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Technical Note

Successful Application of Nanostructured Titanium Dioxide Coating for High-Pressure Acid-Leach Application

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A nanostructured titania coating was specifically developed for ball valves destined for high-pressure acid-leach (HPAL) service. Comparative tests were carried out between titania coatings derived from conventional and nanostructured powder. The nanostructured titania coating provided dramatically superior resistance against abrasive and erosive wear. The enhanced wear performance seemed to be attributed to improved toughness without any compromise in strength or hardness. The nanostructured titania coating has been applied onto ball valve components in ten locations around the world and has performed very well.

Keywords cermic oxide layers, erosion and abrasion resistance, wear, wear and corrosion, nano-powders, nanostructured materials

1. Introduction

1.1 High Pressure Acid Leach

The hydrometallurgical process referred to as high pressure acid leach (HPAL) utilizes autoclaves (vessels), piping, valves, and other equipment to contain and flow-control a very severe service slurry environment. The severe service consists of typical operating temperatures at around 260 °C in Ni/Co HPAL autoclaves, with process designers seeking to further increase the process temperature. In addition to the high temperatures, the service environment consists of highly corrosive sulfuric acid (>95%), high pressures (up to 5,500 kPa), and relatively high solid content (>20 wt.%). Hence, these components suffer significant damage due to factors such as corrosion, thermal stress, erosion, and abrasion, and the profitability of the operation turns on their durability and dependability.

Prior to the start of this effort, extensive failure analyses carried out on existing coatings (Ref 1, 2) for HPAL ball valves showed that there was a need for coatings that could provide superior performance, life, and reliability.

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1.2 Nanostructured Ceramic Coatings

In 1997 Dr. Lawrence T. Kabacoff (Program Officer) at the United States Office of Naval Research (ONR) began a five-year program entitled, ''Thermal Spray Processing of Nanostructured Coatings'' (Ref 3). The work was based on the notion that properties of existing materials drastically change when physical features (i.e., grain size, fiber diameter, layer thickness, particle diameter) of a material are reduced to and kept below 100 nm. ONR's overall objective was to save the Navy money by extending the service life of ship components by incorporating any enhanced properties of nanostructured materials in coating form. The technical objective was to fabricate coatings which exhibit an extraordinary combination of hardness, toughness, abrasion resistance, and adherence.

The findings from the ONR program have led to numerous successes in the use of nanostructured coatings for military applications. The work carried out by Gell et al. (Ref 4, 5) at the University of Connecticut (UCONN) on a nanostructured form of a commonly used wear-resistant coating material, alumina-titania, has yielded very unique properties. These properties include enhanced bond strength, superior wear resistance, and remarkable toughness.

Other research groups have worked on nanostructured ceramic coatings. Several groups (Ref 6-9) have worked on developing nanostructured zirconia-base thermal barrier top coats. The results from these studies showed that the properties of the nanostructured zirconia-base top coats could be tailored to possess notably different thermal properties, as compared to its conventional APS-applied counterpart. Provenzano et al. (Ref 6) carried out preliminary development work on stabilizing nanostructred zirconia top coats with alumina; the results looked promising. Tao et al. (Ref 7) showed the superior wear resistance of APS coatings sprayed with nanostructured YPSZ compared to that of APS conventional YPSZ coatings. Some detailed characterization of APS applied nanostructured YPSZ carried out by Lima et al. (Ref 8) showed that the bimodal microstructure composed of the dense molten regions and porous unmolten agglomerates led to bimodal mechanical properties. Gell et al. (Ref 9) used the approach developed by Karthikeyan et al. (Ref 10) to solution precursor plasma spray YPSZ. These coatings, with very high porosity in both the micro- and nano-range, showed very good thermal cyclic resistance and high coating thickness capabilities.

1.3 Objective

The goal of the collaborative program was to develop and introduce the first nanostructured coating for an industrial application, by incorporating and advancing the knowledge gained from the results of ONR's program.

2. Description of the Process

The general approach to the processing of nanostructured thermal spray ceramic coatings is illustrated in Fig. 1. The main aspects of the approach included processing well-bonded agglomerates of nano- and/or ultrafine particles, thermal spaying of powder to optimize coating properties, and characterization/testing of the coating.

