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Nanoindentation and nanoscratch properties of mullite-based environmental barrier coatings: Influence of chemical composition — Al/Si ratio

C.A. Botero [a,b,*], E. Jimenez-Piqué [a,b], R. Martín [a], T. Kulkarni [c], V.K. Sarin [c], L. Llanes [a,b]

[a] CIEFMA — Departament de Ciència dels Materials i Enginyeria Metallúrgica, Universitat Politècnica de Catalunya, ETSEIB, Avda. Diagonal 647, Barcelona 08028, Spain
[b] CRnE, Campus Diagonal Sud, Universitat Politècnica de Catalunya, C/Pascual i Vila 15, Barcelona 08028, Spain
[c] Department of Mechanical Engineering, Boston University, 110 Cummington Street, Boston, MA 02215, USA

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ABSTRACT

The mechanical properties and structural integrity of mullite ($3Al_2O_3 \cdot 2SiO_2$) environmental barrier coatings (EBCs) are key factors towards the implementation of these systems in real applications. By using chemical vapor deposition, the chemical composition of mullite in these coatings may be tailored to obtain high Al/Si ratios in the outer surface, for an optimum corrosion protection in gas turbine environments. In this work, the influence of such Al/Si ratio on the mechanical properties and structural integrity of different Al-rich mullite coatings is evaluated by means of nanoindentation and nanoscratch tests. It is found that hardness and elastic modulus of the coating increases as the Al/Si ratio raises. On the other hand, an inverse trend is discerned for the apparent fracture toughness, although this is stated to be an indirect consequence of the resulting residual stress state, without any relevant effect on the intrinsic toughness of the mullite coatings. Regarding structural integrity, an increasingly brittle response to the sliding contact is evidenced as chemical composition moves towards higher Al/Si ratios. However, within the load range studied, brittle-like damage at the coating surface did not translate into critical decohesion at the coating/substrate interface. It sustains the effective protective role of the studied layers as EBCs. Therefore, all the studied coatings are found to exhibit a suitable structural integrity for their potential use as EBCs.

1. Introduction

Mullite coatings have proven to be excellent alternatives to protect Si-based substrates from the corrosive environments found in the hot section of gas turbines [1–4]. Mullite is an ideal material for such purpose, particularly because of the similarities between its thermal expansion coefficient and that of SiC, avoiding thermal stresses to build up. In addition, it possesses a high stability at elevated temperatures, an excellent corrosion resistance and a low thermal conductivity [5]. Moreover, mullite has an excellent creep and thermal shock resistance, as well as the ability to retain its strength at elevated temperatures [6]. All these properties make mullite one of the best candidates for being used as environmental barrier coatings (EBCs) of Si-base substrates.

On the other hand, there are also shortcomings on the use of mullite as EBCs. The silica content of mullite coatings might be susceptible to hot-corrosion and recession during extended exposure to combustion atmospheres that contain molten salt and water vapor. Under such conditions, these coatings suffer the preferential loss of silica, leaving behind an alumina skeleton [2,7]. Consequently, there is a strong motivation to decrease the silicon content in mullite, especially in the outermost surface of the coatings, aiming to protect silicon carbide from the corrosive combustion environments. In this regard, an approach based on increasing the Al/Si ratio within the chemical composition of mullite by chemical vapor deposition (CVD) has proven to be effective [8–15]. By tailoring the ratio of the input gases during the deposition process, high Al/Si ratios can be achieved at the top surface of the coatings. Al-rich coatings obtained in this way present high temperature resistance and improved protection of SiC against oxidation at elevated temperatures [10,13,15].

In a recent investigation [15], the hot corrosion of different CVD mullite coatings was studied. Mullite coatings with different Al-rich compositions at the surface (Al/Si from 3 to 16) were covered with Na_2SO_4 acting as a molten salt and subjected to flowing oxygen environments at 1200 °C for 100 h. It was evidenced that protection increases proportionally with the Al/Si ratio at the surface of the tested coatings, approaching the values exhibited by bulk alumina. Thus, by tailoring the Al/Si ratio within the mullite structure of the coatings, their corrosion behavior may be driven to that of alumina.

Beyond the evaluation and understanding of the corrosion behavior of mullite-base EBCs, it must be pointed out that the study and comprehension of the micro/nano-mechanical properties of these coatings,

* Corresponding author.
E-mail address: carlos.alberto.botero@upc.edu (C.A. Botero).

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aimed to guarantee their structural integrity and reliability, are crucial for the practical and effective implementation of the mullite/SiC system in real applications. In this context, it becomes essential not only to investigate the micro/nano-mechanical behavior and integrity of mullite coatings, but also to understand the influence of the mullite composition on such behavior.

Following the above ideas, in this work the effect of chemical composition (given in terms of the Al/Si ratio) on the mechanical behavior of mullite coatings is investigated by using nanoindentation and nanoscratch tests. In doing so, two categories of coatings are studied: 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). Stoichiometric bulk mullite and alumina specimens were also investigated for comparison purposes.

Assessment of the mechanical properties and structural integrity of the studied Al-rich coatings is carried out by means of nanoindentation and nanoscratch tests, using both Berkovich and cube corner tips. Special emphasis is placed on evaluation of film hardness (H_f), elastic modulus (E_f) and fracture toughness (K_f), as well as scratch resistance. Results of the micro/nano-mechanical tests of the coatings are also analyzed and compared with those found for bulk specimens.

