JTTEE5 15:513-517
DOI: 10.1361/105996306X146901
1059-9630/$19.00 © ASM International

Peer Reviewed

Characterization of Microstructure of Nano-TiO_2 Coating Deposited by Vacuum Cold Spraying

S.-Q. Fan, G.-J. Yang, C.-J. Li, G.-J. Liu, C.-X. Li, and L.-Z. Zhang

(Submitted February 27, 2006; in revised form June 11, 2006)

Control of the microstructure of TiO_2 coatings through preparation methods significantly influences the coating performance. In this study, a vacuum cold-spray process, as a new coating technology, is used to deposit nanocrystalline TiO_2 coatings on conducting glass and stainless steel substrates. TiO_2 deposits were formed using two types of nanocrystalline TiO_2 powders with mean particle diameters of 200 and 25 nm. Coating microstructures were characterized by scanning electron microscopy and x-ray diffraction analysis. Results demonstrate that a thick nanocrystalline TiO_2 coating can be deposited by the vacuum cold-spray process. The coating was found to consist of particles stacked as agglomerates that build up to several hundred nanometers. The coating also presents a mesoporous microstructure that could be effective in such applications as photocatalytic degradation and dye-sensitized solar cells.

Keywords ceramic coating, mesoporous structure, nanocrystalline material, TiO_2, vacuum cold spray

1. Introduction

Titanium dioxide, a stable, nontoxic semiconducting material with excellent photocatalytic activity, has attracted much attention (Ref 1, 2) over the years. It has been widely used in photocatalytic degradation of harmful and toxic organic pollutants (Ref 3, 4), dye-sensitized solar cells (Ref 5, 6), solar water splitting (Ref 1), etc. TiO_2 coatings in the immobilized form are more desirable than TiO_2 powders. Moreover, a recent study showed that nanocrystalline TiO_2 coatings had better performance when used in the above-mentioned applications (Ref 7).

Several processing methods, including sputtering, sol-gel processes (Ref 8, 9), vapor deposition (Ref 10, 11), and thermal spraying (Ref 12, 13), have been developed to deposit nanocrystalline TiO_2 powders. In all of these processes, the coatings are deposited at a temperature from 300 up to 2000 °C (Ref 14). High temperatures during processing may change the microstructure of TiO_2, which makes it less effective in photoelectrochemical applications. Previous study revealed that cold spraying could deposit a nanostructured TiO_2 coating with excellent photocatalytic performance when agglomerated nano-TiO_2 powders are used (Ref 15). However, it was found that, under the conventional cold spraying process, the coating thickness was limited to ~10 μm when deposition was performed using an agglomerated nanopowder. A recent study revealed that submicrometer-sized solid ceramic particles can be deposited on a substrate directly in a reduced-pressure atmosphere (Ref 16). However, few reports were concerned with deposition of nanocrystalline ceramic coating using nanometer-sized particles. In the study described herein, a vacuum cold-spray (VCS) system was developed and used to deposit 25 nm diameter TiO_2 powders on the surface of conducting glass. The TiO_2 coatings deposited have potential use in solar water splitting electrodes and dye-sensitized solar cells. TiO_2 powder with a mean diameter of 200 nm was also used to deposit a coating on a stainless steel surface for comparison. Deposition characteristics and microstructure features of the deposited TiO_2 coatings were examined.

This article was originally published in *Building on 100 Years of Success, Proceedings of the 2006 International Thermal Spray Conference* (Seattle, WA), May 15-18, 2006, B.R. Marple, M.M. Hyland, Y.-Ch. Lau, R.S. Lima, and J. Voyer, Ed., ASM International, Materials Park, OH, 2006.

S.-Q. Fan, G.-J. Yang, C.-J. Li, G.-J. Liu, C.-X. Li, and **L.-Z. Zhang,** State Key Laboratory for Mechanical Behavior of Materials, School of Materials Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, P. R. China. Contact e-mail: licj@mail.xjtu.edu.cn.

