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Research Article

Bulk Synthesis and Characterization of Ti_3Al Nanoparticles by Flow-Levitation Method

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A novel bulk synthesis method for preparing high pure Ti_3Al nanoparticles was developed by flow-levitation method (FL). The Ti and Al vapours ascending from the high temperature levitated droplet were condensed by cryogenic Ar gas under atmospheric pressure. The morphology, crystalline structure, and chemical composition of Ti_3Al nanoparticles were, respectively, investigated by transmission electron microscopy, X-ray diffraction, and inductively coupled plasma atomic emission spectrometry. The results indicated that the Ti_3Al powders are nearly spherical-shaped, and the particle size ranges from several nanometers to 100 nm in diameter. Measurements of the d-spacing from X-ray (XRD) and electron diffraction studies confirmed that the Ti_3Al nanoparticles have a hexagonal structure. A thin oxidation coating of 2-3 nm in thickness was formed around the particles after exposure to air. Based on the XPS measurements, the surface coating of the Ti_3Al nanoparticles is a mixture of Al_2O_3 and TiO_2. The production rate of Ti_3Al nanoparticles was estimated to be about 3 g/h. This method has a great potential in mass production of Ti_3Al nanoparticles.

1. Introduction

Intermetallic compounds, especially titanium aluminides, having a positive temperature dependence of yield strength are becoming one of the most promising candidates for a high-temperature material to realize an aerospace plane [1]. This is due to their outstanding engineering performances such as low density, good corrosion resistance, high specific Young's modulus, strength, and their good oxidation and burn resistances [2]. However, their intrinsic low tensile ductility at room temperature and poor high temperature strength have limited their potential applications, particularly in the aerospace field [3]. During recent years, many attempts have been made to improve the ductility. Attempts adapted include techniques such as grain refinement to nanoscale structure [4–6] and microstructure modification [7, 8]. Thus research aiming to produce nanocrystalline materials by improved experimental techniques is relevant. Now, ball mill method is one of the methods used for preparation of titanium aluminium nanoparticles. Calderon et al. have prepared nanocrystalline powders of titanium aluminum by ball milling [9–11]. But ball milling is associated with long periods of milling times in order to obtain crystallite size below 100 nm. The phase composition of titanium aluminum nanoparticles is very difficult to be controlled, and the particles size distribution of them is also very wide. Liu Tong prepared nanocrystalline powders of Ti-Al nanoparticles by hydrogen plasma-metal reaction [12]. Nevertheless, nanoparticles prepared by this method are not pure, and the phase composition is also very difficult to be controlled by this method.

Flow-levitation (FL) method is based on the levitation melting technology [13] and has been used as a successful method for the preparation of some metals [14–16] and zinc oxide nanoparticles [17]. Also, the method has been used for the preparation of alloy nanoparticles. Sivaprahasam et al. used this method for the synthesis of FeCu nanopowders [18]. Recently, we developed this method for the synthesis of intermetallic Ag_2Al, FeAl, and $FeNi_3$ nanoparticles [19–21]. In comparison to the conventional evaporation-condensation methods, the main advantages of the FL method are high purity of the product (due to the containerless nature of the process) and high production rate (due to the rapid heating and continuous manner of the method). FL method is a novel method capable of producing high purity intermetallic nanoparticles with a relatively high production rate.

Until now, little work has yet been reported on the synthesis of high pure Ti_3Al nanoparticles [12]. In the present work, we have developed a novel method for the synthesis of high pure Ti_3Al nanoparticles with the production rate of about 3 g/h in a continuous manner, by using flow-levitation (FL) method. The morphology and structure of the Ti_3Al nanoparticles were investigated. The surface compositions of the samples were also studied.

