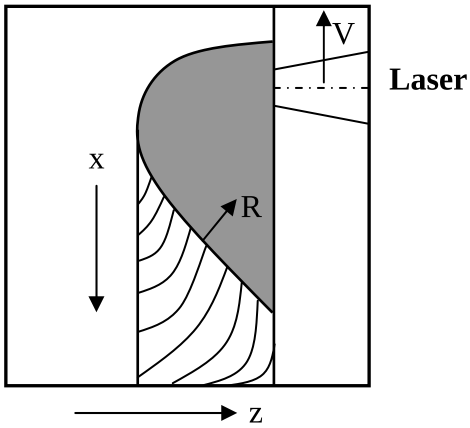

Fig. 1 Schematic diagram of the laser zone remelting for growing ternary eutectic composite. R: solidification direction, V: scanning direction, x, z: worktable moving direction.

3 Results and Discussion

3.1 Microstructure Characteristic

Fig. 2(a) shows the photograph of the as-solidified Al_2O_3/EAG eutectic ceramic plate. The as-solidified eutectic composite presents smooth surfaces with pink color, and contains no pores, cracks and grain boundaries, as shown in Fig. 2(b). There are no bubbles observed in the solidified samples by filling Ar gas during remelting. The thickness of the solidified layer is about 2-4 mm and the density is almost near to the theoretical value (5.4 g/cm^3) of the composite. This indicates that laser zone remelting can achieve full density of the ceramic composite, which is obviously superior than conventional sintering method [16]. The solidified layer thickness is dependent on the laser scanning rate and laser power density.

Fig. 3(a) shows the typical microstructure of the transverse cross-section for the composite. The eutectic microstructure displays a continuous and homogeneous structure with fine entangled eutectic phases in an alternating interpenetrating network of Al_2O_3 (vol. 54%) and $Er_3Al_5O_{12}$ (vol. 46%) of sizes in the submicron range. The dark phase is Al_2O_3, and the grey phase is EAG. No Al_2O_3 solubility in EAG is

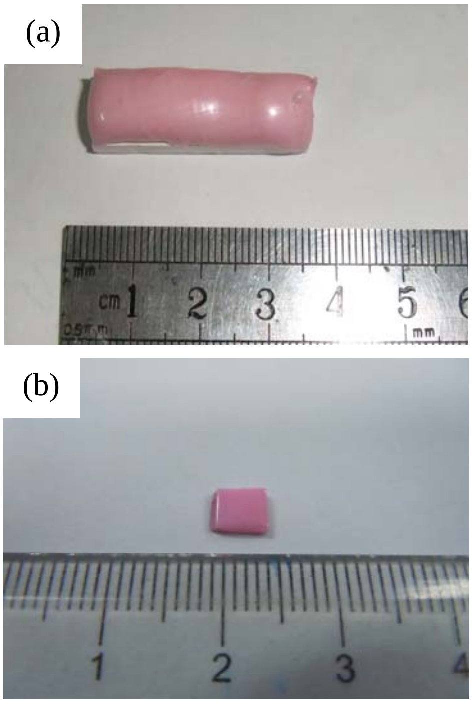

Fig. 2 The macrograph of Al_2O_3/EAG eutectic plate: (a) surface; (b) longitudinal section.

found in the composite determined by XRD and EDS. The eutectic spacing is about 0.1 μm, which much smaller than the results of Nakagawa et al. [13] by Bridgman method (20~30μm) and consequently, improving the properties of the composite. The great refinement of microstructure is mainly contributed to the high temperature gradient and rapid cooling rate. The growth of eutectic interfaces of rapid solidification shows a typical faceted/faceted characteristic. The phase-size is strongly dependent on the laser scanning rate, decreasing at the nanometer range for the samples grown at the highest rate.

