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Wear Characteristics of Plasma-Sprayed Nanostructured Yttria Partially Stabilized Zirconia Coatings

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Reconstituted nanostructured and conventional yttria partially stabilized zirconia coatings were deposited by atmospheric plasma spray. The tribologic properties of the coatings against 100C6 steel were evaluated with a ball-on-disc configuration under dry friction conditions at room temperature. Microstructure and the phase composition of the powders and the coatings were examined using a scanning electron microscope, optical microscope, and x-ray diffraction. Microhardness and the Young's modulus of coatings were measured by indentation testing. Results showed that the wear resistance of the coatings produced using the nanostructured powder is improved compared with the coating produced using the conventional powder. The wear rates of nanostructured zirconia coatings are about four-fifths of those of conventional counterparts under a load of 5 N. The wear mechanism is also discussed.

Keywords coatings, friction and wear, nanostructural, plasma spraying, zirconia

1. Introduction

Yttria partially stabilized zirconia (YPSZ) ceramics, as one of the promising materials with good thermal and mechanical properties, have attracted the interest of many researchers and have been widely used for various applications (Ref 1-6) in past decades. The need for increasing engine efficiencies and environmentally cleaner emissions mandates the use of higher operating temperatures in both land-based and aircraft engines. The YPSZ coatings deposited by atmospheric plasma spray or electron beam physical vapor deposition are used as thermal barrier coatings (TBCs) due to their capability in improving gas turbine performance by allowing higher turbine inlet temperatures and reduced cooling airflow (Ref 7). However, these coatings have still not achieved widespread application in conventional diesel engines. Further efforts are needed to estimate the effect of coatings on exhaust emissions, component wear, and the sensitivity of engines to fuel quality. Wear at high temperatures, where conventional lubricants are not effective, is a serious problem in low-heat-rejection engines. Ceramic materials such as TBCs in cylinder liners must have an acceptable wear rate and coefficient of friction.

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In recent years, nanostructured materials have been considered as a new concept for increasing the performance of engineering components (Ref 8, 9). Research efforts have demonstrated that thermal-spraying processes are effective methods to produce nanoscale coatings (Ref 10-12). Nanostructured coatings exhibit better properties, including tribologic properties, than conventional coatings of the same composition. Zeng et al. (Ref 11), Chen and coworkers (Ref 13-16), Lima and coworkers (Ref 17-19), and Soltani et al. (Ref 20) have investigated nanostructured YPSZ coatings, and have reported improved quality of properties such as increased wear resistance, bond strength, and microhardness. But, a further understanding of the difference of coating properties, as mentioned above, between nanostructured YPSZ coatings and their conventional counterparts is often uninvolved or even ignored.

To examine the toughening and strengthening mechanism of plasma-sprayed nanostructured YPSZ coatings, two different types of powder feedstocks were used: a conventional micron particle size powder and a reconstituted nanostructured powder. The phases and microstructures of YPSZ coatings before and after wear tests against 100C6 steel under dry friction conditions were investigated.

2. Experimental

2.1 Coating Preparation

Two commercially available YPSZ powders were used to deposit coatings by atmospheric plasma spraying with a F4-MB plasma torch (Sulzer Metco AG, Winterthur, Switzerland) onto medium carbon steel. The nanostructured powder (ZrO_2-7 wt.%Y_2O_3) was Nanox S4007 (Inframat Corp., Farmington, CT). This powder consisted of agglomerated particles 15 to 150 μm in diameter with a grain size of approximately 200 nm. The conventional powder was Metco 204NS (ZrO_2-8wt.%Y_2O_3) with a particle size of 11 to 106 μm. Figure 1 illustrates the scanning electron microscope (SEM) micrographs of the two kinds