3. Experimental Methods

- All APS coating samples were applied using Sulzer-Metco's 7 M torch using FW Gartner spray parameters. Coating thickness of approximately 250 μm was targeted for all coatings.
- Vickers microhardness was determined using a Clark CEM microhardness (Crystal Lake, Ill) indenter with loads of 300 g for microhardness measurements and 500 g for crack propagation studies.

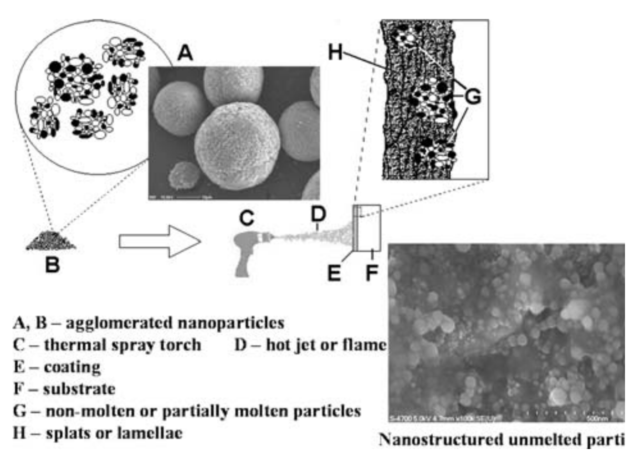

Fig. 1 Generic schematic to thermal spraying of nanostructured ceramic coatings

- Porosity measurements were determined using a Nikon Epiphot light optical microscope at 200× magnification. Ten regions were sampled to attain an average.
- JEOL-840 (Tokyo, Japan) scanning electron microscope, coupled with an EDAX EDS system, was used to characterize cross-sections of coating samples.
- Field Emission Scanning Electron Microscope (FE-SEM Hitachi S-4700 coupled with an Oxford EDS detector with a UTPW allowing the detection of light elements) was also used for higher magnification characterization of coatings.
- ASTM G65 dry sand/rubber wheel abrasion tests were carried out using procedure E. This procedure was selected to ensure that the coating was not worn through the entire thickness during testing of the least resistant coating, without altering the thickness of the coating from that specified for the actual component.
- ASTM C633-01 tensile adhesion tests were carried out using 1″ round titanium buttons coated with a deposit thickness of 125-250 μm. Three tests per coating type were evaluated and averaged using EC-2086 3M adhesive.
- Slurry erosion tests were carried out at the National Research Council of Canada-IMI division with the following test procedures:

  a. Minimum of three tests were carried out on each coating with the scar volume loss measured using laser profilometry

  b. Alumina erosive particle Number 100 (150 μm) were mixed with neutral pH deionised water to form a slurry concentration of 0.66 wt.%

  c. Continuous slurry jet had a constant flow rate of 1 l/min and a constant velocity of 20 m/s

  d. The spray nozzle had a 1 mm inside diameter and 5 cm long barrel, placed 7.6 cm from the test-piece which provided a straight cylindrical shape jet

  e. Impingement angles were 30° and 90°

  f. Exposure durations were 5 min for 90° and 20 min for 30°

4. Results and Discussions

The microstructure for the commercial coating (Fig. 2-top) consists of a lamellar splat structure with vertical microcracks and dense unmelted particles (outlined by dashed box) distributed throughout the coating. The different shades of gray reflect the different phases of TiO_2 in the coating. The porosity determined by image analysis was below 2%, excluding pull-outs resulting from sample polishing. A microhardness of 759 $HV_{0.3}$ was measured. This structure is typical of thermal spray ceramic coatings.

Micrographs of the APS-applied nanostructured TiO_2 coating on titanium substrates (Fig. 2-bottom) have characteristics typical of the APS process: microcracks, lamellar structure, porosity, different phases for TiO_2, etc. There

