JTTEE5 12:523-529

Peer Reviewed

Transmission Electron Microscopy Observation of Microstructure of Plasma-Sprayed Nanostructured Zirconia Coating

Huang Chen and Chuanxian Ding

(Submitted 16 April 2002; in revised form 31 August 2002)

Nanostructured zirconia coatings deposited by plasma spraying technique were observed using transmission electron microscopy (TEM). It was found that the as-sprayed nanostructured zirconia coating had bimodal microstructures in terms of grain size distribution in the direction parallel to substrate surface. One was in the range 30-120 nm, which was the dominative structure of the coating, and the other was about 150-400 nm. The cross-section micrograph of the plasma sprayed nanostructured zirconia coating revealed that the coating still exhibited lamellar structure with columnar grains extending through its thickness. In conjunction with partially molten zirconia grains, amorphous regions were found. Domain structure and superlattice structure were observed in the plasma-sprayed nanostructured zirconia coating. The formations of the domain and superlattice structures are discussed in this paper.

Keywords microstructure, plasma spraying, TEM, zirconia coating

1. Introduction

Zirconia-based coatings partially stabilized with yttria (Y_2O_3) are commonly used for thermal protection and anticorrosion of hot section components due to their low thermal conductivity and high coefficient of thermal expansion as well as their good mechanical properties.[1-4] Recently, the preparation of nanostructured zirconia coating using thermal spraying technique has attracted great attention. Some information on the plasma-sprayed nanostructured zirconia coatings has been reported.[5-9] However, few reports on detailed microstructures of the plasma-sprayed nanostructured zirconia coating have been published. The object of this research was to examine the microstructures and defects presenting in the nanostructured zirconia coating deposited by plasma spraying technique using transmission electron microscopy (TEM).

2. Experimental Procedures

Nanostructured zirconia coatings were deposited on stainless steel substrates by the plasma-spraying technique. The particle sizes of partially stabilized zirconia nano-powders, which are composed of tetragonal phase zirconia with small amount of monoclinic zirconia, are in the range of 70-110 nm, as shown in Fig. 1. To improve the flowability of the nano-powders in plasma spraying, the nano-powders were reconstituted into spherical and near-spherical micrometer-sized granules by the

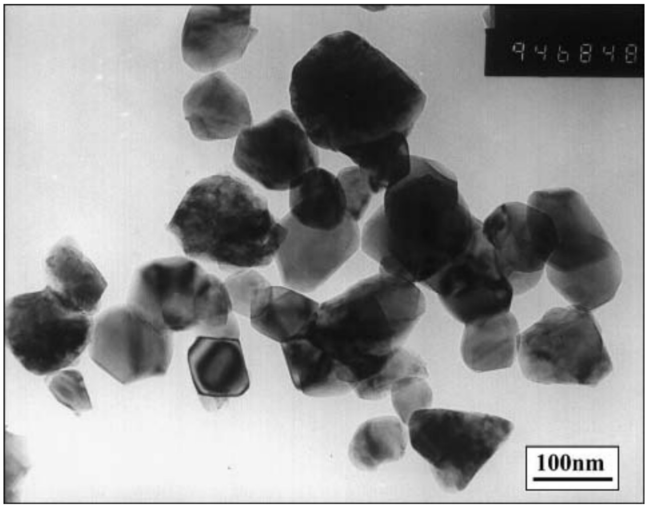

Fig. 1 Micrograph of the starting nano-zirconia powders

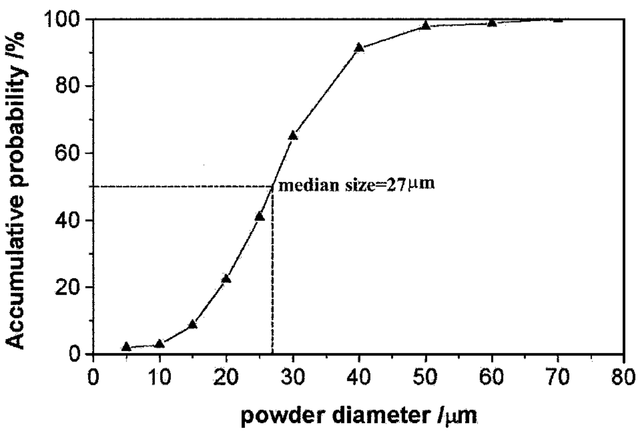

Fig. 2 Particle distribution of the spray-dried powders

Huang Chen and **Chuanxian Ding,** Plasma Spray Laboratory, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, 200050, People's Republic of China. Contact e-mail: jx_chuang@yahoo.com.

spray-drying process before plasma spraying in this experiment. The size distribution of the spray-dried powders was measured by natural depositing method (Fig. 2). As indicated in Fig. 2, the spray-dried powders distribute mainly in the range of 15-40 μm and their median size is about 27 μm. The Metco A-2000 atmospheric plasma spraying equipment with F4-MB plasma gun (Sulzer Metco AG, Wohlen, Switzerland) was selected to deposit the nanostructured zirconia coatings. The spray parameters are tabulated in Table 1. Prior to spraying, the substrates were degreased ultrasonically in acetone and blasted with alumina grit to improve bonding strength.

