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The phase stability and toughening effect of 3Y-TZP dispersed in the lanthanum zirconate ceramics

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ABSTRACT

The low fracture toughness of lanthanum zirconate ($La_2Zr_2O_7$, LZ) greatly impedes its wide application as thermal barrier coatings (TBC). The 3 mol% Y_2O_3-stabilized tetragonal zirconia polycrystals (3Y-TZP) have been introduced to toughen the brittle LZ ceramics. The dispersive 3Y-TZP undergoes a simultaneous t–m transformation upon cooling below a critical volume fraction x of 3Y-TZP, above which its tetragonal phases can however be preserved. The different stabilities of 3Y-TZP second phases arise from a variation of residual tensile stress within them. The fracture toughness has been greatly improved by dispersing the tetragonal particulates (t-3YSZ) in the LZ matrix and the primary toughening mechanisms are phase transformations of the dispersive second phases and the residual compressive stress within the matrix. An anticipated increase of fracture toughness from the ferroelastic toughening and the residual compressive stress toughening highlights the great potentials to improve coating durability by depositing t'-3YSZ/LZ composite TBCs by the industrial non-equilibrium route.

1. Introduction

While lanthanum zirconate ($La_2Zr_2O_7$, LZ) is postulated as an alternative thermal barrier coating (TBC) topcoat material due to its excellent thermal resistance [1,2], its application has been largely hindered by penalties in durability [3], attributable to the following two reasons. Firstly, the LZ topcoat and its underlying thermally grown oxide (TGO) are thermochemically instable and prone to react with each other and form a porous $LaAlO_3$ interphase, which therefore, compromises the integrity of the TBC system and eventually the protective function of TGO [3]. Secondly, the premature failure of LZ topcoat arises from a combination of the low toughness [4] and the low thermal expansion coefficient (TEC) [5] of $La_2Zr_2O_7$. Upon cycling, the lower TEC of LZ topcoat causes a higher thermal stress, which can more easily initiate cracks and promote their growth, thereby leading to an earlier failure [6].

The thermochemical instability problem of LZ and TGO has been solved by inserting an inert layer, typically yttria-stabilized zirconia (YSZ), between LZ topcoats and the TGO layer [7]. Acting as a diffusion barrier layer, as well as a stress alleviation layer, the YSZ transition layer has considerably improved the cyclic life of LZ TBC [8]. It is conceivable that the durability of LZ TBC would be further improved if the LZ ceramics could be toughened. The poor fracture toughness of the LZ ceramic originates from its lack of energy dissipative mechanisms and the essence of various toughening methods is to introduce different energy dissipative channels. Li et al. [9] introduced a ferroelastic phase $BaTiO_3$ to LZ ceramics, attempting to make exploitation of domain wall switching as an energy dissipation pathway. They achieved a 24% increase of fracture toughness. In another study, they incorporated YAG ($Y_3Al_5O_{12}$) nano-phase to the LZ ceramic matrix and obtained a similar improvement of fracture toughness [10]. However, both $BaTiO_3$ and YAG are reactive with LZ matrix at high temperatures. Hence, they are not a desirable second phase inclusion for the LZ ceramics.

Therefore, an ideal toughening phase of LZ matrix should meet the following requirements. Firstly, it should be thermochemically compatible with LZ ceramics; secondly, it should include a certain energy dissipative channels (or have a high intrinsic fracture toughness); and finally, it should have a desirably low thermal conductivity, since the toughening of LZ ceramics should not be at the expense of its thermally insulative capabilities. As a conventional TBC topcoat material, YSZ essentially satisfies all the above requirements, and therefore becomes a qualified candidate for a toughened phase of LZ ceramics. In this study, the commercially available 3 mol%-Y_2O_3 tetragonal zirconia polycrystals (3Y-TZP, or

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3YSZ) has been selected as the toughening agent. The slightly lower stabilizer concentration than that of the standard YSZ TBC (about 3.8 mol%-Y_2O_3 stabilized zirconia [4]) results in a larger tetragonality (c/a ratio) [11], upon which, the high temperature ferroelastic toughening mechanism is dependent. The initial envisagement of this study is to homogeneously disperse the nontransformable tetragonal-prime (t') 3YSZ particulates in the LZ matrix to exploit the ferroelastic domain reorientation as a toughening mechanism. However, the introduced 3Y-TZP particulates are transformable especially with a low addition of the dispersive second phase, attributed not only to the equilibrium route of sample preparations by sintering, but also to the thermal residual stress arisen from the TEC misfit between 3YSZ dispersive particulates and the LZ matrix. The 3YSZ particulates dispersed in LZ ceramics can greatly improve the fracture toughness of the matrix. The primary toughening mechanisms originate from the phase transformation of the dispersive 3YSZ second phases and the residual compressive stress within the LZ matrix.

2. Sample preparation and characterization

The $La_2Zr_2O_7$ polycrystalline powders were prepared by the co-precipitation technique as described in Ref. [12]. Prior to mixing, 3 mol% yttria stabilized zirconia powders (Pi-Kem, 99% pure) were heated at 1423 K for 6 h to homogenize the composition, to yield single tetragonal phase. Then, x3YSZ/$(1-x)La_2Zr_2O_7$ composite powders (where x is volume fraction and x=0.1, 0.2, 0.3, 0.4, 0.5) were mixed by attrition milling (12 h, 300 r.p.m.) with zirconia media in distilled water. The powder suspensions received were subsequently freeze-dried to yield aggregation-free powders. Such powders were then cold-pressed into disc compacts (12 mm in diameter and 2–3 mm in height) and sintered at 1673 K for 2 h.