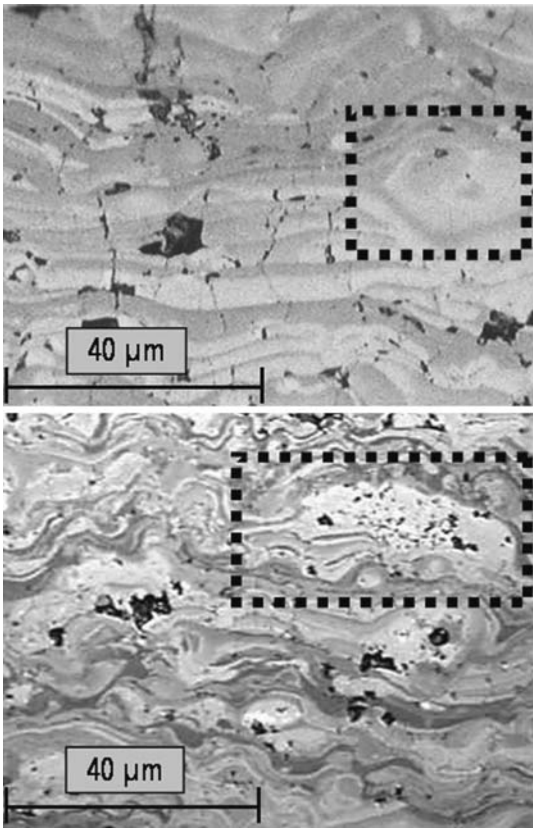

Fig. 2 Cross-sectional view of APS TiO_2 Coatings: conventional (top) and nanostructured (bottom)

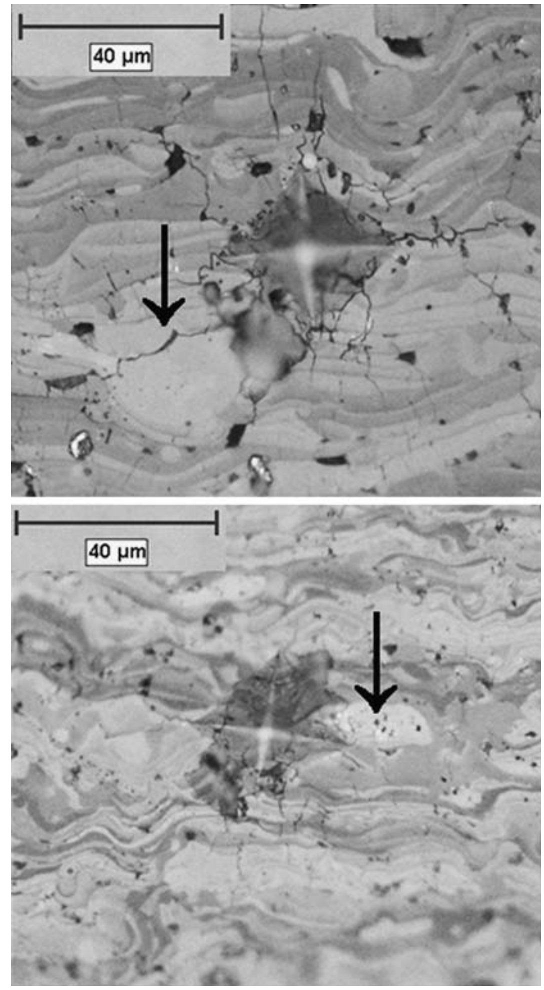

Fig. 3 Micro-indentation crack pattern on commercial (top) and nanostructured (bottom) APS-applied TiO_2 coatings

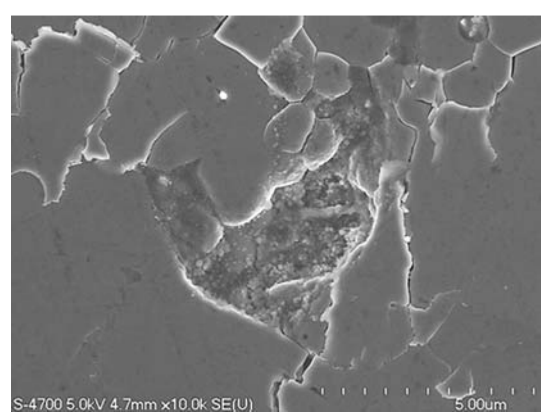

Fig. 4 Field emission-SEM micrograph of cracks in porous nanostructured unmelted particles

were, however, notable differences between this coating and the one deposited using commercial TiO_2 powder. The different features included finer microcracks and a uniform distribution of unmelted particles/agglomerates with fine pores (outlined by dashed box). The average microhardness measured for this coating was slightly higher than its commercial counterpart, at 783 $HV_{0.3}$.