Moreover, for comparison, the interface of the solidified layer and unprocessed zone is shown in Fig. 3(b). It can be seen that the un-processed ceramic by laser remelting presents polycrystalline ceramic structure with obvious pores. At the interface between the sintered layer and solidified layer, the coarse primary EAG phases are assembled and gradually are

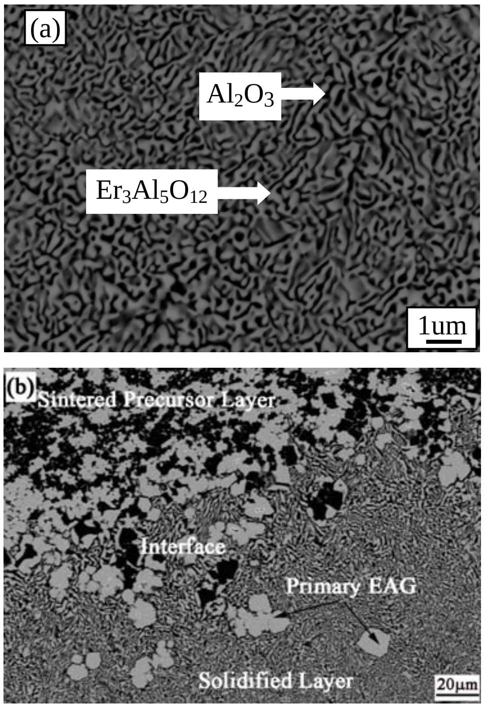

Fig. 3 SEM micrograph showing the near-surface zone of the transverse cross-section of the eutectic $Al_2O_3/Er_3Al_5O_{12}$ grown at laser scanning rate of 800 μm/s (a) and the interface between the solidified layer and sintered precursor layer (b).

branched and refined toward to the solidified layer. The morphology of EAG phases transforms from coarse block to fine lamellae. It means that the growth and evolution of EAG phases basically control the microstructure development of Al_2O_3/EAG eutectic ceramic. Furthermore, the eutectic spacing gradually decreases from the bottom to surface of the solidified layer (Fig.3a and b), which is contributed to rapid increase of solidification rate [14].

3.2 Emission Properties

The emission property is characterized by the absorbance spectrum, as shown in Fig. 4. The result shows that the laser remelted Al_2O_3/EAG eutectic presents strong selective emission bands at wavelength 1.5 μm. In comparison, the laser remelted Al_2O_3/YAG eutectic does not show emission characteristic at any wavelength. This further indicates the produce of emission properties of Al_2O_3/EAG is due to Er^{3+} ion. The wavelength at the energy gap of the GaSb cell is 1.7 μm, as shown by the vertical line in Fig.4. Therefore, the emission bands of this material are basically coincident with the sensitive region of GaSb PV cell, which indicates that the Al_2O_3/EAG eutectic ceramic is one of the promising materials as an emitter material for TPV systems.

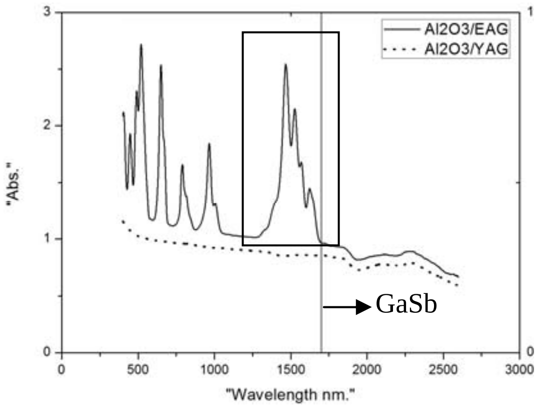

Fig. 4 The absorbance spectrum of laser remelted Al_2O_3/EAG eutectic composite.

4. Conclusions

Directionally solidified Al_2O_3/EAG eutectic ceramic composite is rapidly prepared by laser remelting at high growth rate. The eutectic microstructure presents ultra-fine irregular lamellar structure in the submicron range, which decreases from the bottom to surface of solidification layer. At the wavelength 1.5 μm, the composite shows strong selective emission bands, which can be matched with GaSb PV cell as one of the promising emitter materials used in TPV systems.

Acknowledgments

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References

[1] B. P. Bewlay and M. R. Jackson, “High-temperature in situ composites: processing and properties”. Comprehensive Composite Materials, Chapter 3.22, pp 579-615, 2003.

[2] V. M. Orera, R. I. Merino, J. A. Pardo, A. Larrea, J. I. Peña, C. González, P. Poza, J. Y. Pastor and J. Llorca, “Microstructure and physical properties of some oxide eutectic composites processed by directional solidification”. Acta. Mater., Vol. 48, pp 4683-4689, 2000.

