MONITORING TECHNIQUES OF YTTRIA STABILIZED ZIRCONIA USED AS THERMAL BARRIER COATING

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ABSTRACT

Ceramic materials based on zirconia (ZrO\textsubscript{2}) have attracted attention due to their unique physical properties. Thermal barrier coating is used as thermal protective layer dedicated to metallic components in high temperature region, on engines and gas turbines, leading to high component reliability and operating temperature. The paper proposes the use of an electromagnetic method using a sensor with metamaterial lens for evaluation of zirconia coating on AISI316L stainless steels, in order to evaluate good or no adhesion coating-support and the results obtained by complementary methods.

Key words: ZrO\textsubscript{2}-based ceramics, Yttria, SEM, ND, X-ray diffraction, EM test.

1. Introduction

Thermal barrier coating (TBC) is used as thermal protective layer dedicated to metallic components in high temperature region, on engines and gas turbines, resulting to high component reliability and operating temperature, leading in higher efficiency and better environmental benefits [1]. TBC is a system that consists of a ceramic coating with or without Thermally Grown Oxide (TGO), deposited on a metal support. The weakest part of TBC is the substrate-ceramic interface, where fractures can appear under the action of thermal shock. Previous papers have been focused on behavior analysis of TGO as intermediary layer and later, on the improving of the surface of the top layer submitted to loadings during functioning. The optimization of the substrate surface topography is preferably based on a more complete
characterization in order to achieve a reasonable balance between the level of induced delamination stresses, mechanical bonding as well as a minimization of the defect size.

For better characterization and to monitor TBC failure and detect TBC delamination, NDE methods are used, most of these are based on optical principles including mid-infrared reflectance [2], luminescence spectroscopy [3] and elastic optical scattering [4]. These methods allow detection of TBC delamination and pre-spall condition. Laminar structures of YSZ TBC layers deposited on stainless steels are typically porous and the pore size and character depends on the process parameters. A decreasing of global coating porosities is preferred; especially those opened at the surface, in order to reduce to minimum the permeability of coating to oxidation.

Zirconia doped with rare earths oxides is considered a good TBC material [5] due of its low thermal conductivity, refractory, chemical inertness, and compatible thermal expansion coefficient [6],[7] with metallic support. Zirconia stabilized in tetragonal phase, namely Tetragonal Zirconia Poly-crystal (TZP) have CeO$_2$ and Y$_2$O$_3$ [8],[9] as stabilizers, the dimensions of crystallites being in the range of hundreds of nanometers, conferring a high resistance to breaking. The most frequently used ceramic material for TBC coatings is the zirconia partially stabilized with Yttria [10] (YSZ) which present high resistance to thermal shocks and fatigue until 1150°C. It is known that three low-pressure polymorphic forms of zirconia [6], [11] can be found at temperature over 2370°C: monoclinic state, P2$_1$/c; tetragonal phase, P4$_2$/nmc and the cubic, Fm-3m phase. Despite the success of zirconia in many new applications, it has become apparent that certain zirconia compositions can also have one weakness - their tendency to low temperature degradation in the presence of moisture. Under external stress, as grinding or impact, transition from the tetragonal (t) to monoclinic (m) phase can appear at normal temperatures, being followed by an increase of volume of 3-12%, causing compressive stress of YSZ coating[12].

The purpose of this paper is to emphasize the improvement of zirconia coating based on ceramics properties as a function of addition of Y$_2$O$_3$ in the structure of the original ceramics, deposited on AISI 316L to act as TBC. The substrate AISI 316L stainless steel is nonmagnetic with magnetic permeability equal to 1, allowing electromagnetic (EM) tests. The investigation has been carried out using destructive and electromagnetic nondestructive evaluation (eNDE) at interface between ceramic coating and stainless steel. In order to differentiate the areas with good/inferior coating quality, an EM sensor was used and the results were compared with those from complementary methods of characterization.

2. Studied samples

The system ZrO$_2$-Y$_2$O$_3$ was extensively studied in the last 50 years, the most publications analyzing the special mechanical properties of the structure function of Y$_2$O$_3$ content. By doping with Yttria, a cation substitutive, supplementary oxygen vacancies are added to the molecular structure, increasing the ionic electrical conductivity. When Yttria is alloyed with zirconia in concentration from 3% to 20% (molar percent), the crystalline structure of material in normal conditions is entirely stabilized [13], so that at variation of temperature, microcracking apparition can be avoided. Monolithic coating consisting of various thickness zirconia doped with 3 - 20% Y$_2$O$_3$ deposited on AISI 316L (composition in wt. % as EN 1.4404) have been taken into study.

