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Engineering nanostructured thermal spray coatings: process–property–performance relationships of ceramic based materials

B. R. Marple* **and R. S. Lima**

Nanostructured powders were deposited using thermal spraying to produce coatings having internal features of nanosized dimensions. Several ceramic based materials were studied, including WC–12 wt-%Co, TiO_2, hydroxyapatite, Al_2O_3–13 wt-%TiO_2 and yttria stabilised zirconia. The effect of the thermal spray conditions on the microstructure, phase composition, properties and performance was investigated. Key nanostructural features of the coatings were identified and their potential benefit in contributing to enhanced behaviour explored. Issues relating to design strategies and process control for engineering these types of coatings with performance characteristics tailored for targeted applications are discussed.

Keywords: Nanostructured coatings, Thermal spray, Processing strategies, Process–property–performance relationships

Introduction

The need for materials having enhanced properties and performance characteristics capable of meeting more demanding requirements of existing applications and for use in new functions is a major impetus for research and development in the materials field. This is leading to advances in the science and technology of materials design and engineering for both bulk ceramic components and coatings. In some cases, the focus has been on the processing of materials, where more sophisticated processing routes are being employed, techniques are being combined in a simultaneous, sequential or alternating fashion, and improved process control strategies and diagnostic tools are being applied. In other instances, the emphasis is on the formulation, where new combinations of constituents resulting in new materials or composite structures are being developed. Often the approach focuses on tailoring the structure of a material to produce more complex architectures, layered or laminate structures, and graded materials. There is also a significant effort in engineering the fine structure of materials by closely controlling the scale of the internal features (e.g. grains, pores, and defects or inclusions).

A specific area of interest in materials engineering is reducing the scale of the internal structure from the micrometer level to a size in which at least one dimension of the constituents (grains, particles, fibres, rods, etc.) is below 100 nm. These so called nanostructured materials are being studied to determine if such an approach can lead to improvements in various properties and, hence, an enhanced performance in targeted applications. The present study focused on producing nanostructured coatings; more specifically, on engineering ceramic based, nanostructured coatings by thermal spraying. This paper will outline some of the strategies employed, identify various limitations and challenges, highlight some of the advantages, provide results on process–property–performance relationships obtained with several ceramic based materials, and discuss the potential for using these coatings in a range of applications. This work draws from and builds upon several earlier articles from the same authors. Those articles, cited later in the text, contain detailed information on the processing, characterisation and performance of the various coating systems discussed here.

Background

Thermal spraying

Thermal spray processes involve the use of feedstock materials, in the present case in the form of powders, which are injected into a gas stream and exposed to a heat source where they are heated to induce partial or complete melting and then propelled against the surface to be coated. The droplet/particle jet impinges on the part surface where spreading, rapid solidification and (mainly) mechanical bonding of a portion of the starting material occur. A deposit is built up layer by layer by repeatedly traversing the spray jet over the part surface to produce coatings that are typically a few hundred micrometres thick. Coatings synthesised in this fashion often exhibit a high degree of anisotropy due to the lamellar nature of the structure.

When depositing ceramic based compositions, the approach employed concerning melting of the material can vary, depending on whether the powder is comprised of only ceramic or is a cermet (a combination of

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both a ceramic and a metal). In the latter case, the powder formulation is often composed of a low melting point metal and a high melting point ceramic. For these materials, the goal is often to melt only the metal and use this phase as the matrix to anchor the ceramic phase, which is not melted. This approach has the advantage of enabling the deposition of ceramic materials that can be decomposed or degraded if exposed to higher temperatures and it also offers the possibility of incorporating nanosized ceramic particles in the coating. For ceramic systems in which no metal phase is present, the degree of melting during deposition can be controlled by manipulating the process parameters.

Two important and widely used thermal spray processes are high velocity oxyfuel (HVOF) and air plasma spray (APS). Although a detailed description of these two processes is not required for this paper, a couple of points need to be highlighted. In the HVOF method, heat is generated by a combustion process. The particle temperatures generated are typically relatively low ($<2100^\circ$C) and the velocities relatively high (>600 m s^{-1}). For APS systems, heating takes place within a plasma and the particle temperatures are typically significantly higher ($>2400^\circ$C) while the velocities are considerably lower (<300 m s^{-1}). These differences in temperature and velocity can have a major effect on the deposition process and on the coating properties. A third process, vacuum plasma spraying, involves using a plasma system under a vacuum or partial vacuum. In this case, the particle velocities can be higher than for a regular APS system.

Nanostructured materials

As mentioned in the introduction, nanostructured materials are usually defined as those for which at least one of the dimensions of the internal structure is less than 100 nm. Engineering materials so that at least some of the structure is at the nanoscale is being investigated because of the potential of leading to, for example, enhanced mechanical performance,[1] better osteointegration characteristics in biomedical applications,[2] and improved function of photocatalytic materials.[3] The effect on material performance can arise due to various factors, including the increased number of atoms situated at the surface and at grain boundaries, the higher surface area, and the fineness and distribution of pores. There are a number of relationships that point to the potential improvements in various properties when the scale of the microstructure is decreased from the micrometre to nanometre level.[4–6]

For those applications where only the surface region needs to be tailored to impart specific performance characteristics, surface modification techniques or coatings can be employed to introduce nanostructured features. Such an approach can help limit the amount of material (coating thickness) to only that required to meet the demands of the application. It also provides added latitude in engineering bodies by coupling processes for producing bulk components with deposition techniques controlled and tailored to produce nanostructured coatings.

Experimental

Processing

The starting materials used to produce coatings were powders comprised of agglomerates having a size range suitable for thermal spraying. This varied, depending on the thermal spray process being employed and the type of performance characteristics being sought. Details on the six nanostructured starting powders are provided in Table 1. As indicated in this table, the scale of the internal structure of the powder agglomerates also varied. For each of the ceramic powders, the scale of the structure within the agglomerates was relatively uniform. In the case of the cermet, the WC phase consisted of a mixture containing equal amounts of nanosized and micron sized (>1 μm) grains. (This powder was designated as multimodal by the manufacturer to reflect the range of WC grain sizes.)

As shown in Table 1, coatings were produced using these powders by either HVOF processes or APS. In one case, coatings were deposited using VPS. When ceramic powders were being sprayed by HVOF, only one system (DJ2700-Hybrid, Sulzer Metco, Westbury, NY, USA) was employed. For the cermet, several HVOF systems were used to produce coatings. Additional details on the processing of the WC–12Co coatings can be found elsewhere.[7] For each powder-deposition process combination, the thermal spray conditions were varied in order to generate a range of in-flight particle temperatures and velocities, which were monitored using a diagnostic analysis system (DPV-2000, Tecnar Automation, St. Bruno, PQ, Canada). By varying these key characteristics of the thermal spray jet, coatings possessing differences in the microstructure and properties could be produced and information on the robustness of the process could be obtained.

