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Thermal properties and phase stability of Yttria-Stabilized Zirconia (YSZ) coating deposited by Air Plasma Spray onto a Ni-base superalloy

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ABSTRACT

Thermal properties and microstructure characterization of Yttria Stabilized Zirconia (YSZ) Thermal Barrier Coatings (TBCs) deposited by Air Plasma Spray (APS) onto a Ni-base superalloy (Inconel 625) were studied. Two separate sets of tests were performed. The first one consisted in Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) performed over free-standing TC samples detached from TBCs. The second one included the analysis of the cross section of samples heat treated at 1100 °C with holding times of 600, 1000, and 1700 h. The TC porosity was analyzed for different heat treatment conditions so that inter-lamellar, intra-lamellar and globular pores, as well as cracks, were identified and quantified independently. An initial porosity reduction related to inter-lamellar and intra-lamellar pores, as well as cracks, was observed during the first 600 h of heat treatment, due to sintering. However, porosity continually increased during heat treatment from 600 to 1700 h driven by volumetric changes associated to phase transformations. During this period, yttrium diffused from the metastable tetragonal phase favoring the transformation to cubic phase while monoclinic phase transformed after cooling from the yttrium-depleted tetragonal phase. Energy absorption curves and the variation of heat capacity with temperature were also determined and correlated to microstructural changes.

1. Introduction

Thermal Barrier Coatings (TBCs) define the operational limits and capabilities of gas turbines. The overall performance of such machines is determined by the morphology and microstructural behavior of the Top Coat (TC) when it operates at high temperature. One of the most widely used materials for the TC, particularly in land-based gas turbines, has been 7–8 wt% Yttria-Stabilized Zirconia (YSZ) applied by Atmospheric Plasma Spray (APS) [1]. During turbine operation, the TBCs undergo microstructural and morphological changes. Long-term operation eventually causes a detriment of the TC integrity affecting the mechanical and thermal properties, which directly impacts the reliability of components located in hot gas paths [2]. The lack of precise knowledge about the evolution of the TC microstructure under specific operation regimes (specially non-steady turbine operation) leads to an increment in the repairing costs, as well as a reduction in the efficiency in power generation [2,3]. Determining microstructural and morphological variations of the TC and their effect on the thermal properties under conditions similar to those of operation at gas turbines provides valuable information about thermal efficiency and expected lifetime [4,5]. The variation in thermal properties of YSZ, such as the specific heat at constant pressure (C_p) and the enthalpy of physical-chemical reactions, determine the level of TC degradation and its thermal protection capabilities [6,7]. Wang et al., for instance, reported C_p values between 0.51 ± 0.01 and $0.69 \pm 0.02\ J\,g^{-1}\,K^{-1}$ and thermal conductivity ranging from 1.9 to $2.4\ W\,m^{-1}\,K^{-1}$ for YSZ coatings studied from room temperature up to 1200 °C [5,8].

The relationship between phase transformations and thermal properties plays a significant role on the turbine efficiency and helps to determine when the components must be repaired or replaced. Furthermore, the evolution of the TC morphology has a strong influence on both the thermal conductivity variation and thermo-mechanical properties [9,10]. In consequence, microstructure and morphology of the YSZ-TC must be considered in order to understand their effect on the heat transfer in TBC systems [1,11].

Several works have studied the reduction in thermal conductivity of TBCs due to phonon scattering caused by the increase in the absolute porosity, which reveals the importance of correlating the TC morphology with its thermal properties [6,12,13]. Also, the amount of pores, their morphology, as well as the cracks within the TC generate

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variations in C_P, absorbed energy and thermal conductivity, which are influenced by operating temperatures and pressures [14]. The contribution of conduction and radiation to the heat transfer throughout the porous TC must also be considered to track the evolution of thermal properties under operating conditions. For instance, fine-sized pores cause a decrease in the thermal conductivity close to room temperature. At high temperatures and low pressures, instead, they increase "the air thermal conductivity". Since the conduction mechanisms are influenced by large size globular pores and cracks [14,15], the increase in the number of small pores intensifies the phonon scattering that reduces the TC thermal conductivity [12,15,16]. It is also worth mentioning that some fine-sized pores tend to close under operating conditions due to sintering effects [17].

Variations in the microstructure of YSZ-TC can be monitored with the aid of X-Ray Diffraction (XRD) [18] and neutron diffraction [19]. These techniques can be used to determine the influence of the presence of cubic phase (**c**-YSZ), the yttria content, and the degree of stabilization of tetragonal phases (t-YSZ and t′-YSZ) on heat absorption, among other effects. It has been demonstrated, for instance, that the yttria content depletion from the tetragonal phase during operation favors the transformation of this phase into cubic and monoclinic phases [20]. Several authors have carried out high-temperature XRD studies on TCs deposited by Electron Beam-Physical Vapor Deposition (EB-PVD) and Atmospheric Plasma Spray (APS). It is well known the fact that when the non-transformable tetragonal phase (*t′*) is deficient in yttria it may decompose to tetragonal phase with low yttria content (*t*), which is more susceptible to transform to cubic phase with higher yttria content [21,22]. Transmission Electron Microscopy (TEM) has allowed identifying phase transformations in EB-PVD TC samples after being exposed to temperatures from 1100 to 1500 °C [23]. In this case, metastable tetragonal YSZ phases with low and high yttria contents are formed, and the cubic phase is enriched with yttria. Computer-aided simulation using data obtained from TEM has shown that grain boundaries of the cubic structure have a relatively high concentration of yttrium ions [24].