Table 1 Plasma Spraying Parameters

Parameters	Values
Current, A	620
Voltage, V	72
Ar, slpm	42
H_2, slpm	12
Carrier gas, slpm	3.5
Powder feed rate, g min^{-1}	19
Spraying distance, mm	120

A RAX-10 x-ray diffractometer (Rigaku, Tokyo, Japan) operating with Cu K_α (λ = 1.54056 Å) radiation was used to identify phase composition of the nanostructured zirconia coating.

Thin foil samples of the zirconia coating were prepared for TEM observation. A coating sample with thickness of about 600 μm was attached to a tripod polisher with glue and polished from both side until the thickness of the coating became approximately 30 μm. The specimen was further reduced with a low-angle ion thinning precise ion polishing system (PIPS). The microstructures of the as-sprayed zirconia coatings were examined with a JEM-200CX TEM (Jeol, Tokyo, Japan) at an accelerating voltage of 200 KV.

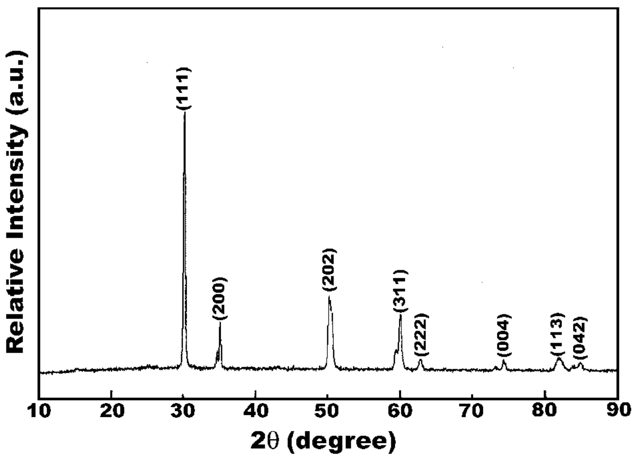

Fig. 3 XRD spectrum of plasma-sprayed zirconia coating

3. Results and Discussion

Figure 3 shows the x-ray diffraction (XRD) pattern of the as-sprayed zirconia coating. From Fig. 3, it can be found that the plasma sprayed zirconia coating is composed of tetragonal phase zirconia. Due to the existing of yttria (Y_2O_3) and high heating/cooling rate of plasma spraying process, the tetragonal phase was retained in the as-sprayed zirconia coating at room temperature.[6,10]

The most frequently observed structures of the plasma-sprayed zirconia coatings are fine crystalline zirconia grains as shown in Fig. 4. It was found that the size distribution of the plasma sprayed nanostructured zirconia coating is heteroge-

