Nondestructive evaluation of the oxidation stresses through thermal barrier coatings using Cr$^{3+}$ piezospectroscopy

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The stresses in the aluminum oxide formed during high-temperature oxidation of a bond-coated superalloy are shown to be measurable through zirconia thermal barrier coatings. The basis for the measurements is the piezospectroscopic shift in the $R$-line fluorescence (photoluminescence) from Cr$^{3+}$ impurities incorporated into the growing aluminum oxide scale. Measurements through the thermal barrier coating are feasible because (partially stabilized) zirconia coatings have some transparency at both the excitation and at fluorescence frequencies. © 1996 American Institute of Physics.

Thick (100 $\mu$m–2 mm) partially stabilized zirconia (PSZ) coatings are increasingly being used in industry to thermally insulate internally cooled metallic components, enabling gas turbines and diesel engines to be operated at significantly higher temperatures. While the coating provides a thermal barrier, it does not block oxidation of the underlying metal because ZrO$_2$ is a fast oxygen-ion conductor at high temperatures. As a result, an oxide [termed the thermally grown oxide, (TGO)] gradually grows at the interface between the metal and the coating. Indeed, in many applications an aluminum-rich coating, termed the bond coat, is applied to the metal prior to the deposition of the thermal barrier coating (TBC) in order to promote the formation of a highly stable, protective aluminum oxide phase upon oxidation. A sample cross section through a TBC coating is shown in Fig. 1.

Knowledge of the stresses in the thermally grown oxide is of importance because the thermal barrier coatings typically fail mechanically by spalling from the oxide, and there is evidence that the coating lifetime is limited by the oxidation kinetics of the bond coat. Unfortunately, as the TGO is buried beneath a thick ceramic coating, the determination of the stresses in the TGO has been intractable. In this letter, we demonstrate that the stresses in the thermally grown oxide under the TBC can be measured piezospectroscopically utilizing the trace Cr$^{3+}$ ions incorporated in the growing alpha-alumina scale. This takes advantage of the transparency of the zirconia coating at optical frequencies, allowing stresses to be probed in the thermally grown oxide.

The thermal barrier coatings examined were typical high-performance coatings deposited by electron-beam evaporation onto a preheated platinum-aluminide bond-coated nickel-based superalloy. Visually, the coatings appear white or cream in color as a result of scattering from the intercolumnar porosity. The porosity is deliberately introduced into the TBC to decrease its lateral elastic modulus and consequently enhance its thermal strain accommodation with the underlying metal. Despite the porosity and grain

FIG. 1. (a) Scanning electron micrograph of a representative cross section of a PSZ thermal barrier coated N5 superalloy with an intermediate bond coat, illustrating the dimensions of the coating and the columnar microstructure of the electron-beam evaporated TBC. (The thermally grown oxide is too thin to be seen in this micrograph but is situated just above the crack running horizontally below the TBC. The bright band well below the TBC is a reaction zone between the bond coat above and the alloy below.) (b) Schematic cross section and the wavelengths used in probing the stresses in the thermally grown oxide (TGO).
boundary scattering, the coatings are partially translucent since the optical band gap of partially stabilized zirconia is \(~12\text{ eV}\) — well above the energy of either those of argon-ion lasers (514 and 488 nm) or the characteristic ruby \(R\)-line fluorescence from \(\text{Cr}^{3+}\) ions in aluminum oxide (at 693 nm). When the coatings are illuminated using an argon ion laser, characteristic ruby \(R\)-line fluorescence from \(\text{Cr}^{3+}\) ions in aluminum oxide can be detected. The fluorescence measurements described in this work were made using an optical microscope-based system with an attached double monochromator and CCD detector for collecting the fluorescence spectrum.\(^4\) The measurements were all made at room temperature. The \(R\)-line spectra recorded were subsequently analyzed using a commercially available software package treating the spectral lineshapes as pseudo-Voigt functions.

Figure 2 compares the spectrum recorded after 700 h oxidation at \(1135^\circ\text{C}\) with that from a spalled coating with the TGO still attached (from the same sample), illustrating the shift and broadening of the \(R\) and \(\overline{R}\) lines. The \(R\)-line spectra recorded from the underlying TGO were similar to those obtained from oxide scales formed by isothermal oxidation of several alumina-forming alloys, including the same superalloy.\(^4\) The spectra were shifted by several wave-numbers with respect to the scale spalled from the metal, and both the \(R\) and \(\overline{R}\) lines were extensively broadened. (The broadening is attributed to the existence of strain gradients through the volume of oxide probed by the exciting laser.)\(^5\) Spectra were recorded from thermal barrier coated samples that were oxidized for different times at \(1135^\circ\text{C}\). The observed frequency shifts of the \(R\) line are reproduced in Fig. 3. The evolution of the piezospectroscopic shift and the calculated biaxial stresses in the TGO as a function of oxidation time at \(1135^\circ\text{C}\) appears to decrease. The cause of this behavior is not fully understood but has been linked to the onset of decohesion of the oxide scale from the alloys in the absence of the thermal barrier coating.

In summary, it is shown that it is possible to measure the stresses in the thermally grown oxide formed underneath thermal barrier coatings after high-temperature exposure to...
an oxidizing atmosphere. The measurement relies on the translucency of thermal barrier coating at visible wavelengths and the piezospectroscopic properties of trace impurities of Cr$_3^+$ incorporated into the thermally grown oxide. Similar observations have also been made through plasma-sprayed coatings, but the greater scattering from porosity in such coatings generally requires the use of more intense laser probes or thinner coatings. The nondestructive nature of the piezospectroscopic technique suggests the possibility of non-contact monitoring of stress development through the life of a thermal barrier coated metal component.

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3 R. H. French (private communication).