2. Experimental Procedures

2.1 Materials

TiO_2 powders of 200 nm (ST-41, Ishihara, Japan) and 25 nm (P25, Degussa, Dusseldorf, Germany) in diameter were used as feedstocks in coating deposition. Powder ST-41 was composed of anatase crystalline structure, and powder P25 was a mixture of 75% anatase and 25% rutile. Figure 1 shows the morphologies of the two powders. Stainless steel and transparent indium tin oxide (ITO) conducting glass (STN-180, Nanbo, Shenzhen, China) were used as metallic and ceramic substrates, respectively, for coating deposition. ITO conducting glass was selected as a substrate for use of a nano-TiO_2 coating as the electrode in a dye-sensitized solar cell (Ref 17). The surface roughness, R_a, of ITO was <0.02 μm. On the other hand, stainless steel with a surface roughness of 0.03 μm was used as a typical metal substrate. Prior to spraying, the substrates were ultrasonically cleaned in acetone.

2.2 TiO_2 Coating Preparation

The TiO_2 coating was deposited using a VCS system developed in our laboratory (Fig. 2). The system consists of a vacuum

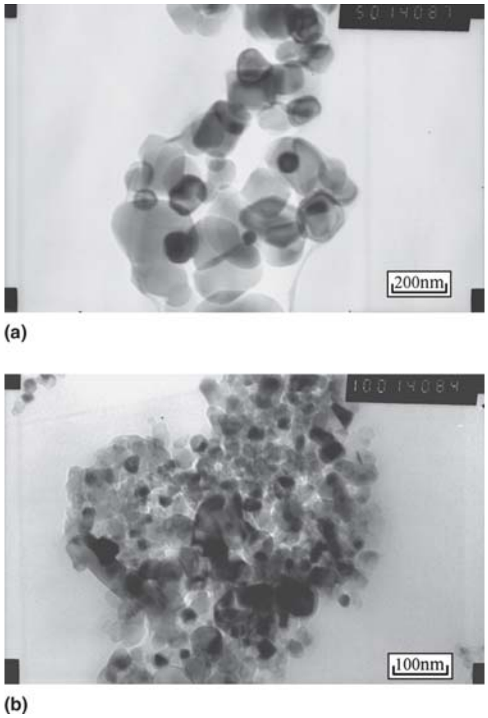

Fig. 1 Morphologies of TiO_2 powders used in the experiment: (a) ST-41 and (b) P25

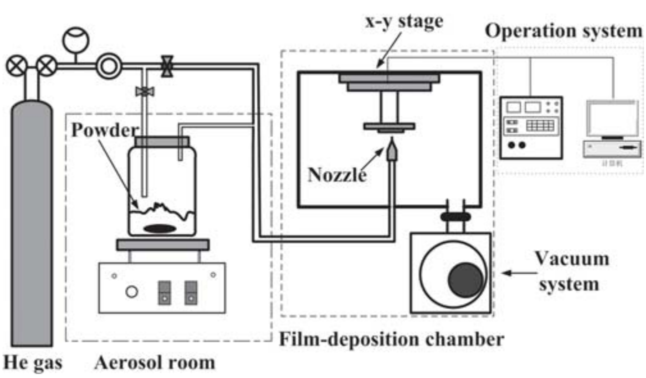

Fig. 2 Schematic diagram of the VCS system

chamber and a vacuum pump, an aerosol room, an accelerating gas feeding unit, a particle-accelerating nozzle, a two-dimensional worktable, and a control unit. TiO_2 particles were accelerated by high-pressure He gas. Spray parameters are given in Table 1.

2.3 Characterization of the Coating

The surface morphology and microstructure of coatings were examined by scanning electron microscopy (SEM) (Quanta 200, FEI, The Netherlands). The crystalline structures of the as-sprayed coating and powder were characterized by x-ray diffraction (XRD) (Shimadzu XRD-6000, Kyoto, Japan) with Cu Kα radiation. The microhardness of the coating was measured by Vickers hardness tester (HV-5, Huayin, Laizhou, China) at a load of 20 grams with loading time of 10 s.

Table 1 Vacuum cold spray parameters

Chamber pressure, Pa	2×10^3
Pressure in the aerosol room, Pa	1×10^6
He gas flow, L/min	3
Distance from nozzle exit to substrate, mm	5
Nozzle orifice size, mm × mm	2.5 × 0.2
Substrate traversal speed, mm/s	5

3. Results and Discussion

3.1 Coating Thickness Growth Characteristics During Deposition of Nanocrystalline TiO_2

Figure 3 shows the cross-sectional morphology of nanocrystalline TiO_2 coatings deposited by VCS using powder P25 at different spray passes. The coatings were deposited on the glass surface and were then fractured after deposition. All coatings in different thicknesses presented good adhesion to the substrate after fracturing. It was found that the thickness of coating increased with the number of the spray pass. A nanocrystalline TiO_2 coating several tens of micrometers thick can be attained by the VCS process using 25 nm TiO_2 particles, as shown in Fig. 3c.

