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Towards Engineering Isotropic Behaviour of Mechanical Properties in Thermally Sprayed Ceramic Coatings

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Towards engineering isotropic behaviour of mechanical properties in thermally sprayed ceramic coatings

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Abstract

It is widely recognized by the scientific community that thermal spray coatings exhibit anisotropic behaviour of mechanical properties, e.g., the elastic modulus values of the coating in-plane (i.e., parallel to the substrate surface) or through-thickness (i.e., perpendicular to the substrate surface) will tend to be significantly different due to their anisotropic microstructures. This work shows that thermally sprayed ceramic coatings may exhibit isotropic mechanical behaviour similar to that of bulk materials even when exhibiting the typical anisotropic coating microstructure. Elastic modulus values on the in-plane and through-thickness directions were measured via Knoop indentation and laser-ultrasonic techniques on a coating produced via flame spray (FS) using a nanostructured titania (TiO₂) powder. No significant differences were found between the coating directions. In addition, four major cracks with similar lengths were observed originating near or at the corners of Vickers indentation impressions on the coating cross-section (i.e., a typical characteristic of bulk ceramics), instead of two major cracks propagating parallel to the substrate surface, which is normally the case for these types of coatings. It was observed by scanning electron microscopy (SEM) that coatings tended to exhibit an isotropic behaviour when the average length of microcracks within the coating structure oriented perpendicular to the substrate surface was about twice that of the microcracks aligned parallel to the substrate surface. Modelling, based on scalar crack densities of horizontal and vertical cracks, was also used to estimate when thermal spray coatings tend to exhibit isotropic behaviour.

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1. Introduction

1.1. Anisotropic microstructure of thermally sprayed coatings

Thermally sprayed coatings are formed by the impact, spreading, resolidification and overlapping of fully molten and/or semi-molten particles on a substrate surface. Consequently, thermally sprayed coatings typically exhibit a lamellar, anisotropic microstructure of randomly stacked splats and well-defined horizontal splat boundaries. It is also possible to observe coarse (globular) pores, which are associated with defects in the structure, such as, the incomplete filling of interstices between previously deposited particles. For ceramic coatings, in addition to these characteristics, it is common to observe a network of intra- and inter-lamellar microcracks or

voids, which are normally generated due to imperfect splat-to-splat contact and quenching stress relaxation [1].

Due to this anisotropic microstructure, it is known that thermally sprayed coatings tend to exhibit anisotropic characteristics of mechanical properties. For example, mechanical properties, such as elastic modulus (E), tend to exhibit different values for the in-plane (parallel to the substrate surface) and through-thickness (perpendicular to the substrate surface) directions [2–4].

This phenomenon can be explained based on the shapes and orientation of pores and cracks. Inter-splat horizontal pores (voids) and intra-splat cracks may be considered as ellipses exhibiting different aspect ratios, i.e., the ratio of the major axis over the minor axis, and regarded as pores parallel or perpendicular to the substrate surface, respectively. For example, a spherical void could be considered as an ellipse exhibiting an eccentricity value of zero or close to zero, whereas, a crack or an inter-splat pore could be considered as an ellipse that exhibits an eccentricity value equal to or near one. It is known that each

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pancake-shaped splat is horizontally deformed/oriented with dimensions of approximately a few microns in thickness and tens of microns in diameter [5]. Due to this geometrical factor, the surface area provided by horizontal inter-splat pores will tend to be higher than that provided by the vertical intra-splat cracks [3,4,6]. As it is known that E values of bulk ceramics are lowered when the internal surface area of the material (i.e., porosity level) increases [7], it is then understandable why ceramic thermal spray coatings tend to exhibit anisotropic E values.

The effect of the orientation and shape of cavities on the E values of materials was extensively discussed and modelled by Kachanov et al. [8]. These models are very effective in helping to better understand the anisotropic character of complex structures like thermal spray coatings. Kroupa et al. [9,10], based on this previous work [8], adapted these mathematical models to describe specifically the relationship between the microstructural characteristics of thermally sprayed coatings with the anisotropy of the E values measured on the in-plane (E_{ip}) and through-thickness (E_{tt}) directions. The modeling is a function of globular pores, inter-splat horizontal pores/cracks and intra-splat cracks. According to the model, the material comprising the splats is isotropic and homogeneous, exhibiting an elastic modulus E_0 and a Poisson's ratio ν_0 . Within the thermal spray coating there are approximately N spherical (globular) pores of radii R_i randomly distributed. The overall coating porosity (p) is given by:

