Measurement of the elastic modulus of ceria yttria co-stabilized zirconia coatings

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Abstract: - Thermal barrier coatings are currently used in stationary turbines of power plants and aircraft engines to improve thermal efficiency through an increase of the inlet temperature. For this reason, air plasma sprayed yttria stabilized zirconia (YSZ) has been often adopted in the last decades. However, the drawback of YSZ is the tetragonal to martensitic (t$\rightarrow$m) transformation occurring at high temperature which induces a disastrous volume expansion (from 3 to 5%) and coating fracture. In order to tackle this problem new alternative material have been proposed. In particular, it has been observed that the addition of ceria to tetragonal zirconia allows to obtain ceria and yttria co-stabilized zirconia (CYSZ) which presents an higher phase stability than YSZ and is particularly promising for technical demanding applications. The basic properties of a coated system, for instance the adhesion strength or its thermo-mechanical behavior, mainly depend on the elastic modulus. In the present paper the elastic modulus of CYSZ plasma spray deposits, measured by means of the impulse excitation technique (IET), is reported. In addition, as the microstructure of the final coating strongly affect the elastic response, the microstructural features of the coating are also analyzed using scanning electron microscopy (SEM).

Key-Words: - Thermal barrier coatings, ceria-yttria stabilized zirconia, Young's modulus, impulse excitation technique

1 Introduction

Surface material in mechanical components is usually weaker than the interior part. The chemical reactions occurring, for instance, during manufacturing or in service (*e.g.* corrosion phenomena), produce a thin surface layer with lower properties with respect to the underlying material [1]. This problem is emphasized when the operating temperature increases. Besides, the surface is the place where the highest stresses are usually experienced thus providing the ideal condition for nucleation and growth of cracks. Therefore, in order to improve the resistance against corrosion, wear and fatigue of mechanical components, metallic as well as non metallic coatings are currently really widespread. In particular, ceramic coatings are suitable for higher working temperatures, *e.g.* $\geq$1000^{o}C. Owing to their low thermal conductivity they are applied as Thermal Barrier Coating (TBC) protecting the substrates in service [2-5]. So far, the ceramic material mostly used as TBC has been yttria stabilized zirconia (YSZ), but in the last decade, new alternative materials have been proposed [6]. In particular, it has been observed that the addition of CeO_2 to tetragonal zirconia allows to obtain a ceramic material, *i.e.* ceria-yttria co-stabilized zirconia (CYSZ), which presents an higher phase stability than YSZ thereby leading to an improvement in durability of TBCs [7-8]. Various techniques have been developed for coating deposition, one of the most widespread is the Air Plasma Spray (APS) process. With such a technology, a gas streaming in a burner through an high energy electric arc is transformed into an high temperature plasma. The individual components of the TBC are thus fed into the burner in the form of powder and are melted and driven by the plasma gas to impact with high velocity on the substrate. The rapid solidification of impacted molten droplets give rise to a highly heterogeneous microstructure consisting of irregular thin lamellae known as 'splats'. This feature has a severe impact on the elastic response of the APS deposit and in particular on the Young modulus [9-10]. As the basic properties of a coated system, for instance the adhesion strength or its thermo-mechanical behavior, mainly depend on the elastic modulus, it follows that APS CYSZ development demands an efficient, reliable and convenient methodology for its measurement. Up to now, several test methods are reported in literature for the elastic characterization of coatings, the most commonly employed are the conventional quasi-static tests like Nano-indentation (NI) or Bending Tests (BT) [10]. Even if NI and BT are currently used in order to obtain the elastic properties of plasma deposits, they are too tedious for a routine and cost-effective application in production. As an alternative, the use of dynamic test methods, in particular the resonant methods, has increased in the last decades [11-13]. In the present paper the elastic modulus of CYSZ plasma spray deposits is determined by means of the impulse excitation technique (IET) [14]. In addition, as the microstructure of the final coating strongly affect the elastic response, the microstructural feature of the coating are also analyzed.