2. Experiments

Ti_3Al nanoparticles were synthesized by the FL method (see Figure 1). In principle, the solid metal wires (Ti and Al) are first heated by a high-frequency electromagnetic induction coil, and a metal liquid droplet is formed. The droplet is levitated and heated continuously under its interaction with the magnetic field generated by another reverse electromagnetic induction coil. Atoms at the surface of the droplet are evaporated when a high temperature (about 2050°C) is reached. These evaporated atoms are quickly cooled through their collision with the inert gas and form nanoparticles. When the inert gas with a special gradient pressure is imposed in the vapour environment, metal atoms and resultant nanoparticles can flow in a definite direction in no contact with the reactor wall and finally enter the collector. Consequently, both high yield and high purity of nanoparticles are expected. In synthesizing nanoparticles by the FL method, the aerosol is rapidly cooled and diluted to prevent extensive sintering and coalescence raise for maintaining nanosized particles and limiting agglomeration. In the present experiments, these synthesized nanoparticles were taken out of the collector and were immediately placed into ethanol to reduce oxidation and coalescence and to improve their dispersion. For synthesizing Ti_3Al nanoparticles, the temperature for evaporation was about 2400°C, resource materials Al and Ti were supplied at a rate of 23.04 Hz and 67.75 Hz, and Ar flow rates v_1 and v_2 are equal to 0.2 and 0.8 $m^3 \cdot h^{-1}$, respectively.

Structures of the nanoparticles were investigated by X-ray diffraction (XRD) method using Cu Kα ($\lambda = 0.15405$ nm) radiation. The morphology and the particle size of the prepared nanopowders were directly observed by transmission electron microscopy. The chemical composition of the particles was examined by induction-coupled plasma spectroscopy (ICP). X-ray photoelectron spectroscope with Mg Kα radiation as exciting source was used to examine the chemical composition of the surface samples.

3. Results and Discussion

The chemical compositions of Ti_3Al nanoparticles were determined by the inductively coupled plasma atomic emission spectrometry (ICP-AES) measurements. There are

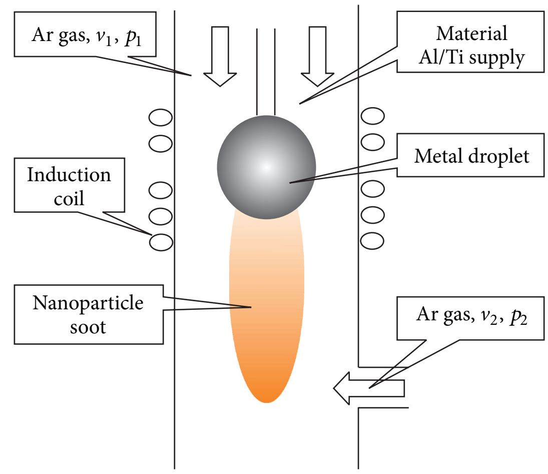

Figure 1: The scheme of the flow-levitation method for synthesizing intermetallic nanoparticles.

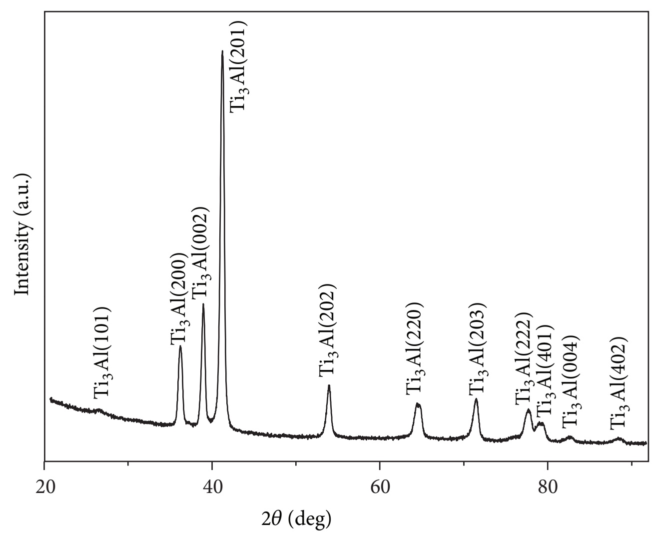

Figure 2: XRD patterns of the as-prepared nanoparticles.

74.42% (molar fraction) Ti and 25.28% Al in the nanoparticles as determined by the ICP analyses. And the Ti/Al atomic ratio of the nanoparticles is about 3 : 1.