$$p = (1/V) \sum_{i=1}^N (4/3)\pi R_i^3 \quad (1)$$

where V is the representative volume element of the coating. According to the model, cracks do not contribute to porosity p . A family of approximately n_3 circular and randomly distributed microcracks of radii r_3 parallel to the substrate surface represents the imperfect bonding between splats along the interfaces (boundaries). Their effect is given in terms of a scalar crack density ρ_3 :

$$\rho_3 = (1/V) \sum_{i=1}^{n_3} r_{3i}^3 \quad (2)$$

A family of approximately n_1 circular and randomly distributed microcracks of radii r_1 perpendicular to the substrate surface represents the vertically oriented cracking. Their effect is given in terms of a scalar crack density ρ_1 :

$$\rho_1 = (1/V) \sum_{i=1}^{n_1} r_{1i}^3 \quad (3)$$

In these equations, which try to represent a thermal spray microstructure, it is important to distinguish the difference between globular spherical pores of radii R_i from microcracks of radii r_i perpendicular or parallel to the substrate surface. The resulting E values are given by two equations. For E_{ip} , the equation is:

$$E_{ip} = \frac{E_0}{1 + \left(\frac{p}{1-p}\right) \frac{3(1-\nu_0)(9+5\nu_0)}{2(7-5\nu_0)} + \left(\frac{\rho_1}{1-p}\right) \frac{8(1-\nu_0^2)(1-3\nu_0/8)}{3(1-\nu_0/2)}} \quad (4)$$

For E_{tt} , the equation is:

$$E_{tt} = \frac{E_0}{1 + \left(\frac{p}{1-p}\right) \frac{3(1-\nu_0)(9+5\nu_0)}{2(7-5\nu_0)} + \left(\frac{\rho_3}{1-p}\right) \frac{16(1-\nu_0^2)}{3}} \quad (5)$$

Based on these equations, the dependencies of the ratios of the elastic moduli E_{ip}/E_0 on ρ_1 and E_{tt}/E_0 on ρ_3 were plotted for different values of porosity (p). It was observed that for the same porosity levels (p) and scalar crack density values (ρ), the E_{ip}/E_0 ratios were higher than those of the E_{tt}/E_0 , i.e., the modeling was able to represent the anisotropic mechanical behaviour of thermal spray coatings.

1.2. Near-isotropic characteristics

Previous works have shown that ceramic thermal spray coatings produced via air plasma spray (APS) and high velocity oxy-fuel (HVOF) from nanostructured and fused and crushed (F&C) powders may exhibit isotropic characteristics of mechanical properties [11–13]. These near-isotropic coatings exhibited at least some of the following characteristics: (i) absence of the typical lamellar microstructure, (ii) high density, (iii) extensive vertical intra-splat crack network, and (iv) tendency to exhibit four major cracks with similar lengths emanating from or near the corners of the Vickers indentation impression produced on the cross-section (when one of the diagonals of the Vickers indenter was positioned parallel to the substrate surface). Concerning this last characteristic (according to the best knowledge of the authors), this behaviour has been observed only for some coatings produced from nanostructured agglomerated ceramic powders by APS [13] and HVOF [12]. These coatings were also shown to exhibit improved wear resistance (however, their E values were not measured in the two directions to confirm the isotropic behaviour). Therefore, there seems to be some type of correlation between the nanostructural character of the feedstock with this type of isotropic crack propagation behaviour of the coating, which may also have influenced the wear performance of this material.

1.3. Isotropic crack propagation

During an ongoing research project on the development of titania (TiO_2) coatings for sliding wear applications, it was observed that a coating developed by flame spray (FS) from a nanostructured powder exhibited isotropic behaviour. During Vickers indentation measurements on the cross-section, with one of the diagonals of the indenter aligned parallel to the substrate surface, four major cracks with similar lengths tended to be observed originating at or near the corners of Vickers indentation impressions. This behaviour, which is typical of that observed in bulk ceramics [14], is shown in Fig. 1.

This is not a typical characteristic of ceramic thermal spray coatings, which tend to exhibit two major cracks parallel to the substrate surface (in-plane direction) propagating from the corners of the Vickers indentation impression, when the indentation is performed on the cross-section with one of the diagonals aligned parallel to the substrate surface [15]. This

Fig. 1. Isotropic behaviour — four major cracks with similar lengths originating near or at the corners of Vickers indentation impressions on the cross-section of a flamesprayed nanostructured titania coating.

anisotropic crack propagation occurs predominantly due to the typical microstructure of thermal spray coatings, with its well-defined splat boundaries, which provide easy crack propagation paths.