The AISI 316L steel may be susceptible to intergranular corrosion in certain corrosive media after it is welded or otherwise heated at temperatures between 430 and 860 °C [14],[15]. It has electrical conductivity $1.3513 \times 10^6$ S·m$^{-1}$ and thermal expansion coefficient $17.2 \times 10^{-6}$ K$^{-1}$ at
473 K. TBC coating were deposited onto AISI 316L samples (20x80 mm$^2$ and 2 mm height) using plasma torch F 400 with commercial atmospheric equipment APS 100 produced by Plasma-Technik AG.

Monolithic coatings of various thickness consisting of zirconia doped with 20 % $\text{Y}_2\text{O}_3$ and sandwich zirconia doped with 20 % $\text{Y}_2\text{O}_3$ and $\text{Y}_2\text{O}_3$ coatings were deposited on AISI 316L. The coating material is produced by Metco as powder Metco$^\text{TM}$ 202NS and Metco 6035A-1 used for plasma spraying, having excellent resistance to oxidation and corrosion at temperature up to 1000 °C and can create excellent TBC. Pure yttrium oxide is a highly stable compound with a high melting point and is very inert chemically and exhibits excellent electrical insulation (volume resistivity and dielectric breakdown strength). The quality of surface of ceramic coating depend on: gas flow, power levels, powder particle size distribution, etc. During the deposition, also samples without good adherence at support were obtained, being analyzed as well.

2.1 Microscopy analyses

For TBC the most important parameters are the thickness, thermal conductivity and density of coatings. In order to minimize the mechanical stresses inside the proper material as well as at the interface with support during the heating/cooling, the coating ZrO$_2$-$\text{Y}_2\text{O}_3$ shall be characterized for each application (following the transformations in the targeted temperature range). It is difficult to achieve the balance at 1200°C in the conditions of low diffusion of cations in YSZ [16].

In Fig. 1a is presented the structure, cross sectional image of the sample deposited with ZrO$_2$ with 20 % $\text{Y}_2\text{O}_3$ with 0.2 mm thick monolithic coating, using Zeiss microscope in polarized light with Axio Imager A1m and in Fig. 1b the cross section of sample deposited with ZrO$_2$ with 20 % $\text{Y}_2\text{O}_3$ with 0.25 mm thick monolithic coating using Zeiss microscope Z1m with Axio-Vision 4.8.

![Fig. 1: Metallography: a) of ZrO$_2$ with addition of 20 % $\text{Y}_2\text{O}_3$ ceramic coating with 0.2 mm thickness; b) of ZrO$_2$ with 20 % $\text{Y}_2\text{O}_3$ ceramic coating with 0.25 mm thickness
1 – substrate AISI 316L; 2 – Zirconia doped with Yttria; 3 – Bakelite(a)/air(b);](image)

The Vickers micro-indentation tests were made using Shimadzu M device to determine the adherence of zirconia coating to support, the measured value being de 470 HV 0.05. Indentations were effectuated on longitudinal and cross section, to determine the effect of diffusion over the adherence to support and the results will be further discussed elsewhere. Information about interface between support and zirconia coating are obtained by SEM and EDX. Usually, information about porosity of coating are obtained by surface microscopy and soft grayscale threshold setting. This technique is subjective, due to the setting of gray level and light intensity, reflection of surface, samples preparation etc. The accuracy of grayscale threshold approach is investigated using image processing in Matlab described in [17].

Taking into account that the structures of YSZ TBC layers deposited on stainless steels are
typically porous, to obtain relevant information about the influence of yttria concentration over the adherence at support, Secondary Electrons (SE) images, as well as Backscattered Electrons (BSE) images have been taken, Fig. 2a and c. In Figs. 2b and d are presented the histograms of voids data.

It can be observed that with the doping with yttria, the voids are larger but their number decreases. Topographical characterization of the specimen is realized with a TESCAN electron microscope (TESCAN LYRA3 GM) operating at an acceleration voltage of 15 kV. The porosity of the tested surface can be evaluated from the SEM images within 0.5% accuracy.