The phase compositions of the composite ceramics were identified by an X-ray diffraction (XRD) facility (Philips X'Pert) with CuK_α radiation and a Raman optical microprobe system (Renishaw 1000, UK) with the 514 nm line of argon laser. The densities of the sintered bodies were measured by Archimedes' method. The microstructure details of the specimens were examined via scanning electron microscope (SEM, Philips XL 30) on the polished and thermally-etched surfaces. The fracture toughness was investigated by the indentation method at room temperature using a diamond Vickers indenter with a loading time 15 s at a constant load 50 N. Since the indenting of low-toughness materials with a Vickers indenter generally forms a half-penny crack [13,14], the fracture toughness (K_{Ic}) is calculated by the following equation [15]:

$$K_{Ic}=0.016\sqrt{\frac{E}{H}}\frac{P}{c^{1.5}} \qquad (1)$$

where E is the elastic modulus, H is the hardness, P is the applied load and c is the sum of crack length (l) and one half of the indenter imprint diagonal (a).

3. Results

3.1. Phase composition

Fig. 1(a) shows the XRD patterns of 3YSZ/LZ ceramic composites in comparison with the raw powders for each constituent. While LZ and 3YSZ exhibit single pyrochlore (P) and tetragonal (t) phase respectively, the monoclinic (m) phase of zirconia can be detected for the composites with a lower 3YSZ addition (i.e. the volume proportion $x \le 0.3$), evidenced by the presence of the characteristic reflections at 31.5° for the monoclinic phase. However, when the volume fraction of 3YSZ exceeds 0.3, the monoclinic phase is absent and the introduced 3YSZ purely exhibits the tetragonal phase. The Raman spectra, Fig. 1(b) further confirms the prior findings. The characteristic bands of monoclinic zirconia, the doublets near 180 cm^{-1}, are present for the volume fraction x lower than 0.3 but absent for x above 0.3.

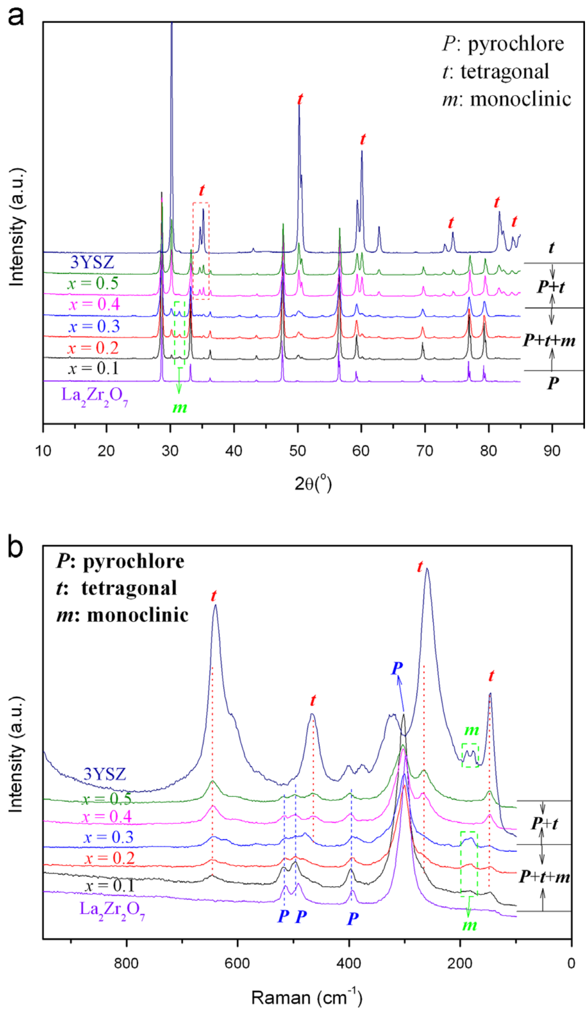

Fig. 1. XRD patterns (a) and Raman spectra (b) of 3YSZ and LZ powders and 3YSZ/LZ composite ceramics. Partial tetragonal phases of 3YSZ has transformed to monoclinic for a lower addition of 3YSZ ($x \le 0.3$).

3.2. Density and microstructure

Fig. 2 shows the theoretical and measured densities of 3YSZ/LZ ceramic composites. The densities of the ceramic composites with a high addition of 3YSZ ($x > 0.3$) are consistent with those predicted by the mixing law. By contrast, the densities of those composites with a relatively low addition of 3YSZ ($x \le 0.3$) are lower than the values predicted from the mixing law. It has been attributed to the partial transformation of the heavier tetragonal phases to the lighter monoclinic phases, which further confirms the simultaneous phase transformation upon cooling for those composites with a lower inclusion of 3YSZ particulates.

Fig. 3 shows the microstructural evolution of 3YSZ/LZ ceramic composites with an increase of 3YSZ volume fraction x. As shown, for a low addition of 3YSZ, the second phases are rather homogeneously distributed in the LZ matrix. For a high inclusion of 3YSZ, on the other hand, aggregations of 3YSZ sub-micron particulates are dispersed in the matrix. The grains of LZ matrix are around 1–2 μm, much bigger than those of the dispersing 3YSZ