Analysis and characterisation

The resulting microstructures (and nanostructures) were characterised using a field emission scanning electron microscope (FE-SEM, Model S4700, Hitachi Instruments Inc., Tokyo, Japan). For certain coatings, X-ray diffraction (XRD) analysis (Model D8, Bruker AXS, Karlsruhe, Germany) with Cu K_α radiation was employed to determine the phase composition. For several compositions, the Vickers microhardness was measured (average value from ten indentations produced, typically, under a load of 300 gf). In some cases,

Table 1 Details on powders and processes used to produce coatings

Material	Agglomerate size, μm	Size of nanoparticles, nm	Coating process
WC–12 wt-%Co	5–40	30–50	HVOF
TiO_2	HVOF: 5–20/APS: 15–50 VPS: 5–20	15–70	HVOF, APS VPS
Al_2O_3–13 wt-%TiO_2	15–200	15–60	APS
ZrO_2–8 wt-%Y_2O_3	50–150	40–200	APS
ZrO_2–15 wt-%Y_2O_3	5–20, 15–45	<150	APS
Hydroxyapatite	5–50	90–140	HVOF, APS

the resistance to crack propagation was determined on the coating cross section using Vickers indentation under a 5 kgf load with the indenter aligned so one of the crack systems emanating from the corners of the indentation propagated in a plane parallel to the substrate surface. The crack propagation resistance was defined as being equal to $P/c^{3/2}$, where P is the indentation load in Newtons and c is one-half the total length of the crack that runs approximately parallel to the substrate surface. This crack emanates from opposite corners of the indentation and its length, tip to tip, is defined as $2c$.[8] To calculate the value for the crack propagation resistance, an average result was determined based on five indentations. The strength of bonding between the coating and substrate (adhesion) was assessed using a standard tensile test.[9] Depending on the targeted application, the wear resistance, bioperformance, or thermal characteristics of the coatings were investigated. In most cases, coatings produced using these nanostructured materials were compared to those deposited by thermal spraying using conventional (microstructured) powders.

Results and discussion

Influence of powder on coating structure

The internal structures (nanostructures) of the agglomerates comprising the various starting powders discussed in this study are shown in Fig. 1. As mentioned earlier, additional details are provided in Table 1. The characteristics of the feedstock, in particular the particle size distribution of the nanostructured agglomerates, could be used to produce coatings having a very broad range of performance characteristics. Details of this will be presented in the following sections; however, in general, it has been shown that to produce relatively dense coatings possessing high structural integrity, powders comprised of smaller agglomerates having a relatively narrow particle size range were preferred. Such coatings were often characterised by regions of well bonded, dense nanostructured material within a microstructured matrix. When nanostructured powders having a much larger agglomerate size distribution were used, coatings having very different characteristics could be deposited. In this case, the nanostructured regions tended to be larger, more porous and more poorly bonded, and the coatings possessed properties suitable for applications quite different from those produced using the finer powders.

The following sections will provide examples of coatings engineered to possess properties and characteristics to enhance their performance for certain applications.

Wear resistant surfaces

Tungsten carbide–cobalt

The wear resistance of a given composition is often dictated by a combination of the hardness and toughness of the material. For many applications, cermets are employed to take advantage of the properties arising from mixing a hard ceramic phase with a tough metal phase. A comparison of the hardness values of various WC–12 wt-%Co (WC–12Co) cermet coatings deposited to a thickness in the range of about 200–500 μm using various HVOF processing conditions, as reflected in the average in-flight particle temperature, is shown in Fig. 2. As seen in this graph, the hardest coatings deposited were those produced using a starting powder that contained a significant fraction of nanograins of WC.

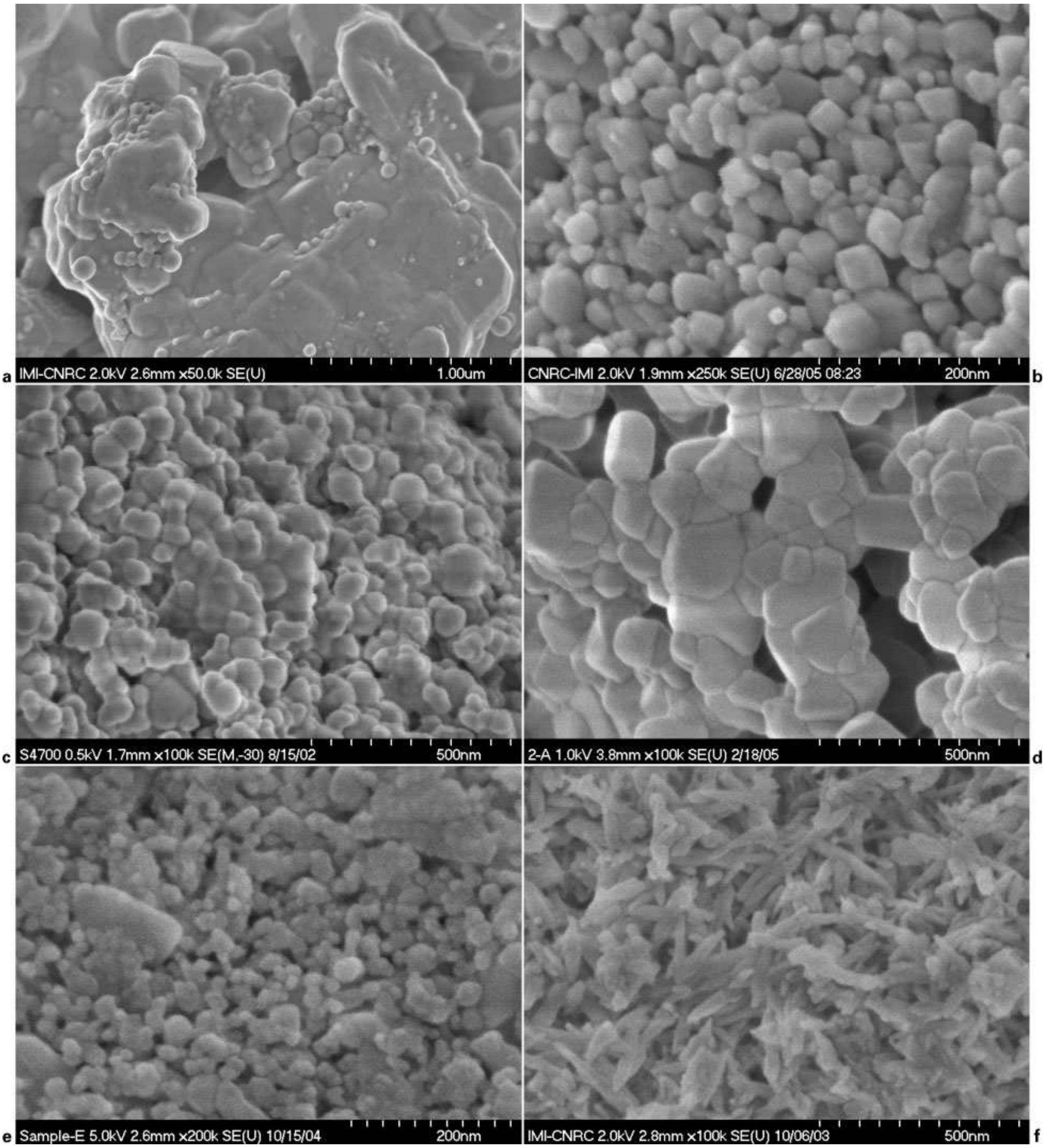
Some of these coatings were also subjected to scratch tests to compare the performance.[10] Differences were observed between coatings produced using starting powders containing predominantly micron sized WC grains and those containing a significant fraction of nanograins. As shown in Fig. 3, the damage within and along the outer edges of five parallel scratches on the polished surface is more severe for the conventional material. The Vickers hardness numbers ($HV_{0\cdot3}$) were found to be 1373 ± 65 and 1440 ± 81 for these coatings produced from the conventional (Fig. 3*a*) and multimodal (Fig. 3*b*) powders respectively. It was also shown that wear scars resulting from abrasion tests of these materials had a lower value of roughness for coatings produced using the multimodal powder. These results from both the scratch and abrasion tests suggest that the machinability of the coatings produced using the multimodal powder would be superior to those deposited using conventional powder containing predominantly micron sized WC grains. Therefore, when using powders containing WC nanograins it was possible to synthesise coatings having a higher hardness and exhibiting characteristics suggesting improved machinability. It is believed that the presence of the finer WC phase in the composite coating gave rise to these effects.