Consequently, it is hypothesized that thermal spray coatings exhibiting isotropic characteristics of crack propagation may respond differently to mechanical stresses, which may lead to new types of applications and improved performances. The evaluation of these coatings will also lead to a better understanding of thermal spray microstructures. Therefore, the objective of this work was to study in more detail the nature and origin of this type of isotropic behaviour of crack propagation. To achieve this objective, measurements of elastic modulus values on the in-plane and through-thickness directions of the coating were carried out using a static, high strain, direct-contact and destructive technique (Knoop indentation), and a dynamic, low strain, non-contact and non-destructive technique (laser-ultrasonics). In addition, modeling of the elastic behaviour of thermal spray coatings was considered and carried out. The results of this research are intended to provide some additional guidance on how to engineer isotropic ceramic thermal spray coatings.

2. Experimental procedure

2.1. Powder and thermal spraying

The nanostructured titania powder (TiCp2, Altair Nanomaterials Inc., Reno, NV, USA) was deposited using an oxy-acetylene FS torch (Metco 6P-II, Sulzer Metco (US) Inc., Westbury, NY, USA). Despite the fact that part of the original nanostructure of the powder is partially destroyed during thermal spraying, the expression “nanostructured coating” will be used in this work to differentiate this type of coating from those produced from conventional powders. Powder particle size distribution was evaluated using a laser diffraction particle size analyzer (Beckman Coulter LS 13320, Beckman Coulter, Miami, FL, USA). The sprayed particles had their velocity and

temperature values measured by using an in-flight diagnostic tool (Accuraspray, Tecnar Automation, Saint Bruno, QC, Canada), which is based on pyrometry and time-of-flight measurements. The particle detector was placed at the same spray distance as used when depositing the coatings, i.e., 10 cm. The coating was deposited onto 1.25 cm-thick low carbon steel substrates that had been grit-blasted before spraying. Coating thickness was approximately 500–600 μm.

2.2. Microstructural characterization

The structural characteristics of the powder and the cross-section of the coating were evaluated by scanning electron microscopy (SEM) (Model S4700, Hitachi Instruments Inc., Tokyo, Japan). In order to better preserve and reveal the true structural features of the coating (cross-section), it was mounted in epoxy resin using vacuum impregnation and polished using standard metallographic procedures. The porosity of the coating was evaluated by using SEM and image analysis on the cross-section. A total of 10 pictures were taken (at 500×) to evaluate porosity levels. The powder and coating phase compositions were determined by means of X-ray diffraction (XRD) using Cu Kα radiation (step: 0.05°/step time: 2.5 s) for values of 2θ in between 20° and 60°.

2.3. Microhardness values measured via Vickers indentation

For Vickers indentations (300 gf — 15 s), one diagonal of the Vickers indenter was positioned parallel to the substrate surface on the coating cross-section. A total of 10 indentations were performed.

2.4. Elastic modulus values measured via Knoop indentation

Elastic modulus values were evaluated on the cross-section of the coating using Knoop indentations according to a technique developed by Marshall et al. [16]. The Knoop indenter is a diamond ground to pyramidal form that produces a diamond shaped indentation having an approximate ratio between long (a) and short (b) diagonals of 7:1. The depth of indentation is about 1/30 of its length. The Knoop technique employed to measure E is based on the measurement of the elastic recovery of the dimensions of the Knoop indentation impressions. The formula for determining the elastic modulus (E , in Pa) is:

$$E = \frac{(-\alpha H)}{\left(\frac{b'}{a'} - \frac{b}{a}\right)} \quad (6)$$

where α is a constant (0.45), H is the Knoop hardness (in Pa), and a' and b' are the lengths of the major and minor diagonals of the Knoop indentation impression.

During unloading, the elastic recovery reduces the length of the minor diagonal of the indentation impression (b'), while the length of the major diagonal of the indentation impression (a') remains relatively unaffected. The known major to minor diagonal ratio (7.11) of the indenter is compared to that of the

Fig. 2. Schematic of E_{ip} and E_{tt} measurements on the coating cross-section via Knoop indentation.

indentation impression. The extent of recovery depends on the hardness-to-modulus (H/E) ratio of the material being indented.