![Fig. 2: SEM images (left) and voids counting (right): a) and b) for specimen with 0.2 mm thick monolithic coating ZrO\(_2\) with addition of 20% Y\(_2\)O\(_3\); c) and d) for specimen with sandwich coating 0.25 mm ZrO\(_2\) with addition of 20% Y\(_2\)O\(_3\) and 0.005 mm Y\(_2\)O\(_3\).](image)

### 2.2. X-ray diffraction (XRD) and Neutron Diffraction (ND)

XRD experiments performed at room temperature on a Philips diffractometer, at JINR Dubna, Russia, allow determination of the phase composition and microstructural parameters by using Fullprof software. The space group and lattice constants were obtained with Ceckcell and proofed by Fullprof software. The comparisons between the diffractogram of the sample formed from a layer of zirconia doped with yttria deposited on a support of AISI316L with the diffractogram of AISI 316L and, respectively, with the diffractogram of zirconia doped with yttria allowed to identify austenite maxima (γ) (Fig. 3) and doped zirconia (t) maxima (Fig. 4).

![Fig. 3: The X-ray diffractograms of support + the layer of zirconia with yttria and of the support](image)

![Fig. 4: The X-ray diffractograms of support + the layer of zirconia with yttria and of the zirconia with yttria](image)
Some ND data were collected by using the HRFD time-of-flight diffractometer from reactor IBR 2 – JINR Dubna, Russia, at room temperature (Fig. 5) corresponding bulk samples of zirconia doped with yttria on bulk samples (ND diffractograms were calculated also by using FullProf and PowderCell software). We have attempted to determine the conditions in which zirconia doped with yttrium can be identified in the diffractogram of a sample formed by a yttrium-doped zirconia layer and a stainless steel support, using the data obtained on zirconia doped with yttria (4% and 8%) bulk sample (Fig. 5).

Transformation of TOF values in 2θ values was obtained using the relation

\[
2\theta = \left[ \frac{360}{\pi} \right] a \sin \left[ \frac{Dtt1 * 0.77026}{\text{TOF} - \text{ZERO}} \right]
\]

(1)

The constants ZERO, Dtt1 and Dtt2 can be determined with a standard (Dtt2=0 in this case). The neutrograms were obtained using \( \lambda = 1.5406 \text{Å} \).

The test performed on zirconia doped with yttria (4 - 8%) bulk samples by neutron diffraction at IBR-2 Dubna, Russia indicated the presence of two phases (Fig. 5).

![Fig. 5: The neutronogram of ZrO\(_2\)+4\%Y\(_2\)O\(_3\) bulk sample. The ND data were acquired by using HFRD diffractometer, IBR-2, Dubna, Russia](image)

The calculated neutronogram for a sandwich of two layer of zirconia doped with 20% yttria (0.25 mm thickness) and a layer of yttria (0.005 mm thickness) is presented in Fig. 6. The both layers are practically transparent for the neutron beam and the volumes of the layers are supposed to be the same. The diffracted intensities corresponding to the layers depend on its relative volumes.

The calculated neutronogram of a mixture between stainless steel, zirconia and yttria, in equal concentrations, was presented in Fig. 6. We have used a neutron beam with a constant wavelength (\( \lambda = 1.5406 \text{Å} \)), the same with the wavelength used to obtain the X ray diffractogram of layer of zirconia deposited on AISI 316 support (Fig. 7). In the first case (XRD) we have a real thin layer of zirconia (about 200 µ), in the second case (ND) the neutron beam sees equal volumes of the three components of the "phase mixture: steel 316, zirconia and yttria" (Fig. 6). In fact, the concentration ratio of the three phases is 1000: 125: 2.5. The intensity of maxima corresponding to yttria cannot be observed in this case. We will investigate the yttria+zirconia layers deposited on stainless steel 316 support by neutron reflectometry or by X-ray diffraction.
The difference between the structure of bulk doped with yttrium zirconia and of the deposited layer of yttrium doped zirconia on 316 support will be discussed elsewhere.

3. Experimental setup and principle of electromagnetic testing

\(\text{ZrO}_2\text{-Y}_2\text{O}_3\) used as top-coating (is nonconductive and nonmagnetic) behaves like an air gap between conductive support and EM sensor, creating a lift-off for the EM sensor. The challenge for the development of new types of EM transducers consists in the obtaining of good detection sensitivity for a minimum 3/1 signal to noise ratio as well as a good spatial resolution.

