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Influence of temperature and hot corrosion on the micro–nanomechanical behavior of protective mullite EBCs

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ABSTRACT

Materials for components installed in the hot section of gas turbines must endure highly aggressive conditions, such as elevated temperatures and corrosive environments. Under these scenarios, CVD mullite coatings enriched in alumina in the outer surface have demonstrated excellent thermal stability and protection to SiC against corrosion and recession. It is essential that, in addition to the excellent protective behavior exhibited by Al-rich mullite coatings, their structural integrity and mechanical properties can be retained after their exposure to such aggressive conditions. This investigation is devoted to the study of the effect of temperature and hot-corrosion on the main micro–nanomechanical properties and performance of mullite-based EBCs. Nanoindentation was conducted to determine coatings' hardness, stiffness and fracture toughness whereas nanoscratch tests allowed evaluating their intrinsic structural integrity. Temperature and corrosion were found to have a minor effect on the mechanical behavior of the studied coatings. Hardness and Young's modulus remained comparable after thermal treatments, and scratch tests show similar damage features. From these results it can be concluded that mullite-based coatings present a satisfactory structural integrity and reliability to be used as environmental barrier coatings for hot environments.

1. Introduction

It has been widely demonstrated that mullite ($3Al_2O_3 \cdot 2SiO_2$) coatings are optimal candidates to protect silicon-based ceramics, such as SiC and Si_3N_4, from the aggressive environments characteristic in the hot section of gas turbines [1–10]. Consequently, mullite is an optimal material as Environmental Barrier Coatings (EBCs). However, several investigations have shown that the silicon present in mullite may be prone to undergo corrosion during long term exposures to atmospheres containing corrosive agents and water vapor [8,11–15], losing its properties as EBC's.

The most effective approach to overcome the problem of Si-corrosion in mullite coatings has been to fabricate alumina-rich coatings by Chemical Vapor Deposition (CVD). This technique allows obtaining columnar mullite coatings in which the Al/Si ratio may be tailored to get alumina-rich compositions (almost silicon-free) at their outer surface, in direct contact with corrosive atmospheres. The alumina rich surface is then resistant to corrosion and recession, making the EBC durable and resistant.

Two different strategies have been done: Al-rich mullite coatings with different Al/Si ratios (obtained by keeping the input gases constant during deposition), and compositionally graded coatings (obtained by grading the input gas ratios during deposition) [1–3,5,7,9,10,16–18].

Under the demanding conditions of gas turbines, mullite coatings are required to exhibit high chemical (oxidation and corrosion resistance) and thermo-mechanical (thermal shock resistance) properties. Moreover, since most of the applications at elevated temperatures operate at long-term, these materials must provide superior long-term stability as well. Within this context, several investigations have been conducted to evaluate the behavior of mullite-containing EBCs deposited on Si-based substrates when subjected to thermal stability, thermal shock and hot corrosion conditions [3,5,10,14–16,19,20].

The thermal stability behavior of compositionally graded CVD mullite coatings was addressed in a previous investigation [3]. Mullite coated SiC samples were subjected to different heat treatments in the temperature range of 1100–1400 °C. Main outcomes of the study include:

1) a tetragonal to orthorhombic transformation in the structure of mullite coatings when exposed to 1250 °C during 100 h, such transformation occurs without compositional changes
2) a transformation of the entire coating microstructure from columnar into equiaxed crystalline grains after the same heat treatment

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3) a precipitation of nanosized α-alumina in the Al-rich regime of the coatings when performing a two-step annealing process of 1250 °C for 100 h, followed by one at 1400 °C during extra 100 h.

In this previous work, compositionally graded mullite coatings were also subjected to thermal cycling between 1250 °C and room temperature for 500 cycles [3]. In this cyclic thermal shock test the adhesion of mullite coatings to the SiC substrate was qualitatively evaluated after the tests. Graded mullite coatings showed no signs of significant cracking and/or spallation.

The hot corrosion of different CVD mullite coatings deposited on SiC has also been studied [10]. Mullite coatings with different Al-rich compositions at the surface were sprayed with Na_2SO_4 and subjected to flowing oxygen environments at 1200 °C for 100 h. It was found that corrosion protection increases with the Al/Si ratio at the surface of coatings; and after the tests, none of the specimens was visibly affected by corrosion even under the severe circumstances simulated in the study. Although there was evidence of some minor reactions at isolated parts of the Al-rich coatings, Na penetration into the bulk was negligible.

In addition to the highly aggressive environments that materials for gas turbines must endure in service conditions, they are required to exhibit an optimum combination of mechanical properties that guarantees their structural integrity. Although the micro–nanomechanical behavior of as-deposited mullite EBCs has been recently documented [21–23], similar information about the influence of temperature and corrosion on the mechanical properties evolution of these coatings is inexistent.

The objective of this work is to evaluate such influence. For doing so, several Al-rich mullite/SiC coated samples are subjected to thermal stability, thermal shock and corrosion treatments; and their micromechanical behavior is subsequently evaluated. Nanoindentation is implemented to assess coatings' hardness (H_f), elastic modulus (E_f) and fracture toughness (K_f), and nanoscratch tests are conducted to evaluate their intrinsic structural integrity. Results are compared with the mechanical properties found for the same materials in the as-deposited condition.