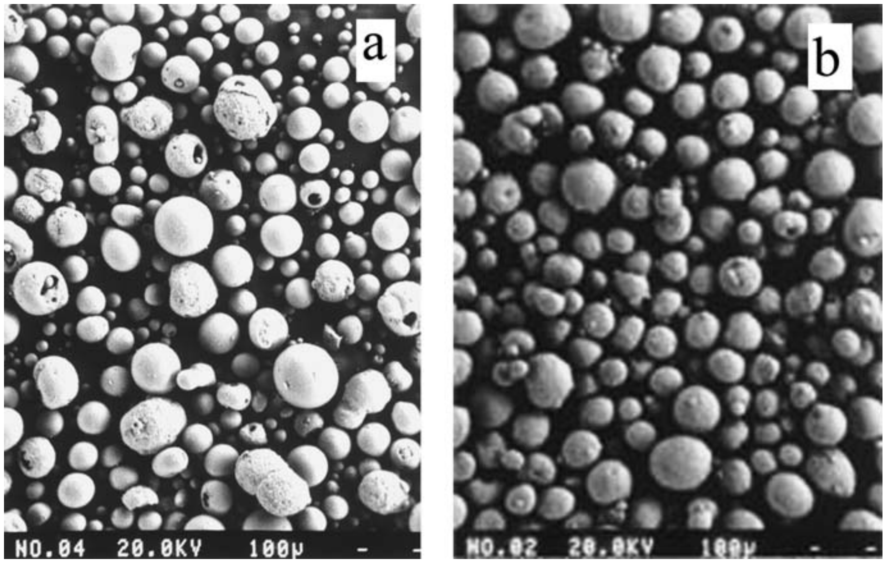

Fig. 1 The morphologies of the (a) as-received Metco 204NS and (b) Nanox S4007 powders

of YPSZ powders. In addition, NiAl (Amdry 956, Sulzer Metco) was used as a bond coating prior to the spraying of YPSZ coatings. The thickness of the bond coating was about 60 μm, and it was about 400 to 500 μm for the top coating. The substrates, Φ 65 × 5 mm medium carbon steel discs and 70 × 20 × 1.5 mm stainless steel plates, were grit-blasted with alumina just before spraying. The spraying parameters are listed in Table 1. A uniform design experiment (Ref 21) was used to optimize the spraying parameters according to the microhardness.

2.2 Coating Characterization

Phase identification of powders and coatings was carried out by x-ray diffraction (XRD) using a D/max 2550V diffractometer (Rigaku, Tokyo, Japan) with Cu-Kα (λ = 0.15418 nm) radiation. The phase composition of worn (after wear test) coatings at worn surface was examined within an irradiated area of 3 × 4 mm.

The microstructure of the YPSZ coating was analyzed with a Nikon optical microscope (OM, Nikon, Tokyo, Japan) and an EPMA-8705QH electron probe microanalyzer (Shimadzu, Tokyo, Japan). Vickers and Knoop microhardness measurements were performed at a 2.942 N load for 15 s on the polished cross section of coatings using a Leitz RZD-DO hardness tester (Leitz, Wetzlar, Germany). For the cross sections, the indentations were applied near the centerline of the coating thickness. The distance between the indentations was 0.5 mm. The reported values of microhardness for the coatings are the means of 20 indentations. The Knoop indenter, with the major diagonal perpendicular to the substrate, was used to determine the calculated Young's modulus E (in GPa) as shown in Eq 1 (Ref 22):

$$E = \frac{(-\alpha H_K)}{\left(\frac{b'}{a'} - \frac{b}{a}\right)} \qquad \text{(Eq 1)}$$

where H_K denotes the Knoop microhardness (Pa), b'/a' denotes the ratio of the short (b') and long (a') indention diagonals after elastic recovery; b/a is the ratio of the known Knoop indenter geometry (1/7.11), and α is a constant having a value of 0.45.

Table 1 The spraying parameters used for zirconia coatings

Parameters	Conventional coating	Nanostructured coating
Current, A	620	620
Voltage, V	66	69
Ar gas flow, slpm	30	35
H_2 gas flow, slpm	13	12
Carrier gas flow, slpm	3.4	3.5
Powder feed rate, g/min	46	26.4
Spray distance, mm	90	120

2.3 Tribologic Tests

Friction and wear tests were conducted on a ball-on-disc arrangement of a tribometer (CSEM, Rue Jaquet-Droz 1, Switzerland). The 100C6 steel balls were 6 mm in diameter. Prior to the tests, the coatings were ground using grit SiC papers and then polished using diamond slurries down to an average surface roughness of 0.1 to 0.4 μm.

