Abrasion Behavior of Nanostructured and Conventional Titania Coatings Thermally Sprayed via APS, VPS and HVOF

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Abrasion behavior of nanostructured and conventional titania coatings thermally sprayed via APS, VPS and HVOF

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Nanostructured and conventional titania feedstocks were thermally sprayed using APS, VPS and HVOF techniques to study the effects of processing, microstructure and properties on the abrasion behavior. The in-flight characteristics (temperature and velocity) of the APS and HVOF-sprayed particles were also investigated. For the nanostructured coatings, a process map was developed relating the in-flight particle characteristics during coating deposition to the abrasion resistance. This map showed that the particle velocity and particle temperature had an important influence on the volume loss in abrasion tests. Coatings were characterized using SEM to investigate the microstructural features, image analysis to measure coating porosity and Vickers indentation to determine hardness. The abrasion behavior of the coatings was evaluated using the ASTM standard dry sand/rubber wheel test. The abrasion results indicated that the VPS and HVOF-sprayed nanostructured titania coatings exhibited the highest abrasion resistance among the 14 coatings studied.

1 Introduction

Titania (TiO_2) thermal spray coatings have been employed in a wide variety of applications. For example, they are used for anti-wear applications in the propeller shaft bearing sleeve of boats and pump seals where they must resist contact with abrasive grains and hard surfaces [1]. It has been shown that titania (as a bioinert material) can be added to hydroxyapatite in order to enhance the mechanical properties of this biomedical coating [2, 3]. As well, titania is a material known for its photocatalytic properties and researchers have demonstrated the potential of nanostructured and conventional titania thermal spray coatings for use in photocatalytic applications [4, 5].

Recent publications have shown that titania coatings can exhibit very uniform microstructures and mechanical properties when sprayed using high velocity oxy-fuel [6, 7]. From a processing point of view, titania is a very interesting material. Because of its relatively low melting point (1855°C) [8] it can be sprayed by air plasma spray (APS), vacuum plasma spray (VPS), high velocity oxy-fuel (HVOF) and flame spray. Therefore, different microstructures can be engineered through processing. This is an interesting feature that has not been fully explored because titania coatings have not been extensively studied like other ceramic thermal spray coatings, such as alumina, alumina-titania, chromia and zirconia-yttria.

Recently the scientific community has focused considerable attention on nanostructured materials. It has been demonstrated that this class of materials can exhibit enhanced hardness, strength, ductility, and toughness [9-11]. These characteristics open interesting possibilities in thermal spray. Indeed, it has already been shown that nanostructured thermal spray ceramic oxide coatings can have a superior wear performance when compared to similar coatings produced from conventional ceramic oxide powders [12-14].

Due to the promising possibilities exhibited by nanomaterials and the wide range of available processing conditions for titania, the present study was undertaken to investigate the wear behavior of different types of titania coatings deposited by thermal spraying. The coatings were produced from nanostructured and conventional titania feedstocks by spraying via APS, VPS and HVOF. The abrasion performance of these coatings was then studied and the possible causes for differences in the behavior between the two classes of coatings investigated.

2 Experimental procedure

2.1 Feedstocks

One nanostructured and two conventional titania feedstocks were employed in this work. The nanostructured titania feedstock (TiNano 40 VHP, Altair Nanomaterials Inc., Reno, NV, USA) was agglomerated and sintered and exhibited a nominal particle size range from 5 to 20 µm. Both conventional titania feedstocks were fused and crushed. One (Flomaster 22.8(99)F4, F. J. Brodmann & Co., Harvey, LA, USA) had a nominal particle size range from 5 to 20 µm and the other (Amperit 782.3, H. C. Starck GmbH & Co. KG, Goslar, Germany) from 5 to 45 µm. In the remainder of this paper these two conventional materials will be designated as C-1 and C-2 for the Flomaster and Amperit powders, respectively.