2 Microstructural analysis

2.1 Substrates preparation and plasma spraying

The elastic modulus of thermal spray deposits is related to the microstructure. This last strongly depends on spray parameters which, therefore, should be carefully specified. In this work, plasma spraying was carried out using a Sulzer Metco APS system, equipped with a F4-MB plasma torch (Sultzer Metco AG, Switzerland) mounted on an industrial robot. The feedstock was the commercial Metco 205NS (ZrO_2-$25CeO_2$-$2.5Y_2O_3$) [15]. Stainless steel plates (310S) (25 mm x 25 mm x 4 mm dimensions) and Inconel superalloy (IN738) disks (25 mm diameter x 5 mm thickness) were used as substrates. Before spraying, the substrates were cleaned and degreased ultrasonically in ethanol and grit-blasted with alumina abrasive, to increase the roughness of their surface and consequently to improve the adhesion of the coatings on substrates. The spray parameters used during the depositions are summarized in Table 1. The resulting coatings show a thickness ranging between 400 and 450 µm. Before CYSZ deposition, a bond coat was applied in order to reduce thermal expansion mismatch between the substrate and the TBC and to enhance the adhesion of the same TBC. The powder used as bond coat was a commercial CoNiCrAlY (Amdry 995C) [15] and the thickness was about 100 µm.

Table 1 – Torch parameters used for Plasma Spraying the CYSZ powder.

Current (A)	600
Turntable velocity (rad/s)	100
Gun velocity (mm/s)	4
Powder carrier gas Ar (nlpm)	2.6
Primary gas Ar (nlpm)	38
Secondary gas H_2 (nlpm)	11
Stand off distance (mm)	120
Powder feed rate (g/min)	44.1

2.2 SEM analyses

In order to analyze the microstructure of the plasma sprayed coating metallographic surfaces and cross-sections were prepared using standard metallographic procedures. The specimens were cut with a low velocity diamond saw, mounted in vacuum with an epoxy resin and polished to 1 µm. Fig. 1 shows the cross-sectional microstructure of the entire TBC.

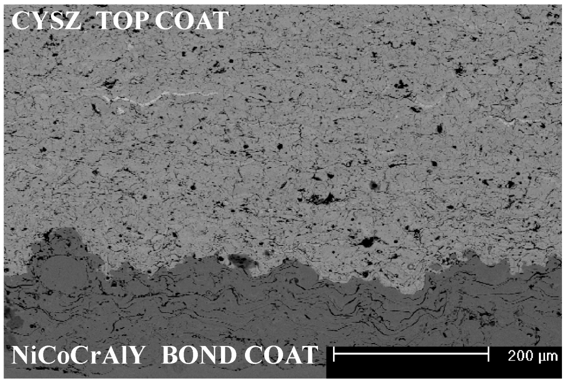

Fig. 1 - SEM micrograph of coating and bond coat.

Fig. 2 shows the complex microstructure of the top coat which consists of irregular thin lamellae known as 'splats' formed by rapid solidification of impacted molten droplets.

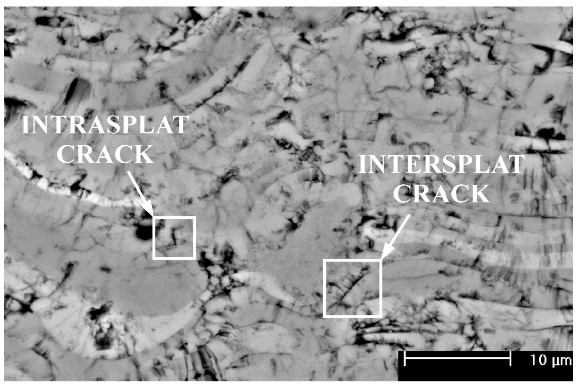

Fig. 2 - SEM microstructure of CYSZ coating.

