Development and implementation of plasma sprayed nanostructured ceramic coatings


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Abstract

A broad overview of the science and technology leading to the development and implementation of the first plasma sprayed nanostructured coating is described in this paper. Nanostructured alumina and titania powders were blended and reconstituted to a sprayable size. Thermal spray process diagnostics, modeling and Taguchi design of experiments were used to define the optimum plasma spray conditions to produce nanostructured alumina–titania coatings. It was found that the microstructure and properties of these coatings could be related to a critical process spray parameter (CPSP), defined as the gun power divided by the primary gas flow rate. Optimum properties were determined at intermediate values of CPSP. These conditions produce limited melting of the powder and retained nanostructure in the coatings. A broad range of mechanical properties of the nanostructured alumina–titania coatings was evaluated and compared to the Metco 130 commercial baseline. It was found that the nanostructured alumina–titania coatings exhibited superior wear resistance, adhesion, toughness and spallation resistance. The technology for plasma spraying these nanostructured coatings was transferred to the US Navy and one of their approved coating suppliers. They confirmed the superior properties of the nanostructured alumina–titania coatings and qualified them for use in a number of shipboard and submarine applications. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The objective of this research was to develop and implement cost-effective plasma sprayed nanostructured ceramic coatings, with superior resistance to wear, erosion, cracking and spallation [1–5]. These attractive properties associated with a nanostructure (a grain size smaller than 100 nm) have been previously documented for bulk materials [6–13]. In this paper, a broad overview of the processing, characterization and testing leading to the development and implementation of the first nanostructured coating is described. With the large number of applications in the US Navy, this program provided a 'market pull' for this new technology.

2. Processing: reconstituted nanostructured powders and plasma spray

The overall processing sequence for the plasma sprayed nanostructured Al₂O₃–13 wt.% TiO₂ coatings is illustrated in Fig. 1. Commercially available nanostructured powders of Al₂O₃ and TiO₂, obtained from Nanophase Technology Corporation™, Burr Ridge, IL, were mixed and reconstituted into plasma sprayable size agglomerates. Using Taguchi design of experiments, large, smooth and relatively dense nanostructured powders were reconstituted with minimum grain growth [1]. The reconstitution process consists of spray drying the slurry that contains nano-particles of appropriate proportion, and subsequent heat treatment at high temper-
Fig. 1. Flow chart illustrating the processing and evaluation sequence for plasma sprayed nanostructured ceramic coatings.

ature (800–1200°C). The resultant Al$_2$O$_3$–13 wt.% TiO$_2$ powders are hereafter denoted as unmodified. In addition, small amounts of other oxides were mixed to further enhance the properties of these nanostructure-derived coatings (hereafter denoted as modified nano-coating). The reconstitution process for modified agglomerates involved an additional step of plasma reprocessing, during which the modified powders were plasma heat-treated and air-quenched in a collection chamber. The reconstituted nanostructured powders were characterized extensively for the size, shape, morphology, phase constituents and composition. For comparison purposes, a commercially available powder (Metco-130) with the Al$_2$O$_3$–13 wt.% TiO$_2$ composition was examined.

Fig. 2 shows the cross-sectional backscattered electron micrographs of Metco-130 and reconstituted, unmodified and modified nano-powders. Using X-ray diffraction (XRD) and scanning/transmission electron microscopy (SEM and TEM) equipped with energy dispersive spectroscopy (EDS), the phase constituents and their compositions were identified for these powders [1–4]. The Al$_2$O$_3$ took the form of α-Al$_2$O$_3$ for all the powders (dark regions in Fig. 2), while the TiO$_2$ was in the form of anatase-TiO$_2$ for the Metco 130 powders and rutile-TiO$_2$ for unmodified powders. TiO$_2$ was dissolved in oxide additives for the modified powders (light regions in Fig. 2). Previous work, using XRD line broadening techniques, has shown that the grain size of anatase-TiO$_2$ was below 100 nm, while grain size of α-Al$_2$O$_3$ and rutile-TiO$_2$ is greater than 100 nm [1]. The particle size estimated by Saltykov analysis and MicroTack™ measurements ranged from 15 to 150 μm for all powders with an average value of approximately 50 μm [4]. Fig. 2 also shows that the commercial Metco 130 powders are dense while the reconstituted nanopowders contain up to 45% porosity.