2.2 Torches and substrate

APS, HVOF and VPS torches were employed to spray the nanostructured and conventional feedstocks, **Table 1**. For the plasma-sprayed samples, the following conditions were changed in order to produce coatings with different structures and properties: (i) torch type, (ii) atmosphere (air or vacuum), (iii) current and (iv) H_2/Ar flow ratio. For HVOF spraying, various O_2/propylene flow ratios were initially tested by monitoring particle temperature using a diagnostic tool (DPV 2000, Tecnar Automation, Saint Bruno, QC, Canada). The parameter set that produced the highest average particle temperature for each of the two feedstocks was selected for coating production.

Table 1. Processes and torches employed for spraying the feedstocks.

Process - Torch	Nano	C-1	C-2
APS - F4-MB*	X	X	
APS – PyroGenesis 40 kW**			X
HVOF – DJ2700-hybrid*	X	X	
VPS – F4VB***	X		X

* Sulzer-Metco, Westbury, NY, USA.
** PyroGenesis Inc., Montreal, QC, Canada.
*** Plasma-Technik AG, Wohlen, Swiss.

The coatings were deposited on low carbon steel substrates (length, 7.62 cm; width, 2.54 cm; thickness, 1.27 cm) that had been grit-blasted to roughen the surface before spraying. A total of 14 different types of coatings, produced using various powder/torch/spray combinations were deposited for this study.

2.3 Particle temperature and velocity

The nanostructured and conventional feedstocks sprayed with the APS torch F4-MB and with the HVOF torch DJ2700-hybrid had their particle velocities (V) and temperatures (T) measured using the DPV2000. A total of 3000 particles were measured for each spray set. The velocity and temperature data were measured at the distance at which the substrate would normally be positioned when depositing a coating.

2.4 Nanostructure, microstructure and porosity

The nanostructures of the titania feedstock TiNano 40 VHP and its coatings were analyzed via a field-emission scanning electron microscope (S-4700, Hitachi, Tokyo, Japan). The overall coating microstructures were also analyzed via scanning electron microscopy (SEM). The porosity of the coatings was measured via image analysis and SEM. A total of ten images per coating were analyzed in order to determine the porosity levels.

2.5 Microhardness and crack propagation resistance

Vickers microhardness measurements were performed under a 300 g load for 15 seconds on the cross-section of the coatings. A total of ten microhardness measurements were carried out for each coating. The crack propagation resistance was determined by indenting the coating cross-section at 1 kg load for 15 seconds. The total length of the major crack (*2c*) parallel to the substrate surface that originated at or near the corners of the Vickers indentation impression was measured. Based on the indentation load (*P*) and *2c*, the crack propagation resistance was measured according to the relation between load and crack length $P/c^{3/2}$ [15], where *P* is in Newtons and *c* is in meters. All the indentations were performed very near the centerline of the cross-section.

2.6 Abrasion resistance

The abrasion resistance of the coatings was tested based on the ASTM standard G65-00 (procedure D – modified) [16] also known as the dry sand/rubber wheel test. In this test a stationary coated sample was pressed against a rotating rubber-coated wheel (11.43 cm radius - 200 rpm) with a force of 45 N. Silica sand (212-300 μm) was fed (300-400 g/min) between the coating and rubber wheel until the wheel traveled over the equivalent linear distance of 1436 m. Prior to being submitted to this test, the surfaces of the coatings were prepared by grinding with diamond wheels to produce a surface finish of ~0.23 μm. Two samples were tested for each of the 14 different coating types produced in the study. The volume of the material abraded away during the test was measured via optical profilometry.

3 Results and discussion

3.1 Feedstock characteristics and particle diagnostics

The morphological characteristics of the nanostructured titania feedstock are presented in a high magnification picture, **Fig 1**. Each microscopic particle is formed by the agglomeration of individual nanosized particles. The agglomerated particle is porous and, due to the low cohesion of the nanoparticles, it is assumed that the particle does not possess a high mechanical strength.