High-temperature characterization of thermal properties and microstructure of APS-deposited 7–8% YSZ-TC samples is conducted in this work with special interest in the influence of cooling and heating rates (which somewhat resemble non-steady turbine operation) on the aforesaid properties. Characterization techniques including high-temperature XRD (up to 1050 °C), Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) (up to 1300 °C) allowed assessing the changes in phase contents, specific heat, thermal conductivity and enthalpy of the TC.

2. Materials and methods

The TBC system studied in this work consisted of Inconel 625 substrate, MCrAlY bond coat applied by High Velocity Oxygen Fuel (HVOF) and 7 wt% Y_2O_3-ZrO_2 top coat deposited by APS. The manufacturing process for the TC used feedstock of vacuum-atomized spherical particles with an average diameter of ~ 60 μm (minimum size 45 μm, maximum size 90 μm), containing circa 68.8 wt% Zr, 31.4 wt% O and 5.8 wt% Y; for the bond coat (BC), the powders consisted of vacuum-atomized spherical particles with an average diameter of 45 μm (minimum size 10 μm, maximum size 60 μm), which were mainly composed of Ni (48.4 wt%), Co (23.1 wt%), Cr (21.9 wt%), Al (5.5 wt %) and O (1.2 wt%). Prior to deposition, the metallic substrate was sand blasted in order to obtain a surface texture with arithmetic mean roughness (Ra) between 3 and 6 μm. HVOF bond coat deposition was done with oxygen flow rate of 4 $m^3\,s^{-1}$, propylene flow rate of 1 $m^3\,s^{-1}$ and the standoff distance was 0.4 m for the spraying. In turn, the top coat was applied using a D.C. plasma torch with anode-nozzle internal diameter of 8 mm, plasma current of 600 A, plasma voltage of 70 V, injection angle of 90°, stand-off distance of 0.9 m and a flow rate of 8.3 $m^3\,s^{-1}$ Ar and 2.5 $m^3\,s^{-1}$ H_2.

2.1. Samples preparation

Two sets of samples were prepared as described below:

i) Free-standing TC samples were detached from the TBC system in order to perform analyses by DSC, TGA, High Temperature X-Ray Diffraction (XRD) and Optical (OM) and Scanning Electron Microscopy (SEM) equipped with Energy-Dispersive X-ray Spectroscopy (EDXS) and Wavelength-Dispersive X-ray Spectroscopy (WDXS) detectors.
ii) Cross sections of TBC samples were vacuum-impregnated in a phenolic resin, ground with emery papers and polished in clothes with diamond particles in order to perform microstructure assessment using XRD together with OM and SEM.

The detachment of the TC specimens from the rest of the TBC system was carried out by controlled chemical dissolution in an acidic aqueous solution (pH 1.5) consisting of 13.2 g $FeCl_3$ + 75 g HCl + 3 g HNO_3 + 22 g deionized water. A surfactant was added in order to reduce the exposure time to the acidic aqueous solution. The sample was exposed to the solution during 5.5 h at 65 °C. In order to remove contaminants, the free-standing TC specimen was cleaned after the detachment process using a basic aqueous solution (pH 7.5) consisting of amines with inorganic fluoride salts at 80 °C during 15 min.

2.2. Thermal analysis and microstructure characterization

The specific heat capacity and enthalpy of the free-standing TC samples were measured at constant pressure using a simultaneous TGA/DSC (SDT) analyzer (TA Instruments, model Q600) with the aid of Universal Analysis® software (TA Instruments). Free-standing TC specimens of 4 × 4 mm and 30 ± 0.1 mg were placed in Al_2O_3 crucibles for TGA/DSC measurements. The specific heat was determined by heating the samples from room temperature to 1450 °C using a sapphire standard reference material. The heating rates were 10, 15 and 20 °C min^{-1}. The C_P was calculated according to the ASTM E-1269 standard [25].

A JEOL 5910LV SEM was used to obtain TBC cross-sectional images. Chemical microanalysis were performed using EDXS and WDXS spectrometers. XRD patterns were obtained in free-standing samples using a Panalytical X'Pert PRO X-ray diffractometer with monochromatic CuKα (λ = 1.5406 Å) radiation. The diffraction patterns were obtained within the $15° \leq 2\theta \leq 90°$ range and step of 0.013° s^{-1} using a standard θ–2θ Bragg-Brentano geometry. Rietveld refinement was performed to measure the phases at different conditions. This analysis was complemented with the General Structure Analysis System (GSAS) package and the EXPGUI interface and included a chi-squared fit of 3.1 ± 0.5 [26,27]. The XRD patterns for the TC were obtained at 100, 200, 400, 600, 800, and 1050 °C both during heating and cooling cycles, with holding time of 10 min at each temperature. The heating rate was set to 10 °C min^{-1} while the cooling rate was determined by the thermal insulation of the equipment as shown in Fig. 1. The temperatures were selected to emulate temperature variations experienced by a gas turbine under operating conditions. In order to analyze phase changes in the TC during longer exposure times at high temperatures, additional X-Ray and porosity analyses were performed for samples exposed at 1100 °C during 600, 1000, and 1700 h. Analyses over an as-sprayed sample at room temperature were also considered for reference purposes.

Four YSZ phases were used for interpretation of the XRD patterns: stable (t′) and metastable (t) tetragonal phases, cubic phase (c) and monoclinic phase (m). The yttria content of the tetragonal phase was calculated using Eq. (1) [20], where *a* and *c* are the tetragonal lattice parameters in angstroms. This information was combined with the results from XRD analyses in order to study the stability of the phase with temperature.