The EM sensor is an absolute send-receiver type [18] and has the principle scheme given in Fig. 8a and its construction in Fig. 8b. EM sensors with metamaterial (MM) lens is made using Conical Swiss rolls (CSR)[19] the operation frequencies depending both by the constitutive parameters of MM lens as well as by the polarization of the incident EM field (TE\(_z\) or TM\(_z\)), in this case TM\(_z\) polarized at normal incidence. The emission part of the sensor is made from a single turn rectangular coil with 20x60mm\(^2\) dimensions, placed at 25 mm distance from the lens.

According to [20] starting at 25mm from the horizontal side of the frame, the Hx component decreases much less than at smaller distances, and on a relatively small distance, the field can be considered approximately constant. In this region, the reception device of the EM sensor is placed. The functioning of the sensor is presented in [18]. The scattered field must be also focused such that it can be detected by the reception part of the sensor placed in image focal point. EM sensor with MM lens has been realized with two CSRs, tuned at 105MHz frequency [18], having a large basis face to face. The MM lens assures the possibility to apply of EM MM in eNDE[21]. As shown in [22], the sensor with a lens realized with CSR, functioning in the range of frequencies such that \(\mu_{\text{eff}}\) is maximum. The detection principle is similar with the one of near-field electromagnetic scanning microscopy (NFESM). NFSEM imaging is a sampling technique, i.e., the specimen (in this case plate with thickness of coating) is probed point by point by raster.
scanning with the sensor over the specimen surface and recording for energy image pixel a corresponding electromagnetic signature. Scattered EM field from other regions is eliminated by using MM lens with CSR with a conductive screen with circular aperture (made from perfect electric conductor material) according to Fig. 9a (right side). The functioning of entire system detection can be described using Fourier optics [23,24]. The skin depth is limited by standard penetration \( \delta = \sqrt{\frac{2/\omega \mu_0 \sigma}{\omega=2\pi f, \mu_0=4\pi\times10^{-7}\text{Hm}^{-1}}, \text{being vacuum magnetic permeability}} \) and \( \sigma \) is the electric conductivity of material. The reception coil functions as a detection antenna, converting localized energy into electromotive force.

Basically, the eNDE of a material consists in the applying a physical field to the object examined and evaluating the interaction between the field and the eventual material flaws. To increase the reliability and assure quality, an automatic scanning system is used, XY displacement system type Newmark together with a high frequency data acquisition [18]. The EM sensor with MM lens, presented above is connected to a Network/Spectrum/Impedance Analyzer type 4395A Agilent USA. During the measurements, the sensor was fixed and the samples is mounted on a XY displacement system. That assures the displacement in plan with \( \pm10 \mu\text{m} \) precision and also assures the scanning of sample with established steps in both directions. A PC allows the command of manipulation and measurement instruments, the data being acquired and stored automatically.

4. Results of EM testing

It is possible to appear a lot of cracks due to the relaxation of residual stresses after deposition. The microstructure obtained by plasma jet can present lamellar or flattened splats with micro cracks through the splats or inter-splats. These splats lie parallel to the surface of the coating due to impact of the high speed molten particles on the substrate. These splats can be at the coating interface being parallel with it and mainly appear due to impact of melted particles with high speed on substrate.

The surface and bonding quality of support-layers are examined. The sensor with MM lens has allowed the identification and estimation of the zones where the nanoparticles have created shear distortions, possible to degenerate in the damage of the coatings. The samples were placed on the displacing system, with emission coil perpendicular on the surface and on scanning direction [18]. Ceramic zirconia top-coating is nonconductive and nonmagnetic, these create a probe lift-off effect. The specimens with 0.2 mm thickness of zirconia coating with and without yttria were fixed on a Newmark X-Y displacement system that assures the displacement in plane with \( \pm10 \mu\text{m} \) precision, for an lift-off of 75 \( \mu\text{m} \). That enables scans of \( 5 \times 5 \text{mm}^2 \) with 0.1 mm step in both directions, and the image delivered by the assembly sensor-equipment is amplified. In order to improve the spatial resolution, in front of the sensor with MM lens has been placed the circularly aperture 0.1 mm diameter. This is due to the diffraction on the aperture of the electromagnetic field generated by scattering on the specimen. That assure for the structure of surface clearly visible. Considering an object placed in the plane \( z = 0 \) and described by the function \( f_0(x,y) \), at passing through an aperture, in the case of Fresnel diffraction (the aperture is closely to the object), the image obtained at the distance \( z \) from the object will be \( f_z(x,y) \) and can be calculated using the algorithm presented in Fig. 10, according to the principle of Fourier optics