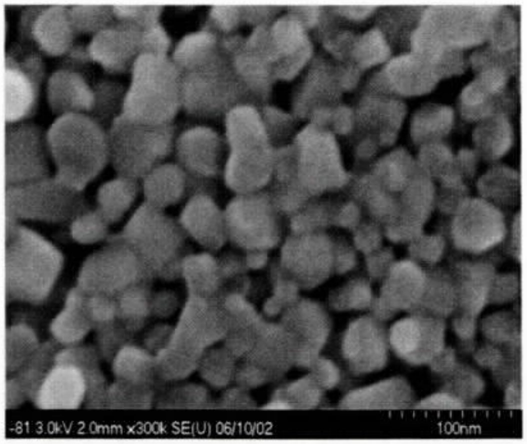

Fig. 1. Individual nanosized particles of titania forming a nanostructured agglomerated particle.

By using APS and HVOF the results of average particle temperature showed that a wide range of values was achieved, from temperatures near the melting point of titania (1855°C) to temperatures up to ~2700°C (see Fig. 2). For the APS-sprayed feedstocks, particle velocities did not exhibit significant differences. The overall particle speed was approximately 250-300 m/s. On the other hand, the HVOF-sprayed particles achieved very high velocities, in the order of 700 m/s.

The intent of using this broad range of velocities, temperatures, equipment, atmosphere (air or vacuum) and feedstocks (nano and conventional) in this work was to enable the engineering of significantly different coating structures. It was hoped that subsequent investigation of the abrasion performance of these nanostructured and conventional titania coatings would help to guide and provide insight for future research in this area.

3.2 Abrasion performance

The abrasion performance (volume loss) results for the 14 titania coatings employed in this study did indeed exhibit notable differences, **Fig. 2**. It is observed that the VPS and HVOF-sprayed nanostructured titania coatings exhibited the highest abrasion resistance of the coatings studied. There is a reduction in volume loss of approximately 25% from the two best conventional coatings (VPS and HVOF-sprayed) to the best nanostructured coatings, which were also sprayed by VPS and HVOF. Concerning specifically the APS-sprayed coatings, there is no significant difference in abrasion performance between the best nano and conventional titania coatings. It is also important to point out that the poorest abrasion performance of all 14 coatings was also a nanostructured one. This characteristic shows the immense importance of processing when engineering nanostructured thermal spray coatings.

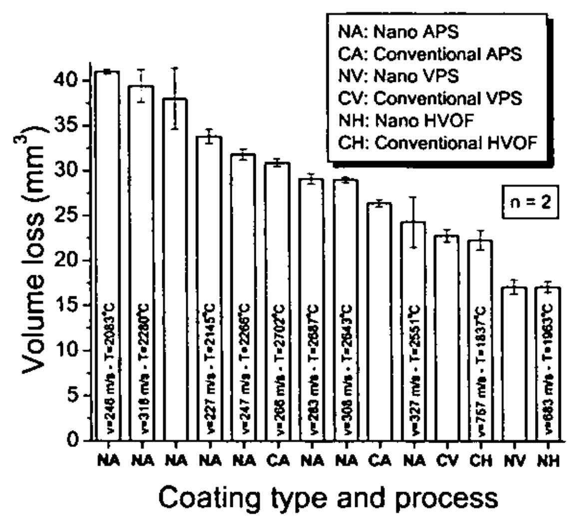

Fig. 2. Volume loss in abrasion test for nanostructured and conventional titania coatings sprayed by APS, VPS and HVOF.

To help identify the reasons for the results shown in Fig. 2 and gain a better understanding of the wear behavior, the abrasion resistance of the APS- and HVOF-sprayed nanostructured coatings was related to the particle in-flight characteristics (T & V). An empirical correlation was found, **Fig. 3**. From Fig. 3 it is observed that when nanostructured particles are sprayed with high T & V the abrasion resistance of the coating tends to be higher.