2. Experimental

2.1. Materials and sample preparation

Chemical vapor deposition was used to deposit columnar mullite coatings on SiC, following the procedure detailed in references [5,7,9]. The resulting microstructure of coatings may be observed in the etched cross section of Fig. 1a.

Al-rich coatings were obtained by both keeping the input gases constant during the deposition process to generate an alumina-rich mullite coating (Al/Si ≈ 7), and by varying the stoichiometry of input gases during the experiment to obtain compositionally graded coatings. For comparison reasons, stoichiometric mullite coatings (Al/Si: 3) were also deposited. Compositions of coatings were determined by chemical analysis through energy-dispersive X-ray spectroscopy (EDX) performed on several points along their cross-sections. Average values of coatings' composition in terms of the Al/Si ratio yield Al/Si: 3, 7 and in the case of graded coatings, Al/Si varies from 3 to 16. Average sample thicknesses, measured in zones far from the edges, range between 15 and 20 μm.

For the nanoindentation tests, top surfaces of coatings were polished with diamond suspension of 6 μm followed by 3 μm, and finished with colloidal silica suspension, in order to achieve a flat mirror-like surface. Similar sample preparation procedure was followed for attaining polished cross-sections and wedge geometries of compositionally graded coatings. For the nanoscratch tests, a lightly polished surface was attained by fine polishing using a 3 μm diamond paste for 20 min and colloidal silica during 5 min. With this polishing, surface irregularities were removed, while keeping the surface and thickness of coatings as close as possible to the non-polished condition.

2.2. High temperature and hot corrosion treatments

Long term stability, thermal shock and hot corrosion treatments were performed on selected coatings as detailed in Table 1. Specimens used for mechanical testing are identified through codes in which the first digit corresponds to the Al/Si ratio; a number in the case of constant compositions (3 or 7) and the letter "G" in the case of graded coatings. The remaining digits are related to the condition of the tested specimen; AD for specimens in the "as-deposited" condition, i.e. without treatments; TS for specimens subjected to the thermal stability test; TSh for specimens subjected to the thermal shock test; and HC to the specimen subjected to the hot corrosion treatment. The scheme of Fig. 1b resumes the temperature conditions for the referred treatments.

2.2.1. Long term stability

Specimens were subjected to a thermal stability test consisting in heating them until 1250 °C and maintaining at this temperature for 100 h in a tubular furnace, with heating and cooling ramps of 5 °C/min. These thermal stability tests were implemented specifically on coatings with Al/Si: 3 and 7, and on the compositionally graded coating.

2.2.2. Thermal shock

Coatings were subjected to a thermal shock treatment consisting in heating the specimens at 1250 °C for 3 h in a tubular furnace (heating

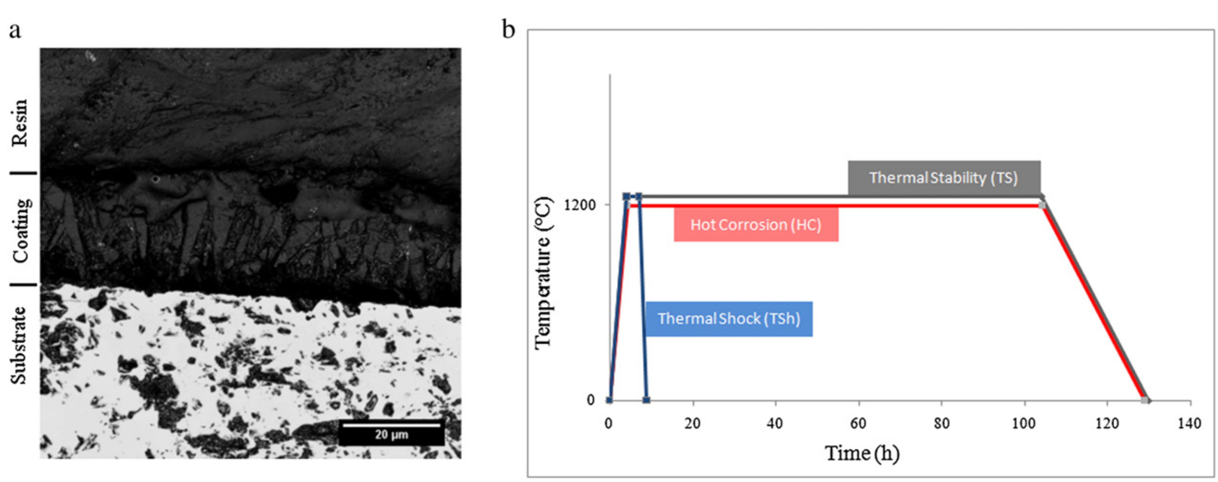

Fig. 1. Cross section of a compositionally graded mullite coating (a). Columnar microstructure is revealed after etching coatings' cross section with HF solution at 60 °C for 10 min. Scheme illustrating conditions for the thermal and hot corrosion treatments performed (b).