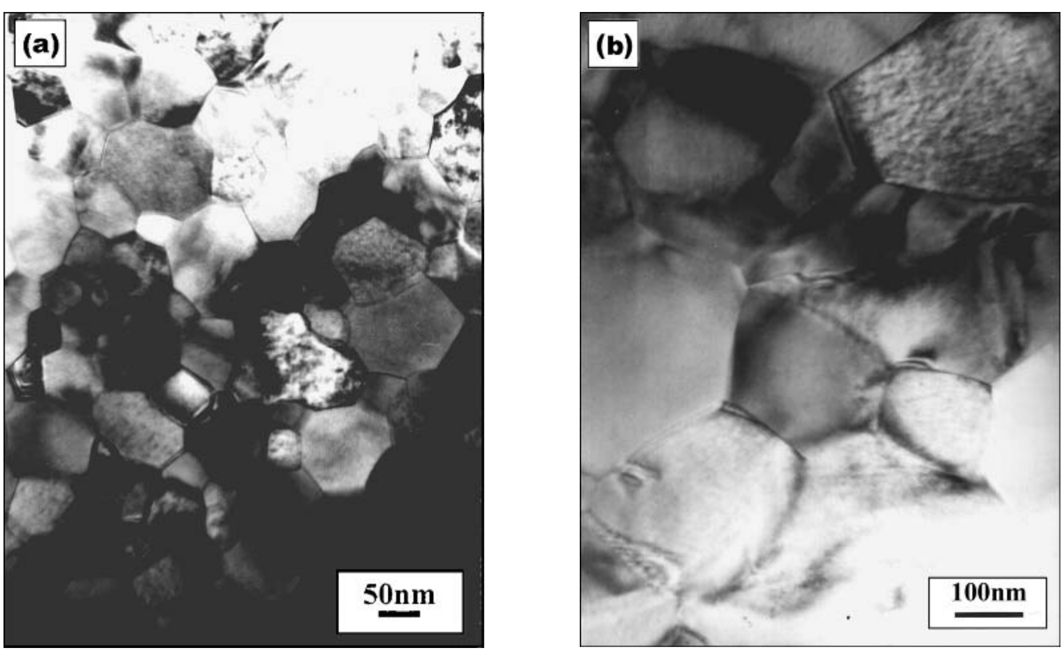

Fig. 4 TEM morphologies of nanostructured zirconia coating

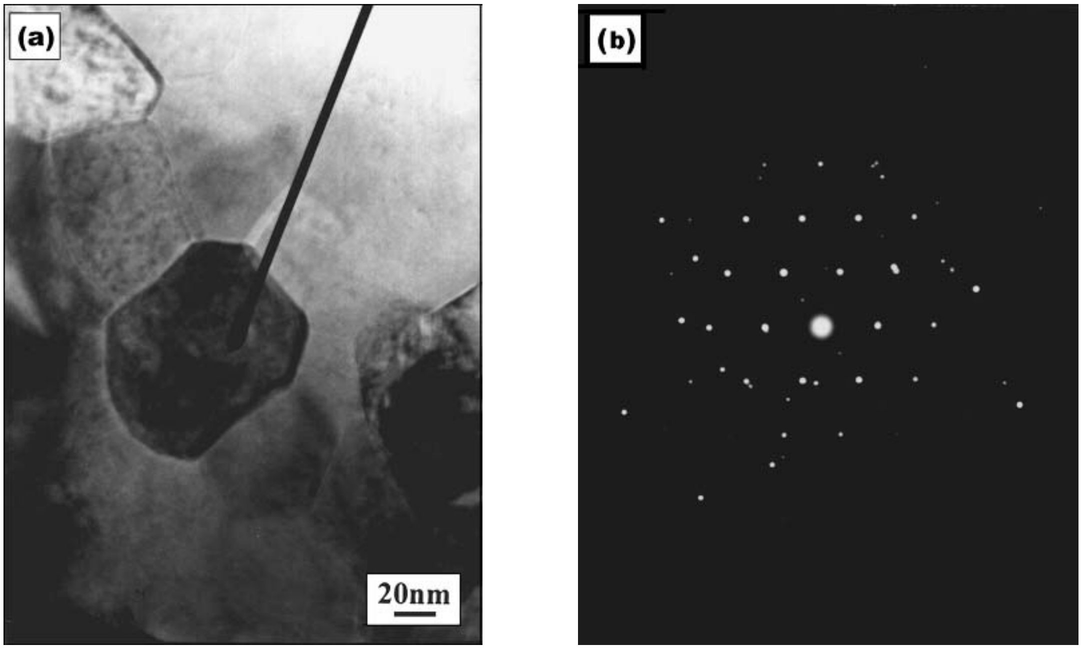

Fig. 5 TEM micrograph of **(a)** zirconia grain and **(b)** corresponding SAD pattern

neous. It had bimodal microstructures in terms of grain size distribution in the direction parallel to substrate surface. One is nanometer grain distributed in range of 30-120 nm (Fig. 4a), which is the dominative structure of the zirconia coating. This structure of Fig. 4(a) is more than 80% as volume fraction as concerned in the as-sprayed nanostructured zirconia coatings. The other is coarser grain with size in the range of 150-400 nm, as shown in Fig. 4(b). The sizes are much bigger than those of primary grains of feedstock, as shown in Fig. 1. This indicates that quick growth happened at some grains during the plasma spraying. Plasma spraying process has high heating and cooling rates. The zirconia grains did not have enough time to grow, so most of the zirconia grain sizes stayed in the nanoscale range. However, it was also noted that some grains grew unavoidably up over 100 nm in the as-sprayed coatings, which is due to their different thermal history during plasma spraying. It is believed that temperature differences of several hundred degrees may exist in the gas flow field.[11,12] The long spraying time is another possible reason for the growth of grain. Tetragonal phase zirconia is the primary phase of the as-sprayed zirconia coating providing proof of the analysis of selected-area diffraction (SAD), as shown in Fig. 5, which corresponds with the result of XRD analysis (Fig. 3).

Figure 6 shows the TEM micrograph standing for the cross section of the plasma-sprayed nanostructured zirconia coating. The micrograph revealed that the zirconia coating still exhibited lamellar structure orientated approximately parallel to the substrate surface.[13,14] The lamellae were typically 0.3-0.6 μm thick with columnar grains extending through its thickness. The microstructure of the lamellae is believed to be determined by the rate and direction of greatest heat removal from the deposited materials and its mode of crystallization.[15] The diameters of the columnar grains were ranging from 60-80 nm and their lengths were in the range of 150-350 nm as shown in Fig. 6. These columnar grains were nucleated firstly on the impact interface and