Therefore, as the measurement of E values via Knoop indentation is largely based on the elastic recovery of the minor diagonal (b'), this technique can be used to measure E values in different directions by simply aligning b' with the desired E direction. Consequently, the indentations were applied with the minor diagonal of the Knoop indenter positioned parallel to the substrate surface to measure E_{ip} and perpendicular to the substrate surface to measure E_{tt} , as shown in Fig. 2. A load of 1000 gf, an indentation time of 15 s and a total of 10 indentations per direction were applied for Knoop evaluation.

2.5. Elastic modulus values measured via laser-ultrasonics

The values of the elastic constants were measured on the in-plane and through-thickness directions of the coating via a laser-ultrasonics technique [17]. The ultrasonic waves are generated by a Nd:YAG (third harmonic: 355 nm) laser pulse. For the through-thickness measurements the generation laser is focused to a spot of about 3 mm in diameter on the back of the substrate (Fig. 3a), whereas, for the in-plane configuration the laser is

focused in a line ($\sim 200 \mu\text{m} \times 5 \text{ mm}$) on the coating surface (Fig. 3b). The detection is done by a long pulse Nd:YAG laser (1064 nm) focused on a region of about 1 mm in diameter on the coating surface for the through-thickness measurement and with a line geometry as in the generation for the in-plane measurements. As the ultrasonic wave reaches the detection spot surface, it modulates the detection light and a two-wave mixing GaAs interferometer is used to demodulate the collected detection light. Fig. 3 also shows signals obtained for in-plane and through-thickness measurements.

The elastic modulus value (E) of a material is directly proportional to its density (ρ) and the velocity (v) of the ultrasonic acoustic wave to the square travelling in the material ($E = \rho \cdot v^2$). By measuring the travel time of a longitudinal wave bouncing within the coating surface and substrate-coating interface (Fig. 3a) an elastic constant in the through-thickness direction can be calculated. Using the C_{ij} notation for elastic constants of anisotropic solids [18], the longitudinal modulus in the through-thickness direction (direction 3) is given by:

$$C_{33} = \rho \left(\frac{2e}{t_t} \right)^2 \quad (7)$$

where e is the coating thickness and t_t is the time delay between echoes bouncing in the coating (see Fig. 3a). For the in-plane measurement, considering in-plane isotropy ($C_{11} = C_{22}$), the longitudinal elastic constant is given by:

$$C_{11} = \rho \left(\frac{d}{t_t} \right)^2 \quad (8)$$

where d and t_t are respectively the travel distance and time of arrival of the longitudinal waves, which are illustrated in Fig. 3b.

It is important to point out that a previous work indicated a “good” correlation between the E values measured via Knoop indentation and the laser-ultrasonics technique for APS and HVOF-sprayed TiO_2 coatings produced from conventional fused and crushed powders [19].

Fig. 3. Schematic of E_{ip} and E_{tt} measurements on the coating via laser-ultrasonics.

3. Results and discussion

3.1. Powder characterization

The nanostructured titania powder exhibits a particle size distribution within the typical microscopic range (10 to 50 μm) found for thermal spray ceramic powders (Fig. 4). By looking at a single particle using SEM (Fig. 5a), it is possible to observe the typical donut shape of spray-dried particles. The nanostructural character of the powder is revealed by analyzing the agglomerate at higher magnifications (Fig. 5b). The XRD pattern shows that the powder is crystalline and anatase is the only detectable phase (Fig. 6).

3.2. Thermal spraying

The range of average velocity and temperature values for the thermally sprayed particles were 70–80 m/s and 2750–2850 $^{\circ}\text{C}$, respectively. The melting point of titania is 1855 $^{\circ}\text{C}$ [20], i.e., the average temperature values measured are significantly higher than this value. However, it has to be pointed out that the particle temperatures were measured via a pyrometer and, therefore, the temperatures measured represent only the temperature at the particle surface, i.e., they do not represent the overall particle temperature. The temperature values of the core of the particles were almost certainly lower than these reported values.

3.3. Coating microstructure

Fig. 7 shows the microstructure (cross-section) of the nanostructured coating deposited via FS. It is important to point out that the scale bar (the overall group of ticks) of the cross-section is oriented parallel to the substrate surface. It is possible to observe the absence of the typical lamellar structure of thermal spray coatings. The microstructure is similar to that previously modeled [8–10], where globular pores are surrounded by a network of vertical and horizontal microcracks. It

Fig. 4. Particle size distribution of the nanostructured titania feedstock.

