Processing Strategies for Tailoring Ceramic-Based Nanostructured Thermal Spray Coatings
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Abstract

New and more demanding applications and higher performance requirements are creating the need for a greater degree of sophistication in engineering coating structures. The use of nanostructured feedstocks provides the possibility of tailoring the structure of thermal spray ceramic-based coatings at the nanoscale. In the present study it has been found that such an approach can produce coatings with enhanced mechanical, thermal and bioproperties. It has been shown that the internal structure and external size of agglomerates as well as the spray conditions employed for deposition play a key role in determining the nature and extent of zones of nanostructured material produced in coatings. The characteristics (such as porosity and bonding) of these zones can have an important effect on the coating performance. This approach has been used to tailor WC-Co, TiO₂, ZrO₂-Y₂O₃, Al₂O₃-TiO₂ and hydroxyapatite coatings targeted for use against wear, as abrasives, on orthopedic implants and as TBCs.

Introduction

The synthesis of nanostructured coatings by thermal spraying offers the possibility of engineering surfaces having superior properties due to the nanocharacter of the structure. However, there are challenges in using such a processing approach for this purpose because inherent to thermal spraying are high temperatures and the melting of material. Therefore, if the idea is to create a nanostructured coating starting from a nanostructured (feedstock) powder, the limitation caused by the loss of the nanostructure when the material passes through the liquid state must be considered. Either the process needs to be controlled in order to retain some of the nanostructured material and incorporate it into the coating, or steps need to be taken to generate a nanostructured phase through precipitation during coating formation. Post-processing treatments may also be employed to modify structures and surfaces and tailor the structural features at the nanoscale.

In the present study the focus was on using nanostructured feedstocks and controlling the thermal spray parameters during coating deposition in order to tailor the coating (nano) structure. The emphasis was on engineering novel ceramic-based coatings having performance characteristics for targeted applications. This paper will discuss some of the strategies that can be employed to produce such coatings as well as some of the challenges and limitations to this approach.

Experimental Procedure

Materials and Processing

Five different ceramic-based systems were investigated during the course of this study: WC-12wt.%Co, Al₂O₃-13wt.%TiO₂, hydroxyapatite (HA), TiO₂, and ZrO₂-7/8wt.%Y₂O₃ (YSZ). Information on the feedstock powders is shown in Table 1. Micrographs showing the nanocharacter of the feedstock materials are presented in Fig. 1. These powders were sprayed

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>POWDER PARTICLE SIZE (µm)</th>
<th>NANO-PARTICLE SIZE (nm)</th>
<th>TS PROCESS</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC-12Co</td>
<td>5-40</td>
<td>30-50</td>
<td>HVOF</td>
</tr>
<tr>
<td>TiO₂</td>
<td>5-20</td>
<td>15-70</td>
<td>HVOF/APS</td>
</tr>
<tr>
<td>Al₂O₃-13TiO₂</td>
<td>15-200</td>
<td>&lt;150</td>
<td>APS</td>
</tr>
<tr>
<td>ZrO₂-8Y₂O₃</td>
<td>50-150</td>
<td>40-200</td>
<td>APS</td>
</tr>
<tr>
<td>ZrO₂-7Y₂O₃</td>
<td>5-20, 15-45</td>
<td>&lt;150</td>
<td>APS</td>
</tr>
<tr>
<td>Hydroxyapatite</td>
<td>5-50</td>
<td>90-140</td>
<td>HVOF/APS</td>
</tr>
</tbody>
</table>

Table 1: Characteristics of nanostructured powders used to produce thermal spray coatings.
using either atmospheric plasma spraying (APS) or high velocity oxy-fuel (HVOF) (see Table 1). In each case, the spray parameters were varied over a range in order to produce different particle temperatures and velocities. For each parameter set, the in-flight particle characteristics were determined using a diagnostic tool (DPV2000, Tecnam Automation, St Bruno, Quebec, Canada). These data were then used to determine the spray parameter settings at which coatings would be produced.

**Characterization and Performance Evaluation**

The structure of the coatings was studied using a scanning electron microscope (SEM) (Model S4700, Hitachi Instruments Inc., Tokyo, Japan). To investigate the nano-features within and at the surface of the coatings, magnification levels of up to 3x10^5 were employed. For some compositions where phase transformations or reactions leading to new phase formation were possible during thermal spraying, x-ray diffraction (XRD) analysis (Model D8, Bruker AXS, Karlsruhe, Germany) was performed on the coatings.

