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Calcia-magnesia-alumino-silicate (CMAS)-induced degradation and failure of air plasma sprayed yttria-stabilized zirconia thermal barrier coatings

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ABSTRACT

Thermal barrier coatings (TBCs) used in gas-turbine engines experience severe degradation by calcia-magnesia-alumino-silicate (CMAS) deposits during high-temperature operation. The present study identified and evaluated the chemical and microstructural changes in air plasma-sprayed (APS) 7 wt.% Y_2O_3 stabilized ZrO_2 (7YSZ) TBCs caused by CMAS attack under isothermal conditions at 1340 °C. Additionally, a 'model' experimental study was conducted by characterizing 7YSZ ceramic powders immersed in molten CMAS glass at 1300 °C for different exposure times. The combined results from both studies highlight the importance of local CMAS glass composition on the 7YSZ/CMAS interaction. Specifically, low Y-content in the glass, caused by a relatively large glass 'sink,' produces Y-depleted ZrO_2 grains that undergo tetragonal (t) → monoclinic (m) phase transformation upon cooling. Alternatively, small pockets of Y-enriched glass induce the formation of t''-ZrO_2, a phase characterized by its high stabilizer content. After prolonged high-temperature exposure, solution-reprecipitation induces the formation of both m-ZrO_2 and t''-ZrO_2 throughout the APS 7YSZ TBC in accordance with the phase diagram. Using a thermomechanical model it is shown that the strain associated with the martensitic $t \rightarrow m$ phase transformation plays an important role in the delamination failure of TBCs attacked by CMAS.

1. Introduction

Ceramic thermal barrier coatings (TBCs) have become indispensible for protecting and insulating hot-section metallic components in gas-turbine engines used in aerospace and power-generation applications [1–4]. The use of TBCs has allowed higher engine operating temperatures, resulting in enhanced engine performance and efficiency [3,4]. However, the high operating temperatures result in the melting of any silicate (sand, dust, runway debris, fly ash, volcanic ash, *etc.*) that may be ingested by the engine [5–14]. These molten silicates, commonly referred to as CMAS (calcium-magnesium-alumino-silicate), cause severe degradation of TBCs and premature delamination, exposing the metallic components to dangerously hot gases.

The most commonly used TBC composition is 7 wt.% yttria-stabilized zirconia (7YSZ), which has been optimized based on years of experience [1–4]. The 7YSZ composition crystallizes as the metastable, non-transformable tetragonal phase (t') under ordinary conditions [15–17], which has high toughness, both at low and high temperatures, as a result of the reversible ferroelastic toughening [16,18,19]. However, prolonged exposure to high temperatures (>1400 °C) results in the destabilization of t' 7YSZ into Y-lean monoclinic (m) and Y-rich tetragonal (t'') ZrO_2 phases (Fig. 1) [20].

The mechanisms involved in the CMAS-induced degradation and failure of 7YSZ TBCs, made by electron-beam physical vapor deposition (EB-PVD) or air plasma spray (APS), have been documented in the literature [5–10,13,21–24]. The general features of CMAS attack on 7YSZ TBCs at temperatures <1400 °C include [5,9,14,21,25]: (i) molten CMAS penetration into the TBC *via* open porosity and cracks, (ii) dissolution of 7YSZ grains in the molten CMAS, (iii) enrichment of Y^{3+} and Zr^{4+} in the CMAS glass, (iv) precipitation of Y-lean ZrO_2 grains, and (v) grain coarsening. The

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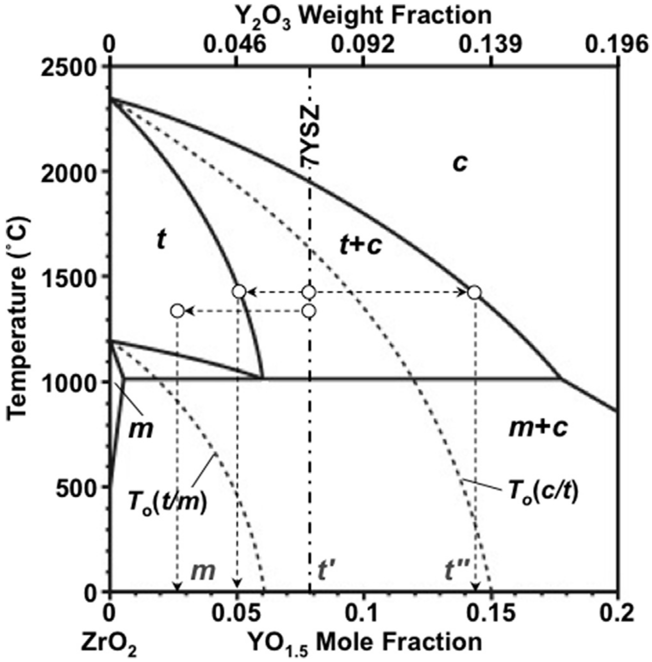

Fig. 1. Phase diagram for the $YO_{1.5}$-ZrO_2 system with the metastable phase transitions superimposed (dashed curves) [15,20]. The conventional 7YSZ (t'-ZrO_2) TBC composition is indicated with a dashed line. The dashed arrows indicate the destabilization pathways of t'-ZrO_2 after: (i) high temperature exposure $\{t' \rightarrow (t + c)\}$, followed by cooling $\{(t + c) \rightarrow (t'' + m)\}$ and (ii) from CMAS attack $\{t' \rightarrow t\}$, followed by cooling $\{t \rightarrow m\}$.

