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The thermal behavior of CMAS-infiltrated thermal barrier coatings

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ABSTRACT

Understanding the mechanisms by which the durability and functionality of thermal barrier coatings (TBCs) are compromised by the infiltration of molten calcium–magnesium alumino-silicates (CMAS) requires an assessment of the effects on the thermal and mechanical properties of the coating. This study focuses on quantifying the effect of CMAS on the thermal properties and heat transport in TBCs. The thermal properties of a 7 wt.% yttria-stabilized zirconia (7YSZ) TBC deposited on a superalloy substrate by air plasma spray (APS) were measured before and after CMAS infiltration. A rise in both volumetric heat capacity and thermal conductivity of the coating was observed upon infiltration. Calculations to explain these trends were performed for a model TBC system and found to be in good agreement with the measured results. The evolution of the phase constitution of the coating was analyzed by Raman spectroscopy and the integrity of the interface was characterized by optical examination of cross sections. These tests determined that the coating remained in good contact with the substrate and experienced no phase change after infiltration.

1. Introduction

Among the mechanisms limiting the durability of thermal barrier coatings (TBCs) identified to date [1], one that has generated considerable concern is the infiltration of molten calcium–magnesium alumino-silicate (CMAS) deposits [2]. The net effect is the crystallization of the molten material within the pore structure of the TBC, degrading its in-plane compliance and increasing the potential for delamination upon thermal cycling [3]. Because silicate deposits can melt at temperatures of ~1200 °C or even lower [4,5], which are on the same order as the surface temperature of TBCs in current technology, CMAS infiltration becomes a fundamental barrier to further increases in turbine inlet gas temperature [2], and hence in engine efficiency. In addition to degrading the in-plane compliance of the coating the penetration of CMAS can attack chemically the insulating oxide, inducing destabilization of the t′ phase [4,6,7] desirable for toughness [8]. Moreover, the thermal insulation ability of the coating is reduced as the coating porosity is filled with solid phases [9], resulting in higher temperatures at the interface with the metallic substrate, and accelerated oxidation rates that can activate other modes of failure such as rumpling [10,11].

Changes in the thermal properties of the coating can also reveal critical information about the coating condition and the extent of CMAS infiltration. The latter is especially relevant since the accumulation of elastic strain that can drive delaminations is related to the depth of infiltration [3]. Hence, limiting the extent of CMAS infiltration has been a key driver in the search for advanced TBC designs [2,12–15]. A particularly promising approach is the use of Gd zirconate ($Gd_2Zr_2O_7$, GZO) in thermal barrier coatings [16], wherein a chemical reaction between molten CMAS and GZO induces rapid crystallization of the melt and inhibits infiltration [9]. If crystallization occurs rapidly within the outer pore structure of the coating and subsequent reaction proceeds slowly, as in GZO TBCs, the remaining issue is whether the thickness of the stiffened layer is sufficiently small to avoid delamination [3].

Proper characterization of the thermal behavior of an infiltrated TBC is essential in developing and validating models to predict the onset of delamination and the associated fail-safe condition [2,3,17,18]. A corollary benefit is a better understanding of the effect of CMAS on the overall heat transport through the coating system and temperatures at critical interfaces, notably those influencing the growth kinetics of the TGO. Photon transport through infiltrated coatings has been investigated previously [19]. That study demonstrated that CMAS infiltration caused an increase in radiation transport through the coating in the spectral range of 0.5–2.5 μm. The large increase in transmission, coupled with the higher gas temperatures in advanced engines where CMAS may be a problem, suggests that radiative heat transport can be significant for infiltrated coatings in an operating engine. The present paper addresses the complementary mechanism of phonon transport through a CMAS impregnated system. The results from both studies can then provide a better overall description of coating thermal performance after CMAS penetration.

Phase of photothermal emission analysis (PopTea) [20], differential scanning calorimetry (DSC) and density measurements are used in this study to determine the thermal properties of a typical thermal barrier coating deposited by air-plasma spray (APS) before and after CMAS infiltration. The experimental procedure outlined in this report yields an

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infiltration of amorphous CMAS, which is determined not to alter the chemical nature of the coating or lead to coating degradations. In real systems, a typical infiltration yields crystallized CMAS caused by high temperature exposure during engine cycles. In these systems, chemical attack can alter the coatings' thermal behavior and is extremely destructive to the coating. Based on bulk properties measurements of both crystallized and amorphous CMAS, the significance of this difference can be estimated for the infiltrated coating system.

2. Experimental details

2.1. Thermal measurements

PopTea is used as the primary technique to measure thermal properties in this paper. The principle of PopTea is to determine coating thermal properties by interrogating the phase of thermal emission from the coating established during modulated heating. The coating is heated with a CO_2 laser (10.6 μm and spot size of 6 mm) and thermal emission is measured with an InSb detector in the mid infrared (5 μm). PopTea measurements are made at 70 °C, controlled by a resistively heated stage. At this temperature there is no risk of inducing delaminations within a TBC or changing the coating thermal properties. Since temperature excursions within the coating caused by modulated heating are small, heat transfer is dominated by conduction and the measurement is not influenced by radiation through the coating. An analytical model has been developed to calculate the transient phase of thermal emission from the TBC as a function of unknown coating properties and known geometric parameters [20]. This model is used to evaluate candidate values of the coating properties from experimental measurements. A single measurement consists of recording the phase of thermal emission as a function of laser frequency. The range of laser frequencies is selected to achieve a wide range of thermal penetration depths, to allow the coating properties to be uniquely determined.

