KINETICS OF THERMAL BARRIER OXIDE INTERACTIONS WITH MOLTEN SILICATES

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The degradation of thermal barrier coatings (TBCs) by molten silicates (CMAS) represents a significant barrier to increased operation temperatures of gas turbine engines and thus fuel efficiency. A promising mechanism for CMAS mitigation has been found in certain TBC chemistries (e.g. $Gd_2Zr_2O_7$) that undergo reactive crystallization – the crystallization of new, thermodynamically favored phases, which contain both melt and TBC constituents (e.g. apatite). Significant work has been undertaken to understand the thermodynamics of TBC-CMAS systems and the possible reaction phases, but little quantitative data on the kinetics of these interactions exists today; this includes: the *(i)* rate of TBC dissolution into the melt, *(ii)* diffusion of TBC constituents within the melt, and *(iii)* reaction product crystallization rates.

To better understand what limits kinetically the rate of thermal barrier oxide (TBO) saturation in the melt (a prerequisite of reactive crystallization), the effect of temperature, melt composition, and TBO composition on the dissolution and diffusion rates were quantitatively studied. TBOs in the $REO_{1.5} - MO_2$ systems (RE=Y & Gd, M=Zr & Hf) were placed in a semi-infinite, 1-D diffusive contact with one of two model silicate melts at either 1300 or 1400°C, an example of which can be seen in Figure 1. The reaction products and morphology were analyzed (Figure 1 (a) inset), and composition profiles of TBC constituents in the melt were measured using an electron microprobe equipped with wavelength dispersive spectroscopy. The resulting compositional data, e.g. Figure 1 (b), was fit to crystal dissolution and diffusion models, which enabled the quantification of TBO dissolution rates and TBO diffusivities in the model silicate melts.

Preliminary work has elucidated that the diffusivities of TBOs are strongly effected by the melt composition (i.e. the melt viscosity), but only weakly effected by the chemistry of the dissolving TBO. However, the TBO composition is seen to be an important parameter for controlling the dissolution rate. Modeling the dissolution and diffusion process on length scales relevant to TBCs (e.g. an EB-PVD intercolumnar gap) reveals that the time to reach melt saturation is only weakly dependent on the diffusivity but is strongly dependent on the dissolution rates. Thus, these results imply that the TBC dissolution rate should be a key optimization parameter for the design of novel TBC chemistries and coating architectures. With further investigation and determination of kinetic data, this work can be coupled with existing thermodynamic, thermomechanical, and infiltration models to enable the development of a fully-integrated, ICME based modeling approach to predict TBC-CMAS interactions and accelerate novel TBC development.
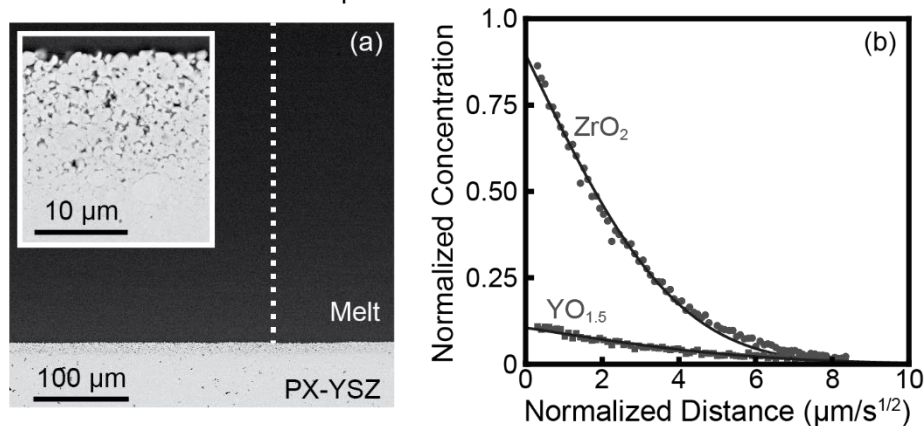

Figure 1 – 1-D TBC-CMAS diffusion couples enables the (a) analysis of the reaction zone (inset) and (b) collection of TBO (e.g. ZrO_2 and $YO_{1.5}$) concentration in the melt.