Fig. 5. (a) Spray-dried titania agglomerate. (b) Individual nano-sized TiO_2 particles.

is particularly noticeable that the network of microcracks is more extensive towards the vertical direction, i.e., perpendicular to the substrate surface. The porosity of this coating was estimated to be $2.0 \pm 0.3\%$ ($n=10$), which is considered to be low, i.e., this is a dense coating. As cited in Section 1.2, the (i) absence of the typical lamellar microstructure, (ii) high density, and (iii) extensive vertical intra-splat crack network are

Fig. 6. XRD pattern of the nanostructured titania powder.

Fig. 7. Cross-section of the FS nanostructured coating.

typical conditions previously observed for thermal spray coatings that tended to exhibit isotropic behaviour of mechanical properties [11–13].

Fig. 8 shows the XRD pattern of the coating. A significant phase change from the powder is observed. The anatase phase present in the powder, was not detected in the coating (Fig. 6). Different phases were detected in the coating. The major phase is crystalline rutile, which can be identified from the diffraction peaks. Based on the characteristically amorphous humps found in the ~ 25 – 30° and ~ 53 – 57° 2θ regions, it can be inferred that amorphous titania is also present in the coating microstructure. The rutile phase probably originated from the melting and resolidification of the powder particles during thermal spraying, as observed by other authors [21,22], whereas, the amorphous titania may have originated from the rapid cooling and resolidification of the molten particles that could have been fast enough (in some cases) to prevent the formation of a crystalline phase from the melt, and/or semi-molten particles that did not fully transform from anatase to rutile phase during thermal spraying. It has to be pointed out that the humps observed in Fig. 8 may also have been caused by an overlapping of peaks of the rutile, anatase and suboxide phases of titanium.

Fig. 8. XRD pattern of the nanostructured titania coating.

3.4. Vickers microhardness

The Vickers microhardness number (300 gf) of the coating is 862 ± 20 ($n=10$), which is within the values typically reported for titania thermal spray coatings, i.e., ~ 800 – 900 [23].

3.5. Elastic modulus

The values of E measured via Knoop indentation and laser-ultrasonics on the in-plane and through-thickness directions of the FS nanostructured coating are listed in Table 1. The values of E measured via Knoop indentation in both directions are not statistically different.

The E values measured via laser-ultrasonics technique agree with the results obtained via Knoop indentation, i.e., the E values on the in-plane and through-thickness directions tend to be similar. The average E_{ip}/E_{tt} ratios measured via Knoop indentation and laser-ultrasonics are 0.99 and 0.92, respectively. This is an important result because these two techniques, which are exhibiting the same isotropic trend, are totally different in their approaches to measure E values, i.e., static, high strain, direct-contact and destructive mode (Knoop) and dynamic, low strain, non-contact and non-destructive mode (laser-ultrasonics).

In early work, isotropic and homogeneous bulk ceramic materials were employed to model and develop crack propagation behaviour on the elastic/plastic field of sharp indenters (e.g., Vickers) [24]. The isotropic elastic modulus behaviour and homogenous microstructures of these materials typically produce a crack pattern of two half-penny cracks represented on the surface as four major cracks with similar lengths propagating from or near the corners of the Vickers indentation impression [14,24]. Typical materials that are known for their anisotropic E values, such as thermal spray coatings [2–4], tend to exhibit two major cracks parallel to the substrate surface propagating from the corners of the Vickers indentation impression, when the indentation is performed on the cross-section with one of the diagonals aligned parallel to the substrate surface [15,25]. This anisotropic crack propagation occurs predominantly due to the well-defined lamellar boundaries, which provide less resistant crack propagation paths. Therefore, the crack propagation behaviour demonstrated by the FS nanostructured coating (Fig. 1) is definitely associated with the isotropic E values observed for this coating.

The differences in the absolute E values obtained by the two techniques (Table 1) are probably related to the microstructure of these ceramic thermal spray coatings and the nature of the two techniques. It is known that under tensile or compressive stresses the microcracks and pores of thermal spray coatings

Table 1

Elastic modulus values measured via Knoop indentation and laser-ultrasonics on the in-plane and through-thickness directions of the FS nanostructured coating

