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In situ Raman spectroscopy studies of high-temperature degradation of thermal barrier coatings by molten silicate deposits

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In situ Raman spectroscopy is used to understand the high-temperature interactions between air-plasma-sprayed 7 wt.% Y_2O_3-stabilized ZrO_2 (7YSZ) thermal barrier coatings (TBCs) and calcium-magnesium-alumino-silicate (CMAS) sand. These interactions result in the depletion of Y^{3+} in the YSZ grains. During cooling the Y-depleted YSZ grains transform to the monoclinic phase starting at ~600 °C. The significant volume expansion associated with this phase transformation could play a role in determining the thermomechanical failure of CMAS-penetrated 7YSZ TBCs during thermal cycling.

Keywords: Thermal barrier coatings; Raman spectroscopy; Zirconia; CMAS

The use of thermal barrier coatings (TBCs) on hot-section metallic components in gas-turbine engines, for both aircraft propulsion and electricity generation, has enabled higher operating temperatures and improved efficiencies [1–3]. However, increased surface temperatures of TBCs engender new materials issues, including melting and adhesion of silicate particles (sand, volcanic ash, fly ash) ingested by the engines on the TBC surfaces, and the subsequent degradation and spallation of the TBCs [4]. TBCs of 7YSZ composition (7 wt.% Y_2O_3 or 7.89 mol.% $YO_{1.5}$; see Fig. 1 [5]), which consist of the non-transformable t'-ZrO_2(*ss*) solid-solution phase that is capable of reversible ferroelastic toughening [6], have been optimized over the past several decades to achieve maximum durability [3]. However, 7YSZ TBCs are highly susceptible to degradation by calcium-magnesium-alumino-silicate (CMAS) attack. This is becoming a critical issue with the ever-increasing demand for higher operating temperatures in future high-efficiency/high-performance gas-turbine engines and the ubiquity of silicate particles in the air and some fuels (syngas) [3,4]. There is ongoing research aimed at furthering our understanding of the mechanisms involved in CMAS attack in 7YSZ TBCs, and a parallel effort in mitigating this attack through the engineering of TBC compositions [3,4,7–20]; this contribution focuses on the former.

It is known that molten CMAS wets and spreads on the hot TBC surface (1200–1300 °C), and penetrates into the pores [4]. It also penetrates the grain boundaries, exfoliating the t'-ZrO_2(ss) grains [4,7,9]. Indirect evidence for dissolution–reprecipitation of ZrO_2(ss) grains has also been provided by local chemical and phase analyses of CMAS-penetrated 7YSZ TBCs using transmission electron microscopy (TEM) and energy-dispersive spectroscopy (EDS), where t'-ZrO_2(ss) grains dissolve in the CMAS glass, enriching the glass with Zr^{4+} and Y^{3+} locally [4,7,9]. It has been suggested that it takes only a small amount of Zr^{4+} to saturate the CMAS glass, whereas the solubility of Y^{3+} is much higher [7], resulting in the reprecipitation (or crystallization) of ZrO_2(ss) grains but in the monoclinic (*m*) form since they are depleted in Y^{3+}. However, to date all the characterization experiments have been performed ex post facto at room temperature, and the evolution of the Y-depleted *m*-ZrO_2(ss) phase is unknown. It is unlikely that the *m*-ZrO_2(ss) phase forms during CMAS interaction even if it is completely depleted of Y^{3+} because the interaction temperature is typically

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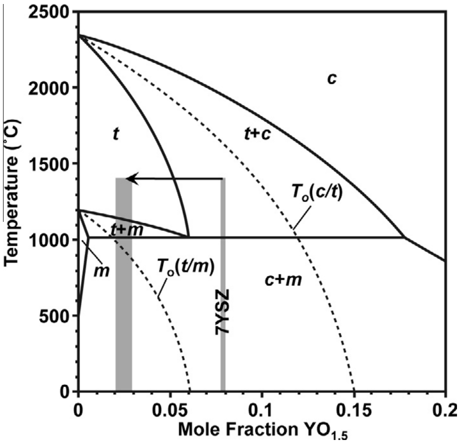

Figure 1. A portion of the $YO_{1.5}$–ZrO_2 phase diagram [5]. The arrow indicates Y-depletion during CMAS interaction.

