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Modeling of elastic modulus and hardness determination by indentation of porous yttria stabilized zirconia coatings

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ABSTRACT

The mechanical properties of materials can be determined by means of the instrumented indentation experiment. However, when the indentation test leads to a regular load–depth curve for homogeneous massive materials, the presence of defects such as roughness, porosity or cracks present in the region close to the indented zone can greatly modify the shape of this curve. To avoid influence of such defects on the indentation measurement, a cautious polishing is generally performed to obtain a smooth surface. However, for the study of coated materials when polishing is not possible, the defects can interfere with the results of the mechanical property determination and they must be definitely taken into consideration for the indentation data analysis. In this work, the indentation test is employed to characterize suspension plasma sprayed porous ZrO_2 + 8 wt.% Y_2O_3 (8YSZ) coatings. By comparing different models for hardness analysis, we selected the most appropriate one allowing the calculation of the macrohardness taking into account the influence of roughness, porosity and cracks. Afterwards, we showed how the roughness interferes with the depth measurement at the beginning of the indentation test where a fast depth increase is observed. We also showed how the presence of confine defects leads to an abnormal effect during the loading, such as a horizontal plate or a jump in depth. Finally, we propose a methodology to avoid the influence of the roughness and of the porosity on the hardness determination and to model a selected part of the loading curve for the determination of the macrohardness and a parameter representative of the indentation size effect.

1. Introduction

The determination of the mechanical properties such as hardness and elastic modulus by instrumented indentation is modified by the presence of defects located in the zone affected by the indentation process. These defects include: (*i*) confined porosity, (*ii*) cracks and/or (*iii*) surface roughness. In the test of macroindentation characterized by applied loads greater than 1 kg, the influence of such defects is often neglected. On the contrary in nano and microindentation, roughness has a predominant effect which starts to play an important role at the beginning of the indentation test. To circumvent such influence, a careful polishing of the surface can be performed. On the other hand, the polishing can modify the material by work-hardening or by introduction of residual stresses [1–4]. This is very important because these effects can be at the origin of the indentation size effect (ISE) which represents the hardness-load dependence [5]. This phenomenon has been associated with various causes such as work-hardening but also roughness, piling-up, sinking-in, shape of the indenter, surface energy, varying composition and crystal anisotropy. To represent ISE, numerous relationships connect the applied load to the indent dimensions, such as those advanced by Meyer [6], Kick [7], Li and Bradt [8], Sangwal et al. [9], and Bull and Page [10]. Other relationships express the hardness value as a function of the indent dimensions which can be either the indent diagonal or the indentation depth. Within this scope, the model of Nix and Gao [11], based on the Strain Gradient Plasticity (SGP) theory, is probably the most widely used ISE models, since it has the advantage of relating the two interdependent ISE parameters to intrinsic properties of the material. To overcome this interdependence, Chicot [12] suggested the use of a hardness length-scale factor based on the SGP theory and only linked to the shear modulus and the Burgers vector of the material. More recently due to the nanoindentation development, Soer et al. [13] show the existence at a nanoscale of new types of ISE phenomena, which become apparent as the indenter approaches a grain boundary. Furthermore, it has been reported in the literature that the microhardness of different materials could: *i*) be independent of load [14,15], *ii*) increase or decrease with load [16–21] or *iii*) exhibit a complex variation with changing load [22–24]. These relations make very difficult the ISE analysis due to the variety of

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effects, especially in nanoindentation where the effect of the extreme surface layers is more pronounced [13,25–29]. According to Gerberich et al. [30], this phenomenon would be due to the variation of the ratio between the energy of newly created surface and plastic strain energy dissipation, whereas the contact surface to plastic volume ratio would remain nearly constant for very low indentation depths. Consequently, as the penetration depth increases, the effect of the bulk material becomes more dominant and eventually there is no change in the value of hardness with the load [31–33]. For all these reasons, it is very difficult to assign one specific phenomenon to an ISE parameter, since several causes can interfere simultaneously with the hardness measurement. As a matter of fact, it is not clear whether the ISE-type behavior arises due to the underlying properties of the material near the surface or due to the indentation measurement process and its interpretation. That is why it seems to be more convenient to study ISE at the microscopic scale. In any case, the ISE phenomenon must be taken into account in each indentation analysis and influence of porosity or roughness can be both analyzed through ISE analysis.