As it can be seen, the coatings prepared by APS are characterized by a highly heterogeneous microstructure where the lamellae, or microsplats, are embedded in a network of cracks and voids, and are able to slide past each other. Usually it is possible to distinguish intersplat cracks and intrasplat cracks. The former are represented by cracks that run across the splat interfaces whereas the latter run inside the splats. These cracks allow a reduction of thermal conductivity and an increase in thermal shock resistance but, at the same time, reduce the corrosion resistance of the coating. Different regions characterized by different grey contrasts can also be observed, this indicates elements and compounds with different atomic weight. In particular, the dark regions correspond to elements with lower atomic weight whereas the bright regions correspond to elements with higher atomic weight. Energy Dispersive Spectrometer (EDS) analyses, not reported herein, demonstrated that the bright areas were more rich of CeO_2 stabilizer than the others. The porosity fraction of the coating was estimated from SEM micrographs using a software suited for image analysis, namely ImageJ [16]. For each metallographic cross-section, 10 measures were carried out. The average of porosity fraction was about 9.1%. Finally, the phase analysis and crystalline structures of the powder and the coating were investigated using an X-Ray diffractometer (XRD). XRD patterns of the powder and as sprayed coating, not reported herein for the sake of brevity, showed that following to the deposition process a small amount of stabilizer evaporated in the plasma plume leading to a stoichiometry variation of the final coating with respect to the original one (ZrO_2-25CeO_2-2.5Y_2O_3).

3 Elastic Characterization

3.1 Introduction and theoretical background

As a results of the deposition process, the coatings present properties quite different from the corresponding bulk materials of the same composition. Indeed, unlike dense ceramics, the final microstructure of plasma sprayed deposits is characterized by the presence of cracks. These last have a severe impact on the mechanical properties as they induce an anisotropic behaviour. In particular, inter-lamellar cracks and pores affect the in-plane elastic modulus, whereas the out of plane elastic modulus is affected by the intra-lamellar cracks [10]. As a consequence, it is necessary to consider the measurement direction in determining the elastic modulus of the deposit or comparing the results of different techniques.

For instance, it has been demonstrated in [10] that the elastic modulus of the APS coatings determined by Nano-Indentation (NI) is different with respect to Bending Test (BT).

BT works at the macroscopic level and provides the in-plane elastic modulus as the tangent of the stress-strain curve of the coating. Owing to splat boundary sliding and propagation of cracks, inelastic deformations occur during testing and, as a consequence, the results of BTs are affected by this non linear stress-strain behaviour.

NI probes the microstructure at the splat level, *i.e.* the microscopic scale, and, owing to the limited test volume, the resulting out of plane elastic modulus is nearly that of the splat itself. Therefore it is different with respect to that of BT (usually higher) and this effect is more pronounced in ceramics than in metals coatings [17].

Even if NI and BT are currently used in order to obtain the elastic properties of plasma deposits, they are too tedious for a routine and cost-effective application in production. As an alternative, the use of dynamic test methods, in particular the resonant methods, has increased in the last decades [11-13]. They allow to determine the elastic modulus if a suitable equation, namely the frequency equation, relating the natural frequencies, the mass and geometrical properties of the specimens is known.

To this aim it is necessary to measure the resonant frequencies of the specimen. From this standpoint sample vibration, in the sonic and/or ultrasonic range, is achieved by continuous variable excitation, generally of sinusoidal or random stationary type, or by impact. With the latter technique, often mentioned as the Impulse Excitation Technique (IET), oscillations are induced in the sample by a single mechanical impact and the resulting transient signal is detected by a microphone and digitally analyzed in order to extract the resonant frequencies. IET has the advantage of being simple, fast and accurate and requires inexpensive experimental equipment and can certainly be used for rapid production process monitoring. In addition, IET allows to determine the elastic moduli subjecting the specimen to lower strains so that they are measured nearly at the origin of the stress-strain curve, thus fracture and non linear material response are then prevented.