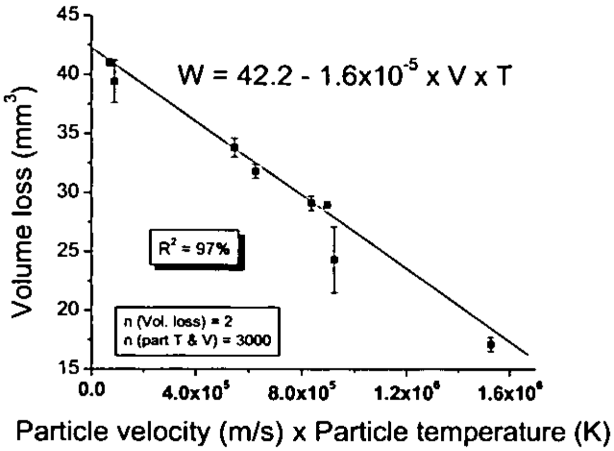

Fig. 3. Linear correlation between volume loss and particle (T & V) for the nanostructured titania APS and HVOF-sprayed particles.

3.3 Factors affecting wear

In order to better understand the wear behavior of these nanocoatings the amount of non-molten nanoparticles retained in the coating structure was determined via SEM for the VPS and HVOF-sprayed nanotitania coatings. It was found that the amount of non-molten nanostructured titania particles retained in these two coatings was less than 1% in volume. For the HVOF-sprayed coating it was found that there were ~3 non-molten agglomerated nanostructured titania particles (radius 0.5 – 1 µm) in each 100 µm^2 of area.

To further investigate the wear behavior, the four most abrasion resistant coatings (nano and conventional VPS and HVOF-sprayed coatings) were carefully analyzed. The hardness and porosity values for the VPS and HVOF-sprayed nanostructured and conventional coatings were found not to differ significantly, **Fig. 4**. Nonetheless, the volume loss in abrasion of the VPS and HVOF-sprayed nanotitania coatings was ~25% lower than the volume loss exhibited for the VPS and HVOF-sprayed conventional titania coatings.

Therefore the argument provided by different authors that nanostructured materials are harder than the conventional ones [10, 11] cannot be used here in order to explain the higher abrasion resistance demonstrated by the VPS and HVOF-sprayed nanotitania. The porosity values for these four coatings were ≤ 1.1%, which indicates that they were all very dense. These very similar values in porosity levels for the four coatings appear to eliminate porosity as a reason to explain the differences in abrasion resistance and the better performance of the two nanostructured samples. However, when the crack propagation resistance of these same four coatings is analyzed, an important observation is made, **Fig. 5**.

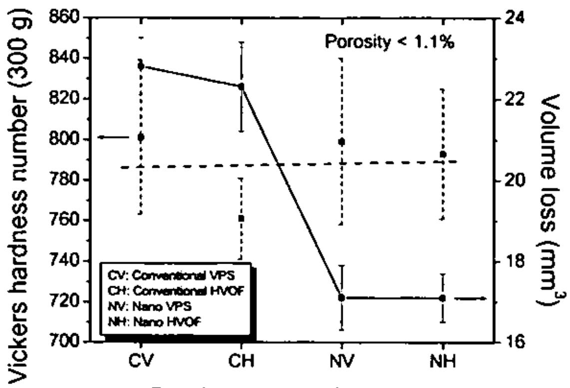

Fig. 4. Vickers hardness number and abrasion resistance for the VPS and HVOF-sprayed nano and conventional titania coatings.

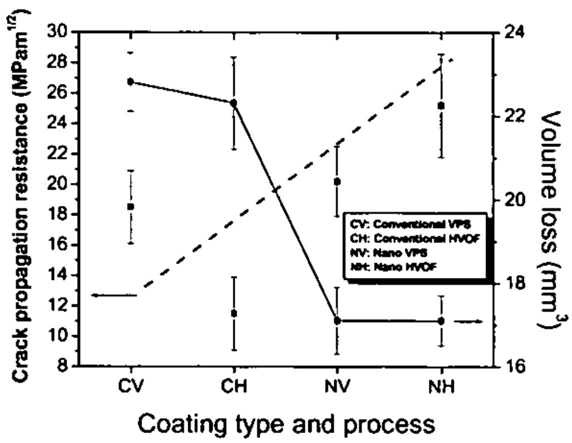

Fig. 5. Crack propagation resistance for the VPS and HVOF-sprayed nano and conventional titania coatings.