Depending on the intended application, various properties and performance characteristics of the coatings were investigated. The microhardness was determined using a Vickers indenter under a 300-gram load and 10 indentations to produce an average value. Resistance to crack propagation was also measured using a Vickers indenter and a higher load (5 kg). Details on determining the crack growth resistance parameter have been presented elsewhere [1]. Bonding between the coating and substrate was evaluated using a standard tensile test [2]. Work was also performed to evaluate the resistance of some coatings to dry abrasion and slurry erosion [3, 4]. A rub-rig test was used to assess the abradability of certain coatings being engineered as high temperature abradables [5]. The thermal diffusivity of selected coatings was determined using the laser flash method [6]. For coatings targeted for biomaterial applications, trials were performed in which the coatings were exposed to simulated body fluid (SBF) [7], human osteoblasts [8] and rat osteoblasts [9]. In most cases, the performance characteristics of the coatings engineered to contain nanostructured regions were compared to those of conventional coatings they were targeted to replace.

**Results and Discussion**

**Selection of Feedstock and Spraying Technique**

The feedstock granulometry and the thermal spray process were found to play a key role in engineering coatings having nanostructured zones. In general, powders having a narrow agglomerate size distribution provided a narrower temperature range for producing such coatings and resulted in smaller zones of nanostructured material and a lower percentage of nanostructured phase in the coating. However, it was also observed that the nanostructured zones in these coatings were often very dense, having been infiltrated to some degree with molten material (Fig. 2a). Infiltration was probably easier due to the shorter distance present in smaller agglomerates and may have been aided by the redistribution of (liquid and semi-molten) material caused by the forces at the point of impact with the substrate.

Powders having broader agglomerate size distributions and larger agglomerates tended to provide a somewhat larger processing window and greater latitude in the extent to which the nanophase could be retained in the coating structure. It also resulted in nanozones that were more porous and in which the nanoparticles were more weakly bonded (Fig. 2b).

**Figure 2:** Micrograph of nanostructured material within thermal spray coatings showing (a) a relatively dense, well-bonded zone in an HVOF titania coating and (b) a more porous region in an 8YSZ coating deposited by APS.
The spray process employed to produce coatings was selected based on the melting point and stability of the material being deposited. For ceramic systems, the goal was to manipulate the temperature reached by the particles during spraying and thereby control the degree of melting. For materials such as TiO₂ that had sufficiently low melting points, the preferred process was HVOF (Fig. 3). This was also the process favored for cermets such as WC-12Co where the approach involved melting only the metal, retaining the nanostructured WC in the solid state and limiting reactions that degraded the WC. Atmospheric plasma spraying was used for ceramic systems with higher melting points. In this case, the “optimum” spray parameter settings were developed using a combination of in-flight particle diagnostics, microstructural analysis and performance evaluation.

It must be noted that varying the spray parameters also affects the deposition efficiency (DE). Frequently, a change in spray conditions that results in a decrease in in-flight particle temperature may lead to an increase in the percentage of nanostructured material in the coating but cause a decrease in DE. It is also important to appreciate that when using HVOF techniques to spray ceramic materials having melting points near the upper temperature capability of the process, there is less latitude for varying the processing conditions. For the spray parameters settings, the limitation is imposed by the need to maintain the particle temperatures high enough to cause sufficient melting to favor deposition. In the case of the feedstock characteristics, it has been found for the ceramic materials sprayed by HVOF in this study that smaller particles, a narrow particle size distribution (e.g., 5-20 μm) and agglomerated powders were preferred over larger particles, a wider particle size distribution and fused and crushed feedstocks.

Case Studies
Coatings were produced using various feedstock compositions. The goal was to engineer coatings having properties and characteristics tailored for specific applications.

Tungsten carbide-cobalt and titania for wear resistance: For producing wear-resistant coatings, the emphasis was placed on engineering dense structures possessing a good combination of hardness and toughness. Due to the melting points of the two materials investigated for this application (1855°C for TiO₂ and ~1500°C for the Co matrix containing the high-melting-point WC (2870°C)), HVOF spraying was employed to produce coatings.