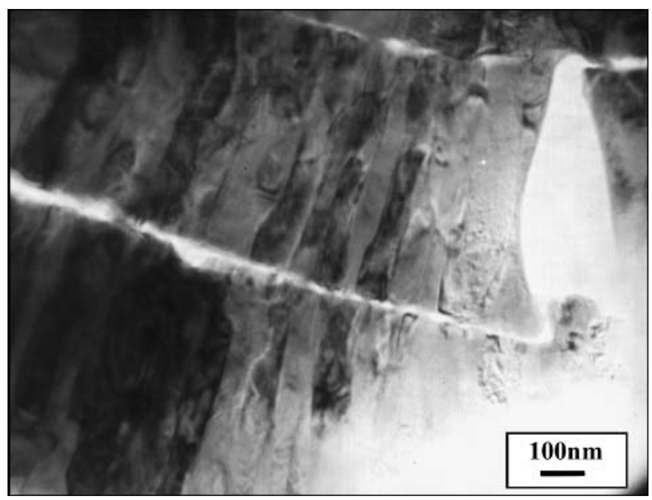

Fig. 6 TEM micrograph showing columnar grain structure of zirconia

grown through the molten splat to the opposite interface.[14,16] The temperature gradient existing in the gas flow also causes the columnar grain growth throughout the thickness of the splat.[11-13]

The lamellar interface in somewhere was found to be discontinuous, resulting in cracks and interlamellar porosity that are about 10-30 nm in width, as shown in Fig. 6. These cracks and interlamellar porosity were believed to arise due to differential thermal contraction rates of two neighboring splats.[14] However, due to the good melting of nanostructured zirconia feedstock in the plasma jet, the splats underwent strong spreading and flattening when they impacted on substrate and previously deposited coating. Hence, the single splat is thinner than traditional plasma-sprayed zirconia coating and the interfaces be-

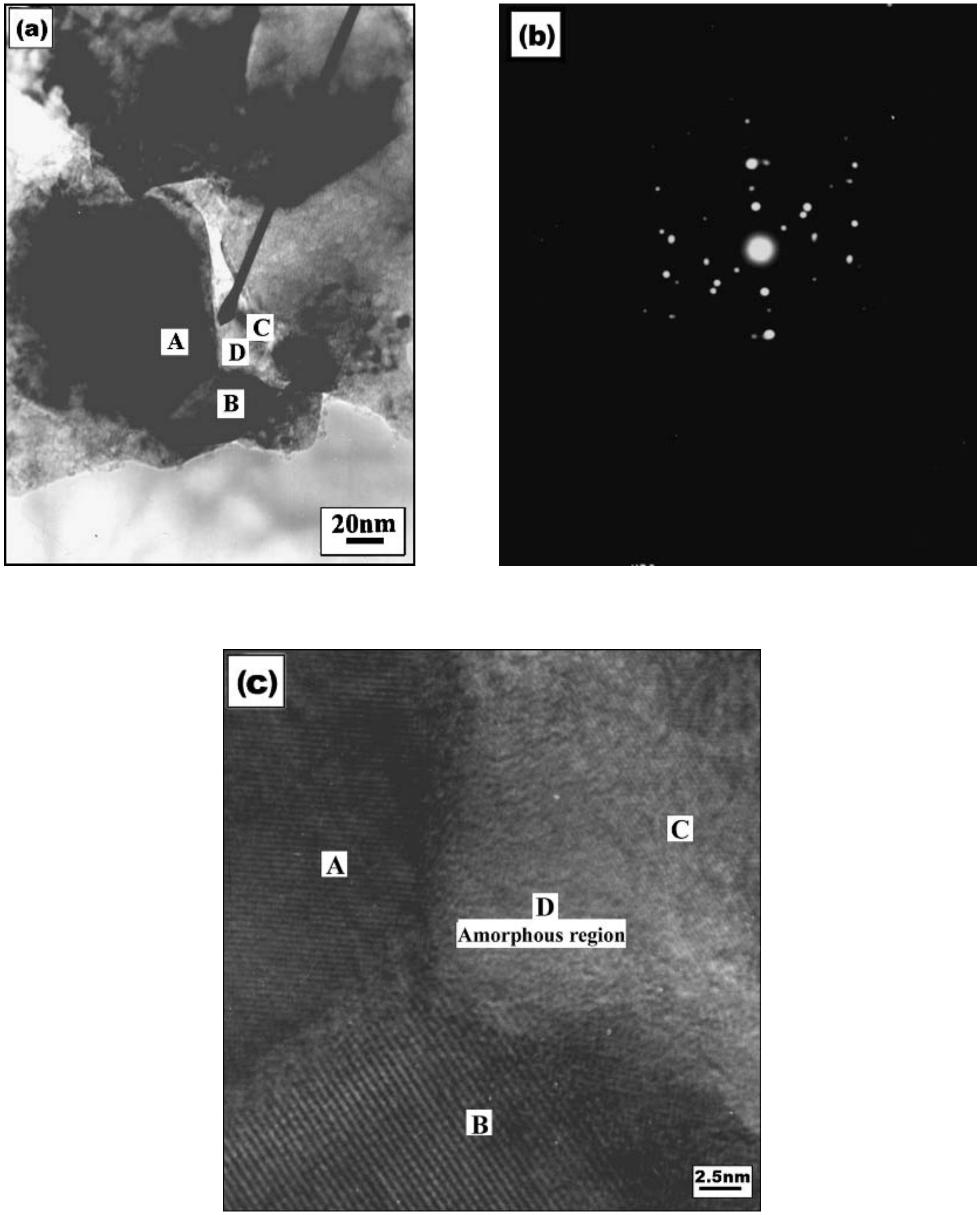

Fig. 7 **(a)** TEM micrographs of nanostructured zirconia coating: morphologies; **(b)** SAD pattern of the amorphous region, and **(c)** corresponding HRTEM image of the interface between crystalline zirconia and amorphous region

tween two splats are narrowed. As a result, more points of contact or anchors between splats were created which will be beneficial to increase the cohesion of coating.[7]

