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$Al_2O_3/GdAlO_3$ eutectic fibers of high modulus of rupture produced by the laser heated pedestal growth technique

Igor Studart Medeiros · Erika R. M. Andreeta · Antonio C. Hernandes

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Abstract Eutectic $Al_2O_3/GdAlO_3$ composites in the form of fibers were produced by the laser heated pedestal growth technique at high pulling rates ranging from 48 to 240 mm/h. Fibers 0.8 mm in diameter and 25 mm in length, devoid of pores or cracks, were pulled in an air atmosphere without seeding or pedestal rotation. ''Chinese script'' and complex-regular microstructures were present in all the fibers. The Jackson–Hunt relationship, $\lambda^2 v$ = constant, applied very well to the eutectic $Al_2O_3/GdAlO_3$ fibers. The modulus of rupture values varied from 800 to 1,780 MPa. The effects of high pulling rate, average phase spacing and modulus of rupture on the microstructure were studied.

Introduction

Eutectic oxide composites produced from liquid phase have high structural stability, good mechanical strength and are free of porosity. Their mechanical properties render these composites more advantageous than single crystals or ceramic materials [1, 2]. Phase alternations in eutectic microstructures increase the energy required for crack propagation and are responsible for these materials' high mechanical strength [3–5]. However, processing difficulties still limit experimental data for oxide eutectics, often rendering them inconclusive.

Eutectic $Al_2O_3/GdAlO_3$ fiber composites have been obtained by micro-pulling down (μ-PD) and laser heated pedestal growth (LHPG) techniques [1, 3–8]. A feature of these composites is their irregular microstructure, called ''Chinese Script''. Fibers having only ''Chinese script'' can be considered isotropic material. $Al_2O_3/GdAlO_3$ fibers also showing the presence of a complex-regular fibrous microstructure in combination with the ''Chinese script'' pattern are considered anisotropic material. The modulus of rupture (MOR) of isotropic $Al_2O_3/GdAlO_3$ fibers shows values similar to the Al_2O_3 polycrystalline ceramic (600 MPa) [9, 10]. The presence of a complex-regular fibrous pattern increases the MOR, but this phase is difficult to control because the fibers are pulled far from their thermodynamic equilibrium.

In previous works in our laboratory [6, 9, 11], we were able to produce $Al_2O_3/GdAlO_3$ fibers with ''Chinese script'' and complex-regular fibrous microstructure using the LHPG technique at a low pulling rate ranging from 4.2 to 48 mm/h. The pedestals used were extruded and not pre-sintered. The characteristics of these pedestals were responsible for limiting our pulling rate to 48 mm/h due to the presence of bubbles in the molten zone, which were eventually incorporated into the fibers. This pulling rate was identified as a critical experimental condition for the $Al_2O_3/GdAlO_3$ produced with our LHPG equipment,

I. S. Medeiros
Departamento de Materiais Dentários, Faculdade de Odontologia, Universidade de São Paulo, São Paulo, SP, Brazil

I. S. Medeiros (✉) · A. C. Hernandes
Grupo de Crescimento de Cristais e Materiais Cerâmicos, Instituto de Física de São Carlos, Universidade de São Paulo, Caixa Postal 369, 13560-970 São Carlos, SP, Brazil
e-mail: igorsm@usp.br

E. R. M. Andreeta
Departamento de Física, Universidade Federal de São Carlos, São Carlos, SP, Brazil

compromising the modulus of rupture. The maximum MOR obtained was 1,320 MPa. A correlation was found between a smaller average spacing between phases and the higher MOR [9].

In this paper, we report on the results of eutectic $Al_2O_3/GdAlO_3$ fibers pulled at high pulling rates (48–240 mm/h) without the incorporation of bubbles. The effects of the high pulling rate, average phase spacing and modulus of rupture on the microstructure were studied.