The abrasion resistance as a function of the processing conditions (temperature) and the hardness for the WC-12Co coatings produced using a feedstock powder in which approximately half of the WC was nanostructured is shown in Fig. 4. Carbide-containing materials of this type are prone to degradation during high-temperature exposure when thermal spraying. Such reactions may be exacerbated by increasing the surface area of WC, which could result from decreasing the carbide grain size. The work in engineering these coatings has indicated that with regard to abrasion resistance, the performance is similar to that of the best conventional coatings [4]. It has also been shown that for coatings produced at higher temperatures (above approximately 1950-2000°C) the abrasion performance decreases. However, for those results there was no clear indication that the deterioration in performance was more pronounced for coatings produced from nanostructured powders than for those deposited using conventional powders. Further, no in-depth analysis was performed to determine to what extent the nanostructured phase present in the feedstock was retained in the coatings.

It was found that the use of powders having a nanostructured WC phase could produce coatings with higher hardness
Zirconia and alumina-titania coatings for abrashables: A micrograph of a zirconia coating engineered to have a combination of properties suitable for use as an abrashable material under high temperature conditions is shown in Fig. 6a. A higher magnification image of a nanostructured region of this coating is shown in Fig. 2b. The coating was produced by the APS process using conditions selected to provide relatively low temperatures and thereby control the degree of melting. By varying the spray settings, coatings could be produced having amounts of nanostructured material in the structure ranging to above 30% [5].

As mentioned earlier when discussing the structure shown in Fig. 2b, a characteristic of the nanostructured regions in these coatings was weak bonding and the presence of porosity. These zones impart a low wear resistance. Rub-rig tests to evaluate the abradability of the coatings have indicated that depending on the coating and the test conditions, the wear scars can be quite smooth and blade wear relatively low [5].

Similar coatings have been engineered using the APS process and a nanostructured Al2O3-13TiO2 feedstock [13] (Fig. 6b). Coatings of this composition would be intended for use in medium-temperature (up to ~800°C) applications under corrosive conditions where metals could be attacked by the corrosive species and polymers would not survive because of the temperatures. It should be noted that it has been shown in other work that nanostructured coatings of this composition can also be tailored to provide superior wear resistance [14].

As discussed earlier and shown in Table 1, an important aspect of engineering these abrashable coatings is the use of a nanostructured feedstock having a relatively broad agglomerate size range. This allows for sufficient melting of an outer shell of material in larger agglomerates, which become embedded in a matrix of resolidifying material originating from fully molten smaller agglomerates. The non-molten or semi-molten nanostructure within the larger agglomerates is retained and becomes part of the coating structure, producing a deposit with poor wear resistance. When correctly engineered, these materials can exhibit attributes making them suitable for use as abrashable coatings.
Hydroxyapatite and titania coatings for biomedical implants: Some of the structures identified within HA coatings produced by the HVOF spraying of a nanostructured powder are shown in Fig. 7. The traditional approach for depositing HA coatings for biomedical applications is APS. This higher temperature approach results in the formation of a range of phases and decreases the level of crystallinity. Coatings deposited using the feedstock and spray process employed in the present work were relatively dense and well bonded to the substrate and exhibited high levels of crystallinity (84%) [7].

Concerning the bioperformance of these coatings, initial tests using simulated body fluid have suggested an accelerated nucleation of apatite on coatings engineered to contain nanostructured zones [7]. Other work has pointed to the potential for enhanced bioperformance in nanostructured materials [15]. This appears to be related to the scale of the structure, which more closely approximates that of the nanosized proteins playing a key role in the osteointegration process [15].

The titania coatings produced for use in orthopedic implant applications were also deposited using HVOF and nanostructured feedstocks. The coatings were found to have various nanofeatures, including nanoparticles, nanoroughness and nanoprotuberances (Fig. 7). These were present at the coating surface, within the coating and at the coating-substrate interface. It was determined that the strength of bonding between these coatings and the substrate was more than twice that found for HA coatings. This is obviously an important characteristic for coatings on orthopedic implants where premature failure requires additional invasive surgery.