In general, the zirconia grains were piled tightly in the as-sprayed nanostructured zirconia coating, as can be seen from Fig. 4. However, in conjunction with partially molten zirconia grains, amorphous regions were observed as shown in Fig. 7. Due to the thickness of amorphous regions is about 10 nm, which is less than the diameter of diaphragm of the transmission electron microscopy, its diffuse rings do not appear in the pattern of SAD shown in Fig. 7(b). Further evidence of the amorphous phase was provided by high-resolution TEM examination. Figure 7(c) is a lattice image taken from the small area indicated by the needle in Fig. 7(a). The ordered and disordered structure regions represented crystalline zirconia (A, B, C) and amorphous region (D), respectively. C is a fine nano-grain

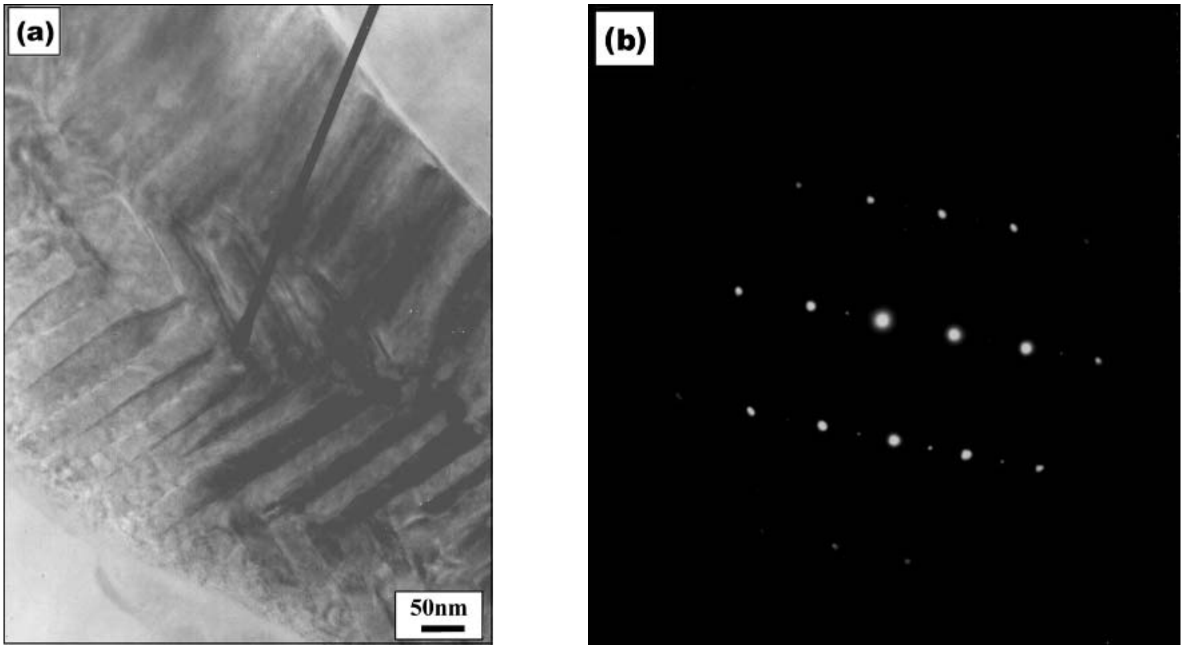

Fig. 8 **(a)** Domain structure of as-sprayed nanostructured zirconia coating; **(b)** SAD pattern [011] reveals it is composed of monoclinic zirconia phase