Figure 2 shows the XRD pattern of nanoparticles obtained by the FL method. All of the diffraction peaks can be indexed according to the JCPDF card no. 14-0451l, indicating the hexagonal Ti_3Al (space group: P63/mmc (194), cell parameters: $a = 0.577$ nm, $b = 0.577$ nm, and $c = 0.462$ nm) [22]. The prominent diffraction peaks at the scattering angles of 26.4°, 36.1°, 39.0°, 41.2°, 53.9°, 64.6°, 71.5°, and 79.4° are assigned to scattering from the 101, 200, 002, 201, 202, 220, 203, and 401 planes, respectively, of the Ti_3Al crystal lattice [22]. The XRD results indicate that the products we obtained were Ti_3Al nanoparticles. The purity of titanium aluminide nanoparticles produced by FL method is higher than that by HPMR [12], in which some quantities of TiAl and Al were still present in the Ti_3Al samples from XRD patterns. According to the XRD patterns of Ti_3Al

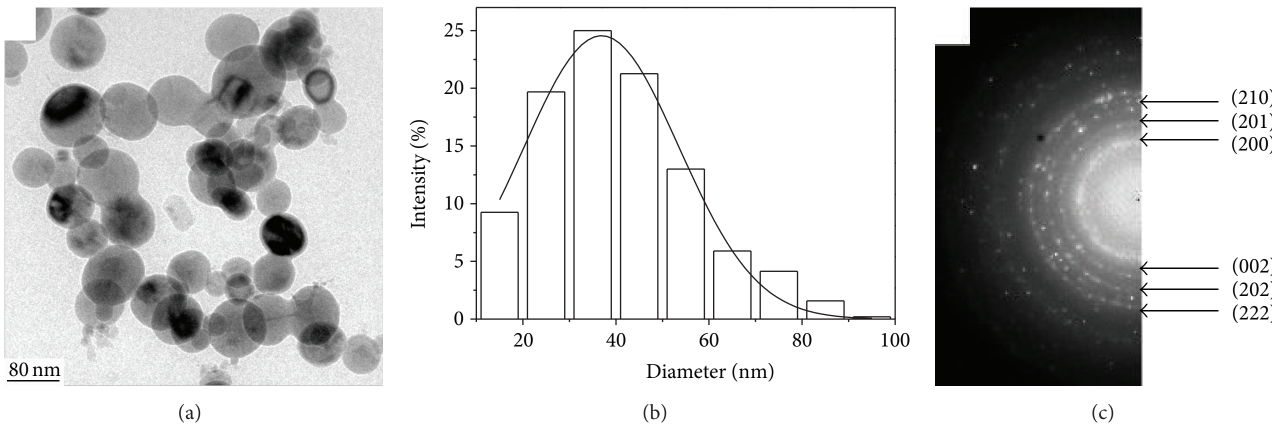

Figure 3: (a) TEM images of Ti_3Al nanoparticles, (b) the particle size distribution of Ti_3Al nanoparticles, and (c) SAED images of Ti_3Al nanoparticles.

nanoparticles, the average crystalline size can be calculated based on the Scherrer equation $D = 0.89\lambda/\beta\cos\theta$ [23], where λ is the X-ray wavelength, D is the average diameter of the crystals in Angstroms, β is the full width at half maximum (FWHM) in radians, and θ is the Bragg angle in degrees. According to Scherrer's relation, the average crystalline size of Ti_3Al nanoparticles is about 25 nm. Also, we have estimated the crystallite size using the Williamson-Hall equation [24]. Result of W-H calculation shows that the crystallite size of Ti_3Al samples is 23 nm, which is similar and consistent with Debye-Scherrer's calculations.

Figures 3(a) and 3(b) show the typical TEM image along with the particle size distribution of the Ti_3Al nanoparticles. Statistically, Ti_3Al nanoparticles are spherical in shape, and the particle size ranges from several nanometers to 100 nm in diameter, with a lognormal particle size distribution typical of other vapor phase synthesized nanopowders [25]. It is worth to note that these primary spherical particles often occur as chain aggregates of several individual nanoparticles. The selected area electron diffraction (SAED) patterns of samples which were conducted in the whole areas of Figure 3(a) are shown in Figure 3(c). The observation of multiple rings indicates no preferential orientation within the nanoparticles sample. The SAED pattern exhibits the diffraction peaks from (200), (002), (201), (202), (210), and (222) planes of Ti_3Al, which further confirms the results of XRD pattern.

Structural information from a single Ti_3Al nanoparticle was obtained using high resolution TEM (HRTEM). Figure 4 shows the high resolution TEM images of samples. In Figure 4, well-developed lattice fringes are resolved in Ti_3Al nanocrystals, which indicate that Ti_3Al particles are well crystallized. Lattice fringes are measured to be 0.2365 nm, which are very close to the (002) lattice spacing of the hexagonal Ti_3Al phase. The existence of lattice planes on the HRTEM image further confirmed the crystallinity of Ti_3Al nanoparticles.