Experimental procedure

Primary Al_2O_3 (Alfa Aesar, 5N) and Gd_2O_3 (Reacton, 6N) oxides were used as starting materials and weighed in the eutectic composition (77 mol% of Al_2O_3 and 23 mol% of Gd_2O_3). To ensure compositional homogeneity, the oxides were ball milled for 24 h prior to preparing $50 \times 10 \times 10$ mm^3 green-ceramic bars. These were pre-sintered at 1,300 °C for 4 h and then cut into 1×1 mm transversal sections to produce the pedestals and seeds for the LHPG pulling process. The experiments were performed without crystallographically oriented seeds (the pedestal was also used as a seed) in an air atmosphere, without pedestal rotation, at a fiber pedestal pulling ratio of 1.0. Details of the LHPG pulling process are described in reference [6].

The pre-sintered pedestals allowed for the application of pulling rates exceeding 48 mm/h, thus eliminating our earlier critical experimental conditions. Several eutectic $Al_2O_3/GdAlO_3$ fibers were obtained at upward pulling rates of 48–96 mm/h. Pulling rates exceeding 96 mm/h led to instability of the molten zone as a result of bubbles. To solve this problem, we inverted the pulling direction (pulling down) and $Al_2O_3/GdAlO_3$ fibers were pulled up to 240 mm/h—the maximum pulling rate allowed by our experimental setup.

After mechanical polishing (using 3–0.3 μm diamond), the fibers' microstructures were analyzed in the longitudinal direction by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis (EDX) (DSM 960, Zeiss). The average spacing between the eutectic phases was determined by image analyzing computer software made in-house. To determine the moduli of rupture (MOR), the specimens were centrally loaded using a support span of 20 mm. The fibers, eight for each parameter, were subjected to a 3-point bending test using a universal testing machine (Instron, model 3362) with a crosshead speed of 0.5 mm/min. The runs were carried out in the direction perpendicular to the pulling axis of the fibers.

Results and discussion

The $Al_2O_3/GdAlO_3$ fibers had an average (0.80 ± 0.02) mm diameter and 25 mm length. Our SEM analysis indicated that the microstructure of these fibers was devoid of pores and cracks, with very well-defined Al_2O_3 and $GdAlO_3$ phases. All the fibers showed two types of microstructural patterns in the entire range of pulling rates. The ''Chinese script'' patterns, where the phases were isotropically distributed, and a complex-regular pattern consisting of ''Chinese script'' in combination with a fibrous regular pattern. The Al_2O_3 phase predominated in the fibrous patterns and was aligned parallel to the fibers' pulling axis.

Irregular eutectic patterns such as ''Chinese script'' are related to faceted–non-faceted interface solidification associated with each component's melting entropy, as described by Jackson–Hunt in 1966 [12]. The presence of complex-regular microstructures is possible when alloys are rich in faceted components over small areas.

In a previous paper, it was shown that regions of complex-regular and ''Chinese script'' microstructure contained a volume fraction of 47 and 51% of $GdAlO_3$, respectively [6]. This means that there was a slight excess of Al_2O_3 when the microstructure was complex-regular, providing evidence that Al_2O_3 is a faceted component [6, 8]. Fibers with a greater relative quantity of complex-regular regions were produced at high pulling rates, indicating that rapid cooling was beneficial to keep an excess of Al_2O_3 at the solidification interface. Hence, if the purpose is to obtain an anisotropic fiber, one must have a molten zone containing a slight excess of Al_2O_3.

Figure 1 shows the patterns on the eutectic fibers pulled at different rates. The magnitude of the pulling rates was a determining factor for defining the average phase spacing. A higher pulling rate produced smaller phase spacing. The average phase spacing was measured on the ''Chinese script'' as well as on the complex-regular fibrous microstructures for fibers pulled upward and downward. The Jackson–Hunt relation [12], which expresses the dependence of the average spacing between the eutectic phases (λ) on the pulling rate (v), $\lambda^2 v$ = constant, was found to be highly appropriate for the $Al_2O_3/GdAlO_3$ fibers pulled under our new experimental conditions (Fig. 2), despite the microstructure's complexity. The Jackson–Hunt constant value for these experimental conditions was 11 μm^3/s. However, both ''Chinese script'' and complex-regular microstructures were observed in regions under the same macroscopic solidification conditions, as indicated in Fig. 3.