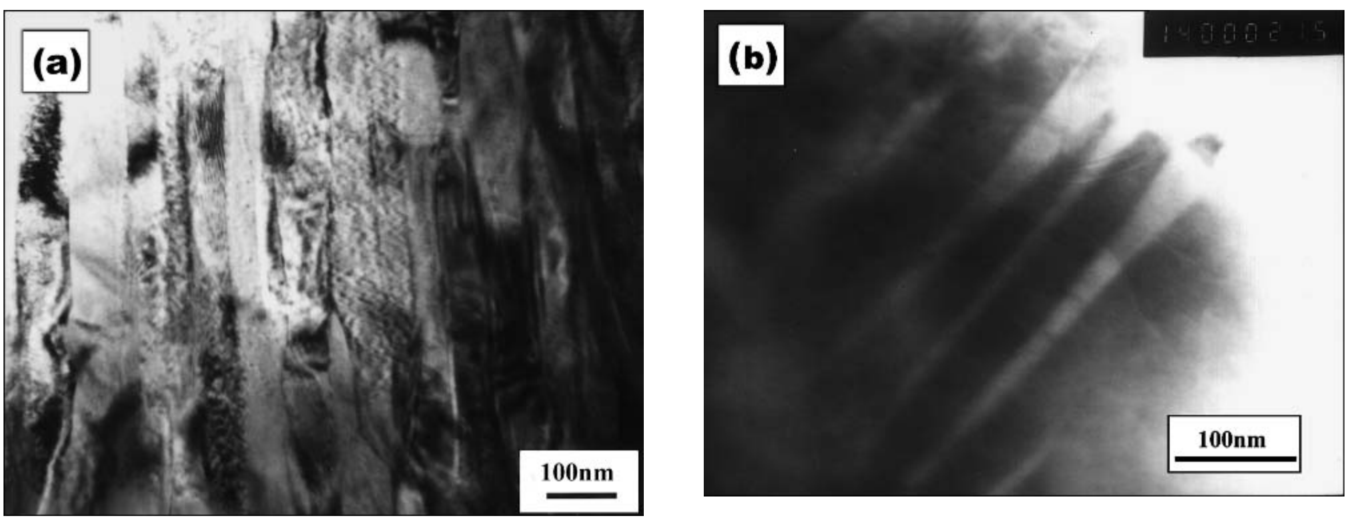

Fig. 9 Twin-related plate of nanostructured zirconia coating

(about 10 nm) crystallizing from the amorphous region. It is attributed to the high heating/cooling rate of plasma spraying process; there is little time for the crystalline zirconia to grow. The amorphous region is believed to contribute to the cohesion strength of the plasma-sprayed coatings.[14]

Two kinds of interesting structures were found in the plasma-sprayed nanostructured zirconia coating. One is domain structure shown in Fig. 8 and 9. The change of grain shape and embossment effect occurred on the surface of grains. This structure was once reported in bulk zirconia ceramics.[17-22] However, it has not been reported in plasma-sprayed nanostructured zirconia coating. This kind of domain structure is believed to be the results of martensitic transformation from tetragonal to monoclinic, which led atomic or ion moving in phase as a whole.[17,21]

A plate of martensite was formed firstly at the defects of grains by means of heterogeneous nucleation, and then grew up quickly in vertical. The growing orientations changed when the tip of the plate met grain boundaries or other inner defects. The "N" or "Z" shape monoclinic zirconia appeared in the coating, as shown in Fig. 8(a). The corresponding SAD pattern shown in Fig. 8(b) revealed that the domain structure was composed of monoclinic zirconia phase. It was reported that low content of stabilizer caused the nuclei to grow up to neighboring plate laterally and formed the lath martensite which were similar to the