\[
\begin{align*}
  f_z(x,y) & \rightarrow \text{2D Fourier Transform} \rightarrow F_{m}(u,v) \rightarrow x\exp\left(-\frac{j2\pi^2}{k'(u^2+v^2)}\right) \rightarrow F_{z}(u,v) \rightarrow \text{Inverse 2D Fourier Transform} \rightarrow f_z(x,y)
\end{align*}
\]

Fig. 9: The image modification by an aperture due to Fresnel diffraction

To ensure that \( f_z(x,y) \) might represent exactly the figure of Fresnel diffraction through the a radius aperture, between the Fourier variables and the spatial ones must be
where \( N \) and \( M \) represent the maximum number of measurement points along \( x \) and \( y \) direction and \( dx_0 \) and \( dy_0 \) are the scanning step along \( x \) and respective \( y \) directions. Inverting the operation from Fig. 9, the object \( f_0(x,y) \) can be determined knowing the diffraction figure \( f(z)(x,y) \). The measurements effectuated with the aperture make that the signals recorded shall represents \( f(z)(x,y) \). The shape of the object that scatters the electromagnetic field created by the emission coil can be determined.

Figs 10 a and b show the amplitude of the voltage induced in the reception coil of the electromagnetic transducer at the scanning of the two specimens presented above. Figure 10 c present the scanning of a specimen with no adherence from 0.25mm thick monolithic coating \( \text{ZrO}_2 \) with addition of 20 \( \% \) \( \text{Y}_2\text{O}_3 \).

It can be observed that the values of emf induced in the reception coils are affected by the material microstructure and by the presence of inhomogeneities on/in the surface of support. The image corresponding to 0.2 mm thick monolithic coating \( \text{ZrO}_2 \) with addition of 20 \( \% \) \( \text{Y}_2\text{O}_3 \) do not present nonadherence regions. The amplitude of voltage induced in the reception coil has relatively constant value, excepting the regions where variations appear most probable due to agglomeration of oxides. Sandwich coatings 0.25 mm \( \text{ZrO}_2 \) with addition of 20 \( \% \) \( \text{Y}_2\text{O}_3 \) and 0.005 mm \( \text{Y}_2\text{O}_3 \) show that at doping with yttria, the voids are more extended but their number decreases, fact confirmed also by the SEM images.

Fig. 10: The amplitude of the voltage induced in the reception coil of the electromagnetic transducer: a) 0.2 mm thick monolithic coating \( \text{ZrO}_2 \) with addition of 20 \( \% \) \( \text{Y}_2\text{O}_3 \); b) sandwich coating 0.25 mm \( \text{ZrO}_2 \) with addition of 20 \( \% \) \( \text{Y}_2\text{O}_3 \) and 0.005 mm \( \text{Y}_2\text{O}_3 \); c) specimen with nonadherence from 0.25mm thick monolithic coating \( \text{ZrO}_2 \) with addition of 20 \( \% \) \( \text{Y}_2\text{O}_3 \).

It can be shown that the region with nonadherence is well emphasized. For specimens without adherence to support, the insular shape emphasized by the complementary methods is found on the representation of amplitude of voltage induced in the reception coil when the surface is scanned.

5. Conclusions
TBC potential depends not only by the intrinsic properties of TBC’s material but of the coating microstructure that is determined by the deposition process. Using a MM lens, CSR type, and following the method described above, from the zone inspected, the results allow the characterization of the surface microstructure and possible spallation/delamination at the interfaces of deposited layers. Also small roughness can be emphasized. The results of the NDT method have been confirmed by complementary methods. Further tests on a larger number of specimens with different coating aspects of the surface, influence of surface roughness on stress intensity factor, number of layers are needed to establish
the accuracy of the results and also the correlation between the located very small defect in size and the results of MM sensor response. Also, the results can be further continues by complementary investigation as ND, X ray diffraction or other methods that can emphasize indications about phase composition and structure parameters.

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7. References