[3] J. Zhang, H. Su, K. Song, L. Liu and H.Z. Fu, “Microstructure, growth mechanism and mechanical property of Al_2O_3-based eutectic ceramic in situ composites”. J. Eur. Ceram. Soc., Vol. 31, pp 1191-1198, 2011.

[4] M. Asta, C. Beckermann, A. Karma, W. Kurz, R. Napolitano, M. Plapp, G. Purdy, M. Rappaz and R. Trivedi, “Solidification microstructures and solid-state parallels: recent developments, future directions”. Acta Mater., Vol. 57, pp 941-971 2009.

[5] J. Llorca and V. M. Orera, “Directionally solidified eutectic ceramic oxides”. Prog. Mater. Sci., Vol. 51, pp 711-809, 2006.

[6] L. Mazerolles, L. Perriere, S. Lartigue-Korinek, N. Piquet and M. Parlier, “Microstructures, crystallography of interfaces, and creep behavior of melt-growth composites”. J. Eur. Ceram. Soc., Vol.28, pp 2301-2308, 2008.

[7] J. H. Lee, A. Yoshikawa, S. D. Durbin, D. H. Yoon, T. Fukuda and Y. Waku, “Microstructure of Al_2O_3/ZrO_2 eutectic fibers grown by the micro-pulling down method”. J. Cryst. Growth, Vol. 222, pp 791-796, 2001.

[8] H. Su, J. Zhang, Y.F, Deng, L. Liu and H.Z. Fu, “A modified preparation technique and characterization of directionally solidified $Al_2O_3/Y_3Al_5O_{12}$ eutectic in situ composites”. Scr. Mater., Vol. 60, pp 362-365, 2009.

[9] P. B. Oliete, J. I. Peña, A. Larrea, V. M. Orera, J. LLorca, J. Y. Pastor, A. Martín and J. Segurado, "Ultra-high-strength nanofibrillar Al_2O_3-YAG-YSZ eutectics". Adv. Mater., Vol. 19, pp 2313-2318, 2007.

[10] K. Hirano, "Application of eutectic composites to gas turbine system and fundamental fracture properties up to 1700°C". J. Eur. Ceram. Soc., Vol. 25, pp 1191-1199, 2005.

[11] J. I. Peña, M. Larsson, R. I. Merino, I. de Francisco, V. M. Orera, J. LLorca, J. Y. Pastor, A. Martín and J. Segurado. "Processing, microstructure and mechanical properties of directionally solidified Al_2O_3-$Y_3Al_5O_{12}$-ZrO_2 ternary eutectics". J. Eur. Ceram. Soc., Vol. 26, pp 3113-3121, 2006.

[12] H.J. Su, J. Zhang, L. Liu and H.Z. Fu, "Microstructure and mechanical properties of a directionally solidified $Al_2O_3/Y_3Al_5O_{12}/ZrO_2$ hypo-eutectic in-situ composite". Comp. Sci. Tech., Vol. 69, pp 2657-2667, 2009.

[13] N. Nakagawa, H. Ohtsubo, Y. Waku and H. Yugami, "Thermal emission properties of $Al_2O_3/Er_3Al_5O_{12}$ eutectic ceramics". J. Eur. Ceram. Soc., Vol. 25 pp 1285-1291, 2005.

[14] H.J. Su, J. Zhang, J.Z. Yu, L. Liu and H.Z. Fu, "Directional solidification and microstructural development of $Al_2O_3/GdAlO_3$ eutectic ceramic in situ composite under rapid growth conditions". J. Alloy Compd., Vol. 509, pp 4420-4425, 2011.

[15] M. Mizuno, "Phase diagrams of the systems Al_2O_3-Ho_2O_3 and Al_2O_3-Er_2O_3". Yogyo Kyokai Shi, Vol. 87, pp 405-412, 1979.

[16] Y. Waku, N. Nakagawa, H. Ohtsubo, A. Mitani and K. Shimizu, "Fracture and deformation behaviour of melt growth composites at very high temperatures". J. Mater. Sci. Vol. 36, pp 1585-1594, 2001.

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