There are only two thermal parameters important to fit results from the PopTea method [21]:

$$a_{sub} = \sqrt{\frac{\alpha_{sub}}{\alpha_{coat}}} \quad \gamma = \sqrt{\frac{\left[k\rho C_p\right]_{sub}}{\left[k\rho C_p\right]_{coat}}}. \tag{1}$$

Both parameters, a_{sub} and γ, reflect the contrast between the two key thermal properties of the coating and substrate, i.e. the thermal diffusivity (α) and the thermal effusivity ($\sqrt{k\rho C_p}$).

While the capabilities of PopTea are well demonstrated, several complementary thermal measurements were used in this study to demonstrate the reliability of the results. Independent measurements of specific heat and density were made for comparison with PopTea. Specific heat values were determined by differential scanning calorimetry (DSC, Netzsch 404 C Pegasus). DSC measures specific heat by comparing the amount of heat necessary to raise the temperature of a sample and a known reference. The samples and reference used for these measurements were cylindrically polished pellets 3 mm in diameter and ~50 mg in weight. Sapphire was used for the reference and has a well-defined specific heat over the temperature range scanned. To make comparisons between specific heat (C_p) measured by DSC and volumetric heat capacity (ρC_p) measured by PopTea, the density (ρ) of each sample was measured using Archimedes principle with water as the fluid.

2.2. Specimen preparation and characterization

The sample used for CMAS infiltration was a 7 wt.% yttria-stabilized zirconia (7YSZ) coating deposited by air plasma spray on a Rene 80 Nickel-base superalloy (provided by Siemens Power, Inc.). The coating thickness was 300 μm, which is representative of TBCs deposited on turbine airfoils used in power generation. Measurements were made on this coating for three different coating conditions, as seen in Fig. 1. The first measurement (1) was made before infiltration to acquire baseline thermal properties needed for a pre/post infiltration comparison, and to determine the pristine coating density (ρ_{coat}) and corresponding pore volume fraction ($v_{coat} = 0.27$). Part of the coating surface was then infiltrated locally with CMAS in a high temperature furnace. A second measurement (2) was made on an un-infiltrated area of the coating to assess possible changes in thermal properties from the as-deposited condition due to temperature effects alone. The final measurement (3) was made on an area of the coating experiencing the full CMAS infiltration.

In addition to the coating measurements, dense amorphous and crystallized CMAS pellets were thermally characterized to help understand the changes caused by coating infiltration. Both CMAS pellets used for characterization were made from CMAS powder with the composition shown in Table 1. The pellets were formed by pressing the powder into flat discs and melting them on platinum foil in a high temperature controlled furnace. Amorphous CMAS was generated by rapidly ramping up and down (~10 °C/min) from the melting point (~1250 °C). To create crystallized CMAS from amorphous stock, the pellet was held within the crystallization range previously determined by DSC (~1080 °C) for 6 h and slowly cooled at 2 °C/min.

The amorphous pellet was used for infiltration of the TBC and polished into a 1 cm diameter disc, 80 μm thick. The pellet thickness was dictated by requirements for full infiltration of the coating ($h = L \times v_{coat}$) where L is the coating thickness and the void fraction v_{coat}. The coating thickness was measured from micrographs of the TBC cross-section and the void fraction was determined from measurements on the as-deposited, un-infiltrated coating. To infiltrate the coating, the amorphous CMAS pellet was placed at the center of the coupon and heated uniformly in a temperature controlled furnace to 1250 °C at 10 °C/min followed by immediate cooling at 10 °C/min to 1000 °C. To prevent thermal shock or "desktop spallation" [22] of the infiltrated coating, the sample was cooled slowly (2 °C/min) for temperatures below 1000 °C in order to allow the glass stresses, induced by the thermal expansion mismatch, to relax [23]. This treatment permitted full infiltration of the coating porosity without evidence of YSZ decomposition or coating delamination, as shown below.

The integrity of the coating microstructure and bond coat is revealed in the optical micrographs of the coating sectioned after the measurements, shown in Fig. 2. The infiltrated region appears to be in perfect contact with the substrate (i.e. no spallation, or coating separation). Furthermore, the condition of the infiltrated coating is uniform and without cracks. The extent of the infiltrated CMAS can be readily identified by a contrast in the image between the infiltrated and uninfiltrated regions, created by differences in polishing properties of the two regions.

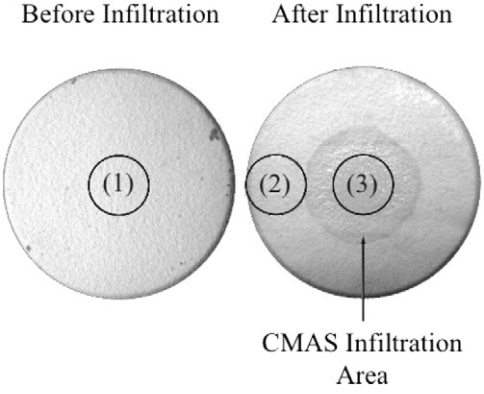

Fig. 1. Top view of TBC before and after CMAS infiltration. Locations of PopTea measurements are highlighted. (1) Baseline, before infiltration; (2) uninfiltrated region after high temperature exposure; (3) infiltrated region of coating.