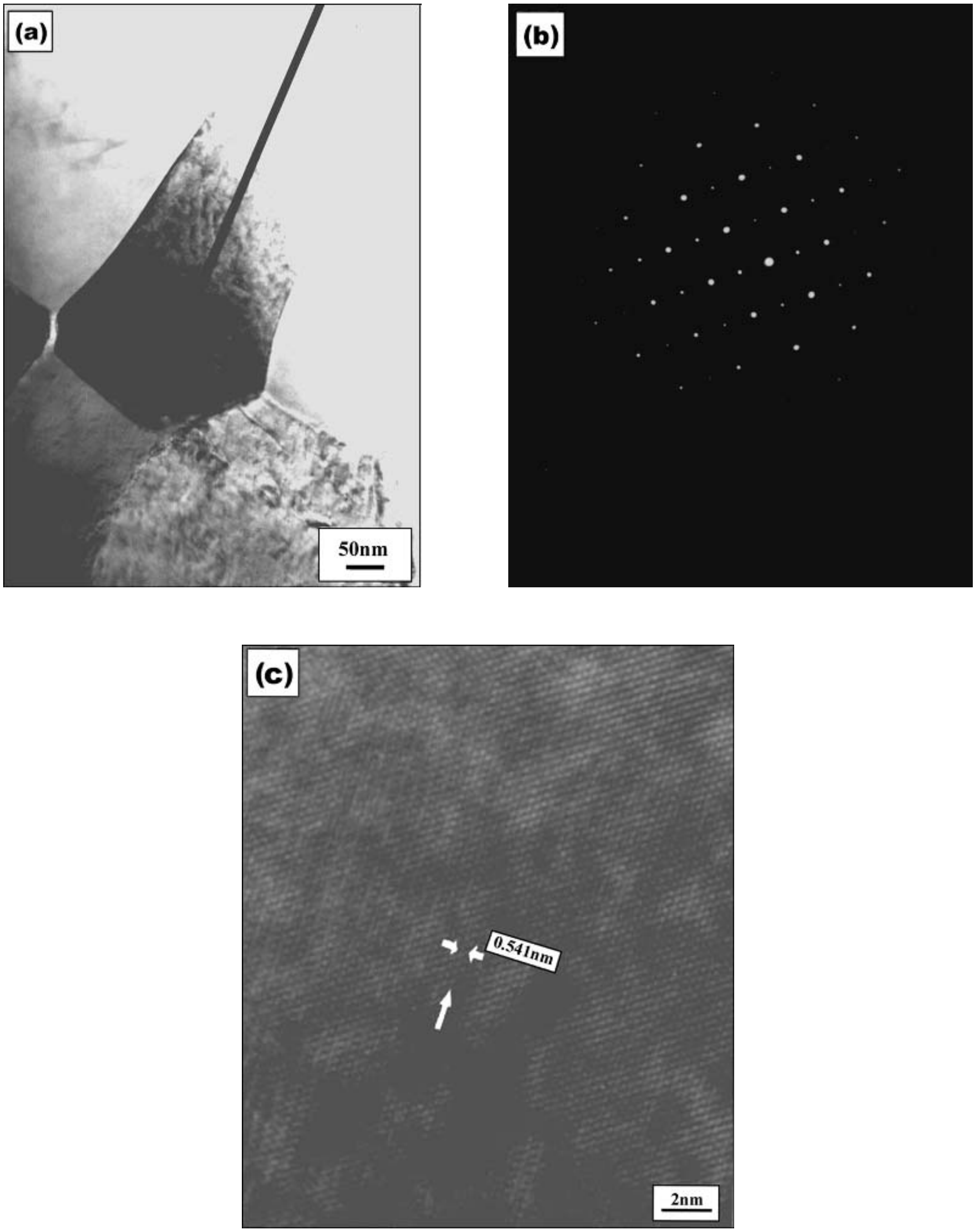

Fig. 10 **(a)** TEM micrograph; **(b)** [111] SAD pattern of tetragonal zirconia and **(c)** corresponding HRTEM image

parallel twin plates in zirconia bulk ceramics observed by Bansal and others.[17,18,21] The neighboring lath martensites have a parallel twin relationship as shown in Fig. 9. It was believed that twin-related plates were evidence of the lattice invariant shear associated with the martensite from tetragonal to monoclinic transformation.[21] This transformation may play an important role on the improvement of mechanical properties of coatings, such as strength and toughness.[19,20] The domain structures in nanoscale were formed because the time of cooling and solidifying of molten particles was very short during plasma spraying.

The other interesting structure is superlattice structure, which was obvious in the plasma-sprayed nanostructured zirconia coatings (Fig. 10). From the SAD pattern and the high-resolution TEM image of the [111] zone of tetragonal zirconia, it was found that except for the normal diffractive spots, another set of diffractive spots was appeared in the SAD pattern of tetragonal zirconia grain (Fig. 10b). From Fig. 10(c), it can be seen that a superlattice plane appeared between two crystal plans of (110) direction, as indicated with an arrow. Superlattice structure is a derivative structure,[23] which was caused by the strong perturbation of the plasma spraying. The derivative structure has larger unit cell than that of the base structure. It is calculated that the interplanar distance of superlattice structure in $(1\bar{1}0)$ direction of the grain is 0.541 nm, which is about twice of the normal structure grains. Usually, zirconia grains in range of 80-120 nm had superlattice structure in the plasma-sprayed nanostructured zirconia coating.

4. Conclusions

Plasma-sprayed nanostructured zirconia coating was observed by transmission electron microscopy. It was found that the nanostructured zirconia coating has bimodal microstructures in terms of grain size distribution in the direction parallel to substrate surface. One is in the range 30-120 nm, which is the dominative structure of the coating, and the other is 150-400 nm. The cross-section micrograph of the nanostructured zirconia coating revealed that the coating still exhibited lamellar structure with columnar grains extending through its thickness. Amorphous regions were found in conjunction with partially molten zirconia grains. The domain structure was also observed in the plasma-sprayed nanostructured zirconia coating, which is explained in terms of the phase transformation of martensite from tetragonal to monoclinic. In addition, superlattice structure appeared in the plasma-sprayed nanostructured zirconia coating.

Acknowledgments

The authors would like to thank Ms. Xiaming Zhou for kind cooperation in the preparation of the coating specimens and Ms. Meiling Ruan for the TEM observation.