The crack propagation resistance values of the nanostructured coatings tend to be higher than those for the conventional material. As the crack propagation resistance is an indirect indication of the fracture toughness, it can be claimed that the fracture toughness is the key factor in causing the higher abrasion resistance of the nanostructured coatings.

Although these nanotitania coatings appeared to have higher fracture toughness than the other coatings, it is important to recall that the amount of non-molten nanostructured particles in these two coatings was found to be less than 1%. In order to identify how these nanostructured particles were acting to increase the crack propagation resistance, the Vickers indentation impressions made when determining the crack propagation resistance were investigated via high magnification SEM. An example of an indentation impression and crack pattern is shown in **Fig. 6a**. It is observed that the crack propagating from the left side of the impression is longer than the one at the right side (Fig. 6a). When examining the tip of the left crack at high magnification (200,000 X) it is observed that it ends without having any interaction with non-molten nanostructured particles, **Fig. 6b**. However, the shorter crack that propagates from the right side of the Vickers indentation impression ends at a non-molten nanostructured particle, **Fig. 6c**.

It is believed that these non-molten nanostructured particles randomly distributed throughout the coating structure act as crack arresters, impeding crack propagation. The crack arresting process takes place when a crack tip reaches a porous non-molten nanostructured particle (Fig. 6c). The porous non-molten nanostructured particle increases the radius of curvature of the crack tip, lowering the maximum stress at the tip [17], impeding subsequent crack propagation. Another identified crack arresting mechanism was crack branching [18], which takes place when a crack tip reaches a packed non-molten nanostructured particle, **Fig. 7**. When the crack begins to travel across the nanoparticle region it deflects or branches into several cracks absorbing the crack energy.

In Fig. 6a it is interesting to observe that the coating does not exhibit the typical lamellar structure of ceramic thermal spray coatings. In fact, the coating is so dense and uniform that its microstructure resembles a bulk structure. Even the crack propagation under indentation has characteristics of a bulk isotropic material, with four major cracks originating at or near the corners of the Vickers indentation impression (Fig. 6a). Ceramic thermal spray coatings may exhibit isotropic characteristics of mechanical properties when their microstructures are very dense and uniform. A key factor in producing such structures is ensuring that the sprayed particles have a narrow particle size distribution and fine cut (e.g., 5–20 μm), which results in a more uniform particle heating during spraying [6, 7]. The VPS and HVOF-sprayed nanotitania coatings achieved all these characteristics. Therefore it is thought that these nanostructured coatings are exhibiting not only a bulk-like behavior but also a toughening mechanism caused by the presence of non-molten nanostructured particles randomly dispersed in the coating structure. It is important to point out that the VPS and HVOF-sprayed conventional coatings are also dense and uniform like the nanocoatings, however, they do not possess non-molten nanoparticles in their structure. Therefore they have a good abrasion behavior when compared to the rest of the coatings but inferior to the abrasion behavior of the VPS and HVOF-sprayed nanocoatings.

