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Step-by-step investigation of degradation mechanisms induced by CMAS attack on YSZ materials for TBC applications

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ABSTRACT

Over the past decades, Thermal Barrier Coatings (TBCs) have become essential parts in gas turbine engines. In working conditions, TBCs are subject to many kinds of degradation (erosion, foreign object damage (F.O.D), oxidation, etc.) which deteriorate integrity and mechanical properties of the whole system. Moreover, with the aim to increase the turbine inlet temperature, a new type of damage has been highlighted: corrosion by molten Calcium–Magnesium–Alumino Silicates, better known as CMAS. In this paper, interactions between yttria-stabilized zirconia (YSZ) materials synthesized via sol–gel process and synthetic CMAS powder were investigated via a step-by-step methodology. The approach was conducted starting from the more severe conditions of interactions and then gradually gets closer to the interactions taking place in service. It was proved that CMAS can induce faster densification of the ceramic leading to a loss of strain tolerance of the protective coating. Besides, a dissolution/re-precipitation mechanism can also take place between YSZ and CMAS leading to the transformation of the initial tetragonal yttria-stabilized zirconia into globular particles of monoclinic zirconia. CMAS were also found to infiltrate the entire thickness of both EBPVD and sol–gel YSZ coatings at 1250 °C for 1 h. Nevertheless, the original non-oriented microstructure provided by sol–gel route leads to a different way of interaction due to the high reactivity of sol–gel precursors and materials. The behaviors of EBPVD and sol–gel coatings under CMAS exposure are discussed in this paper.

1. Introduction

Since many years, engine manufacturers are focused on the improvement of engine performance and fuel efficiency. The increase of the turbine inlet temperature was made easier by three main factors relative to material or process improvements: i) advances in superalloy compositions, ii) casting technology, and iii) the incorporation of Thermal Barrier Coatings (TBCs) in the whole systems [1,2]. TBCs are now widely used to insulate and protect critical metallic parts in hot sections of gas turbine engines by decreasing their surface temperature [3].

TBCs are multilayered systems consisting of a ceramic top-coat with a low thermal conductivity (generally yttria-stabilized zirconia (YSZ)) which provides thermal insulation. This coating is deposited on an oxidation resistant aluminide metallic bond-coat. Currently, the ceramic layer is industrially realized by either Air Plasma Spraying (APS) or Electron Beam Physical Vapor Deposition (EBPVD) resulting in lamellar or columnar microstructures respectively. The first quoted technique is generally used to produce TBCs on combustion chamber parts and vanes, whereas the blades are normally covered with the second one. These protective coatings allowed engines to reach temperatures as high as 1600 °C, thereby improving engine efficiency and lifetime of the underlying superalloys. Nevertheless, this increase of working temperature has induced new degradation phenomena. Indeed, in working conditions, engines can ingest various kinds of particles (dust, sand, volcanic ashes, etc.). Most of them are Calcium–Magnesium–Alumino Silicates, called CMAS (relative to the main chemical components Ca, Mg, Al and Si). Actually, with the increase of the usual operating temperatures, TBC surface temperature is now able to be locally higher than the melting point of these CMAS. Because of their excellent wettability characteristics and their low viscosity [4], these contaminants can infiltrate internal porosity of the TBCs. This is particularly true for EBPVD coatings in which the vertically oriented microstructure eases the infiltration.

Upon cooling, the molten CMAS solidifies and causes high thermomechanical stresses in the ceramic layer [5–7]. The protective coating develops progressive and crossing cracks which lead to its progressive delamination during thermal cycling and premature degradation of the superalloy. Otherwise, the chemical interactions between CMAS and YSZ top-coat result in a complex dissolution/re-precipitation mechanism. Krämer et al. [4] investigated the thermochemical degradation of YSZ coatings. They explained that zirconia can re-precipitates as yttria-depleted ZrO_2 grains after interaction with CMAS. As a result, the allotropic transformation of zirconia (which is no longer stabilized) is likely to happen and thus could generate microcracks within the TBC.

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Our aim in this study is to describe the effects of CMAS on sol–gel YSZ materials exhibiting specific morphology compared to an industrial EBPVD TBC system. A "reference" YSZ material prepared by sol–gel route has been chosen for this investigation. This soft chemical process has already shown a real potential to make high purity nanocrystalline materials with a controlled morphology. Associated with dip-coating or any appropriate coating technique, this process allows producing either thin or thick ceramic coatings with a non-oriented microstructure [8,9] (in opposition to EBPVD or APS coatings).

Because of the complex mechanisms involved in the interaction between CMAS and YSZ, we decided to split our investigation in three different steps starting from the more severe conditions of interactions and then gradually get closer to the interactions taking place in service. A flowchart of the methodology is presented in Fig. 1.