E_{ip} (Knoop)	E_{tt} (Knoop)	E_{ip} (laser)	E_{tt} (laser)
(GPa)	(GPa)	(GPa)	(GPa)
$n=10$	$n=10$	$n=10$	$n=3$
159 ± 19	161 ± 18	120 ± 10	130 ± 15

open or close elastically, which will lead to a non-linear stress–strain relation [9,10]. Concerning Knoop indentation, during the loading half-cycle, the adjacent microstructure surrounding the indenter undergoes elastic-plastic deformation, i.e., this technique is based on high strain when compared to laser-ultrasonics, which is based on a dynamic, low strain, non-contact and non-destructive mode. Therefore, some pores will probably be healed/compacted by this indentation action. During the unloading cycle, elastic recovery takes place, reducing the length of the minor diagonal of the indentation impression (with relatively little change in the major one). Therefore, the elastic deformation (stress–strain relation) that occurs during the unloading cycle is also probably non-linear due to the non-linear stress–strain relation. Consequently, the E values measured via Knoop indentation may be considered as an overall average of the non-linear elastic recovery of the coating, which could explain the different values measured by the two techniques. Another factor that might have caused or contributed to this difference is the indentation size effect. This can arise when the size of the indentation impression is not sufficiently large to represent and encompass the overall microstructure of the coating. In that case defects like pores, splat boundaries and cracks can be minimized, and therefore higher E values may be measured, as observed by Singh et al. [26] for zirconia-based thermal barrier coatings.

3.6. Understanding the isotropic behaviour

In an attempt to gain insight into the behaviour of the titania coating being evaluated in the current study, bulk values for titania, E_0 (282 GPa) and ν_0 (0.278), were taken from the literature [20] and substituted into Eqs. (4) and (5) [8–10]. The elastic modulus (E_0) and Poisson's ratio (ν_0) values corresponded to those of the rutile phase of titania, which was the major phase of the coating (Fig. 8), i.e., they are an approximation to the actual E_0 and ν_0 values of the coating if it were dense. The plots of the E_{ip} and E_{tt} values versus scalar crack density were carried out for a porosity value of 2.0%, which was the porosity of the coating (measured by image analysis). Fig. 9 shows these plots.

It was observed that the coating tended to exhibit isotropic values of elastic modulus when the through-thickness scalar crack density (vertically oriented towards the substrate surface) is approximately two times that of the in-plane scalar crack density (horizontally oriented towards the substrate surface). For example, using the dotted lines found in Fig. 9, it is observed that to exhibit a hypothetical isotropic E value of 160 GPa, the in-plane scalar crack density of the coating should be ~ 0.15 , whereas, that of the through-thickness should be ~ 0.30 . For a hypothetical isotropic E value of 110 GPa, the in-plane scalar crack density of the coating should be ~ 0.30 , whereas, that of the through-thickness should be ~ 0.60 . This same type of correlation was already observed in previous work, when the porosity levels of the coatings were considered to be 0 and 1% [11].

Therefore, when the effect of the scalar crack density created by the vertical intra-splat cracks is large enough to balance the

Fig. 9. Modelling of elastic modulus values on the in-plane and through-thickness directions versus the scalar crack density for a titania thermal spray coating that exhibits a porosity level of 2%.

effect of the scalar crack density created by the horizontal inter-splat pores and cracks, the elastic behaviour of the coating will tend to be isotropic. To achieve this type of microstructure, the cross-section of the thermal spray coating would have to exhibit a significant vertically oriented intra-splat crack network, similar to that of Fig. 7, to balance the surface area of the horizontal inter-splat pores and cracks. A dense coating, such as that produced in this study, also would be important because it would reduce the scalar crack density of the horizontal pores and cracks. It is important to point out that the scheme proposed by Kroupa et al. [9,10] (based on the model of Kachanov et al. [8]) was originally developed to explain the nature of the anisotropic behaviour of thermal spray coatings. However, the same model may be used to predict by which conditions thermal spray coatings may exhibit isotropic behaviour, but as thermal spray coatings are considered inherently anisotropic, this possibility was not considered.

It is difficult to measure experimentally the vertical and horizontal scalar crack densities of a thermal spray coating. A simple experimental technique was employed to provide a better understanding about this isotropic behaviour via the measurement of the vertical-to-horizontal crack length ratio of the coating. To accomplish this objective, a total of 10 SEM cross-section pictures were taken at a magnification of 6 kX at randomly selected regions of the coating. One of these pictures is shown in Fig. 10. It has to be stressed that the scale bar (the overall group of ticks) of the cross-section is oriented parallel to the substrate surface. Via image analysis (carried out manually), the total lengths of the vertical and horizontal cracks were measured for each picture. Of course, by looking at Fig. 10, it is possible to observe that the cracks are not perfectly aligned horizontally or vertically in relation to the in-plane and through-thickness directions. Therefore the following simple approach was applied. Cracks at angles between 0 and 45° to the substrate surface were considered as parallel cracks, whereas, cracks at angles between 45 and 90° to the substrate surface were

Fig. 10. Cross-section zone of the FS nanostructured coating used for determination of the vertical-to-horizontal crack length ratio.

considered as vertical cracks. This same type of approach was also employed by Antou et al. [27].