Titania

The results from abrasion tests are shown in Fig. 4 for a number of titania coatings deposited to a thickness of ~400 μm using different thermal spray processes and both nanostructured and microstructured starting powders. This graph shows only the coatings produced after optimisation for each powder–process combination. Although this graph provides only a general comparison between the different process–powder combinations without giving detailed information on the underlying differences, what it does show is that regardless of the process employed, the coatings produced using nanostructured powder are more abrasion resistant than those deposited using a microstructured powder.

To investigate the reasons for this improved performance, the hardness values for the best coatings produced from the nanostructured and microstructured feedstocks were measured. Similar values for Vickers microhardness number (HV0·3) of 810 ± 26 (coating N–H in Fig. 4) and 833 ± 30 (coating C–H in Fig. 4) were determined for coatings produced from the nanostructured and microstructured powders respectively. Therefore, the better wear resistance of the coating synthesised using a nanostructured powder could not be explained in terms of hardness. It should also be noted that both coatings were shown to be relatively dense, exhibiting porosity levels below 1% as determined using image analysis.

To further investigate the reasons for these differences in performance, Vickers indentation at higher loads on the cross-section of the coatings was employed to study the crack propagation characteristics (toughness). Examples of the behaviour of the two coatings when subjected to this test are shown in Fig. 5. The values calculated for the crack propagation resistance were 28·4 ± 1·4 and 17·2 ± 3·3 MPa $m^{1/2}$ for the coatings produced using the nanostructured and conventional

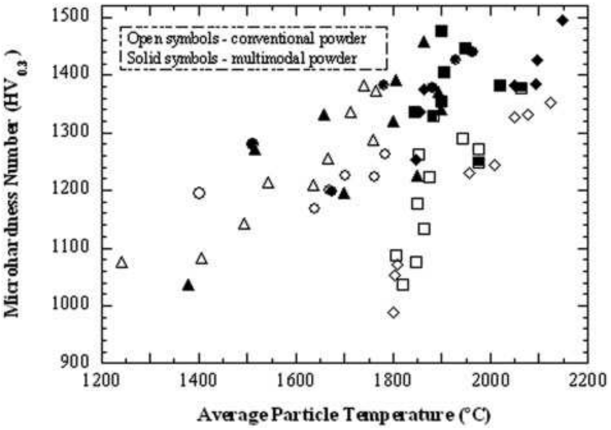


a WC–12Co; *b* TiO2; *c* Al2O3–13TiO2; *d* 7YSZ; *e* 15YSZ; *f* HA

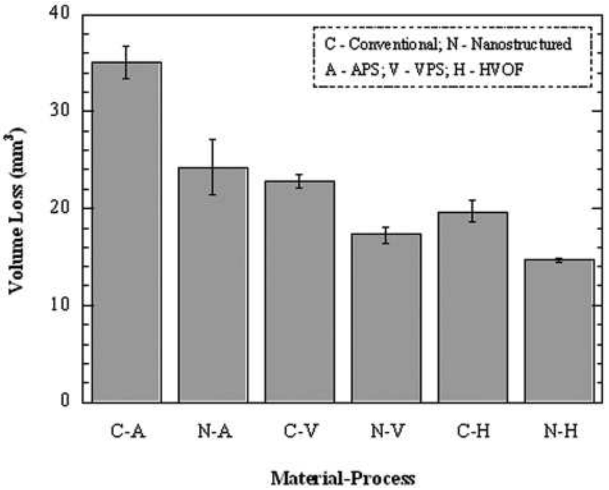
1 High magnification SEM images of nanostructured powders used to synthesise coatings by thermal spraying; scale: number represents combined distance across 10 divisions

powders respectively. When observed at high magnification with an SEM, it became apparent that the coating produced from the nanostructured feedstock contained zones of nanostructured material. Propagating cracks tended to pass through and interact with these zones. In some cases, as shown in Fig. 6, crack tips were situated within one of these zones. It is believed that these nanostructured zones, which are distributed throughout the structure, may serve to aid in crack arrest and thereby toughen the coating. This helps explain the difference in the abrasion resistance and crack propagation resistance between the two coatings. Such zones of nanostructured material were not present in coatings produced using conventional powders.

In addition to producing toughening within the coating, it is thought that these nanozones contribute to enhanced toughening in the coating/substrate interface region, giving rise to improved adhesion between the coating and the substrate.[11] The bond strengths for the C–A, C–H and N–H coatings shown in Fig. 4 were 34 ± 9, 23 ± 5 and 56 ± 22 MPa (check standard deviation value). Because the nanozones are distributed throughout the coating, including in the region of the coating/substrate interface, it is believed that enhanced crack propagation resistance in this region contributes to the higher bond strength of the nanostructured (N–H) coating.

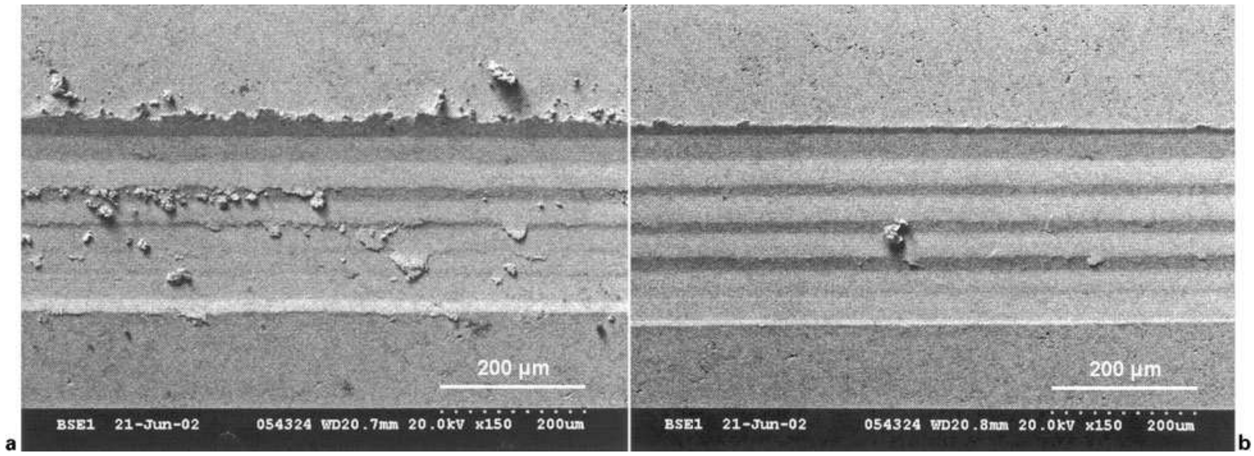


2 **Coating hardness number as function of in-flight particle temperature during HVOF spraying of multimodal (mixture of nanoscale and micron scale WC grains) and conventional (predominantly micron scale WC grains) WC–12Co powders**