The wear tests were performed under the following conditions: room temperature; air environment; applied load of 5 N; and sliding velocity of 1.08 m/s. The friction force was directly measured with a sensor, which was connected to a computer, and the data were collected at a frequency of 12 values per minute. The coefficients of friction were acquired from the values for the friction force divided by applied loads. Wear rates were calculated using the mean measurement value of two samples in terms of the volume of material removed (mm^3) per unit load (N) and the distance of sliding against the 100C6 steel (m). The cross-sectional area of the worn tracks was measured using a Hommel T8000 surface roughness tester (Hommel, Villingen-Schwenninger, Germany) and then was multiplied by the length (perimeter) of the worn tracks to give the total worn volumes.

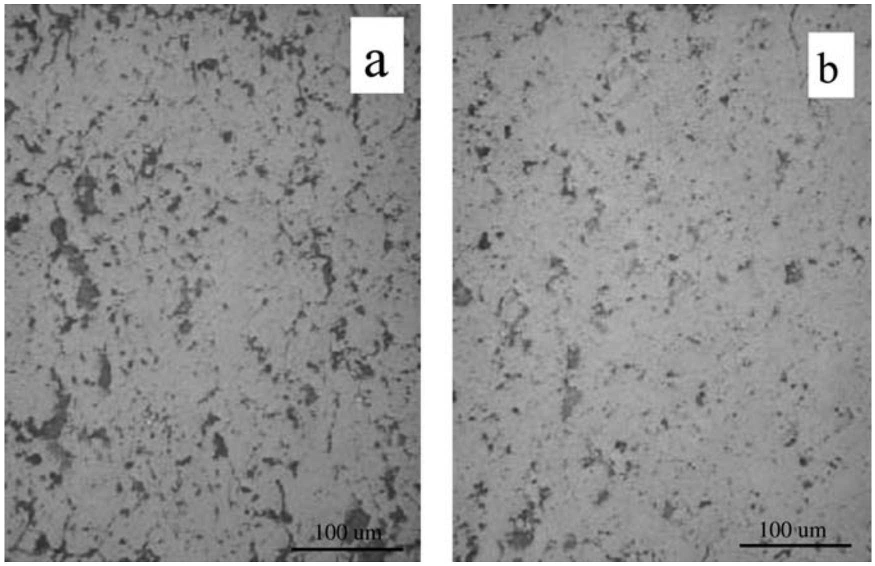

Fig. 2 The optical microscope micrographs of the cross sections of (a) the conventional YPSZ coating and (b) the nanostructured YPSZ coating (the direction of spraying is horizontal)

3. Results and Discussion

3.1 Coating Characterization

Figure 2 shows the cross-sectional OM micrographs of nanostructured and traditional YPSZ coatings. The nanostructured coating exhibits fewer pores and interlamellar and intralamellar cracks.

Table 2 summarizes the mechanical properties of the coatings investigated. There is no obvious difference in microhardness between these two coatings. However, the s.d. of microhardness for the nanostructured coating is less than that of the conventional coating, which implies that the microstructure of nanostructured coatings is more homogenous than that of conventional coatings. As expected, the elastic modulus of nanostructured coatings is higher than that of conventional coatings.

Figure 3 shows XRD patterns of the as-received powders and as-sprayed coatings. Besides the tetragonal and cubic phases, there is some monoclinic phase in the Metco 204NS powder. But, it is undetectable in the nanostructured powder. Plasma spraying often results in the formation of metastable phases in the deposits (Ref 4). It has been proved that the metastable composition is a mixture of the tetragonal and cubic phases rather than only the tetragonal phase (Ref 23, 24). Both of the as-sprayed coatings are composed of tetragonal and cubic phases, without any traces of the monoclinic phase.

3.2 Friction and Wear

The coefficient of friction for coatings against 100C6 steel balls at room temperature are shown in Fig. 4. No obvious difference can be found for both coatings deposited with the nanostuctured powder and conventional powder.

The wear rate of the coating sprayed with the conventional powder is 4.49×10^{-6} mm^3/N/m. While the wear rate of the nanostructured coating is 3.56×10^{-6} mm^3/N/m. It follows that nanostructured coatings have great potential to provide substantial improvement in wear resistance over their conventional counterparts (Ref 13, 20).