A very interesting feature was noted when viewing the crack patterns formed by micro-indentations. Figure 3 provides views of the indentation (at 500 g load) regions for both APS coatings. It was apparent that the commercial coating had higher degrees of crack density, width, and length, as compared to the nanostructured coating. A closer look at the region around the cracks in the APS-applied nanostructured coating (Fig. 4) reveals interesting associations between the presence of nano- or fine-pored unmelted or partially melted particles and crack propagation. These porous particles seem to deflect the crack and blunt the crack tip, thus hindering its propagation, unlike the dense unmelted particles found in the commercial coating (arrow in Fig. 3-top).

The ASTM G65 (procedure E), dry sand rubber wheel abrasion test results for the coatings are presented in Fig. 5. It is well understood that abrasive wear resistance is a reflection of strength/hardness and toughness. Although there is a slight increase in hardness for the nanostructured coating, it is likely the dramatic enhancement in toughness that provides such a drastic increase in abrasive wear resistance. This increased toughness seems to be related to the microscopic crack blunting and deflection observed in Fig. 4. Unlike conventional materials/coatings, where increase in hardness is often accompanied by a decrease in toughness, these nanostructured coatings seem to defy this trend by possessing an increase in both properties.

The results from the slurry erosion test showed improved resistance for the n-TiO_2 coating (Fig. 6). A unique feature was observed which substantiates the hypothesis derived from the abrasion test results of enhancing the toughness without compromising on the hardness. Thus, unlike conventional materials/coatings, the n-TiO_2 showed improved erosion resistance at both low- and high-angle slurry impingements.

Once the information from the tests were analyzed and the mechanisms for n-TiO_2 coating enhancement were understood, the focus shifted from developing and applying novel nanostructured titanium dioxide coating using a conventional thermal spray process (APS) to select and develop a deposition process to further enhance the attractive properties of the coating. The goal was to further increase the toughness of the coatings without compromising their hardness or strength. This would mean that the deposition process would incorporate a higher level of unmelted, nanostructured, porous particles within a well-bonded matrix. The difficult task would be in introducing these fine-pored particles without detracting from the cohesive strength of the overall coating structure.

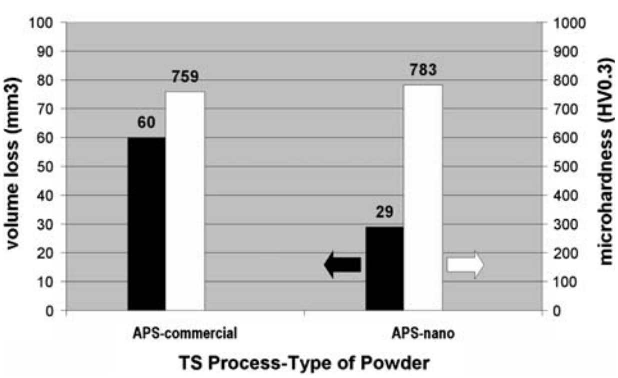

Fig. 5 Abrasive wear volume loss and microhardness (HV300) of commercial and nanostructured TiO_2 coatings applied via APS

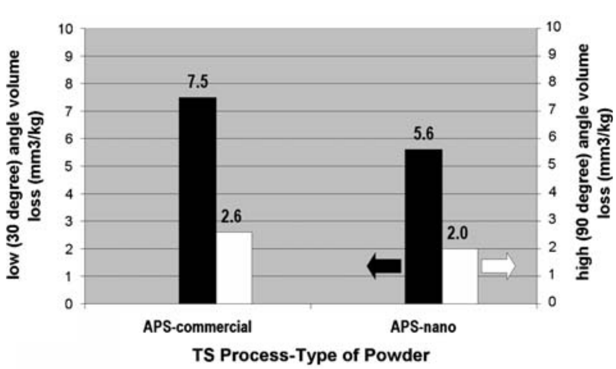

Fig. 6 Slurry erosion volume loss at low and high impingement angles for commercial and naostructured TiO_2 coatings applied via APS

Figure 7 provides a cross-sectional view of the n-TiO_2 coating deposited by the proprietary process.