$\geqslant 1200$ °C where t-ZrO_2 is stable (see Fig. 1). Thus, m-ZrO_2(ss) phase must form by $t \rightarrow m$ phase transformation during cooling to room temperature. However, the onset temperature and the evolution of the $t \rightarrow m$ phase transformation is not known. There is a significant volume change (~5% increase) associated with the $t \rightarrow m$ phase transformation [6], which could play a role in determining the thermomechanical failure of CMAS-penetrated 7YSZ TBCs [4,8]. Thus, it is important to gain insight into the evolution of the m-ZrO_2(ss) phase during cooling, furthering our understanding of CMAS degradation of 7YSZ TBCs. To that end, we have used confocal Raman microscopy to study the $t \rightarrow m$ phase transformation in CMAS-interacted air-plasma sprayed (APS) 7YSZ TBCs *in situ* during cooling. Both t'/t and m phases of ZrO_2 are highly Raman active, each with a unique spectrum, and confocal Raman microscopy is capable of locally interrogating interfaces buried under optically transparent top layers.

Pieces (~3 × 3 mm^2) of free-standing APS 7YSZ TBC (~300 μm thickness) and CMAS glass of composition 39.2CaO–5.2MgO–4.1Al_2O_3–51.5SiO_2 (mol.%) from previous studies [14,20] were used here. The

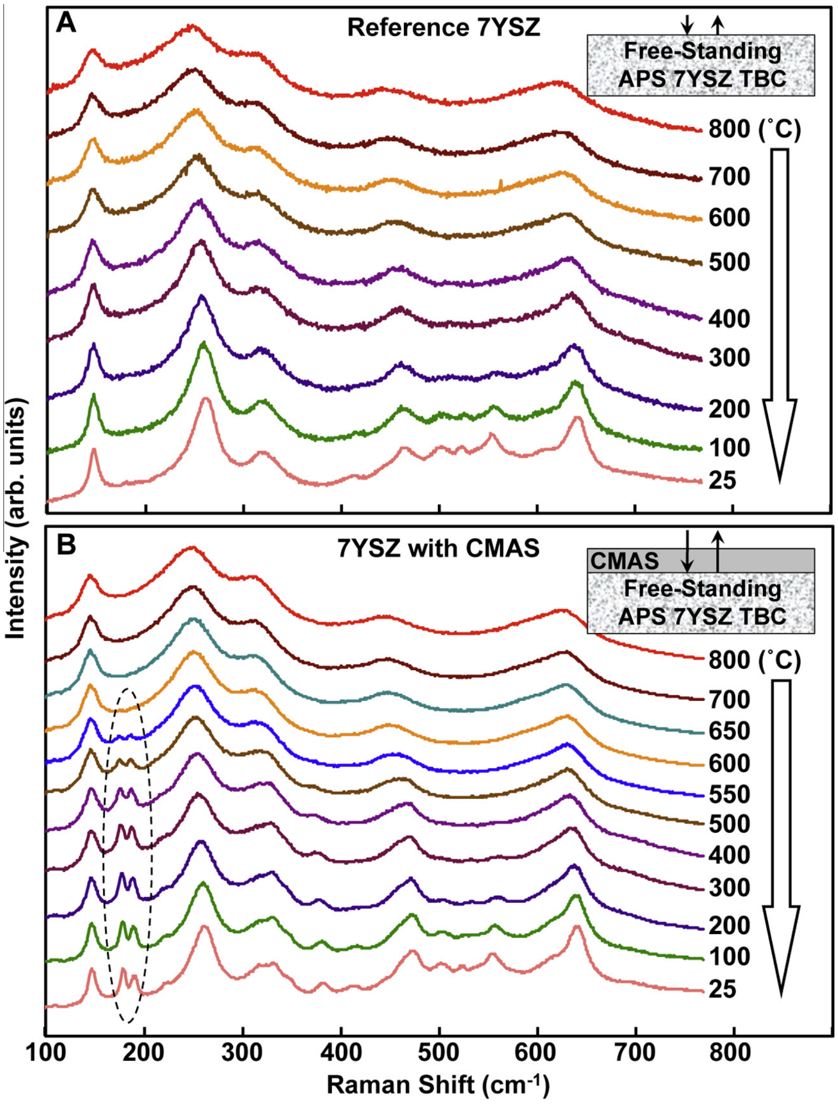

Figure 2. *In situ* Raman spectra collected at temperatures from 800 to 25 °C during cooling (from 1400 °C heat treatment) for: (A) reference 7YSZ APS TBC and (B) 7YSZ APS TBC with CMAS. The m-ZrO_2 peaks marked in (B).