References

1. R.A. Miller: "Oxidation-Based Model for Thermal Barrier Coating Life," *J. Am. Ceram. Soc.,* 1984, *67*(8), pp. 517-21.
2. R.B. Brandt, I. Paudowski, G. Neuer, and P. Facchais: "Specific Heat and Thermal Conductivity of Plasma Sprayed Yttria Stabilized Zirconia and NiAl, NiCr, NiCrAl, NiCrAlY, NiCoCrAlY Coatings," *High Temp-High Press.,* 1986, *18*(1), pp. 65-77.
3. M. Tamura, M. Takahashi, J. Lshii, K. Suzuki. M. Sato, and K. Shimomure: "Monoclinic Zirconia Distributions in Plasma-Sprayed Thermal Barrier Coatings," *J. Therm. Spray Technol.,* 1999, *8*(1), pp. 68-72.
4. T. Brzezinski, A. Carasin, S. Grenier, E. Kharlanova, G. Kim, and P. Tsantrizos: "Vacuum Plasma Sprayed ZrO_2-Based Thermal Barrier Coatings for Aerospace Applications" in *Thermal Spray: Meeting the Challenges of the 21st Century,* C.C. Berndt, ed., ASM International, Materials Park, OH, 1998, pp. 1645-52.
5. J. Karthikeyan, C.C. Berndt, J. Tikkanen, S. Reddy, and H. Herman: "Plasma Spray Synthesis of Nanomaterial Powders and Deposits," *Mater. Sci. Eng.,* 1997, *A238,* pp. 275-86.
6. H. Chen and C.X. Ding: "Nanostructured Zirconia Coating Prepared by Atmospheric Plasma Spraying," *Surf. Coat. Technol.,* 2002, *150,* pp. 31-36.
7. R.S. Lima, A. Kucuk, and C.C. Berndt: "Evaluation of Microhardness and Elastic Modulus of Thermally Sprayed Nanostructured Zirconia Coatings," *Surf. Coat. Technol.,* 2001, *135,* pp. 166-72.
8. R.S. Lima, A. Kucuk, and C. Berndt: "Bimodal Distribution of Mechanical Properties on Plasma Sprayed Nanostructured Partially Stabilized Zirconia," *Mater. Sci. Eng.,* 2002, *A327,* pp. 224-32.
9. Y. Zeng, S.W. Lee, L. Gao, and C.X. Ding: "Atmospheric Plasma Sprayed Coatings of Nanostructured Zirconia," *J. Eur. Ceram. Soc.,* 2002, *22,* pp. 347-51.
10. C.H. Perry and D.W. Kiu: "Phase Characterization of Partially Stabilized Zirconia by Raman Spectroscopy," *J. Am. Ceram. Soc.,* 1985, *68*(8), pp. C-184-87.
11. J.R. Fincke, D.C. Haggard, and W.D. Swank: "Particle Temperature Measurement in the Thermal Spray Process," *J. Therm. Spray Technol.,* 2001, *10*(2), pp. 255-66.
12. I. Ahmed and T.L. Bergman: "Thermal Modeling of Plasma Spray Deposition of Nanostructured Ceramics," *J. Therm. Spray Technol.,* 1999, *8*(2), pp. 315-22.
13. P. Bengtsson and T. Johannesson: "Characterization of Microstructural Defects in Plasma-Sprayed Thermal Barrier Coatings," *J. Therm. Spray Technol.,* 1995, *4*(3), pp. 245-51.
14. P.D. Harmsworth and R. Stevens: "Microstructure of Zirconia-Yttria Plasma-Sprayed Thermal Barrier Coatings," *J. Mater. Sci.,* 1992, *27,* pp. 616-24.
15. R. Mcpherson: "The Relationship Between the Mechanism of Formation, Microstructure, and Properties of Plasma Sprayed Coatings," *Thin Solid Film,* 1981, *81,* pp. 297-310.
16. R. Mcpherson: "On the Formation of Thermally Sprayed Alumina Coatings," *J. Mater. Sci.,* 1980, *15,* pp. 3141-49.
17. G.K. Bansal and A.H. Heuer: "On a Martensitic Phase Transformation in Zirconia (ZrO_2)-I Metallographic Evidence," *Acta Metall.,* 1972, *20,* pp. 1281-89.
18. V. Lanteri, R. Chaim, and A.H. Heuer: "On the Microstructures Resulting From the Diffusion Less Cubic-Tetragonal Transformation in ZrO_2-Y_2O_3 Alloys," *J. Am. Ceram. Soc.,* 1986, *69*(10), pp. C-258-61.
19. A.H. Heuer: "Transformation Toughening in ZrO_2-Containing Ceramics," *J. Am. Ceram. Soc.,* 1987, *70*(10), pp. 689-98.
20. M. Shibata-Yannagisawa, M. Kato, H. Seto, N. Ishizawa, N. Mizutani, and M. Kato: "Crystallographic Analysis of the Cubic-to-Tetragonal Phase Transformation in the ZrO_2-Y_2O_3 System," *J. Am. Ceram. Soc.,* 1987, *70*(7), pp. 503-09.
21. O.L. Ge, T.C. Lei, J.F. Mao, and Y. Zhou: "In Situ Transmission Electron Microscopy Observation of the Tetragonal-to-Monoclinic Phase Transformation of Zirconia in Al_2O_3-ZrO_2 (2mol%Y_2O_3) Composite," *J. Mater. Sci. Lett.,* 1993, *12,* pp. 819-22.
22. P.M. Kelly and C.J. Wauchope: "The Tetragonal to Monoclinic Martensitic Transformation in Zirconia," *Key Eng. Mater.,* 1998, *153-154,* pp. 97-124.
23. W.D. Kingery, H.K. Bowen, and D.R. Uhlmann: *Introduction to Ceramic,* 2nd ed., John Wiley & Sons, New York, 1976, p. 69.