The nanostructured titania feedstock was predominantly in the anatase (low-temperature) phase. When heated to high temperatures, anatase transforms to rutile. Analysis of the coatings produced in this work indicated the presence of approximately 25% anatase phase [16]. Therefore it was deduced that roughly 25% of the coating structure had a nanocharacter originating from that found in the feedstock. This indicates that the process temperature/time was sufficiently low to limit melting and enable the retention of a significant fraction of the nanostructure.

Evaluation of the bioperformance of these dense titania coatings using an osteoblast cell culture indicated a higher cell proliferation than on HA coatings produced by APS [9]. It is believed that the presence of nanostructured regions in these coatings is contributing to this enhanced performance.

As discussed earlier, a key aspect of engineering these dense hydroxyapatite and titania coatings having a bimodal structure is the use of a nanostructured feedstock with a relatively narrow agglomerate size range. The relatively low melting points of TiO₂ and HA enable the use of HVOF as the spray process. This combination results in the presence of nanostructured features in the coatings that appear to enhance their bioperformance. The scale of these nanostructured regions more closely mimics that found in bone and aids in promoting interaction with specific proteins essential for the osteointegration process.

Zirconia coatings for thermal barriers: A comparison of the microstructures of thermal barrier coatings (TBCs) produced using conventional and nanostructured powders is shown in Fig. 8. The preliminary work in this area has shown that the thermal diffusivity of the best coatings produced from nanostructured powders was 25% less than that for the best conventional coatings. The thermal diffusivity values increased for both coatings following a 24-hour heat treatment at 1200°C. However, the value for the coating deposited using the nanostructured powder was still 10% below that for the conventional coating.

![Figure 7: Micrographs of features identified in HA (a-c) and TiO₂ (d-f) coatings produced by the HVOF spraying of nanostructured powders: (a) porous zone (b) fibrous material (c) globular structure (d) nanoparticles (e) nanoprotuberances and (f) nanoroughness.](image)

![Figure 8: Microstructures of TBCs produced from two powders: (a) nanostructured and (b) conventional.](image)
Although quantitative measurements of the porosity levels in these coatings have not been performed, the appearance of the coating structures suggested that the coating produced from the nanostructured powder was denser. The microstructure of this coating was also finer. It is believed that the higher level of interfaces in this coating contributes to the reduction in thermal diffusivity. Further work is required on this topic to fully understand the role of the nanostructured feedstock on the microstructure and performance of the coating. The work does seem to suggest that the use of nanostructured feedstocks for tailoring the coating structure to increase the presence of interfaces may serve to enhance the thermal properties of coatings for TBC applications.

Summary and Conclusion

In this work, coatings engineered to contain zones of nanostructured material have been shown to exhibit enhanced performance characteristics for some applications. The strategies for producing these ceramic-based coatings by the thermal spraying of nanostructured powders involve the use of a carefully selected powder granulometry and processing windows for thermal spraying that limit the extent of particle melting. Depending on the intended application, coatings containing zones of nanostructured material that is relatively dense and well bonded or porous and weakly bonded can be engineered. Hydroxyapatite, WC-Co, TiO₂, ZrO₂-Y₂O₃, and Al₂O₃-TiO₂ coatings produced using feedstocks containing a nanophase exhibited improved performance in various tests. The structures of the various coatings were tailored to provide enhanced wear resistance, thermal resistance, abradability, or bioperformance. The results point to the potential for using nanostructured powders as thermal spray feedstocks for synthesizing novel, higher performance coating structures.

References

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The increase in research activity in the field of nanostructured materials is leading to the development of new strategies and processes for producing bulk materials and coatings having some fraction of the internal structure of nanosized dimension. The size and extent of these nanostructured zones depend on both the nature of the starting material and the process conditions employed during production. The present study was undertaken to investigate the use of thermal spraying to produce a range of ceramic-based coatings in which zones of nanostructured material were an integral part of the coating structure. The material systems studied included WC-12Co, Al₂O₃-13TiO₂, hydroxyapatite, TiO₂, and yttria-stabilized zirconia. By employing a range of values for the thermal spray process parameters, information was obtained on the extent to which the nanocharacter of the coatings could be engineered and controlled. The effect of these parameters on the phase composition, properties and performance, in addition to the microstructure, was also investigated. Specific nanostructural features of the coatings were identified and their potential benefit in enhancing the behavior explored. Aspects concerning engineering these types of coatings to have performance characteristics for targeted applications will be discussed.

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