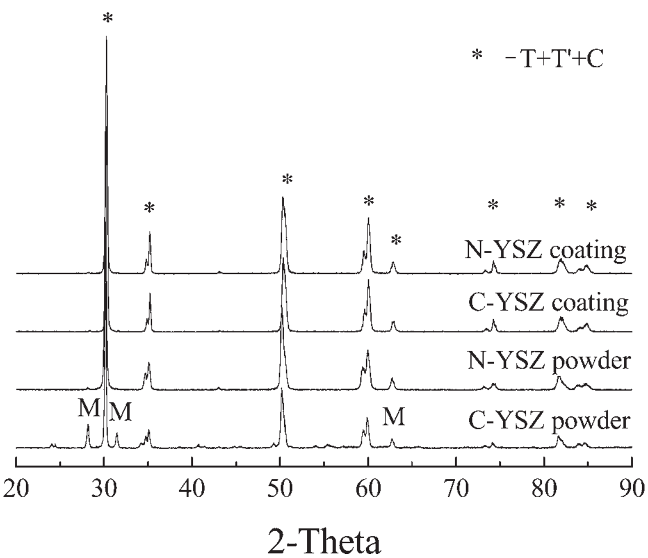

Fig. 3 The XRD patterns of the as-received powders and the as-sprayed coatings. The as-received powders are C-YSZ and N-YSZ powders. The as-sprayed coatings are C-YSZ and N-YSZ coatings

Table 2 The mechanical properties of the as-sprayed YPSZ coatings

Coating	H_{v300}, GPa	E, GPa
Conventional	7.4 ± 1.8	92.9 ± 31.1
Nanostructured	7.4 ± 1.1	113.5 ± 47.6