At first glance, it is obvious that this structure differs greatly from previous coatings. The structure seems denser (<1% porosity) at this magnification and uniform (non-lamellar and single phase), with no signs of microcracks at these magnifications. The high magnification view of the dark spots within the structure (Fig. 7-center) reveals the presence of the familiar fine porous agglomerates, distributed uniformly throughout the coating. Due to the very fine porous structure associated with the nanostructured coating, it is difficult to determine the true porosity without carrying out density measuring tests. The crack pattern around the Vickers indent (Fig. 8) shows very low degrees of crack density, width, and length, as compared to the APS coatings. This apparent increase in toughness was in addition to a notable increase in average microhardness (1150 $HV_{0.3}$). The enhanced toughness and

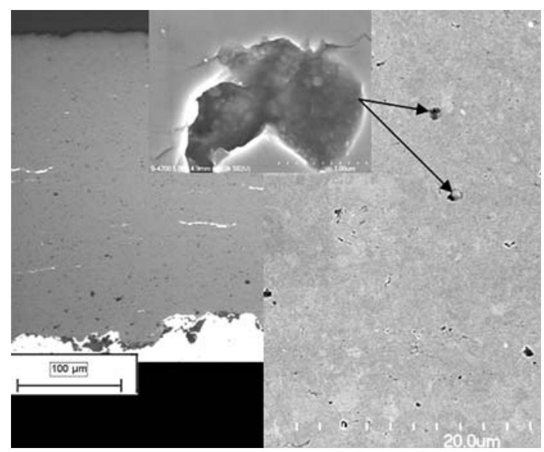

Fig. 7 Cross-sectional view of n-TiO_2 coating deposited using a proprietary process: LOM (left); FE-SEM of coating (right) and porous particles (center)

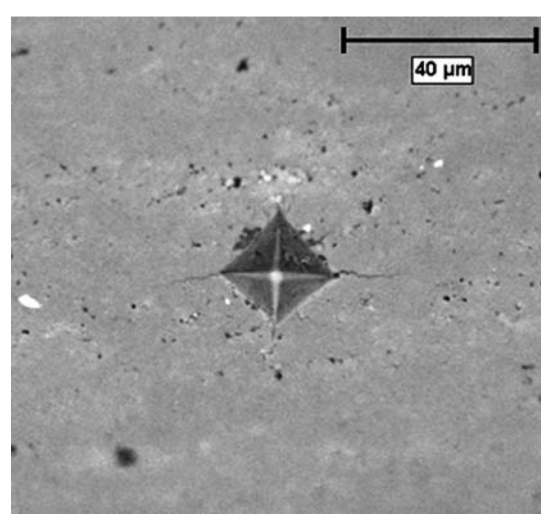

Fig. 8 Micro-indentation crack pattern on n-TiO_2 deposited using a proprietary process

hardness translated, as expected, to a very impressive increase in abrasion and slurry resistance, as presented in Fig. 9 and 10, respectively. The preliminary findings seem to point to the unmelted agglomerates of the coating, with the very fine pores, as the source of the increase in apparent toughness; these regions may provide blunting or changing the direction of the propagating crack tip. Dense regions of the coating from the same feedstock do not provide these effects and thus do not exhibit the same apparent toughness.

A critical component to the performance and longevity of any coating is its bond strength with the underlying substrate. The bond strengths for APS commercial and proprietary nanostructured coatings were 35 MPa and 80 MPa, respectively. The source for the difference in bond strengths between the two coatings has yet to be

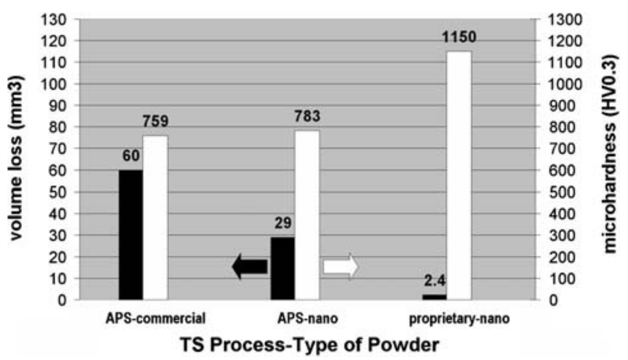

Fig. 9 Abrasive wear volume loss and microhardness (HV300) of commercial and nanostructured TiO_2 coatings applied