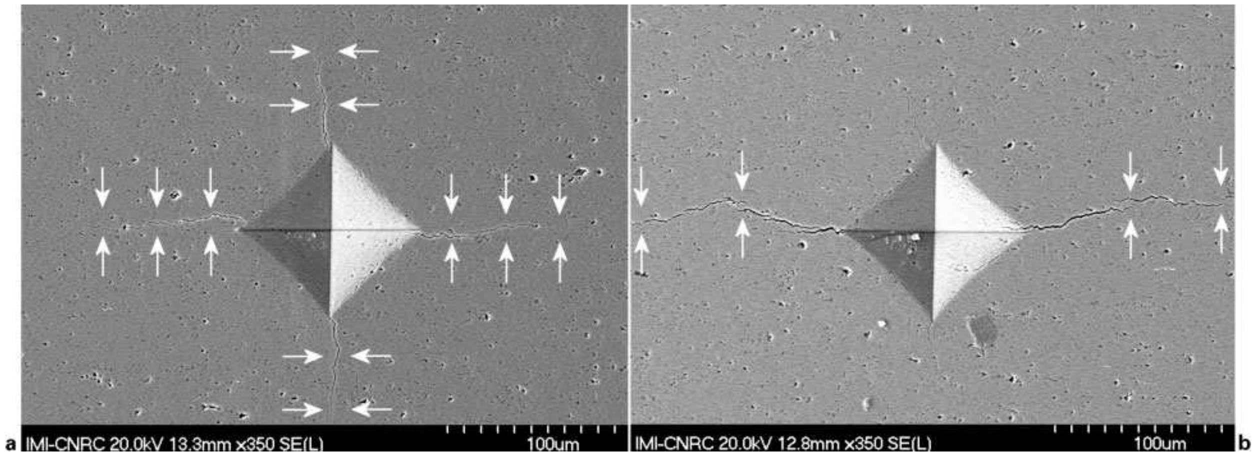


4 **Comparison of dry abrasion performance of TiO_2 coatings produced using different spray processes and nanostructured and conventional feedstocks: volume loss represents average volume (two tests) of wear track, i.e. material abraded away during test**

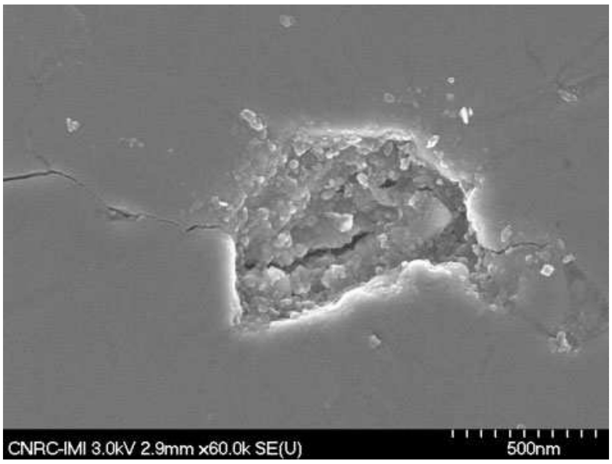
It is important to note that these coatings were produced using nanostructured powders having a relatively narrow agglomerate size distribution (*see* Table 1). Through careful selection and control of the conditions employed for thermal spray, the degree of melting could be controlled so that relatively dense, well bonded zones of nanostructured material were incorporated into the coating structure. These zones appear to



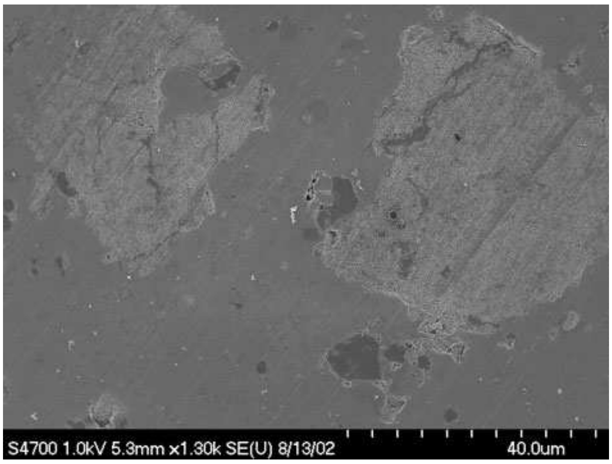
3 **Images of *a* conventional and *b* multimodal WC–12Co coatings showing scratched surface of best performing coatings: micrographs were taken at point where load was 100 N; direction of scratching is from right to left**



5 **Micrographs showing crack formation under Vickers indenter for 5 kg load in titania coatings produced using *a* nanostructured and *b* conventional powder: indentations were made on cross-section of coatings; sample and indenter were situated so main crack plane runs approximately parallel to plane of substrate surface**



6 **Image of interaction of propagating crack with zone of nanostructured titania**



7 **Image of polished top surface of Al_2O_3–$13TiO_2$ coating comprised of regions of porous, finely structured material surrounded by denser, more coarsely structured material**

have resulted from only partial melting of some agglomerates. Some of this molten material may have infiltrated into the remaining core of the agglomerate when the particle impacted the substrate. Some densification may also have occurred at the point of impact due to particle rearrangement within the agglomerate. The molten agglomerate surface helped ensure good bonding between this nanostructured zone and the surrounding matrix produced by the resolidification of molten material. What is important is that such coatings can be engineered to enhance the wear performance and that a significant factor in this improved performance is the use of nanostructured powders.

One factor that can affect the behaviour of coatings deposited by thermal spray is the presence of residual stresses that develop during the deposition and cooling process. An investigation of the residual stresses in these coatings has not been a focus of this study; however, preliminary work on this aspect has been performed using Almen strips[12] to evaluate the nature of the residual stresses present in some of the coatings used to produce the results shown in Figs. 4–6. Of the six coatings included in Fig. 4, only the four coatings deposited by APS and HVOF were evaluated to determine the stress state. This approach does not provide absolute stress values but it does indicate whether the coatings are under tension or compression. The measurements indicated that the two coatings (APS and HVOF) produced using the conventional powder were both in compression. For the coatings deposited using the nanostructured material, the stress states were compressive and neutral for the HVOF and APS coatings respectively. In comparing the degree of curvature for the various Almen strips, no correlation could be found between the stress state of the coatings and the performance in the abrasion tests or the extent of cracking under an indenter. Therefore, although residual stress can affect these values, it is believed that this factor is not playing a dominant role in the performance of these materials.

Abradable coatings

Abradable coatings are engineered to have properties very different than wear resistant coatings. They are employed in applications in which they are meant to be removed or worn in and therefore must have poor wear resistance. As such, they are a sacrificial surface intended to conform rather easily to a mating part. Such coatings are used in some gas turbines to help accommodate dimensional changes associated with heating and cooling cycles, limit damage to the underlying components, and minimise the clearance between rotating and stationary parts.[13] The goal is to limit gas leaks that can lead to a decreased efficiency. Two coating chemistries were investigated using nanostructured powders to determine the feasibility of engineering coatings having properties suitable for abradable surfaces.