3.2 Microstructure of the Coating

Figure 4 shows a typical cross-sectional morphology of the deposited coating using 200 nm TiO_2 powder. It was found that an apparently dense TiO_2 coating was formed with a uniform thickness on the stainless steel substrate using the present system under the conditions shown in Table 1.

Figure 5 shows typical surface morphology of a TiO_2 coating deposited using 200 nm powders. It was clear from the surface morphology that the coating deposited using 200 nm TiO_2 particles was formed by stacking of agglomerates with diameters on the order of hundreds of nanometers. Despite the dense microstructure observed in the cross section (Fig. 4), it is possible to observe pores at the coating surface (Fig. 5). This result suggests that the coating was formed mainly by agglomeration of small particles upon impact at high velocity with limited particles aggregation. An average Vickers microhardness of 235 HV was obtained for the coating deposited using 200 nm powders under a 20-gram load. This hardness number is much lower than that of the sintered bulk TiO_2 and comparable to that of the green body preform before sintering. This fact suggests weak bonding between deposited particles. However, the coating shows good enough adhesion with the substrate as well as good cohesion within the coating to be used in photocatalytic degradation and dye-sensitized solar cell applications.

Deposition of a Ti coating by VCS revealed that a tamping effect through successive impact of sprayed particles on the deposited coating is one mechanism responsible for densification of the cold spray coating (Ref 18, 19). Although it is impossible for ceramic particles to deform under the impact of spray particles, the tamping effect will compact the coating through slipping of the nanoparticles in the coating under high impact pressure. As a result, an apparent dense coating is formed with successive deposition of spray particles. Because of insufficient compaction and lack of aggregation between nanoparticles, the coating formed in the current study is considered to have a mesoporous microstructure.

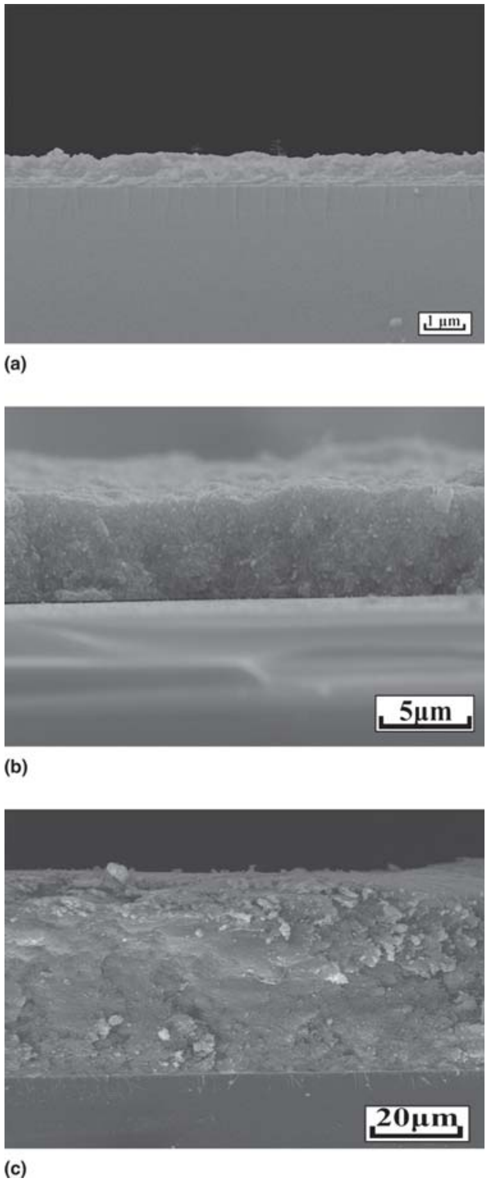

Fig. 3 Cross-sectional view of the nanostructured TiO_2 coating deposited on ITO glass substrate using 25 nm TiO_2 powder by the VCS process at different spray passes: (a) 1, (b) 4, and (c) 12