As shown in Fig. 1, our approach consisted in the first part to put YSZ fine powders in close contact with CMAS. This first step was set up in order to highlight if new crystalline phases can be formed after interaction. The high specific surface area of the YSZ aerogel powder increases its reactivity allowing a strong interaction with silicates. These conditions of mixture are the more severe to quantify the interactions and reactivity between CMAS and yttria-stabilized zirconia. Then, prior to studying the interaction taking place between CMAS and YSZ coatings (3rd step), an intermediate step was performed. In this case, dense YSZ pellets were exposed to the CMAS powder (2nd step) so as to evaluate the infiltration of contaminants within a dense ceramic and the microstructural changes induced by CMAS. This intermediate step allows us to understand the mechanisms and determine the interaction at the interface while avoiding capillary effects which can occur with porous TBCs. Finally, the degradation of YSZ EBPVD TBC and YSZ sol–gel coating was compared (3rd step).

2. Characterization methods

X-ray diffraction (XRD) and Rietveld refinement were performed for phase identification. X-ray diffraction patterns were collected with a *Bruker D4 ENDEAVOR* diffractometer in standard θ–2θ Bragg–Brentano geometry. Copper radiation was used as X-ray source ($\lambda(\mathrm{Cu}_{K\alpha1}) = 0.15406$ nm; $\lambda(\mathrm{Cu}_{K\alpha2}) = 0.15444$ nm). Diffraction intensity was measured at room temperature in the 2θ interval between 10° and 100°, with a step of 0.016° and 23 s by step. The X-ray diffraction diagrams were refined with the Rietveld method using the FullProf software package. For the tetragonal and monoclinic phases the space groups used for Rietveld refinement were $P4_2/nmc$ (137) and $P2_1/C$ (14) respectively. The microstructural analyses were carried out using a scanning electron microscope (SEM) *JEOL JSM6400* and a SEM with Field Emission Gun (SEM-FEG) *JEOL-6700F*. The specific surface area of YSZ powder was determined by the Brunauer–Emmett–Teller (BET) method using the N_2 absorption–desorption at 77 K. The powder was first degassed at 250 °C for 3 h.

3. Starting materials

3.1. Preparation of YSZ materials by sol–gel route

The sol–gel process is a wet chemical technique widely used to synthesize nanostructured materials. In our study, YSZ sol–gel materials were prepared in the form of powder, dense pellets and thick coatings.

The precursors used to synthesize 9.7 mol% yttria-stabilized zirconia (YSZ) sols were zirconium (IV) propoxide ($Zr(OPr)_4$, 70%wt solution in 1-propanol), and yttrium (III) nitrate hexahydrate in 1-propanol (solvent). In order to control the kinetics of zirconium alkoxide hydrolysis which is much faster than condensation, acetylacetone (AcAc) is

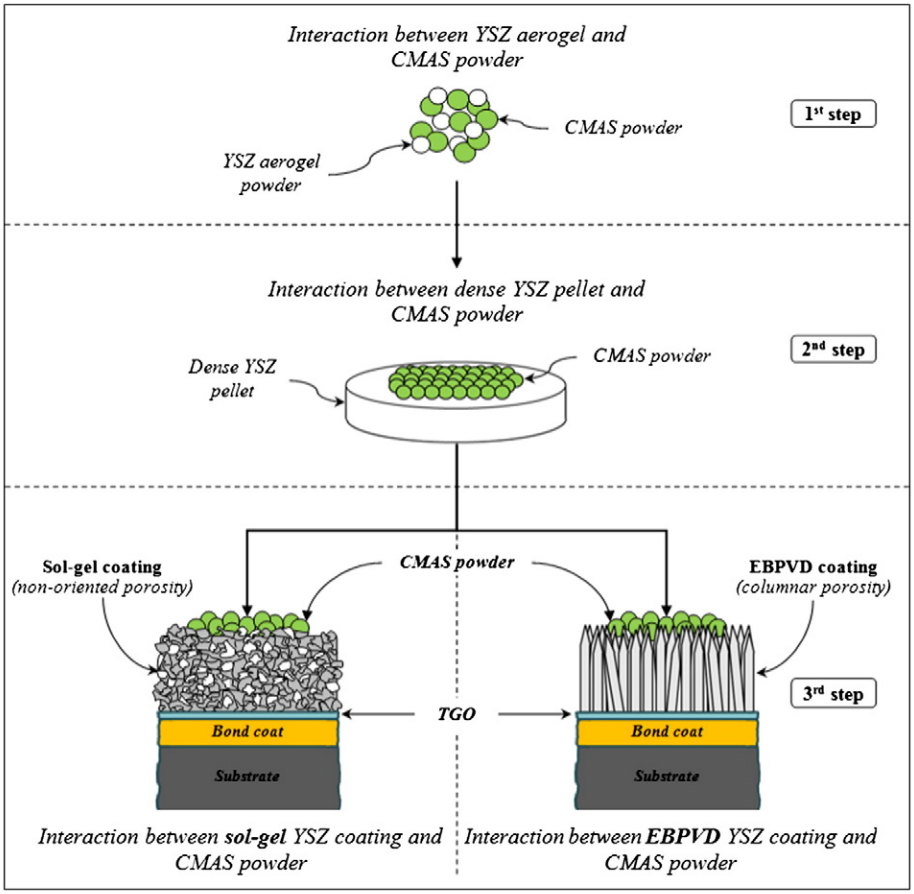

Fig. 1. Flowchart of the methodology followed in our step-by-step investigation.