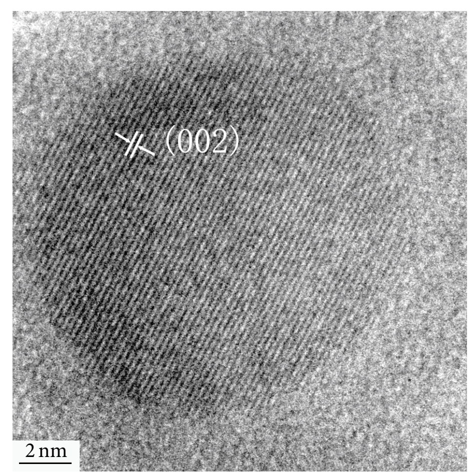

Figure 4: High resolution TEM image of sample.

We also attempted to characterize the amorphous coating using X-ray photoelectron spectroscopy (XPS) measurements. Figure 5 displays XPS of the Ti_3Al nanoparticles. We can see that the main elements contained in the sample surface are Ti, Al and O, and C. To compensate for sample charging, binding energies were referenced to that of the adventitious carbon 1s peak at 285.0 eV. The Ti 2p spectrum is treated as two doublet peaks, which are assigned to Ti^{4+} and metallic Ti, respectively [26, 27]. The Al 2p spectrum (Figure 5(c)) exhibits a doublet peak with binding energy of 71.5 eV and 74.1 eV, corresponding to metallic Al in metallic Ti_3Al, and the oxide state of Al in Al_2O_3 [28, 29]. In the O 1s spectrum (Figure 5(d)), only two peaks could be resolved. The first peak at 530.4 eV has a relatively large intensity and is probably due to O^{2-} ions in TiO_2, and the other smaller peak at 532.2 eV could be due to O^{2-} ions in Al_2O_3 [26]. Thus, the results from XPS measurement confirm that the chemical composition of the Ti_3Al nanoparticle surface could most likely be a mixture of Al_2O_3 and TiO_2.

4. Conclusion

In summary, stoichiometric Ti_3Al nanopowder has been successfully synthesized by the flow-levitation (FL) method.

