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Influence of microstructural size on the thermal shock behavior of Al_2O_3-$Er_3Al_5O_{12}$ directionally solidified eutectics

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ABSTRACT

We analyze the thermal shock resistance of directionally solidified eutectics. When quenching in water, the resistance starts to deteriorate with temperature differences in the range 260 to 300 K, almost independent of the microstructure size (or initial flexural strength). Unlike other strong, dense ceramics, the loss of strength is gradual upon quenching in boiling water. The onset of crack propagation seems to be controlled by the mismatch of the thermal and elastic properties of the component phases, while the length of the propagated cracks is limited by their quantity, which is estimated to scale approximately with the interface density.

In the recent decades, Al_2O_3-based eutectic ceramics have received much attention as structural materials, particularly because of excellent microstructural and chemical stability, creep resistance and mechanical strengths in high-temperature oxidizing atmosphere [1–8]. Very high values of flexural strength have been observed. Flexural strength increases with decreasing interphase spacing (λ), being proportional to $\lambda^{-1/2}$. The high strength comes about by the homogeneous two-phase microstructure with fine control over the microstructural size that is achieved by directional solidification procedures, together with strongly bonded interphases. Alumina-rare earth garnet eutectics present also selective emissivity and have been proposed and investigated as selective thermal emitters for thermophotovoltaic devices. [9–12] Appropriate thermal stress resistance is required in the aforementioned application, but the detailed study of the thermal shock behavior has not been performed previously.

Experiments to measure thermal emission done by laser heating rods of the material up to 1600 °C, which were followed by fast cooling in ambient air, show that they can support moderate thermal shock conditions without apparent degradation. Al_2O_3-aluminium garnet directionally solidified eutectics have typically a high degree of brittleness (with $K_{IC} \approx 2$ MPam$^{1/2}$), relatively low thermal conductivity, and high Young's modulus, being susceptible to catastrophic failure under severe thermal transients [13]. The purpose of this work is to study, using standard quenching test methods, the thermal shock behavior of directionally solidified Al_2O_3-$Er_3Al_5O_{12}$ eutectic selective emitters with emphasis on the microstructural size dependence. The outcome will be applicable to similar alumina-garnet eutectics.

Ceramic feed rods with the eutectic composition of 81 mol% Al_2O_3 + 19 mol% Er_2O_3 were prepared by mixing, compaction and sintering of the Al_2O_3 (Aldrich 99.99%), Er_2O_3 (Alfa Aesar 99.99%) powders, similarly as elsewhere [7]. Eutectic rods of diameters 1.2 to 1.6 mm were directionally solidified from the melt in nitrogen atmosphere [14] by the laser floating zone method at 25 mm/h and 750 mm/h processing rates. The solidified samples had an interpenetrated microstructure of Al_2O_3 and $Er_3Al_5O_{12}$ phases. The values of interphase spacing measured by the line interception method are given in Table 1.

The rods were cut to a length of 45 mm and both cross-sections were carefully polished for thermal shock tests. As the severity of the thermal shock depends on the sample size and the properties of the quenching media and heat transfer coefficient (h), [15–18] here we have always used cylindrical-rod shaped samples with similar sizes (diameters from 1.2 to 1.6 mm) and we have done quenching experiments in both, room temperature (RT) and boiling water. The thermal shock resistance was assessed by measuring the retained flexural strength of the samples after quenching from a given holding temperature into large volume baths of RT water (T = 18 °C to 20 °C) or boiling (T = 95 °C) water. The test specimen temperature was maintained at least 15 min before quenching and then transferred to the quenching bath within 3 s [19]. Three-point flexural tests were carried on Electronic Universal Testing Machine (Instron 5565, UK), with a span of 16 mm and 30 μm/min strain rate. A minimum number of three valid data were measured to calculate the average flexural strength. [5] Microstructure and fracture surfaces were observed by Scanning Electron

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Table 1
Values of thermomechanical parameters for AE25, AE750. R has been calculated using Eq. (2), the flexural strength data given in the table (first column) and the following values for E = 311 GPa [5], coefficient of thermal expansion $\alpha = 7.3 \times 10^{-6}\,K^{-1}$ [33–35], and $\nu = 0.24$ [34,36,37].

Material	Flexural strength (MPa)	Fracture toughness ($MPam^{1/2}$) [5]	Interphase spacing (μm)	R (K)	Measured ΔT_C (K)
AE750	1580 ± 280	1.8 ± 0.2	0.71 ± 0.1	530	290
AE25	710 ± 60	2.1 ± 0.3	5.1 ± 1.2	240	260

Microscopy (MERLIN Field Emission Scanning Electron Microscope (FE-SEM) from Carl Zeiss).

Fig. 1 shows the retained flexural strengths together with the corresponding standard errors of Al_2O_3/EAG eutectics solidified at 25 mm/h (denoted AE25 from now on) and 750 mm/h (AE750) as a function of thermal shock total temperature difference ($\Delta T = T_{hold} - T_{bath}$). The samples quenched in RT water show a sharp, catastrophic degradation of strength at $\Delta T = \Delta T_C = 260$ K (AE25) and $\Delta T_C = 290$ K (AE750). According to the unified theory presented by Hasselman [13,20], this is the expected behavior of strong ceramics, with very small initial cracks (flaws). Once a short crack starts to propagate at a critical temperature difference, it continues propagating kinetically. Crack propagation continues longer for smaller initial flaws, and causes a sharp drop of strength. The original strength of AE750 was 2.2 to 2.6 times higher than that of AE25, as usual for this material [5] but the ΔT_C of AE750 was only 1.1 times the one of AE25.