In order to control the plasma spray process, extensive spray trials were carried out to investigate the effects of a wide range of processing variables on the microstructure and properties of the nanostructured alumina–titania coatings. Several processing parameters of the plasma spray such as: carrier gas flow rate; spray distance; flow rate ratio of Ar to H$_2$; powder feed rate; and gun speed, were held constant during this investigation. It was found that the microstructure and properties could be related to an empirical parameter that is defined as the critical plasma spray parameter, CPSP [Eq. (1)]:

$$\text{CPSP} = \frac{\text{voltage \cdot current}}{\text{primary gas (Ar) flow rate}} \quad (1)$$

CPSP can be directly related to the plasma torch/particle temperature, which was measured by two-color pyrometer [14]. Using various CPSP, alumina–titania coatings were plasma sprayed and the resulting microstructure and properties were evaluated. In addition,
CPSP was employed in computational fluid dynamics analyses [15] to validate the experimental results and to optimize coating deposition.

3. Phase constituents and microstructure of nanostructured coatings

All coatings, Metco-130, unmodified and modified alumina–titania coatings, consisted of γ-Al2O3 and α-Al2O3 [2–4]. TiO2 was found to be in solid solution with γ-Al2O3 [2–4,7,16]. Fig. 3 shows the volume percent of γ-Al2O3 determined by quantitative X-ray diffraction [4] as a function of CPSP, and, in turn, a function of plasma torch/particle temperature [14]. The volume percent of γ-Al2O3 increases with increasing CPSP for coatings plasma sprayed with reconstituted nanostructured powders up to CPSP = 390. The volume percent of γ-Al2O3 for the Metco-130 coatings remains unchanged as a function of CPSP up to CPSP = 390. But, all coatings show a slight decrease in the percent of γ-Al2O3 at CPSP = 410. These variations in the phase constituents as a function of CPSP can be explained based on the starting powder morphology and the plasma spray process (i.e. melting and splat quenching) [2–4]. Metco 130 coatings were sprayed using dense (i.e. high thermal conductivity) α-Al2O3 powder. This powder melts in the torch and is splat-quenched to form metastable γ-Al2O3 in the coating [17–20]. However, for porous reconstituted nanostructured powders with lower thermal conductivity, the amount of γ-Al2O3 increased with CPSP up to 390. This observation indicates that the nano-powder agglomerates are partially melted and retain α-Al2O3 from the powder in the coating [2–4].

The increase in the amount of α-Al2O3 at CPSP = 410 can be attributed to a solid phase transformation (γ → α) that occurs after rapid solidification as a result of substrate heating [4,17–20].

The results from the quantitative XRD on the phase constituents were confirmed by electron microscopy (SEM/EDS and TEM) [2–4]. While the Metco 130 coatings exhibited splat-quenched single phase (γ-Al2O3) microstructure, plasma sprayed alumina–titania coatings from the reconstituted nano-powders exhibited a bimodal microstructure. An example of the bimodal microstructure of the plasma sprayed modified alumina–titania coating is shown in Fig. 4. Region ‘F’ corresponds to fully melted and splat-quenched regions (γ-Al2O3 supersaturated with TiO2) while region ‘P’ corresponds to a partially melted region where the initial microstructure of the reconstituted nanostructured agglomerates is retained. The partially melted region consists of α-Al2O3 particles (black; less than 1 μm in size) embedded in γ-Al2O3 (white) supersaturated with
Ti\textsuperscript{4+} as presented in Fig. 4b. The presence of Ti in \(\gamma\)-Al\textsubscript{2}O\textsubscript{3} (i.e. supersaturated with Ti\textsuperscript{4+} in \(\gamma\)-Al\textsubscript{2}O\textsubscript{3}) was observed from EDS. The modified nanostructured coatings were similar in microstructure with slightly larger \(\alpha\)-Al\textsubscript{2}O\textsubscript{3} particulates (0.5–3 \(\mu\)m). This unique, bimodal microstructure is only obtained by plasma spray of reconstituted nanostructured powders [2–4].

Extensive transmission microscopy [4] also confirmed the bimodal microstructure. While coatings plasma sprayed from Metco 130 powders contain mostly \(\gamma\)-Al\textsubscript{2}O\textsubscript{3}, the coatings plasma sprayed with reconstituted nanostructured powders contained both splat-quenched \(\gamma\)-Al\textsubscript{2}O\textsubscript{3} and retained \(\alpha\)-Al\textsubscript{2}O\textsubscript{3}. It was also found that the grain size of the splat-quenched \(\gamma\)-Al\textsubscript{2}O\textsubscript{3} was extremely small (20–70 nm) while that of the \(\alpha\)-Al\textsubscript{2}O\textsubscript{3} was approximately 0.5–3 \(\mu\)m. Fig. 4c,d shows the microstructure of plasma sprayed nanostructured coating (unmodified) that includes nanograined \(\gamma\)-Al\textsubscript{2}O\textsubscript{3} and submicron/micron-grained \(\alpha\)-Al\textsubscript{2}O\textsubscript{3}.

