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Hardness of thermal sprayed coatings: Relevance of the scale of measurement

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ABSTRACT

The coatings obtained by thermal spraying can present a large variety of geometrical parameters (*thickness*, *roughness*…), of microstructures (*constituents*, *nature of phases*…), of mechanical properties (*hardness*, *elastic modulus*…) and of morphological defects (*cracks*, *pores*…) depending on the spraying conditions. In order to determine the mechanical properties of the coating, one of the most relevant techniques is probably the instrumented indentation test. Nowadays this technique is very attractive since it allows the determination of numerous parameters. Moreover, recent developments allow the use of a phenomenological approach and modeling at different scales of measurement, from nano (even ultra-nano) to macro scale, i.e. from few milligrams to several kilograms of loading. However, the information, which can be extracted at the different regimes of loading can be the same or lead to different values of the mechanical properties, which can be complementary or contradictory depending on the nature of the coating and the preparation of the sample. For example, roughness, porosity and cracks present in the coating will affect the mechanical characterization since the indentation data analysis is based on how a rigid indenter penetrates into the material. So, an important question arises: Should the influence of these defects to be taken into account, or neglected, for the mechanical characterization?

The present work proposes different methodologies for determining the hardness of coated materials by considering or not the influence of both the porosity and roughness of the surface. In the first part, results of microindentation experiments performed on the rough surface of alumina coatings are compared to those obtained on a polished cross-section. Although the surface of the cross-section is irregular even after caution polishing, the hardness can be measured. A decrease of about 30% of the hardness number on the cross-section is observed. The second part is related to the microstructured yttria-stabilized zirconia analysis. A methodology based on the indentation size effect analysis is presented to avoid the influence of roughness and the defects, which can be crossed by the indenter during the indentation. This methodology allows the hardness determination of the coating exempt of defects. In the last part, a statistical analysis using nanoindentation data resulting from the continuous stiffness measurement mode applied to nanostructured yttria-stabilized zirconia shows that, even if the hardness number varies to a great extent according to the applied load and the location of the indent, the hardness can be represented by means of a unique hardness number independent of the sense of the hardness variation during the indenter displacement.

1. Introduction

Thermal sprayed coatings are nowadays widely employed due to their large variety of geometrical and microstructural parameters like thickness, porosity, roughness, hard and soft phases, which could be present into the coating. These parameters are recognized to influence significantly the mechanical properties [1–3]. Therefore, their determination is necessary for studying the mechanical behavior of coated materials according to their usage [4]. Therefore, the researcher has to face some problems for determining the mechanical properties of the coating in relation to its heterogeneity, porosity content, roughness and the cracks network, all of which depend on the thermal spraying conditions [5,6].

Usually for mechanical characterization, the instrumented indentation test is employed since it allows the determination of a large variety

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of parameters like hardness [7,8], elastic modulus [7,8], indentation toughness [9], tensile properties [10], fatigue and creep behavior [11] and the interfacial indentation toughness [12] for characterizing the adhesion of a thick coating onto its substrate. Moreover, the materials can be studied at different scales of measurement, from nano to macroindentation, which renders this mechanical test very popular. As an example, nanoindentation is mostly used to study the mechanical properties of a particle, a local phase or a very thin film, whereas microindentation can give mechanical properties at an intermediate scale of measurement. On the other hand, macroindentation can be employed for characterizing the global behavior of a material since the material under indentation can be considered as to a homogeneous one. However, problems arise when studying rough and porous coatings. For such type of materials, nanoindentation is very sensitive to the roughness and the presence of pores under the indenter. Contrarily, macroindentation is less sensitive to porosity, but the results can be influenced by the presence of the substrate, which can interfere into the measurement. In this case, models for separating the influence of the substrate should be applied but their efficiency and accuracy must be considered. It seems that microindentation could be the most appropriate technique for analyzing such a coating even if the presence of pores and defects also modifies the indenter penetration way and, subsequently, the mechanical properties' determination.