Alumina–titania

Coatings were deposited by APS using Al_2O_3–13 wt-%TiO_2 (Al_2O_3–$13TiO_2$) powders (Table 1) to produce layers ~400 μm thick. An example of the microstructure of a coating of this composition produced in this work that was found to be easily abraded[14] is shown in Fig. 7. This coating is characterised by the presence of relatively large zones of porous, weakly bonded material within a denser matrix. Such a structure results from some of the agglomerates being only partially melted during spraying. These coatings can be synthesised by using a combination of relatively large nanostructured agglomerates (*see* Table 1) and thermal spray conditions that limit the degree of melting. This produces relatively large regions of nanostructured, porous material that impart a degree of abradability to the coating.

Coatings engineered in this fashion can be easily worn by another contacting surface. The nanostructured material helps to generate relatively fine wear debris and create a smooth wear surface. These attributes are often important, because the debris may come in contact with other components in the system and can damage the surface through erosive action. Smooth wear surfaces help limit the gap between the two contacting surfaces thereby maintaining a tighter seal and providing a lower leak rate, an important consideration in some cases. This Al_2O_3–$13TiO_2$ composition could be considered for use as an abradable for temperatures up to ~800°C and in applications where corrosive species that could attack metallic abradables are present.

It is important to note that these nanostructured (bimodal) coatings can also be engineered to possess excellent wear resistance.[15] In that case, a smaller agglomerate size and narrower size distribution of the nanostructured powder is required.

Zirconia–yttria

Coatings were also produced by APS using ZrO_2–8 wt-%Y_2O_3 (8YSZ). In this case, much thicker coatings (~2 mm), were deposited to more closely correspond to those used in industry. Micrographs showing both the microstructure and the nanostructure of these coatings are presented in Fig. 8. It is clear from these micrographs that there is a bimodal structure comprised of two distinct types of zones. One zone consists of dense regions of material having a micron scale structure that originated from the resolidification of fully molten droplets. The second zone is nanostructured, porous and probably less well bonded. By varying the thermal spray conditions it was possible to control the amount of nanostructured material incorporated into the coating. Percentages of nanostructured material of up to 40% were attainable. This could be controlled by adjusting the thermal spray conditions to change the temperature experienced by the particles during deposition. Hotter conditions led to a higher degree of melting and a lower amount of nanostructured material in the coating. Figure 9 shows the microstructures of two coatings having very different levels of nanostructured material. The in-flight particle temperatures when producing these coatings were determined to be 3110 ± 232 and 2632 ± 174°C for the 7 and 30% nanostructured levels respectively.

Some of these 8YSZ coatings engineered in this fashion were evaluated to determine their suitability as abradables and investigate their potential for use in higher temperature environments (>1000°C). For the coatings targeted for use as abradable surfaces the hardness was found to be in the range 75–85 when measured on the Rockwell Y scale using a 15 kgf load. These relatively low values for a ceramic material are similar to those of metallic based abradables currently in use.[16] Rub rig tests involving the controlled incursion of a rotating metal blade into the coating to simulate what might occur in a turbine indicated uniform wear of the ceramic coating, limited wear of the metal blade and relatively smooth wear scars.[17]

The ability to alter the properties of these coatings by changing the spray conditions to adjust the amount of nanostructured material present provides relatively broad latitude in engineering these structures and tailoring them to meet the performance requirements of a given application. Of course, there is a limit to the amount of nanostructured material that can be incorporated using this approach. Higher amounts of nanostructured material in the coating are produced by lowering the temperature of the thermal spray jet. However, at some point the temperature reaches a point where little or no material is deposited because there is insufficient melting to create a bond between the substrate and the material.

Biomedical coatings

Thermal spray surfaces are being employed as coatings on orthopaedic implants for replacing worn, diseased and injured body parts. For example, hydroxyapatite (HA) is widely used on the femoral stem and acetabular cup of hip replacement devices.[18] Various studies have indicated that nanostructured surfaces may aid in promoting osteointegration of implanted devices.[19] Two systems have been studied in this work for this type of application.

Hydroxyapatite

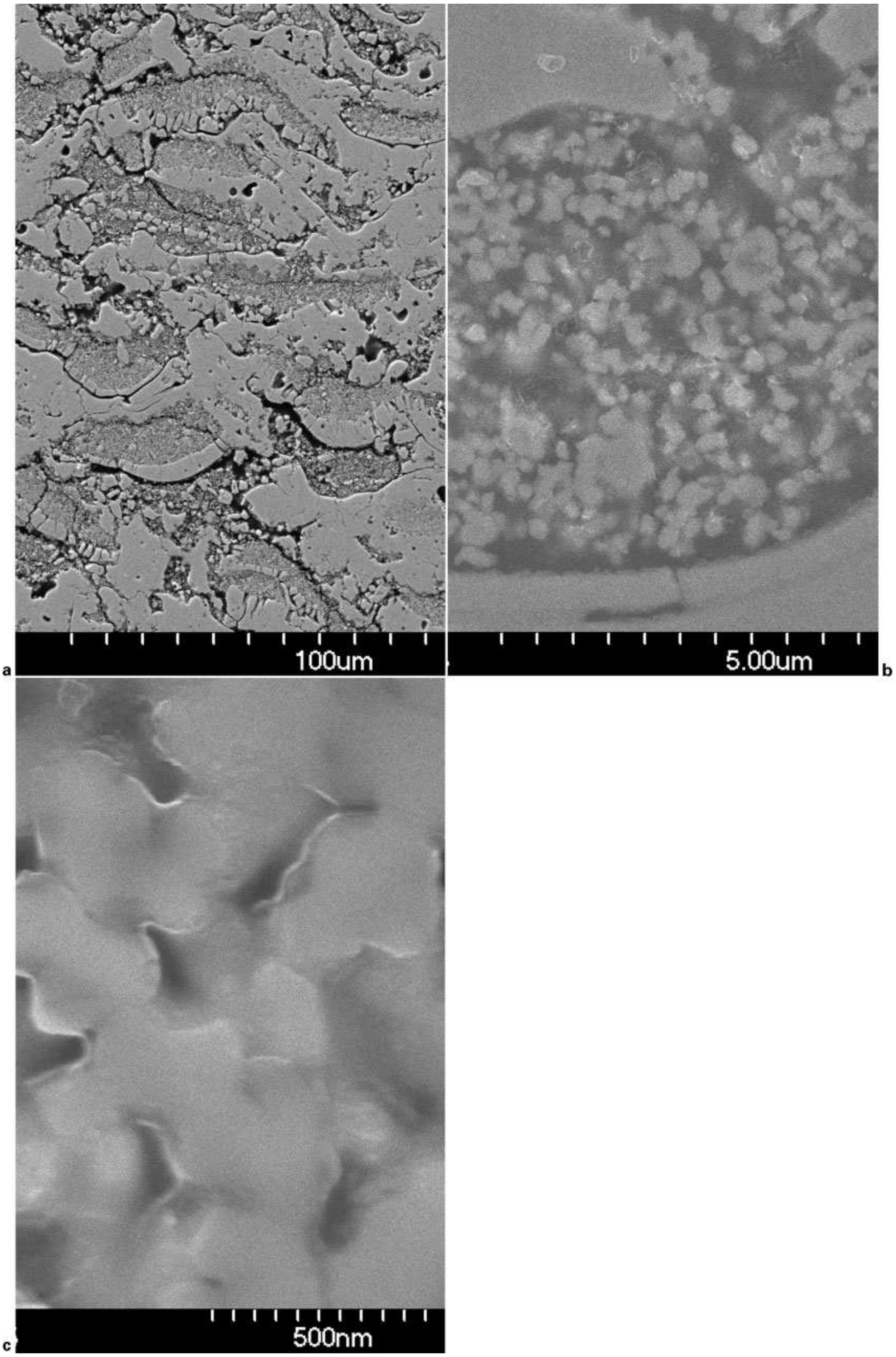
Nanostructured hydroxyapatite $[Ca_{10}(PO_4)_6(OH)_2]$ powders were deposited using both APS and HVOF techniques. The goal was to investigate if some of the nanostructure of the starting powder could be retained to produce nanostructured zones in the coating. Figure 10 shows a series of micrographs of some of the nanostructured features observed in the coatings. When comparing these various structures to that of the starting powder, which was comprised of elongated fibre-like nanoparticles (*see* Fig. 1), it can be observed that the different morphologies appear to result from various degrees of melting. In some cases, the fibre-like characteristics are still present, in other cases the degree of melting has been sufficient to produce a globular shape. Some of the zones are relatively dense and others are more porous. This work showed that HA coatings produced by thermal spray could be engineered to produce regions of nanostructured material. Follow-up studies are now required to assess the effect of these zones on the bioperformance.