2. Experimental

2.1. Materials and sample preparation

Mullite coatings were deposited on SiC bars by using the CVD technique, in a hot-wall reactor. Deposition was carried out under the system of gases $AlCl_3$–$SiCl_3$–CO_2–H_2, at a temperature of 975 °C and a total reactor pressure of 75 Torr. A more detailed description of the deposition process and its parameters is given somewhere else [13]. The Al/Si ratio of the input gases was sustained constant during the course of the experiment to obtain different Al-rich coatings with varied Al/Si ratios (3, 5, 7, 10, 11). In addition, compositionally graded coatings were deposited by varying the stoichiometry of input gases ($SiCl_4$ and $AlCl_3$) from 3 to 11 during the experiment.

The obtained microstructure is columnar, as it may be discerned in Fig. 1. Coating thickness varied across the surface at the different faces of samples, especially at the edges. Average thicknesses measured on the cross-section of coatings, in zones far from the edges, are listed in Table 1. Composition of coatings was investigated by chemical analysis through energy-dispersive X-ray spectroscopy (EDX). Such analyses were performed on at least 5 points along cross-sections of studied coatings. Average values for the molar Al/Si ratio of each coating are also included in Table 1, together with the corresponding input gas ratio used for their deposition.

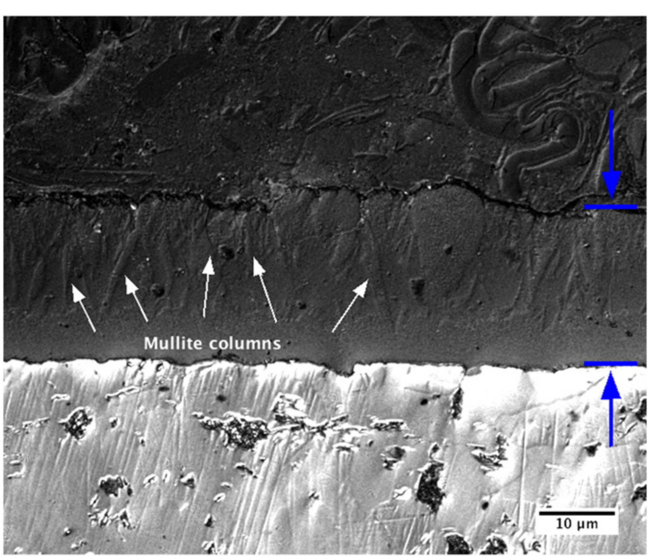

Fig. 1. Polished cross section of sample *M8*, where the columnar microstructure of the coatings is revealed.

The nomenclature of the coated specimens investigated in this work (Table 1) is defined by means of codes combining the letter "*M*" (from mullite) and a number equivalent to the Al/Si ratio in the coatings (3, 5–8). Regarding the cases of compositionally graded samples, they are referred to as "*Graded*". A final digit (I, II or III) is added to the code (only for *M3* and graded conditions) to indicate different specimens for a given composition.

The top surfaces of coatings with constant Al/Si ratios were slightly polished with diamond suspension of 6 μm followed by 3 μm, and finished with colloidal silica suspension, in order to achieve a flat surface necessary for nanoindentation. Similar sample preparation procedure was followed for attaining polished cross-sections and wedge geometries of compositionally graded samples.

For comparison purposes, bulk specimens of stoichiometric 3:2 mullite ($3Al_2O_3 \cdot 2SiO_2$) and alumina (α-Al_2O_3, mean grain size around 2 μm) were also tested.

2.2. Nanoindentation tests

Hardness and elastic modulus were evaluated as a function of the penetration depth on the basis of Oliver and Pharr's model [16]. Tests were performed at a constant strain rate of 0.05 s^{-1}, using a Berkovich indenter with its area function calibrated by means of a fused silica standard. The continuous stiffness measurement (*CSM*) modulus was activated so that the load (P) — penetration (h) data and the contact stiffness (S) were continuously recorded.

Matrices of 3×3 Berkovich indentations were performed at $h_{max} = 2000$ nm and 100 nm on the polished top surface of samples *M3-I*, *M3-II*, *M3-III*, *M5*, *M6*, *M7* and *M8*. Tests were conducted in at least four different (randomly selected) locations at the surface of the coatings, yielding similar results for each specific composition.

The variation of H_f and E_f across the thickness was evaluated in the compositionally graded samples. In doing so, two approaches regarding the nanoindentation tests, named "cross-sectional" and "wedge", were implemented. They are illustrated in Fig. 2. Tests were performed at a penetration depth of $h_{max} = 100$ nm in all the cases. As schematically shown in Fig. 2a, in the cross-sectional approach indentation matrices of 3 columns, with a separation between indents of 2.5 μm, were performed across the thickness of samples *Graded-I* and *Graded-II*. Moreover, to avoid the substrate influence, in the specific case of sample *Graded-II* a portion of the coating was mechanically detached from the substrate, embedded in resin, polished and indented through its free-standing cross section. In addition, similar indentation matrices were conducted following the wedge approach (exclusively in sample

Table 1
Sample designation, Al/Si ratios in the input gases, final composition of coatings and average thickness in the "as-deposited" state for all the coatings studied.

Sample designation	Al/Si input ratio	Al/Si coating composition	Thickness (average value, μm)
M3-I	3	3 ± 1	9 ± 3
M3-II			8 ± 2
M3-III			16 ± 8
M5	5	5 ± 1	6 ± 3
M6	7	6 ± 1	21 ± 3
M7	10	7 ± 2	15 ± 4
M8	11	8 ± 1	20 ± 3
M11	11	11 ± 3	20 ± 2
Graded-I	Changing 3 to 11	Increasing 3 to 18	15 ± 4
Graded-II			15 ± 5