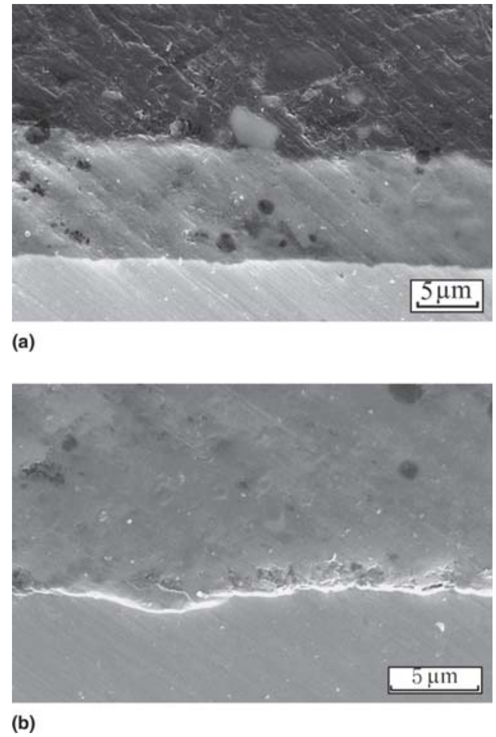

Fig. 4 Cross-sectional view of the nanostructured TiO_2 coating deposited on a stainless steel substrate using 200 nm diameter powders by the VCS process: (a) low magnification; (b) high magnification

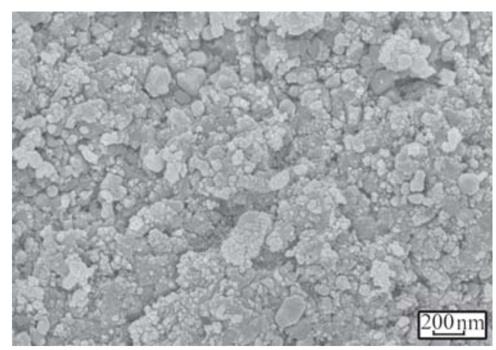

Fig. 5 Surface morphology of the nanostructured TiO_2 coating deposited on a stainless steel substrate using 200 nm diameter powder by the VCS process

Figure 6 shows the typical morphology of a TiO_2 coating deposited using 25 nm powders. This surface morphology suggests formation of a denser coating than that which occurs when using the 200 nm TiO_2 powder. Detailed examination showed that the coating was formed by successive stacking of nanostructured agglomerates having diameters of ~100 nm. SEM examination of the as-deposited surface shows that the surface pores are much smaller in the coating deposited using 25 nm TiO_2 powders (Fig. 6b) than 200 nm TiO_2 powders (Fig. 5). Therefore, it can be considered that, the smaller the particles, the more compact the coating that is formed. Consequently, a dense coating can be deposited using smaller sized particles.

Figure 7 shows the XRD patterns of TiO_2 coatings deposited by VCS compared with those of the starting powders. The crystalline structure did not change after deposition, with full retention of the original anatase structure. This result indicates that the original crystalline structure of the powder can be retained after vacuum cold spray to form a deposit. Therefore, the crystalline structure of deposit can be controlled through design of the structure of the starting powder.

The present results showed that, when using a stream of solid, ceramic, nanometer-sized particles under low-pressure conditions, a nanocrystalline TiO_2 coating can be built up on both metal and ceramic substrates. The hardness test result suggests that the coating behaves mechanically as ceramic green body preform. This fact implies that nanoparticles in the coating are weakly bonded together. Preliminary study of dye-sensitized so-

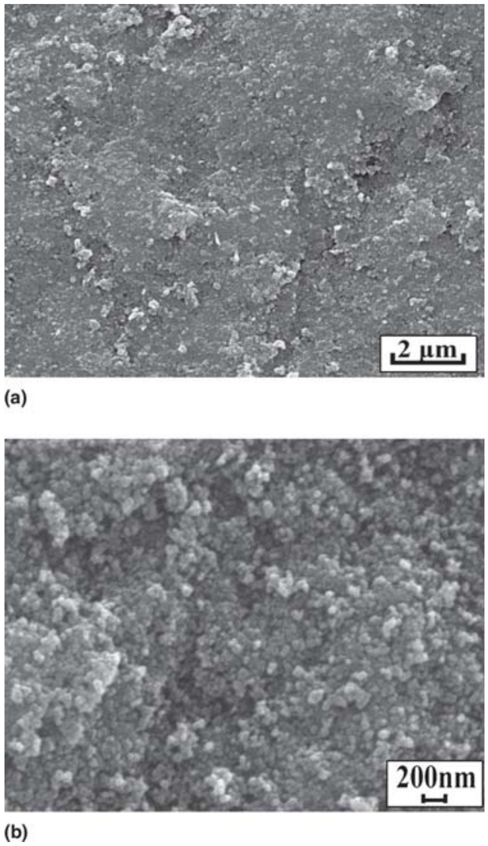

Fig. 6 Surface morphology of the nanostructured TiO_2 coatings deposited on ITO glass substrate using 25 nm diameter powder by the VCS process: (a) low magnification; (b) high magnification