Fig. 1 shows also the retained flexural strength of the samples upon quenching in boiling water versus temperature difference. The degradation of flexural strength is more gradual. The 3-point flexure load-displacement curves registered to measure the retained strength had the same slope as before the quenching, compatible with Young's modulus values equal to the one of the as-grown samples [5]. Therefore, there is no extensive cracking of the samples even if their retained strength has clearly diminished. Fracture surfaces of quenched specimens, showing brittle fracture, are given in Fig. 2, a and b for AE25, c and d for AE750. All the observed surfaces are similar: the fracture initiates at the surface, without evidence of changes in the way the cracks propagate between quenched and unquenched samples. The absence of catastrophic failure in the specimens quenched into boiling water is to be associated to the different ways of heat transfer in both procedures [17]. Upon quenching in RT water, the heat flux is far larger and less homogeneous, favoured by a transient regime with vigorous boiling and solid-liquid bubble contacts.

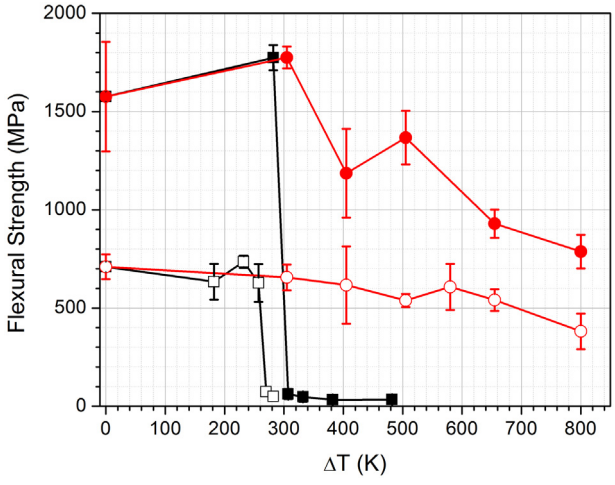

Fig. 1. Retained strength of AE25 (open symbols) and AE750 (closed symbols) as a function of total temperature difference (ΔT), after quenching in water baths at RT (squares) or boiling (circles). When error bars are given, the value corresponds to averages of at least 3 valid measurements of 3-poing flexural strength.

From the values of the retained flexural strength, we have estimated the radius of the critical flaw size after thermal shock (Fig. 3) using Expression 1 [3].

$$a = \frac{1}{\pi}\left[\frac{K_{IC}}{0.65\sigma}\right]^2 \quad (1)$$

K_{IC} is the fracture toughness. Clearly, when the critical flaw size is of the order of 1 mm, the samples have lost all their strength ($\Delta T > \Delta T_C$ in RT water). Upon quenching in boiling water, as ΔT increases we observe a gradual increase in the size of the critical flaw, starting from values of the order of the phase size of the eutectic composite. Moreover, the cracks start to propagate at about the same ΔT in both composites, irrespective of which was the size of this initial flaw.

A so similar value for ΔT_C (quenching in RT water) or ΔT to start to propagate cracks (boiling water), for both samples might seem surprising for composites with so different flexural strength. The critical temperature to initiate fracture in a rod of material subjected to severe thermal quenching is determined by the thermal shock resistance parameter R, Eq. (2), which for rod shaped samples is given by the temperature decrease causing a thermal tensile stress equal to the sample strength (σ_f) [13,15,21–23],

$$R = \frac{\sigma_f(1-\nu)}{\alpha E} \quad (2)$$

where σ_f is the fracture resistance, ν the Poisson's ratio, α the thermal expansion coefficient and E the Young's modulus. Calculated R values for AE25 and AE750 are 240 K and 530 K (see Table 1). While the R value for AE25 is near to the corresponding ΔT_C (quenching in RT water) or ΔT to start to propagate cracks (boiling water) found experimentally, ΔT_C for AE750 is much smaller than its R value. It is well known that strong and fragile ceramics tend to show catastrophic rupture under severe thermal quenching, very frequently with temperature quenching differences smaller than the calculated R parameter. Therefore, instead of increasing strength, the strategy to increase the thermal shock resistance to damage of strong ceramics is to minimize the extent of crack propagation [13,20,24–27]. Often this is done by introducing second phase particles (or microstructural inhomogeneities) into the matrix that increase the toughness and/or decrease the Young's modulus of the material [13,22] and slow crack propagation. These inhomogeneities also concentrate thermal stress at the second phase leading to microcracking and avoiding catastrophic failure [28–31].

The present directionally solidified eutectic is already a two-phase material, whose microstructural distribution and size do not affect to its fracture toughness or Young's modulus, but can contribute to its thermal shock behavior through the inhomogeneity of the thermomechanical properties associated to the two-phase material. Upon quenching, each phase will experience a different time-dependent thermal contraction, according to their different thermal expansion, thermal conductivity, and elastic constants. Stresses larger than the ones corresponding to the homogenized body and large enough to initiate fracture could develop at the interfaces during the transients due to mismatch in thermal properties of the adjacent phases, as suggested by Zimmerman [32] in SiC-ZrB_2 composites.

In the tests perfomed, the volume of sample subjected to the fastest temperature variation is the one adjacent to the outer surface, therefore