solution-reprecipitation process has been used to describe the formation of Y-lean ZrO_2 grains, where the CMAS wets the TBC surface and dissolves the grains, introducing Y^{3+} and Zr^{4+} into the glass. The low solubility of Zr^{4+}, compared to Y^{3+}, in CMAS leads to the precipitation of Y-depleted ZrO_2 grains [9,26]. However, the small amount of Y^{3+} solute available in 7YSZ TBCs (0.08:1:Y:Zr atomic ratio) is not sufficient to alter the composition of the CMAS and its flow behavior significantly, resulting in full TBC penetration by the CMAS. This leads to a significant reduction in the 'strain-tolerance' (compliance) of the 7YSZ TBCs during cooling, causing them to fail [14,27]. Furthermore, CMAS-induced depletion of ZrO_2 grains results in the $t \rightarrow m$ martensitic phase transformation during cooling (Fig. 1), which is associated with a 3–5% volume expansion that can influence the stress state in the CMAS-penetrated TBC [28].

Here we present new insights into the nature of the CMAS/TBC interactions at high temperatures, based on results from experiments on free-standing 7YSZ TBCs and 'model' experiments involving 7YSZ powders. Most significantly, we find that the formation of m-ZrO_2 is highly dependent on the Y^{3+} and Zr^{4+} concentrations in the CMAS. We also analyze the influence of the strain arising from the $t \rightarrow m$ martensitic phase transformation on the delamination of a CMAS-penetrated TBC subjected to thermal excursions under a temperature gradient across the TBC.

2. Experimental procedure

The APS method was used to deposit 7YSZ composition (t'-ZrO_2 phase) TBCs (~300 μm thickness) on aluminum (Al6061) substrates. Hollow-sphere plasma-densified (HOSP) feedstock powder (Metco 204NS, Oerlikon Metco, Westbury, NY) (Fig. 2A) and spray parameters listed in Table 1 were used. APS was performed with an atmospheric DC plasma torch with an 8-mm diameter nozzle and a swirl flow as distribution ring (F4-MB, Oerlikon Metco, Westbury, NY). The substrates were dissolved in acid to obtain free-standing TBCs, which enabled the use of high temperatures for isothermal TBC/CMAS interaction studies. Polished cross-sections of as-sprayed free-standing APS 7YSZ TBCs were thermally etched at 1400 °C for 10 min in a box furnace to reveal the grain boundaries.

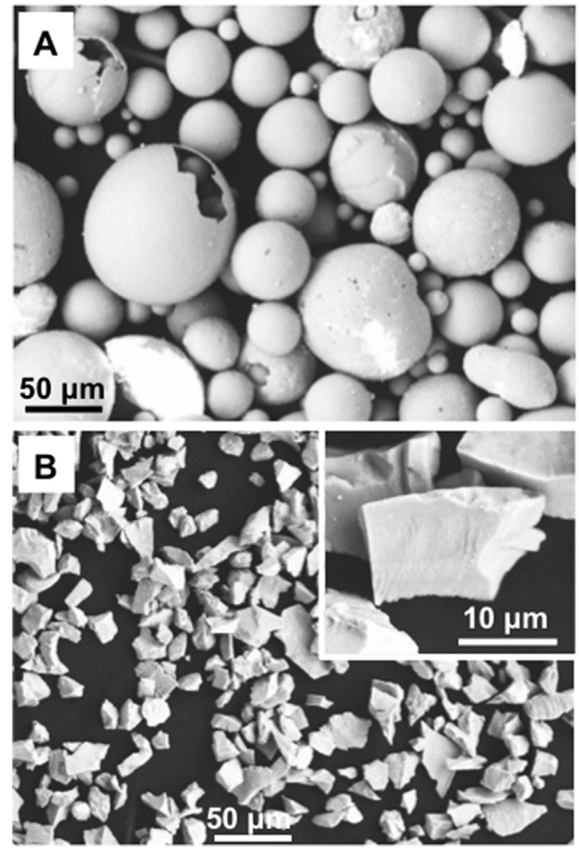

Fig. 2. SEM micrographs of the 7YSZ (t'-ZrO_2) (A) HOSP feed powder and (B) F&C powder used for depositing the TBCs and the 'model' experiments, respectively.

The CMAS powder used here is from previous studies, and the composition (Table 2) is based on sand from the field [21,29,30]. Briefly, a mixture of the oxide constituents in their stoichiometric amounts were mixed and melted at 1550 °C for 4 h in a platinum crucible, and then quenched to room temperature in water. The glass was then crushed using a mortar and pestle, and remelted again to ensure chemical homogeneity. The final CMAS powder was formed by crushing the glass and then ball-milling it for 72 h in ethanol with ZrO_2 milling media. (The composition of the CMAS glass was measured after ball-milling using inductively-coupled plasma atomic-emission spectroscopy (ICP-AES; JY2000, Horiba Jobin Yvon, Edison, NJ), and the amount of Zr^{4+} in the glass was found to be below the detection limit (<0.1 wt.%).) The CMAS glass frit was mixed in ethanol to form a paste, which was then applied over a small circular area at the center of top surfaces of the as-sprayed free-standing APS 7YSZ TBCs (30 mg/cm^2 loading). The isothermal TBC/CMAS interaction studies were performed at 1340 °C for 24 or 72 h in a box furnace, using heating and cooling rates of 10 °C/min. Cross sections from the center of the interaction regions were cut using a low-speed diamond saw, and then polished to a 1 μm finish using standard procedures.

As mentioned earlier, the t'-ZrO_2 phase in 7YSZ TBCs destabilizes when exposed to high temperatures for long periods of time without any CMAS [20]. Therefore, control samples of free-standing APS 7YSZ TBCs were exposed to the same heat