In this work, we collect some results obtained on three thermal sprayed coatings presenting heterogeneity, roughness at the surface and pores in the coating. The microstructural analyses together with the mechanical characterization of these coatings are presented in three distinct sections. In the first section, we compare the hardness of an alumina coating deduced from microindentation tests performed at the top surface and on a cross-section. On the top surface in order to circumvent any change of the mechanical properties, no polishing has been conducted. Note that in this case, the origin of a load–displacement curve corresponds to the contact of the indenter with the material, which can be located at the top or in a hollow of the rough surface, thus leading inevitably to a discrepancy of the results. On the other hand, indentation tests have been performed using the same range of loads on a polished cross-section but the results equally show a large variation because the surface is not smooth enough even after polishing. In the second section concerning the analysis of an yttria-stabilized zirconia coating, we proposed a methodology, which allows the separation of the influence of roughness, which predominantly appears at the beginning of the loading and the influence of pores and cracks, which lead to a shift of the load–displacement curve toward the high depths when the indenter crosses the defect. This methodology is based on the analysis of the loading curve by means of the Proportional Specimen Resistance (PSR) model proposed by Li and Bradt [13] and the Strain Gradient Plasticity (SGP) model proposed by Nix and Gao, [14] afterwards extended by Chicot [15] for representing the indentation size effect equally at nano and micrometer regimes. The last section is devoted to the analysis of a nanostructured yttried zirconia coating. The hardness results from the continuous stiffness measurement mode in nanoindentation, which allows the plot of hardness versus the indenter displacement. In this situation, a statistical approach allows the determination of a representative hardness value. The different approaches presented here can be reasonably employed according to the scientific objective, i.e. obtaining the mechanical properties of the global coating, with or without the consideration of the defects, or the mechanical properties of a specific phase or particle.

2. Experiments

The hardness determination has been performed by instrumented indentation experiments both at a microscale and a nanoscale. The microindentation tests were performed with a micro-hardness Tester CSM 2-107 equipped with Vickers and Berkovich indenters. The maximum loads were chosen within the range 100 mN to 10 N and close to 50 indentation tests were randomly conducted at the top surface and on the cross-section of the coating. The indentation on the non-polished top surface of the coating has been motivated in order to avoid any modification of the microstructure and possible changes in the indentation data analysis, i.e. modification of the residual stress state, filling or plugging of the pores, generation of cracks and work-hardening. To study the influence of the preparation mode of the sample, hardness tests have been performed on a polished cross-section. The values of the loading and unloading rates (expressed in mN/min) were set at twice the value of the maximum applied load, according to the rule proposed by Quinn et al. [16]. A dwell-time of 15 s was imposed according to the standard indentation test procedure conducted in classical indentation tests according to the ASTM E92 and E384-10e2 standards.

Nanoindentation experiments have been conducted employing a Nano Indenter XP™ (MTS Nano Instruments) with a Berkovich indenter. 30 indentation tests have been conducted randomly at the surface of the polished coated system by applying the same indentation testing conditions. The maximum indentation depth reached by the indenter was fixed at 800 nm and the strain rate was equal to 0.05 s^{-1}. The instrument was operated in the Continuous Stiffness Measurement mode (CSM) allowing the determination of the hardness at each data point during the indentation loading. The harmonic displacement was 2 nm and the frequency is equal to 45 Hz. The sample was fixed on a metallic support using the heat softening glue crystal bond 509.

3. Results and discussion

3.1. Comparison between top surface and cross-section hardness determination of an Alumina coating

The alumina coating under investigation has been manufactured by Atmospheric Plasma Spraying (APS) with a conventional d.c. plasma gun PTF4 from Sulzer Metco. The powder used is α-Al_2O_3 agglomerated nanometric powder with a size ranging between 200 and 500 nm agglomerated into 25 to 100 μm (d_{50} = 55 μm) grain-size [17]. The powder is sprayed onto a low carbon steel (XC38) as substrate. The substrate was firstly grit blasted with corundum alumina then cleaned in an acetone bath with ultrasonic stirring before the spraying. The resulting roughness was 5.3 ± 0.1 μm. The anode nozzle diameter was 7 mm. The powder was injected perpendicularly to the plasma jet axis through a 1.8 mm i.d. injector located 3 mm upstream of the torch nozzle exit. The plasma jet parameters used are presented in Table 1.

The microstructure analysis of the coating was performed by X-ray Diffraction (XRD) for identifying the phases present into the coating and with a SEM-JEOL JSM-6490LV microscope to observe the microstructure and the defect distribution through the coating. The coating obtained with the agglomerated nanometric powder has a large surface mean roughness, Ra = 9.4 ± 1.8 μm. The XRD analysis using the SIEMENS D5000TM equipment shows that the coating is composed of both α and γ alumina phases, 81.8 and 18.2%, respectively. The SEM

Table 1
Plasma jet parameters used to obtain the Alumina sprayed coatings deposited onto a low carbon steel substrate.

Parameters	Unit	Value
Arc current	A	600
Voltage	V	65
Argon flow rate	slm	45
Hydrogen flow rate	slm	15
Spray distance	mm	100
Gun Traverse speed	m/s	1
Powder flow rate	g/min	25
Argon carrier gas flow rate	slm	5
Number of cycles	–	39
Spray time	min	4