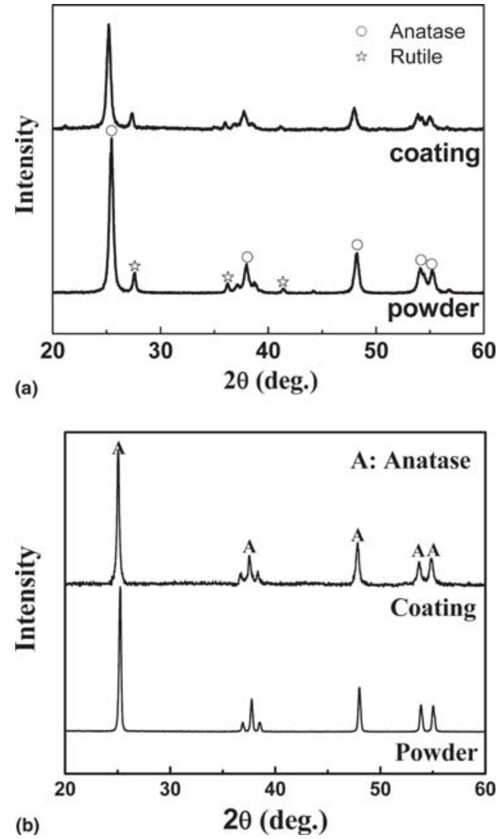

Fig. 7 XRD patterns of (a) 25 nm TiO_2 powder and the coating deposited on ITO conducting glass substrate by the VCS process, and (b) 200 nm TiO_2 powder and the coating deposited on a stainless steel substrate by the VCS process

lar cell performance shows comparable high solar energy conversion efficiency between the VCS-sprayed TiO_2 coating and the coating prepared with the doctor blading process (Ref 17). The TiO_2 coating in the study is 11 μm thick and had been applied by VCS with 25 nm powders. The previous result (Ref 17) shows that the VCS nanocrystalline TiO_2 coating has sufficient electron transfer ability, which implies good contacts among nanoparticles in the coating. These results also suggest that the present coating adheres well to the substrate, with bonding mechanisms that are similar to other conventional wet ceramic coating processes, such as tap-casting and doctor blading. Although the local damage to brittle substrate surface upon impact of nanoparticles (Ref 20) may benefit the mechanical interlocking between particles and substrate, the bonding mechanisms of the nanoceramic particles with their substrates may not depend solely on mechanical interlocking. On the other hand, ceramic particles may be embedded into the steel surface, creating mechanical bonding. Future study is needed to examine the bonding mechanisms between nanoparticles and substrates and between nanoparticles within the deposit.

4. Conclusions

In this study, the authors demonstrated the successful deposition of nanocrystalline TiO_2 coatings on ITO conducting glass and stainless steel substrates using two types of nanocrystalline TiO_2 powders by vacuum cold-spray process. The TiO_2 coating deposited by this method was formed by stacking of nanostructured TiO_2 agglomerates having diameters on the order of hundreds of nanometers. The coating thickness can easily be controlled through spraying passes. The nanostructured TiO_2 coatings exhibited an apparent dense microstructure. The low microhardness values of the coating suggest the formation of weak bonding among nanoparticles. The original nanocrystalline structure of the starting powder can be completely retained in the coating.

Acknowledgment

The authors thank Dr. Siu Ching Lui (Advanced Technology, Honeywell International) for kind review of the text.

References

1. A. Fujishima and K. Honda, Electrochemical Photolysis of Water at a Semiconductor Electrode, *Nature,* 1972, **238,** p 37-38
2. Y. Ohko, T. Tatsuma, and A. Fujishima, Characterization of TiO_2 Photocatalysis in the Gas Phase as a Photoelectrochemical System: Behavior of Salt-Modified Systems, *J. Phys. Chem. B,* 2001, **105**(41), p 10016-10021