It should also be noted that these types of HA coatings produced by HVOF had a high degree of crystallinity (>80%) as determined by XRD.[20] This is an important attribute because the amorphous phases that can arise during this type of thermal exposure are less stable in the human body.[21] The bonding of these HVOF sprayed coatings to the substrate was found to be ~24 ± 8 MPa for a coating thickness of ~150 μm. Although this value is typical of that found for HA coatings deposited by thermal spray, it will be shown in the following section that newer coatings under development offer the potential for enhanced bonding with the substrate.

Titania

Titania was investigated as a potential replacement or alternative for HA as a biomedical coating. Some of the attributes of the coatings developed for this application have already been discussed in the section on 'Wear-resistant surfaces'. In the present phase of the study, the area of interest was the structure, bonding and bioperformance of the coatings. For this application, a coating thickness of ~150 μm was produced. Figure 11 shows various nanostructured features found at the surface and within the titania coating produced by HVOF. It is believed that these features may help promote interaction with key proteins (e.g. fibronectrin) involved in the osteointegration process. These proteins also have nanoscale features and other work has shown accelerated activity when nanostructured oxide ceramics are used.[22]

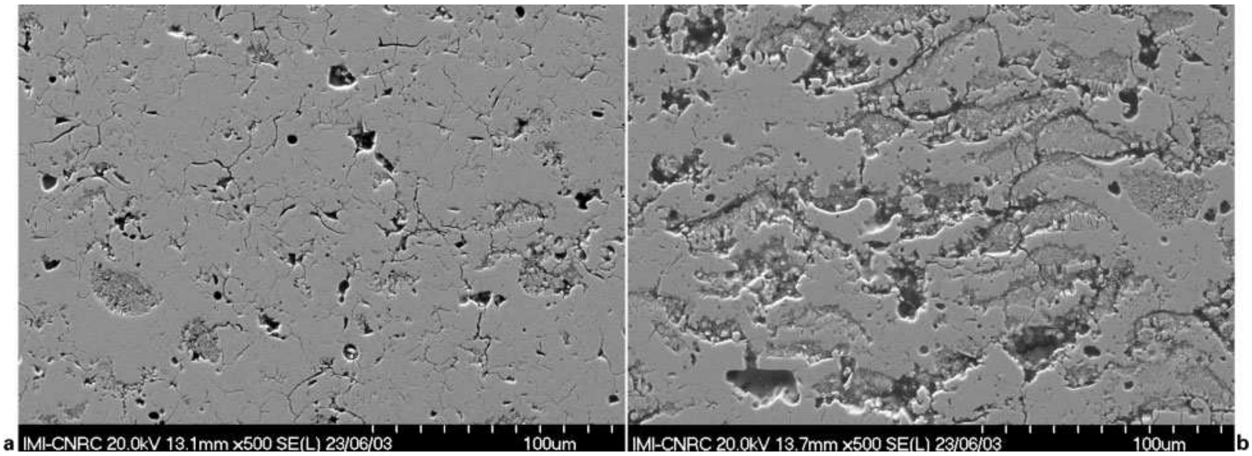
The bonding between these coatings and the underlying Ti–6Al–4V substrate was found to be >77 MPa. The exact value could not be determined because the technique being employed involved using an adhesive that failed before the bond between the coating and substrate. However, what is important to note is that a value of 77 MPa is more than twice the value of bond strength reported for HA,[23] the material currently being



a relatively low magnification and nanostructured region; *b* intermediate magnification; *c* high magnification
8 Micrographs showing cross-section of 8YSZ coating

employed on various orthopaedic implants. The improved adhesion of titania is believed to be due in part to the presence of zones of nanostructured material at the interface between the coating and substrate, giving rise to improved resistance to crack propagation, as discussed in the section on 'Titania'.

Evaluation of the bioperformance of these coatings using fetal rat calvaria cells has shown a rate of proliferation and a degree of adherence similar or superior to HA coatings.[24] These preliminary results on bioperformance, combined with the excellent mechanical properties, bonding and long term stability,