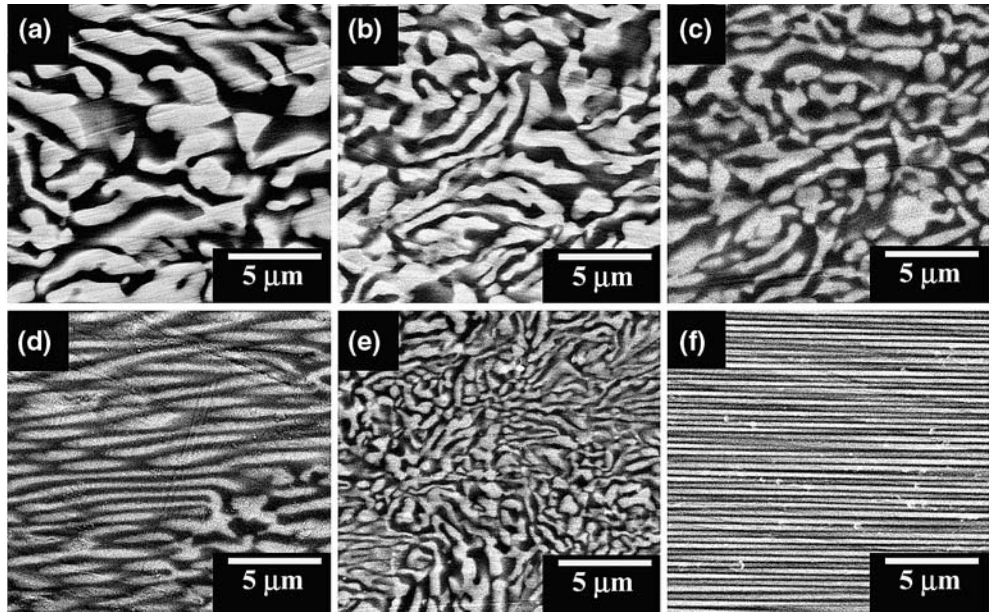

Fig. 1 Microstructural patterns of $Al_2O_3/GdAlO_3$ fibers. (**a**) ''Chinese script'' pattern at a fiber pulling rate of 48 mm/h; (**b**)''Chinese script'' pattern at a pulling rate of 72 mm/h; (**c**) ''Chinese script'' pattern at a pulling rate of 96 mm/h; (**d**) complex-regular microstructure in a fiber with a pulling rate of 96 mm/h; (**e**) complex-regular and Chinese script microstructure in a fiber with a pulling rate of 240 mm/h; (**f**) region showing a fibrous pattern in fiber pulled at a rate of 240 mm/h

The 3-point bending test indicated that eutectic $Al_2O_3/GdAlO_3$ fibers have a high modulus of rupture (Table 1). A tendency for higher MOR values was observed at higher pulling rates. The MOR values ranged from 880 to 1,780 MPa and were higher than those of polycrystalline alumina, whose values vary from 100 to 650 MPa [10].

In Table 1, the deviations in eutectic sizes and MOR between up and down direction pulled at 96 mm/h were recorded. The differences probably are related to the different thermal gradients obtained in each process. Even using the same growth rate, the lower thermal gradient obtained in pulling up process results in lower average spacing between the eutectic phases and consequently higher MOR. In addition, in the rupture region of 96 mm/h pulling down fibers, it was observed an alternation of both microstructures (''Chinese script'' and Complex regular) resulting in a higher standard deviation of spacing between phases.

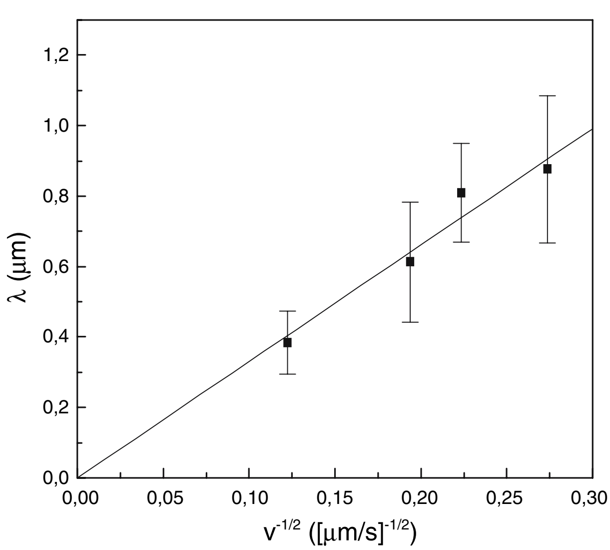

Fig. 2 Dependence of the average spacing between the eutectic phases (λ) of $Al_2O_3/GdAlO_3$on the pulling rate (v), $\lambda^2 v$ = constant = 11 $\mu m^3/s$