Based on this approach, the average vertical-to-horizontal crack length was found to be 2.24 ± 1.07 ($n=10$), i.e., the total length of the through-thickness-oriented cracks is approximately two times that of the in-plane-oriented cracks. It is recognized that the standard deviation of this value is high, therefore, to obtain a very accurate number, more SEM pictures would probably have to be taken and a more rigorous analytical approach employed. However, this approximate value serves the intent of this specific study in regard to providing insight into the isotropic behaviour of thermal spray coatings.

Therefore, the mathematical model [8–10] and the experimental data are based on two different approaches (i.e., scalar crack density and crack length) and cannot be directly related. However, both show that when vertical scalar crack density or vertical microcracking outweigh horizontal scalar crack density or horizontal crack/inter-splat pores by a ratio of approximately 2 to 1, thermal spray coatings tend to exhibit an isotropic behaviour of E values.

Finally, it has to be pointed out that according to Sharma et al. [28] the anisotropic microstructures of thermally sprayed coatings do not only affect the mechanical properties of the coatings but also the electrical properties. Properties like current-voltage characteristics and electrical resistivities tend to be different when measured on the in-plane and through-thickness directions. It is hypothesized that a microstructure that promotes isotropic behaviour of mechanical properties may also induce isotropic characteristics of electrical properties.

3.7. Through-thickness crack network formation

As previously discussed, one of the key microstructural factors to generate the isotropic behaviour of mechanical properties is the formation of an extensive vertical (through-thickness) crack network to counterbalance the effect of the surface area created by the horizontal inter-splat pores and cracks. The formation of the vertically oriented intra-splat crack network, such as that of Fig. 7, is predominantly caused by quenching stress relaxation effects [1]. When individual molten and/or semi-molten ceramic particles impact and spread over

the substrate surface or previously deposited layers, they contract upon rapid resolidification. This contraction tends to be constrained by the underlying surface. As the particle cools down, the degree of constraint is highly dependent on the nature of the bonding at the splat/underlying surface interface. This quenching stress is always tensile in thermal spray splats.

According to Clyne and Kuroda [1], the maximum quenching stress developed in a splat is given by the formula:

$$\sigma = \alpha \times E \times \Delta T \quad (9)$$

where σ is the maximum quenching stress, α is the coefficient of thermal expansion, E is the elastic modulus and ΔT is the temperature drop. Based on rutile properties (bulk) at room temperature ($E=282$ GPa; $\alpha=9.4 \times 10^{-6}/K$), it can be estimated that for each temperature drop of 100 K and completely constrained strain (i.e., perfect splat/underlying surface contact), the maximum quenching stress generated on a single titania splat would reach values around 265 MPa. As the modulus of rupture of rutile titania is approximately 100 MPa [20], adding the fact that ceramics do not exhibit high plasticity, the tensile/quenching stress generated is definitely higher than the mechanical strength of the splat, which would tend to crack vertically to release stress.

Another factor that may play a role in increasing quenching stress levels is the deposition per pass rate, which can be achieved by increasing the powder feed rate and/or lowering the traverse torch speed, as proposed by Matejcek et al. [29]. At higher deposition rates, more particles undergo impact on splats that had been previously deposited during the same torch pass.

Therefore, one of the possible ways to generate an increased vertical-to-horizontal microcrack ratio is via thermal spraying particles at high temperatures to (i) produce higher levels of quenching stress within each splat, by improving the splat/underlying surface bonding via the lowering of particle viscosity, (ii) reduce the surface area of the horizontal pores and cracks, leading to an enhanced splat contact adherence and thermal conductivity and (iii) increasing the deposition rate. Prystay et al. [30] were able to tailor horizontally and vertically oriented crack distributions in zirconia coatings deposited via APS by controlling the temperature and velocity of the sprayed particles. It was observed that to produce higher amounts of vertically oriented cracks, the generation of high particle temperatures was a key issue. The particle temperature levels of the FS nanostructured titania coating of Fig. 7 reached values of 2750–2850 °C (measured at the substrate distance). In a previous study, an APS coating produced from a fused and crushed titania powder also exhibited an extensive vertically oriented crack network. The average particle temperature in that work (measured at the substrate distance) was 2702 °C [11], i.e., a similar value. These temperatures are much higher than that of the melting point of titania (1855 °C) [20]. Therefore, these results seem to agree with those of Prystay et al. [30].