The frequency equation, can generally be obtained integrating the equation of motion in accordance with the prescribed boundary conditions. For example, an exact solution of the three dimensional form of the differential equation of motion was obtained for the axial and the torsional vibrations of an infinite length isotropic circular bar with free edge conditions. For finite length isotropic bars (circular or rectangular cross sections) and other simple geometries, such as circular thick plates, only approximate numerical solutions exist and these approximate numerical solutions are recommended in ASTM standards for the elastic characterization of isotropic materials [14]. Nevertheless, different geometries could also be used if the corresponding frequency equations are known. For example, a procedure that extends resonant method to isotropic samples in the form of thin rectangular plates was proposed in [18] and subsequently it was applied to a free standing diamond coating in [11,19]. However, the methodologies mentioned above are not suited for coated samples (*i.e.* coating/substrate system), like those analyzed in this paper. For this class of specimens the resonant method was extended in [20]. In particular, considering a bi-layer sample with free ends conditions and neglecting shear or rotary inertia effect, a frequency equation suitable for the elastic characterization can be written as follows

$$f_1 = \frac{k_1^{\,2}}{2\pi}\left\{\frac{E_c I_c + E_s I_s}{\rho_c A_c + \rho_s A_s}\right\}^{1/2} \qquad (1)$$

where k_1 is a constant equal to $k_1L=4.73004$, L is the length of the composite beam, A_i is the cross sectional area, E_i represent the in-plane elastic modulus, ρ_i the mass density, I_i the second moment of area of the cross section with respect to the neutral axis while the subscripts c and s refer to the coating and the substrate, respectively. Therefore, the in-plane elastic modulus of the coating can be obtained using Eq. 1. As it is in implicit form an iterative procedure should be used, however, in this work, as it will be shown later, the function *Solve* available in the software package *Mathematica*® [21] will be used.

3.2 Experimental procedures

For mechanical properties investigation, stainless steel plates (100 mm x 25 mm x 4 mm) were used as substrates and coated with CYSZ. In order to simplify the identification procedure, the bond coat was not applied. Nevertheless, the adhesion between coating and substrate was excellent. Other authors showed that the elastic modulus of the coating does not depend on coating thickness [22]. For each specimen a deposit thickness approximately equal to 350 μm was chosen. So, the tests were carried out on nominally identical coated samples whose dimensions are reported in Table 2.

Table 2 - Geometrical and mass properties of the samples

Specimen dimension	[ν]	P1 $\bar{x}$	P1 $u(\bar{x})$	P2 $\bar{x}$	P2 $u(\bar{x})$	P3 $\bar{x}$	P3 $u(\bar{x})$
length, L [mm]	2	100.53	0.01	100.55	0.05	99.73	0.03
width, B [mm]	4	25.08	0.02	25.09	0.01	24.92	0.01
thickness, t_s [mm]	5	3.986	0.012	4.021	0.004	4.027	0.003
thickness, t_c [mm]	5	0.362	0.017	0.357	0.019	0.367	0.014
density, ρ_s [g/cm^3]	∞	7.78	0.02	7.78	0.01	7.78	0.01
density, ρ_c [g/cm^3]	∞	5.40	0.01	5.40	0.01	5.40	0.01

$\bar{x}$: mean value of n measurements;
$u(\bar{x})$: standard uncertainty [23];
ν= n-1: degree of freedom;

Thickness measurement is always critical for the quality of the results therefore a digital micrometer with a resolution of one-thousandth of a millimeter was used. For all the other length measurements a standard caliper with a resolution of one-fiftieth of a millimeter was used.

The mass density of the steel substrates has been determined from the plate volume and mass. This last has been measured by a precision digital balance which is accurate to one-hundredth of a gram. The mass density of the coating is that specified by the manufacturer [15].