For porous coated materials, polishing is not achievable without important modifications of the mechanical behavior of the coating. In this case, there are two possibilities of analyzing. One of them consists to perform nanoindentation in a region without defects to estimate the properties of the bulk material. The other one consists in modeling the mechanical property as a function of the porosity rate. On the other hand by studying the loading curve, some authors suggest a methodology to separate the influence of the defects in the indentation measurement in order to calculate the actual hardness of the coating [34,35]. Indeed, when the indenter comes across a pore during its displacement into the coating, the load–depth curve shows a singularity that is traduces by a horizontal plate, i.e. a fast increase of the depth under the same applied load. In this case, the authors suggest the shift of the curve toward the low indentation depths within the objective to rebuild a regular loading curve. The authors thus reconstructed a “normal” loading curve from which they calculate the true hardness of the material. Another approach consists of representing the loading curve using the Proportional Specimen Resistance (PSR) model of Li and Bradt [8], originally used to characterize ISE, to highlight the influence of the defects on the mechanical properties. The load to indenter displacement ratio is then plotted as a function of the indentation depth for representing ISE. For a homogeneous material, the PSR model leads to a straight line for which the slope is directly connected to the hardness of the material and the coordinate at the origin represents the indentation size effect [36,37]. Nowadays, the PSR model lacks of physical meaning of the fitting parameter traducing the ISE. That is why the model of Nix and Gao [11] modified by Chicot [38] could replace advantageously the PSR model since the ISE parameter represents plastic deformation toughness. Based on this model describing the indentation size effect, Chicot et al. [38] suggested a model for representing the loading part of a load–depth curve leading to three fitting parameters, i.e. the macrohardness, the hardness length-scale factor and the shift load.

In this paper, we propose the application of these different methodologies allowing the characterization of the mechanical behavior of a porous material. We discussed about the efficiency to separate the influence of roughness, porosity and cracks on the hardness measurement within the objective to give suitable values for characterizing the hardness of yttria stabilized zirconia coating obtained by suspension plasma spraying.

2. Materials

The commercial powder Metco 204NS of a composition ZrO_2 + 8 wt.% Y_2O_3, prepared by spray drying was ball milled to obtain fine particles useful to formulate the suspension. The initial volume–surface mean diameter of the coarse powder is equal to d_{vs} = 38 μm. After 2 h of milling, the resulting powder has a mean size equal to d_{vs} = 4.6 μm and a monomodal size distribution.

The suspension used for the spray experiments was formulated with the use of 20 wt.% of powder, 40 wt.% of water and 40 wt.% of ethanol. The suspension feed rate at spray experiment was of about 39 g/min. The suspension was introduced via internal injection mode using a continuous-stream injector (with an internal diameter of 0.5 mm) installed inside the anode-nozzle of the plasma torch. Plasma spraying was performed using an *SG-100* (*Praxair S.T.,* Indianapolis, In, USA) DC single cathode torch mounted on a 5-axis *IRB-6* robot of *ABB* (Zürich, Switzerland) using an Ar + H_2 (45 + 5 slpm) plasma gas mixture with electric power of 40 kW. The suspension spraying was performed in order to obtain coatings of the thickness up to 100 μm. Stainless steel disks (diameter 25 mm and thickness about 8 mm), initially cleaned with ethanol and sand blasted using corundum grit under a pressure of 0.04 MPa from a distance of 100 mm, were used as substrates. Table 1 collects the spray conditions for obtaining YSZ coatings on stainless steel substrate.

The deposits were sprayed by 3 passes in one scan over the substrate, with a scan step of 10 mm and after each scan the deposition was interrupted and the coatings were cooled down to about 60 °C. This experiment was made with a spray distance of 40 mm and a velocity of 300 mm/s. There were 6 sand blasted stainless steel substrates which were sprayed simultaneously to obtain the desired thickness of about 100 μm. Fig. 1a and b shows the surface of the suspension plasma sprayed coatings. The figure reveals presence of some microporosity and cracks at the top of the coating. It is also clear that the surface is heterogeneous according to the shape of the splats and that the size of the particles is randomly distributed at the surface of the coated sample.

3. Indentation experiments and analysis

The instrumented indentation experiments were performed with a micro-hardness Tester CSM 2-107 equipped with a Vickers indenter. The maximum loads were chosen within the range 100 mN to 10 N and more than 20 indentation tests were conducted only in the as-sprayed top surfaces of the coating and not on the cross-section. This choice has been motivated in order to avoid modification of the coating microstructure and possible changes in the indentation data analysis, i.e. the modification of the residual stress state after cutting and/or polishing, the filling or the plugging of the pores by polishing, the generation of cracks by cutting and the work-hardening by polishing. 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. [39]. 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.

Table 1
Operational processing parameters used to obtain suspension plasma sprayed YSZ coatings on stainless steel substrates.

Process parameters, units	Values
Electric power	40 kW
Working gas composition	Ar + H_2
Working gas flow rate	45 + 5 slpm
Spray distance	40 mm
Torch scan speed velocity	300 mm/s
Number of scans	9 scans (27 passages)[a]
Injector type	Nozzle inserted in the torch
Nozzle injector internal diameter	0.5 mm
Static pressure in suspension container	0.03 MPa
Coatings' thickness	100 μm
Maximum surface temperature	692 °C

[a] after each scan interruption until temperature drops down to 60 °C.