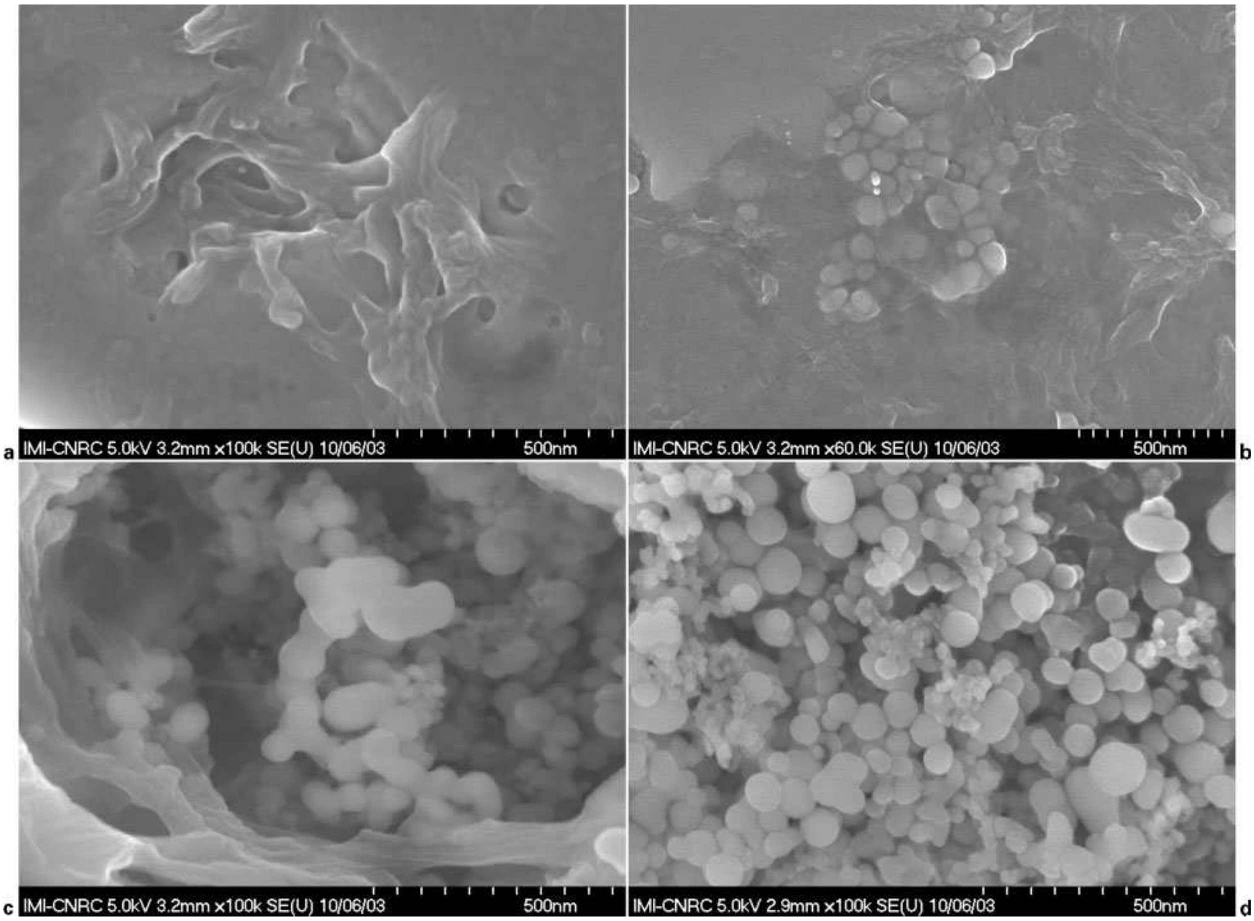


9 Micrographs showing cross-sections of two 8YSZ coatings having approximately *a* 7% and *b* 30% of area encompassed by nanostructured regions

make this bimodal titania coating an interesting candidate for further research for biomedical applications.

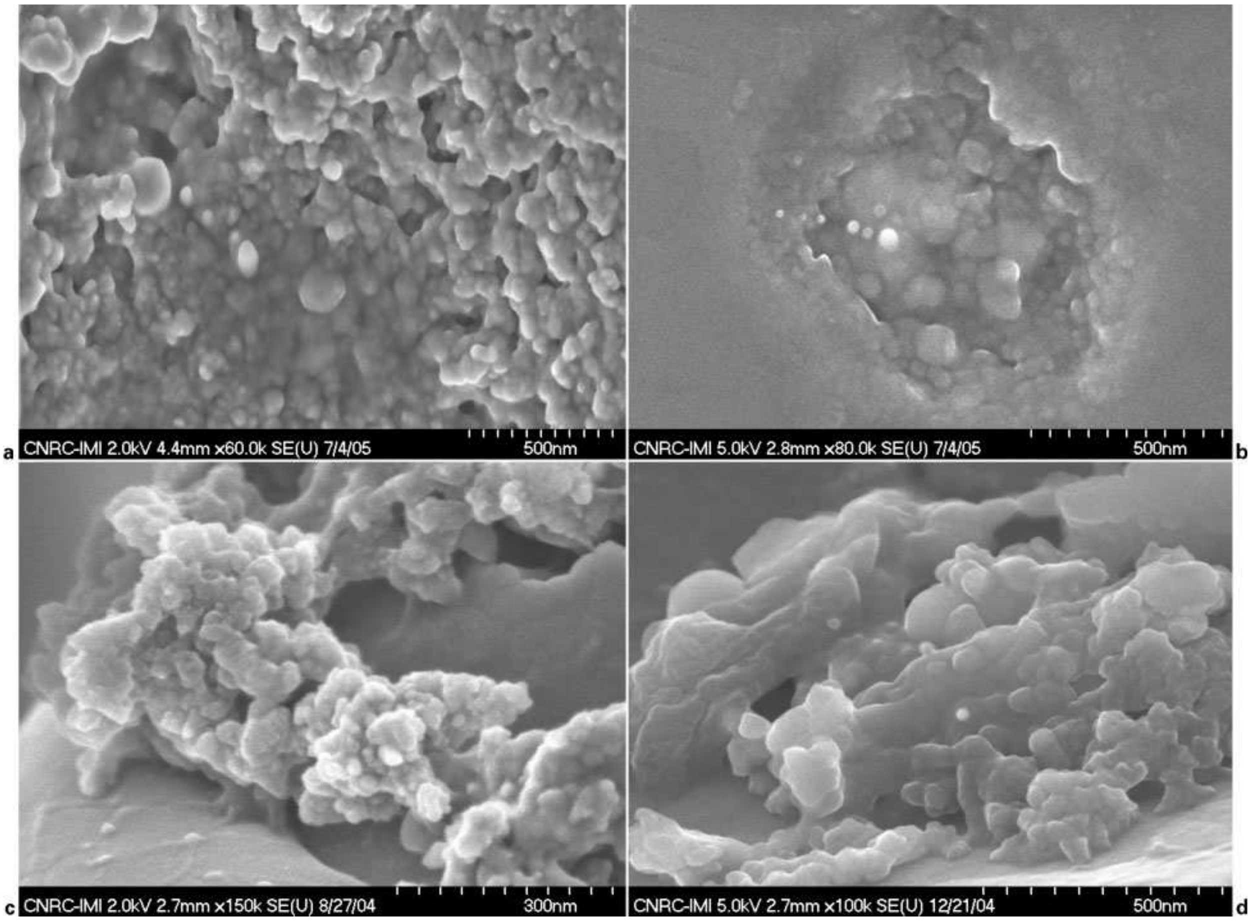
Thermal barrier coatings

Some preliminary research has been performed on synthesising thermal barrier coatings (TBCs) by APS using nanostructured feedstocks. These types of coatings are employed to protect underlying components from hot combustion gases in gas turbines used in the aerospace field and for land based energy generation. Details on the nanostructured 15YSZ powder are provided in Table 1. An example of the microstructure of a coating produced using this powder is shown in Fig. 12 along with that of a typical 8YSZ coating currently in use and produced using powder having a coarser (micron scale) internal structure. Thermal diffusivity measurements indicated that the coating produced using the nanostructured powder had a value 25% lower than the conventional coating. It is believed that this difference is due to a finer structure and an



a fiber-like structure; *b* closely packed globules; *c* region of porous, partly coalesced globular material; *d* zone of denser globular material

10 Micrographs showing regions of nanostructured material found within hydroxyapatite coatings produced by depositing powder shown in Fig. 1*f* by thermal spraying



a dense region; *b* nanostructured zone surrounded by denser material; *c* nanostructured pores and grains; *d* dense zone at surface