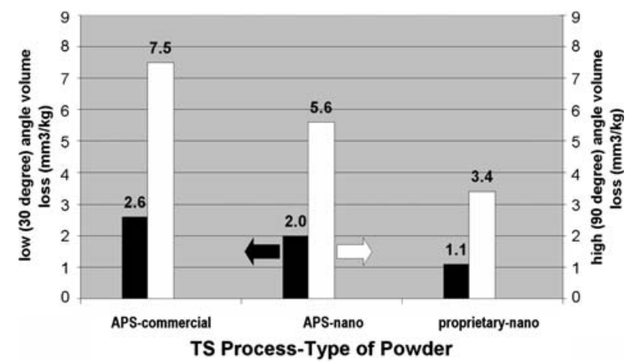

Fig. 10 Slurry erosion volume loss at low- and high-angle impingement for commercial and naostructured TiO_2 coatings

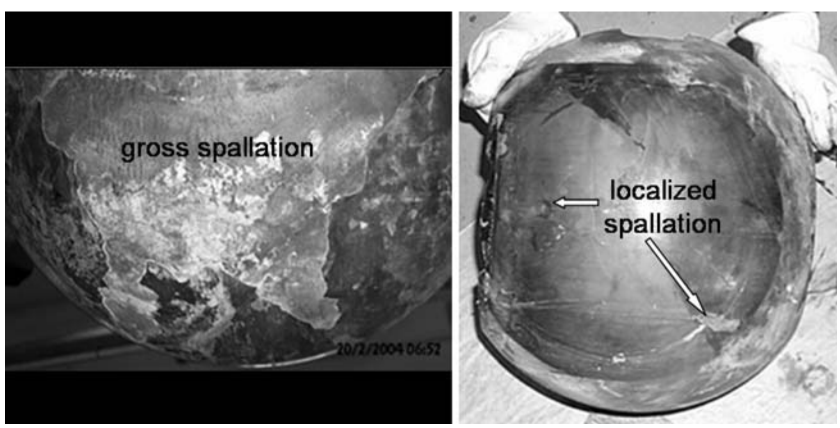

Fig. 11 Photographs of the ball surfaces with Cr_2O_3-blend coating (left) and with n-TiO_2 coating (right) after same service exposure and conditions

Fig. 12 Mines with Mogas' n-TiO_2 coated valves

determined; however, Gell et al. (Ref 4, 5) have also noted an increase in bond strength for nanostructured Al_2O_3-TiO_2 coatings over its microstructured counterparts.

5. Field Results

In 2003, Lihir installed two 10″ ID Ti Gr5 Mogas ball valves (with n-TiO_2 and Cr_2O_3-blend coatings) into the same service exposures and conditions for the same duration. Figure 11 provides photographs of the ball surface upon inspection after 10 months of service.

It was clearly evident that the n-TiO_2 coating was in a far superior state when compared to the non-nanostructured Cr_2O_3-blend coating (Fig. 11). The surface of Cr_2O_3-blend coated ball had large regions without coating. In contrast, the n-TiO_2 coated ball had a few isolated regions without coating which did not inhibit it from being returned into service.

Figure 12 is a schematic of the world map pointing to mines using n-TiO_2 coated valves.

6. Summary

- A novel nanostructured titania coating has been developed for the HPAL industry. In nanostructure form, the coating exhibits a unique characteristic not seen in many conventional materials—increase in both hardness and toughness. This coating possesses superior abrasion and erosion wear resistance, in addition to superior bond strength.
- The presence of unmelted, nanostructured, porous particles in the well-bonded matrix (derived from fully or partially molten particles) is the source for the enhanced toughness of the nanostructured coating.
- A proprietary process has been developed to optimize the qualities associated with the unmelted, nanostructured, porous particles; the results show a dramatic improvement in wear resistance.
- A patent on the coating (Ref 11) has been attained and the coating is successfully being applied to valves in ten locations around the world. Other HPAL components are being targeted for application with the same coating.
- Since this group's initial introduction of n-TiO_2 coatings to the public, at least one other group has focused their effort in developing a similar coating (Ref 12). Their results mirror those of this work.

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