Before plasma spraying the elastic properties of the substrates were determined following the procedures and the recommendation of the ASTM standards for the elastic characterization of isotropic materials [14]. Subsequently, the Young modulus of the deposit has been determined using Eq. 1. In both case the measurement of the fundamental natural frequency is needed. From this standpoint, specimens suspension is of critical concern in order to achieve good quality frequency measurement. The procedure adopted herein requires specimens with all the edges free in order to accommodate the boundary conditions prescribed from Eq. 1. Therefore, each samples were supported on direct contact supports made of soft material (*e.g.*, cotton pad, soft sponge) showing a minimal contact area with the specimen. They were placed in locations that allow the plate to oscillate without significant limitation in the desired mode (see Fig. 3). Impact excitation was imparted lightly hitting the beam and the resulting vibration was picked up using a microphone (Trust MC200, frequency bandwidth from 50Hz to 14000 Hz) placed near the surface of the sample under examination. The dynamic response detected by the microphone was then analyzed and processed by a suitable program written in MATLAB™ [24] environment. It transforms the sampled time functions into a frequency spectrum by a Fast Fourier Transform (FFT) algorithm allowing the identification of the fundamental natural frequency. The resolution of the measurement system depends on the time length (t_a) of the signal acquired. In this work, each measurement was carried out using an acquisition time equal to 10s. Using a sampling frequency of 44100Hz a resolution equal to $\Delta f = 1/\Delta t = 0.1$ Hz is achieved. No significant deviation were observed among the values of repeated measurements. In order to mitigate the environmental noise and to better illustrate the peaks of the frequency spectrum, the average signal obtained by impacting the plate three times has been analyzed.

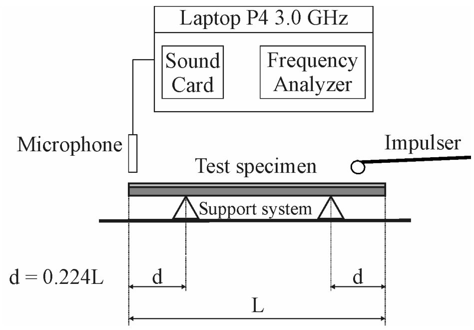

Fig. 3 - Block diagram of the test set-up

3.3 Results and discussion

The results obtained using the procedure described in the previous section are reported in Tables 3 and 4. In particular in Table 3, the fundamental natural frequency of the substrate before coating deposition is reported. This last together with the geometrical dimension and the mass density of the substrate material (see Table 2) allow to determine the Young modulus following the procedure and the recommendations reported in [14]. The results present a reduced scatter and are in agreement with the common values reported for steel. In a similar manner, Table 4 presents the fundamental frequency of the coated samples, which introduced in Eq. 1 and considering the geometrical and mass properties reported in Table 2, allows to obtain the elastic modulus of the coating. The Young modulus of the coating, E_c, presents a relatively large scatter that could be addressed mainly to the measurement error in determining the thickness, t_c.

4 Conclusion and perspectives

In this work, the elastic modulus of plasma sprayed ceria yttria co-stabilized zirconia coatings (CYSZ) was determined using the impulse excitation technique (IET). In addition, as the microstructural features strongly affect the elastic response, microstructural analyses of the final coating were executed. In particular, SEM analyses revealed a lamellar microstructure characterized by the presence of intra-lamellar and inter-lamellar cracks and high porosity.

The results obtained for the Young modulus of the coating are characterized by relatively large scatter. However, they fall within the range of values reported for coatings presenting similar composition and obtained with different test methods [10]. In addition, IET has the advantage of being simple, fast and accurate, it requires inexpensive experimental equipment and can certainly be used for rapid production process monitoring.

Table 3: Fundamental natural frequency and Young's modulus of the steel substrates

	f_{1s} [Hz]	E_s [GPa]		
		$\bar{x}$	$u(\bar{x})$	$U(\bar{x})$ (95%)
P1	2104.5	212.13	1.90	4.87
P2	2107.1	208.92	0.70	1.71
P3	2148.9	209.95	0.51	1.24

U(x): combined standard uncertainty (coverage factor k=t_{95}, t is the t-student distribution) [23]

Table 4: Fundamental natural frequency and Young's modulus of the CYSZ coating

	f_{1sc} [Hz]	E_c [GPa]		
		$\bar{x}$	$u(\bar{x})$	$U(\bar{x})$ (95%)
P1	2092.0	25.10	4.53	11.09
P2	2094.7	25.50	2.20	4.50
P3	2134.1	23.41	1.52	3.14

U(x): combined standard uncertainty (coverage factor k= t_{95}, t is the t-student distribution) [23]

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