3. A. Hagfeldt and M. Grätzel, Light-Induced Redox Reactions in Nanocrystalline Systems, *Chem. Rev.,* 1995, **95**(1), p 49-68
4. Z.H. Han and H.Q. Zhao, Progress in Applied Research of the Heterogeneous Photocatalysis on Semiconductors, *Prog. Chem.,* 1999, **11**(1), p 1-10
5. M. Grätzel, Dye-Sensitized Cells, *J. Photochem. Photobiol C: Photochem. Rev.,* 2003, **4,** p 145-153
6. B. O'Regan and M. Grätzel, A Low-Cost, High Efficiency Solar Cell Based on Dye-Sensitized Colloidal TiO_2 Films, *Nature,* 1991, **353,** p 737-740
7. P.Y. Zhang, G. Yu, and Z.P. Jiang, Preparation of Photocatalytic Titania Film and Its Application, *Adv. Environ. Sci.,* 1998, **6**(5), p 50-56
8. J.G. Yu and X.J. Zhao, Effect of Surface Treatment on the Photocatalytic Activity and Hydrophilic Property of the Sol-Gel Derived TiO_2 Thin Films, *Mater. Res. Bull.,* 2001, **36,** p 97-107
9. B. O'Regan, J. Moser, M. Anderson, and M. Grätzel, Vectorial Electron Injection into Transparent Semiconductor Membranes and Electric Field Effects on the Dynamics of Light-Induced Charge Separation, *J. Phys. Chem.,* 1990, **94**(24), p 8720-8726
10. Y.A. Cao, T.F. Xie, X.T. Zhang, Z.S. Guan, Y. Ma, Z.Y. Wu, Y.B. Bai, T.G. Li, and J.N. Yao, Investigation on Surface States of TiO_2 Nanoparticulate Film, *Acta Phys.-Chim. Sinica,* 1999, **15**(8), p 680-683
11. S. Takeda, S. Suzuki, H. Odaka, and H. Hosono, Photocatalytic TiO_2 Thin Film Deposited onto Glass by DC Magnetron Sputtering, *Thin Solid Films,* 2001, **392,** p 338-344
12. L. Kavan and M. Grätzel, Highly Efficient Semiconducting TiO_2 Photoelectrodes Prepared by Aerosol Pyrolysis, *Electrochim. Acta,* 1995, **40**(5), p 643-652
13. G.J. Yang, C.J. Li, F. Han, and A. Ohmori, Microstructure and Photocatalytic Performance of High Velocity Oxy-Fuel Sprayed TiO_2 Coatings, *Thin Solid Films,* 2004, **466,** p 81-85
14. G.J. Yang, C.J. Li, F. Han, and X.C. Huang, Effects of Annealing Treatment on Microstructure and Photocatalytic Performance of Nanostructured TiO_2 Coatings Through Flame Spraying with Liquid Feedstocks, *J. Vacuum Sci. Technol. B,* 2004, **22**(5), p 2364-2368
15. C.J. Li, G.J. Yang, X.C. Huang, W.Y. Li, and A. Ohmori, Formation of TiO_2 Photocatalyst Through Cold Spraying, *Thermal Spray 2004: Advances in Technology and Application,* May 10-12, 2004 (Osaka, Japan), ASM International, 2004, p 315-319
16. J. Akedo and M. Lebedev, Piezoelectric Properties and Polling Effect of $Pb(Zr,Ti)O_3$ Thick Films Prepared for Microactuators by Aerosol Deposition, *Appl. Phys. Lett.,* 2000, **77**(11), p 1710-1712
17. S.-Q. Fan, C.-J. Li, C.-X. Li, G.-J. Liu, G.-J. Yang, and L.-Z. Zhang, Primary Study of Performance of Dye-Sensitized Solar Cell of Nano-TiO_2 Coating Deposited by Vacuum Cold Spraying, *Mater. Trans.,* 2006, **47**(7), p 1703-1709
18. C.J. Li and W.Y. Li, Deposition Characteristics of Titanium Coating in Cold Spraying, *Surf. Coat. Technol.,* 2003, **167**(2-3), p 278-283
19. C.J. Li and W.Y. Li, Microstructure Evolution of Cold-sprayed Coating during Deposition and Through Post-Spraying Heat Treatment, *Trans. Nonferrous Met. Soc. China,* 2004, **14** (Suppl 2), p 49-54
20. J. Akedo and M. Lebedev, Microstructure and Electrical Properties of Lead Zirconate Titanate ($Pb(Zr_{52}/Ti_{48})O_3$) Thick Films Deposited by Aerosol Deposition Method, *Jpn. Appl. Phys.,* 1999, **38,** p 5397-5401