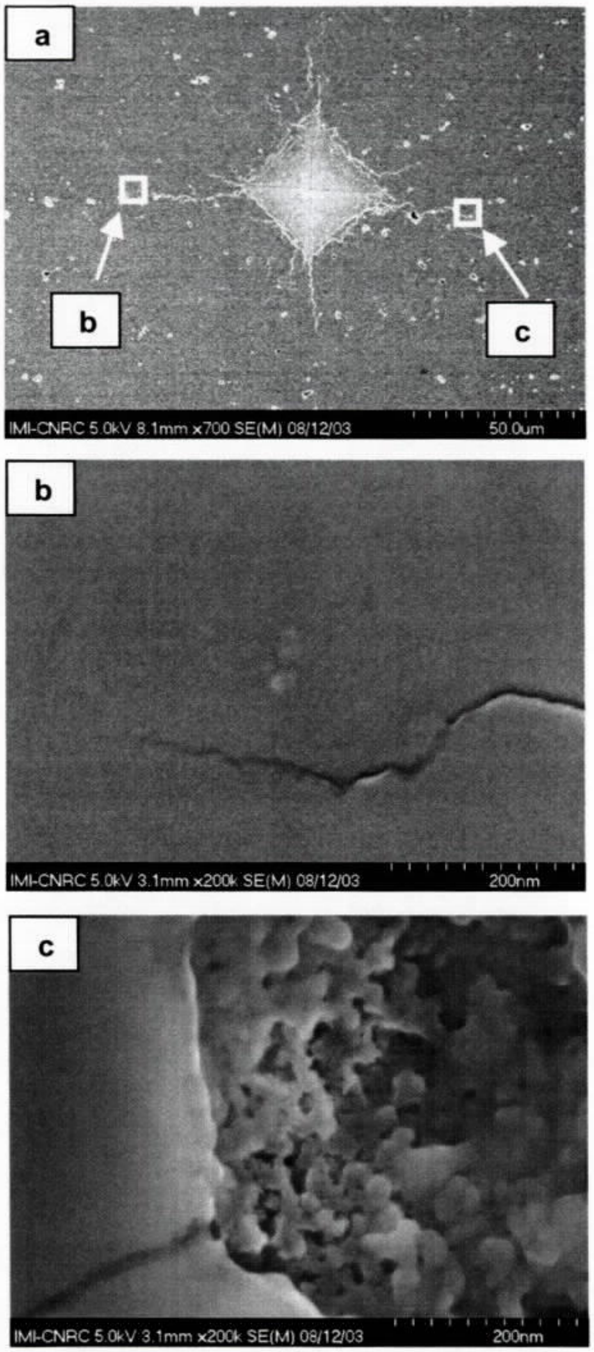

Fig. 6. Vickers impression on the cross-section and crack propagation pattern for the HVOF-sprayed nanostructured titania coating (a), and the tips of the left (b) and right (c) cracks at high magnification. The right crack ends in a porous non-molten nanostructured particle (crack blunting).

Some of the characteristics of the toughening mechanism caused by the presence of non-molten nanostructured particles may be similar to those found in toughened ceramics, where fine particles (submicron to a few microns in size) are uniformly dispersed in the ceramic matrix structure [18]. In this type of toughening mechanism, in order to obtain maximum toughness, the volume fraction of dispersed inclusions must be at an optimal level, i.e., a high volume fraction of the dispersed inclusions in the ceramic matrix lowers the fracture toughness of the material [18] due to the interaction of the inclusions.

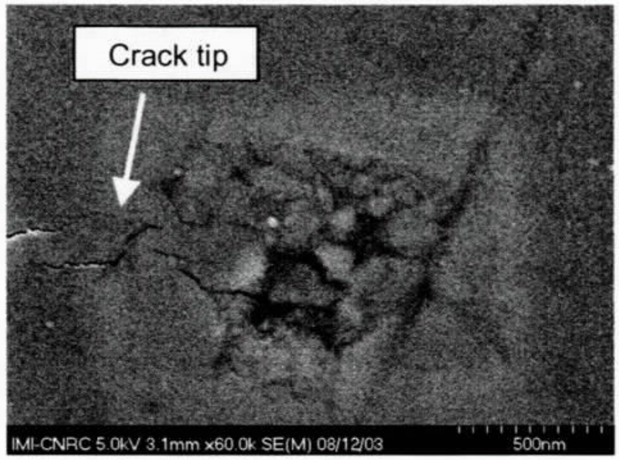

Fig. 7. Crack arresting via crack branching in a packed non-molten nanostructured particle.