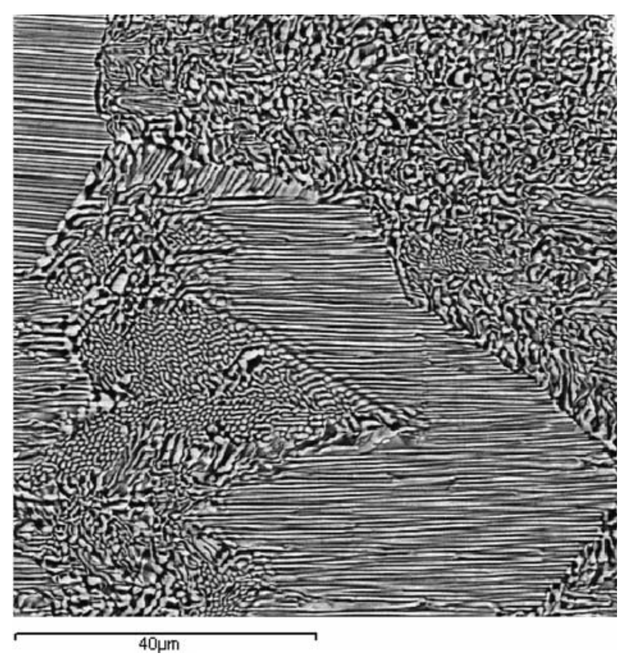

Fig. 3 Heterogeneous microstructure of a region of a $GdAlO_3$/Al_2O_3 fiber pulled at 96 mm/h, showing the presence of islands of complex-regular and Chinese script patterns

Table 1 MOR and average spacing between phases (λ) measured in $Al_2O_3/GdAlO_3$ fibers with eutectic composition

		Pulling direction	λ (μm)	MOR (MPa)
Pulling rate (mm/h)	48	Up	0.90 ± 0.15	880 ± 100
	72	Up	0.80 ± 0.12	1,000 ± 130
	96	Up	0.60 ± 0.17	1,080 ± 190
	96	Down	0.70 ± 0.22	900 ± 120
	240	Down	0.40 ± 0.13	1,780 ± 130
Microstructure	Chinese script		0.70 ± 0.23	1,000 ± 200
	Complex regular		0.40 ± 0.14	1,600 ± 300

The microstructures of the fibers obtained were classified in Chinese Script and Complex Regular, independently of the growth rate, in according to quantity present in the fracture region. Thus it was possible to identify as Complex regular the microstructure resulting in a high MOR (Table 1).

An examination of the $Al_2O_3/GdAlO_3$ fibers' microstructure revealed that the ''Chinese script'' microstructure was predominantly observed at 48 mm/h and its presence decreased with the increase of growth rate. Moreover, increasing the pulling rate led to a tendency for elongation of the eutectic phases parallel to the pulling direction (Fig. 1). This microstructural anisotropy was responsible for the high average MOR. Filaments of sub-micrometric diameters ($\approx$ 0.4 μm), observed in Fig. 1f, of Al_2O_3 and $GdAlO_3$ phases were positioned in perpendicular alignment with the loads applied in the bending tests, working as micro-fiber-reinforced ceramics, which led to the high energy necessary to crack propagation and consequently high modulus of rupture [13, 14].

Conclusions

Eutectic $Al_2O_3/GdAlO_3$ fibers free of macroscopic defects such as pores and cracks and with an irregular microstructure were pulled using the laser heated pedestal growth technique at a high pulling rate. An excess of Al_2O_3 on the solidification interface at pulling rates exceeding 96 mm/h produced more complex-regular regions inside the fibers, resulting in a high average modulus of rupture (1,780 MPa). Filaments of the $GdAlO_3$ phase with a 0.4 μm diameter present in these regions worked as fiber-reinforced ceramics and were responsible for the high MOR.

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