3.8. Integrity of the feedstock

Based on the high particle temperatures reported in this study (2750–2850 °C) and the melting point of titania (1855 °C [20]),

it can be hypothesized that the nanostructured powder particles were molten during thermal spraying. It is important to point out that the temperatures measured (via pyrometry) represent those at the particle surface; therefore, the inner particle temperatures may be lower (or even higher) than those measured.

Fig. 11 shows SEM pictures of the fracture surface of the cross-section of the FS nanostructured titania coating. It is possible to observe that semi-molten nanostructured particles were embedded in the coating microstructure, aided by the action of fully molten particles (Fig. 11a). It is also possible to observe that the molten part of the semi-molten agglomerates tended to penetrate into the capillaries (porosity) of the structure (Fig. 11b). Therefore, despite the high average particle surface temperatures, at least part of the original nanostructural character of the feedstock is preserved in the coating microstructure.

This result tends to agree with that of Zhu et al. [31]. In that study, nanostructured titania particles were deposited onto stainless steel substrates to form coatings via vacuum plasma spray (VPS). It can be considered that the temperatures of particles sprayed via VPS systems can be as high as those produced in FS. However, semi-molten nanostructured titania particles were observed in the coating microstructure via transmission electron microscopy (TEM). Gell et al. [32] sprayed nanostructured alumina–titania particles via APS, which also

tends to generate high particle temperatures. It was observed via SEM and TEM that previously semi-molten particles in the spray jet were embedded in the coating microstructure in percentages (vol.%) varying from about 10 to 50%. Therefore, the retention of at least part of the nanostructured character of the feedstock in the coating microstructure is possible, even when the particles are sprayed at high temperatures.

In the present study, the percentage of semi-molten particles embedded in the coating microstructure was not quantified. Consequently, further analysis would be required to confirm if these semi-molten particles are creating any important effect on the cracking behaviour of this coating.

4. Conclusions

- Thermally sprayed ceramic coatings may exhibit isotropic characteristics of mechanical properties on the in-plane and through-thickness directions. These characteristics include (i) similar E values in both directions (measured via Knoop indentation and laser-ultrasonics techniques) and (ii) the tendency of four cracks of similar length to propagate from or near the corners of the Vickers indentation impression (when one of the diagonals of the indenter is aligned parallel to the substrate surface).
- These characteristics may be achieved if at least some the following microstructural characteristics are observed: (i) uniform microstructure, (ii) absence of lamellar structure, (iii) low porosity values (dense coatings), and (iv) extensive formation of through-thickness crack network (i.e., perpendicular to the substrate surface).
- Experimental verification demonstrated that ceramic coatings will tend to exhibit isotropic values of elastic modulus when the total length of through-thickness cracks (vertically oriented with respect to the substrate surface) is approximately two times that of the in-plane cracks (horizontally oriented with respect to the substrate surface). The surface area generated by the vertical intra-splat cracks has to counterbalance that of the horizontal inter-splat pores and cracks.
- Modelling also indicated that when vertical scalar crack density outweighs the horizontal scalar crack density by a factor of approximately 2, thermal spray coatings tend to exhibit an isotropic behaviour of E values.
- The extensive through-thickness (vertical) intra-splat crack network was probably caused by high tensile stresses generated within individual splats during quenching. High particle temperatures lower particle viscosity and favour the formation of a vertical crack network, by enhancing the contact between the splats and underlying surfaces and consequently the constraint in between them.
- Concerning specifically the isotropic crack propagation under Vickers indentation on the coating cross-section, it has been observed only in some coatings produced from ceramic nanostructured-based particles, which tend to exhibit larger surface areas when compared to other types of ceramic thermal spray particles. This large surface area probably translates into a better capacity to absorb heat from

Fig. 11. (a) Fracture surface (cross-section) of the FS nanostructured coating showing a semi-molten particle embedded in the coating microstructure by the action of a molten particle. (b) Another semi-molten particle embedded in the coating microstructure.

the thermal spray jet, thereby lowering the viscosity of the particle near the surface. This would result in increased quenching rates and improved splat-to-splat adhesion. Further analysis would be required to confirm this hypothesis. Other factors that were not investigated in this study, such as residual stress and phase orientation (texture), may also play a role in this vertical microcrack formation.

- Thermal spray coatings exhibiting isotropic characteristics of crack propagation and E values will probably respond differently to mechanical stresses when compared to typical coatings. Such behaviour may lead to new types of applications and improved performances.

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