Thus applying this toughening concept for the specific case of this study, it can be stated that if the number of non-molten nanoparticles (e.g., the zones shown in Figs. 6c and 7) increases above an optimal level they will interact with one another resulting in a decrease of toughness and strength.

The VPS-sprayed nanostructured titania coating (picture not shown) has the same type of bulk-like microstructure as that of the HVOF-sprayed nanocoating. VPS-sprayed particles are known for exhibiting high velocity. And as the VPS and HVOF-sprayed nanocoatings exhibit similar non-molten nanoparticle distribution, microstructure, porosity, crack propagation resistance and hardness, it is not difficult to imagine why they exhibit similar high abrasion resistance.

It is important to discuss the reasons why the APS-sprayed nanostructured coatings exhibited a poor performance in abrasion behavior. The porosity of the nano APS-sprayed nanotitania coatings reached levels up to 4%, i.e., much higher than the porosity levels of the VPS and HVOF-sprayed nanotitania coatings. Due to these higher levels of porosity the ceramic coatings do not have high strength (cohesion). Therefore the presence of non-molten nanoparticles in their structures (for the low particle T APS-sprayed coatings) is outweighed by the effect of porosity and lower strength of the coatings.

In this study, the highest abrasion resistance was achieved when non-molten nanostructured particles (radius 0.5-1 μm) were randomly spread throughout the coating structure. It is important to point out that in order to achieve the highest performance in applications involving other types of wear mechanisms the amount and distribution of non-molten nanostructured particles may need to be radically different than that observed in this work. In other words, for each application the optimum number and distribution of non-molten nanostructured particles should be found. Having a structure containing high levels of non-molten nanostructured particles is not a guarantee for optimal performance.

4 Conclusions

In this work on nanostructured and conventional titania coatings produced using APS, VPS and HVOF processes it was found that the VPS and HVOF-sprayed nanostructured titania coatings exhibited the highest abrasion resistance of all the 14 coatings studied. The improvement in abrasion performance of the best nanostructured coatings over the best conventional ones was determined to be ~25%.

Hardness properties alone cannot be used for explaining the higher abrasion resistance of the VPS and HVOF-sprayed nanostructured titania coatings. The best conventional and nanostructured titania coatings exhibited similar hardness values but the best nanostructured coatings had a higher abrasion resistance.

The best nanostructured coatings had higher crack propagation resistance levels than those exhibited by the best conventional coatings. It is believed that this difference plays an important role in producing the higher abrasion resistance of the VPS and HVOF-sprayed coatings.

The VPS and HVOF-sprayed nanostructured coatings exhibited very dense and uniform microstructural characteristics. A lamellar structure is not evident, i.e., these coatings exhibit characteristics of bulk isotropic materials.

The percentage in volume of non-molten nanoparticles in the VPS and HVOF-sprayed coatings is less than 1%. These non-molten nanostructured titania particles are randomly dispersed within the coating structure. For the HVOF-sprayed nanocoating ~3 particles (radius 0.5-1 μm) are found per 100 μm^2.

The non-molten nanostructured particles present within the coating act as crack arresters either by (i) blunting when the crack tip reaches a porous non-molten nanostructured particle, causing an increase in the radius of curvature of the crack tip and a lowering of the maximum stress at the tip or by (ii) crack branching that takes place when a crack tip reaches a packed non-molten nanostructured particle. When the crack begins to travel across the nanoparticle region it branches into several cracks, absorbing the crack energy.

The APS-sprayed nanostructured titania coatings do not exhibit high abrasion resistance. The high porosity of the APS-sprayed coatings lowers the mechanical strength, which outweighs the effect of the presence of non-molten nanostructured particles.

It is suggested that in order to obtain maximum crack propagation resistance an optimal level of non-molten nanostructured particles retained in the coating structure must be achieved. A high number of non-molten nanostructured particles would result in a decrease of the toughness and strength of the coating.

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