Based on quantitative image analysis, the two regions of the microstructure were examined as a function of CPSP, as presented in Fig. 5. The fraction of the coating microstructure, represented by region ‘P’ decreases with increasing CPSP and the corresponding increase in plasma torch/particle temperature. Near-complete melting followed by splat quenching was observed at relatively high CPSP, corresponding to increase in the microstructural region ‘F’ with increasing CPSP. Therefore, it can be concluded that splats, which formed through melting the feed powder and rapid solidification, consisted of nanometer-sized \(\gamma\)-Al\textsubscript{2}O\textsubscript{3}, whereas the particulate microstructure, which was formed via partial melting and liquid phase sintering, consisted of submicrometer-sized \(\alpha\)-Al\textsubscript{2}O\textsubscript{3} with small amounts of nanometer-sized \(\gamma\)-Al\textsubscript{2}O\textsubscript{3}. Furthermore, the bimodal
distribution of the microstructure in nanostructured coatings can be controlled by CPSP [2–4]. The phase transformations during the plasma spray deposition of reconstituted alumina–titania, as a function of CPSP, can be summarized as shown in Fig. 6 [4].

### 4. Properties of nanostructured coatings

Physical and mechanical properties of the plasma sprayed coatings including: density; hardness; indentation crack resistance; adhesion strength; spallation resistance in bend and cup-tests; and resistance to abrasive and sliding wear, were evaluated as a function of CPSP [2,3]. In all tests, coatings with bimodal microstructures made from nanostructured powders showed unique and superior properties. Specifically, significant improvement in indentation crack resistance, spallation resistance and wear resistance was consistently observed. Typical results from cup and bend tests are presented in Figs. 7 and 8, respectively. While significant spallation is observed for Metco-130 coatings, nanostructured Al$_2$O$_3$–13 wt.% TiO$_2$ coatings exhibit minor damage.

This drastic improvement in cracking can be understood from the results of indentation tests performed on these coatings. At selected CPSPs, improved crack resistance, defined as reciprocal of the crack length, was observed for coatings plasma sprayed from reconstituted Al$_2$O$_3$–13 wt.% TiO$_2$ as shown in Fig. 9. In Metco-130, long and well-defined splat boundaries provide easy crack propagation paths. In the nanostructured alumin
Indentation cracks observed for (a) Metco-130 and (b,c) nanostructured alumina–titania coatings. (a) Long, wide cracks along the splat boundaries were observed for Metco-130 coatings; (b,c) short, narrow cracks arrested at partially melted regions (arrow) were observed for nanostructured alumina–titania coatings.

Fig. 11. Abrasive wear resistance of plasma sprayed Al₂O₃–13 wt.% TiO₂ coatings at CPSP = 350.

Fig. 12. Surface morphology of (a,c) Metco-130 and (b,d) reconstituted nanostructured Al₂O₃–13 wt.% TiO₂ coatings after the (a,b) abrasive wear and (c,d) scratch test (courtesy of Dr T.E. Fischer).

5. Implementation of plasma sprayed nanostructured coatings

The technology for plasma spraying the nanostructured coatings was transferred to the US Navy and one of their approved coating suppliers. From independent tests carried out at the US Navy as well as at the coating supplier, superior properties of the nanostructured Al₂O₃–13 wt.% TiO₂ coatings were consistently confirmed. The modified nanostructured alumina–titania coatings have been qualified for use in a number of shipboard and submarine applications such as: arm weldment; bulkhead pivot arm; bearing sled; front and aft door support; magnet arm; sockets and arm pivot pins; periscope guides; hydraulic piston; and reduction gear set. The successful and efficient technology transfer was carried out by the use of CPSP and process diagnostic tools. The relationship between the plasma torch temperature and CPSP in a pre-specified industrial setting (i.e. different plasma systems, torches, etc.) was quickly established by process diagnostics. Then, an optimum CPSP for the coating supplier was defined to
deposit nanostructured coatings with a partially melted microstructure.

6. Summary

A broad overview of the science and technology leading to the development and implementation of the first nanostructured coating with superior properties was presented. The use of a critical plasma spray parameter (CPSP) permitted an efficient integration of multidisciplinary engineering efforts to produce nanostructured Al$_2$O$_3$–13 wt.% TiO$_2$ coatings that are unique in microstructure, superior in properties and readily technology transferable. The key to the improved properties is the production of a bimodal microstructure, which imparts improved toughness to the coating. The nanostructured Al$_2$O$_3$–13 wt.% TiO$_2$ coatings have been approved by the U.S. Navy for shipboard and submarine applications.

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References