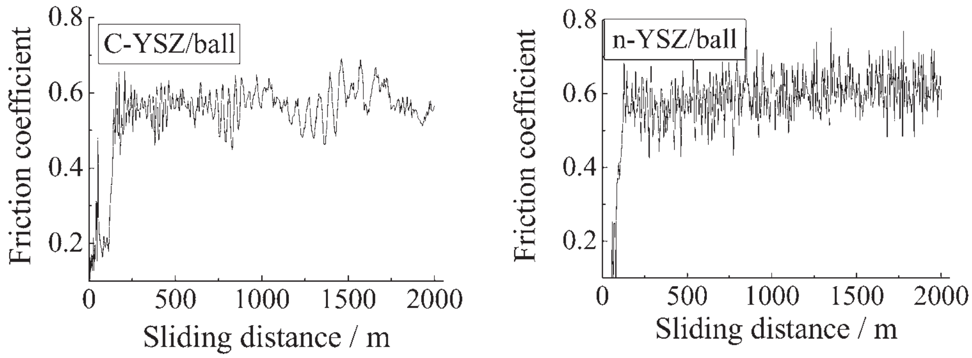

Fig. 4 Comparison of the friction coefficients of the two frictional pairs

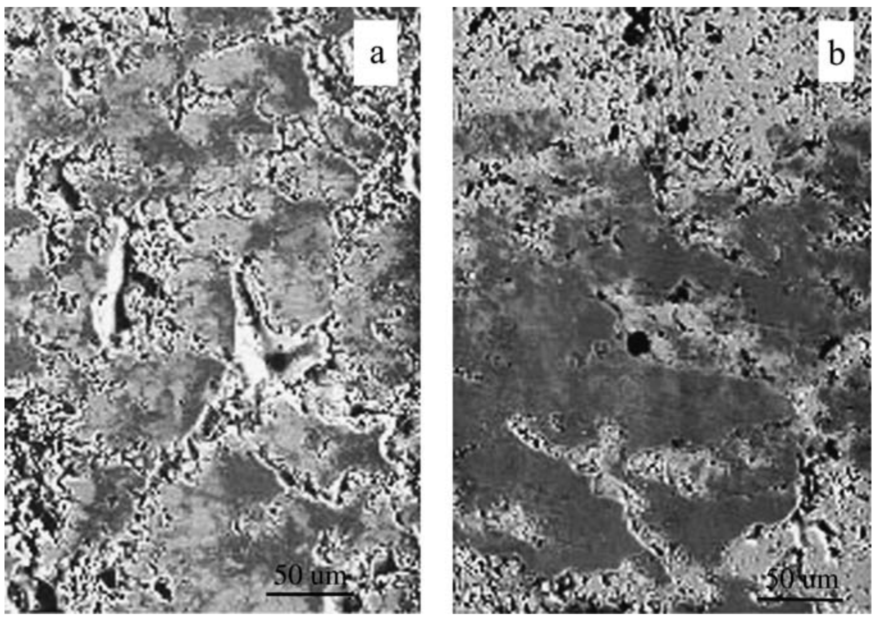

Fig. 5 The SEM micrographs of the worn surfaces of (a) conventional coatings and (b) nanostructured coatings

Many studies have suggested that a high degree of hardness is desirable for both brittle and ductile materials, while the brittle material has the benefit of its high degree of toughness (Ref 25, 26). That is to say, the wear resistance of brittle materials such as YPSZ coatings can be effectively improved by promoting their toughness rather than their hardness. This will be discussed later.

3.3 Worn Surface Morphology

Figure 5 shows the worn surface morphologies of the YPSZ coatings. There is an obvious difference between the coatings sprayed with the conventional powder and the nanostructured powder. The worn track on the conventional material coating is rough. Some grooves, plastic deformation, and intergranular microfracture features can be found on the worn surface of the conventional coating, as is shown in Fig. 5(a). However, the nanostructured coating is smooth without obvious grooves and microfracture features, despite the microcracks and plastic deformation, as shown in Fig. 5(b).

There is a brown transferred film observed during the wear test, which is made of the wear debris and consists of Fe_2O_3. This transferred film appears to act as a lubricating layer and to play an important role in these two frictional pairs. In the case of the nanostructured coatings, the film is more integrated and seems more effective in reducing the friction and wear than in the conventional coatings, as is shown in Fig. 5.

3.4 X-Ray Diffraction Results before and after Wear Tests

Figure 6 shows the XRD patterns of the as-sprayed, polished, and worn coatings. It can be found that both of the as-sprayed coatings are composed of tetragonal and cubic phases, while the polished coatings are composed not only of tetragonal and cubic phases, but also contain some monoclinic phase. In the case of worn surfaces, the peak of the monoclinic phase disappeared. The phase transformation in YPSZ ceramics is an essential research and development issue for the application of TBCs. It is generally recognized that there is a so-called nontransformable tetragonal phase (T′) in the as-sprayed state, and a stress-induced martensitic phase transformation will not take place in the T′ phase (Ref 24). This implies that the M phase occurring in the ground and polished surface is transformed from the T phase, and the T phase disperses in a phase transformation zone with a considerable volume. Hence, the YPSZ coating in this area consisted wholly of the nontransformable T′ phase, M phase, and some C phase. The transformed zone along the worn track was then thinned during the friction and wear tests. The amount of M phase decreased. The peak of the M phase disappeared in the XRD pattern of the worn surface, indicating that the depth of the phase transformation zone is less than that of the worn track (i.e., less than 500 to 700 nm), which was tested by a surface roughness tester. The friction and wear under the applied load of 5 N are not high enough to induce further deeper phase transformation.

3.5 Effect of Grain Size and Phase Composition on Wear Resistance

Nanostructured grain could be retained in as-sprayed YSZ coatings by using reconstituted nanostructured powder feedstock (Ref 11). It is generally recognized that the wear of polycrystalline ceramics varies significantly with mean grain size, with the wear rate increasing rapidly with increasing grain size (Ref 27, 28). The fine grain causes not only decreases in defect size (including microcracks and pores in the materials) but also defect size distribution narrowing, as is shown in Fig. 2. External stress such as thermal and friction usually causes cracks to propagate along grain boundaries. These cracks propagated in nanostructured coatings are just like zigzags. The larger the boundary volume, the more the cracks can propagate, and the more energy can be absorbed. Therefore, the finer the grain size, the greater the wear resistance that the materials might offer. It follows that the semimolten nanostructured particles embedded in the coating microstructure arrest crack propagation, causing an increased crack growth resistance and enhanced wear resistance (Ref 29).