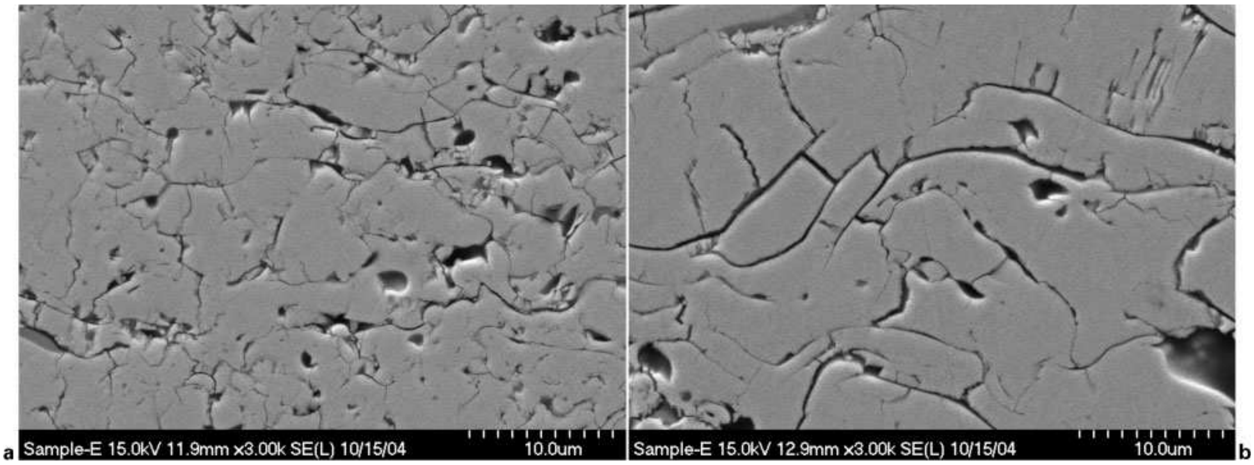
11 Micrographs showing zones of nanostructured material in titania coatings

increased number of interfaces in the coating produced from the nanostructured material. In practice, this lower value would lead to lower heat transfer to the component being protected by these TBCs.

Although further work is required to investigate the fine features of the microstructure, determine if further improvements are possible and study the long term stability of these materials when exposed to high temperatures and cyclic heating and cooling treatments, these initial results provide evidence that engineering TBCs by the thermal spraying of nanostructured powders may lead to improvements in performance.

Summary and conclusions

This work has outlined the concepts and strategies employed for engineering thermal spray coatings using nanostructured powders as the starting material and discussed some of the process–property–performance relationships. In general, the methodology for ceramics



12 Micrographs of YSZ coatings produced using *a* nanostructured and *b* conventional powder

has been to control the temperature of the particles in the thermal spray jet so they are in the vicinity of the melting point of the material. By adjusting the thermal spray conditions around this point, the degree of melting and the amount of nanostructured material formed in the coating can be varied. This approach results in coatings having a bimodal structure comprised of nanostructured material, originating from agglomerates that were only partially melted, held within a coarser (micron scale) matrix, arising from the resolidification of fully molten material.

A second important aspect for tailoring nanostructured coatings for specific applications is the agglomerate size and size distribution of the starting powder. To produce dense coatings having well bonded, relatively dense nanostructured regions, smaller agglomerates and a narrower agglomerate size distribution is preferred. To produce larger zones of nanostructured material that are more porous and more poorly bonded, larger agglomerates and a broader size distribution are favoured.

Using these guidelines, a range of coating compositions were employed to tailor coatings for specific applications. Titania, hydroxyapatite, alumina–titania, and yttria–stabilised zirconia ceramic materials, as well as a tungsten carbide–cobalt cermet, were included and used to produce coatings for use as wear resistant, biomedical, abradable and thermal barrier applications. The results indicate that the use of nanostructured powders for synthesising ceramic based thermal spray coatings holds promise for engineering surface layers with enhanced properties and performance characteristics.

References

1. K. Jia and T. E. Fischer: *Wear*, 1996, **200**, 206–214.
2. T. J. Webster, C. Ergun, R. H. Doremus, R. W. Siegel and R. Bizios: *Biomaterials*, 2000, **21**, 1803.
3. C. Lee, H. Choi, C. Lee and H. Kim: *Surf. Coat. Technol.*, 2003, **173**, 192–200.
4. W. D. Kingery, H. K. Bowen and D. R. Uhlmann: 'Introduction to ceramics', 2nd edn, 739; 1976, New York, John Wiley & Sons.
5. A. H. Cottrell: 'The mechanical properties of matter', 326–332; 1981, New York, Robert E. Krieger Publishing Co.
6. A. H. Cottrell: 'The mechanical properties of matter', 345; 1981, New York, Robert E. Krieger Publishing Co.
7. B. R. Marple and R. S. Lima: *J. Therm. Spray Technol.*, 2005, **14**, (1), 67–76.
8. G. R. Anstis, P. Chantikul, B. R. Lawn and D. B. Marshall: *J. Am. Ceram. Soc.*, 1981, **64**, (9), 533–543.
9. 'Standard test method for adhesion or cohesion strength of thermal spray coatings', ASTM standard C 633-01, ASTM, West Conshohocken, PA, USA, 2001.
10. B. R. Marple, H. M. Hawthorne and Y. Xie: 'Thermal spray 2004: advances in technology and application', 846–851; 2004, Materials Park, OH, ASM International.
11. P. Bansal, N. P. Padture and A. Vasiliev: *Acta. Mater.*, 2003, **51**, 2959–2970.
12. J. P. Sauer and P. Sahoo: Thermal Spray 2001: New Surfaces for a New Milennium (ed. C. C. Berndt, K. A. Khor and E. F. Lugscheider) 2001, Materials Park, OH, USA, ASM International, p. 791–796.
13. M. O. Borel, A. R. Nicoll, H. W. Schlapfer and R. K. Schmid: *Surf. Coat. Technol.*, 1989, **39–40**, 117–126.
14. R. S. Lima and B. R. Marple: Proc. 1st Int. Surf. Eng. Cong. and 13th IFHTSE Cong., (ed. N. Dahotre *et al.*), 495–504; 2003, Materials Park, OH, ASM International.
15. E. H. Jordan, M. Gell, Y. H. Sohn, D. Goberman, L. Shaw, S. Jiang, M. Wang, T. D. Xiao and P. Strutt: *Mater. Sci. Eng. A*, 2001, **A301**, 80–89.
16. 'Sulzer Metco 2043 – CoNiCrAlY-boron nitride/polyester composite powder', Technical Bulletin no. 10-636, Sulzer Metco, Westbury, NY, USA, 2000.
17. Building on 100 years of success: Proc. 2006 Int Thermal Spray Conf., (ed. B. R. Marple *et al.*); May 15–18, 2006, (Seattle, WA, USA), ASM International, Materials Park, OH, 2006.
18. K. A. Gross, W. Walsh and E. Swarts: *J. Therm. Spray Technol.*, 2004, **13**, 190–199.
19. T. J. Webster, R. W. Siegel and R. Bizios: *Biomaterials*, 1999, **20**, 1221–1227.
20. R. S. Lima, K. A. Khor, H. Li, P. Cheang and B. R. Marple: *Mater. Sci. Eng. A*, 2005, **A396**, 181–187.
21. L. Cleries, J. M. Fernandez-Pradas, G. Sardin and J. L. Morenza: *Biomaterials*, 1998, **19**, 1483–1487.
22. T. J. Webster, C. Ergun, R. H. Doremus, R. W. Siegel and R. Bizios: *J. Biomed. Mater. Res.*, 2000, **51**, 475–483.
23. H. Li, K. A. Khor and P. Cheang: *Mater. Sci. Eng. A*, 2000, **A293**, 71–80.
24. J. G. Legoux, F. Chellat, R. S. Lima, B. R. Marple, M. N. Bureau, H. Shen and G. A. Candeliere: *J. Therm. Spray Technol.*, 2006, **15**, 628–633.