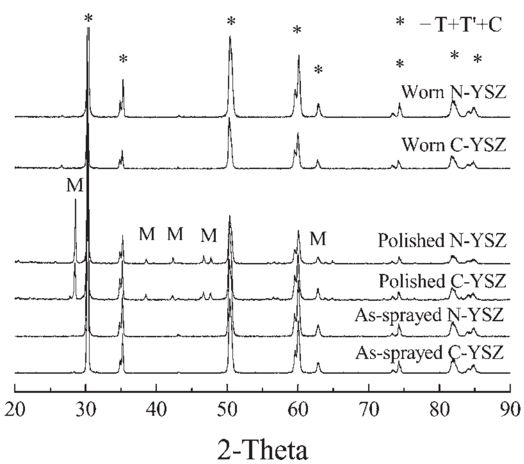

Fig. 6 The XRD patterns of the two coatings before and after wear tests

Toughening and strengthening have been extensively studied in bulk ceramic materials, especially in yttria-stabilized zirconia ceramics (Ref 1). It is recognized that the stress-induced martensitic phase transformation (T → M) is important for structural applications because it is the basis for phase transformation toughening (Ref 30). As shown in Fig. 6, a T → M phase transformation occurred on the ground and polished surfaces of both nanostructured and conventional coatings. This indicates that the stress of grinding and polishing induced the transformation. Owing to the coarse grain and those submillimeter cracks in the conventional coating, as shown in Fig. 7, the progressive growth of multiple cracks link up to cause microfractures and grain pull-out, while in the case of the nanostructured coating more friction heat was absorbed accompanied by phase transformation and crack propagating during friction, with the coating exhibiting a greater wear resistance.

4. Conclusions

The plasma-sprayed nanostructured YPSZ coating exhibits a better wear resistance than its conventional counterpart. The

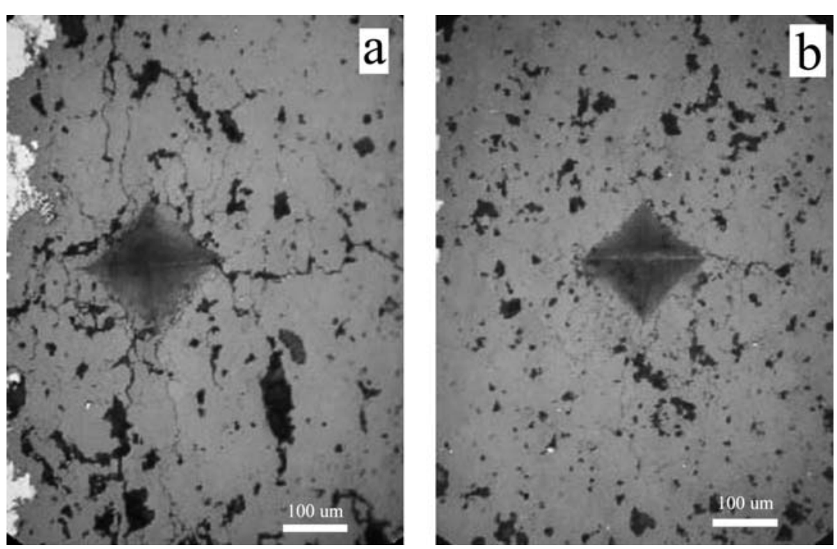

Fig. 7 Microcracking propagation from the Vickers indentation in (a) the conventional coating and (b) the nanostructured coating

wear rates of nanostructured coatings are about four-fifths of those of their conventional counterparts under a load of 5 N. The improved wear resistance of nanostructured coatings is attributed to the mechanisms of microcrack toughening and phase transformation toughening. The finer grain size and the phase composition of the nanostructured coating not only optimize the microstructure but also enhance the mechanical properties of the coating.

The XRD data indicate that the depth of the phase transformation zone caused by grinding and polishing is less than that of the worn track (i.e., less than 500-700 nm). The stresses occurring during friction and wear under the applied load of 5 N are not high enough to induce a further, deeper phase transformation.

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