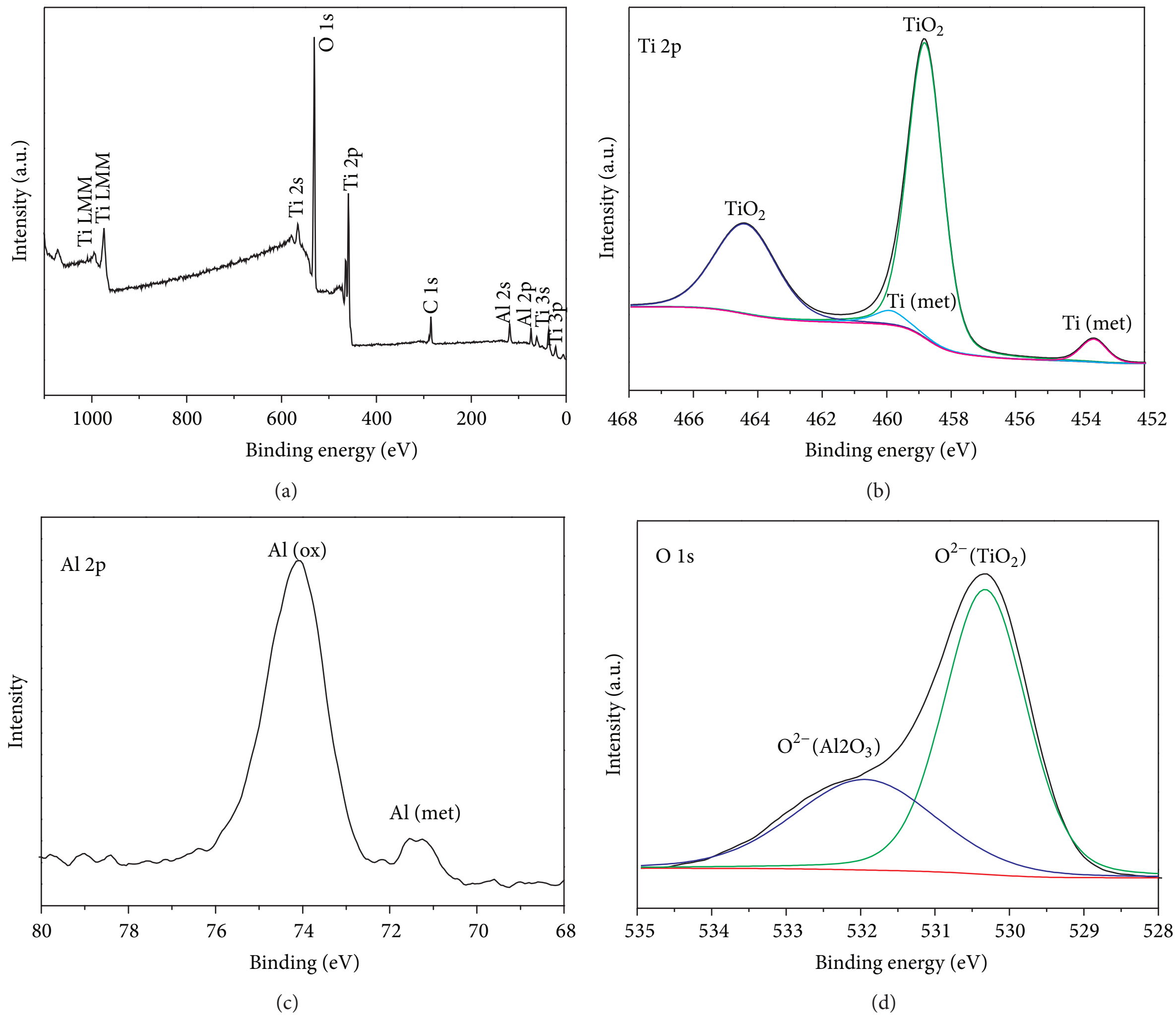

Figure 5: XPS spectra of the nanoporous surface of Ti_3Al nanoparticles. (a) Full spectrum; (b) Ti 2p; (c) Al 2p, and (d) O 1s.

TEM images indicate that the nanoparticles are nearly spherical and the particle size ranges from several nanometers to 100 nm in diameter. The as-synthesized nanoparticles have a hexagonal structure. The ICP results show that the Ti/Al atomic ratio of the nanoparticles is about 3 : 1. The Ti_3Al nanoparticles contain an amorphous layer of 2-3 nm in thickness surrounding the crystalline core after exposure to air. Results from XPS measurement show that the amorphous layer of the Ti_3Al nanoparticles could most likely be a mixture of Al_2O_3 and TiO_2. This work showed a simple and effective method to synthesize Ti_3Al nanopowders, and this method has a great potential to be used in mass production of Ti_3Al ultrafine particles.

Acknowledgments

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References

[1] M. Yamaguchi, H. Inui, and K. Ito, "High-temperature structural intermetallics," *Acta Materialia*, vol. 48, no. 1, pp. 307–322, 2000.

[2] N. S. Stoloff, C. T. Liu, and S. C. Deevi, "Emerging applications of intermetallics," *Intermetallics*, vol. 8, no. 9–11, pp. 1313–1320, 2000.

[3] G. Hénaff and A.-L. Gloanec, "Fatigue properties of TiAl alloys," *Intermetallics*, vol. 13, no. 5, pp. 543–558, 2005.

[4] R. M. Imayev, N. K. Gabdullin, G. A. Salishchev, O. N. Senkov, V. M. Imayev, and F. H. Froes, "Effect of grain size and partial disordering on ductility of Ti_3Al in the temperature range of 20–600°C," *Acta Materialia*, vol. 47, no. 6, pp. 1809–1821, 1999.

[5] G. Fanta, R. Bohn, M. Dahms, T. Klassen, and R. Bormann, "The effect of ultrafine grained microstructures on the hot-workability of intermetallic/ceramic composites based on γ-TiAl," *Intermetallics*, vol. 9, no. 1, pp. 45–49, 2001.

[6] F. H. Froes, O. N. Senkov, and E. G. Baburaj, "Synthesis of nanocrystalline materials—an overview," *Materials Science and Engineering A*, vol. 301, no. 1, pp. 44–53, 2001.

[7] X. H. Wu, "Review of alloy and process development of TiAl alloys," *Intermetallics*, vol. 14, no. 10-11, pp. 1114–1122, 2006.

[8] S. Karthikeyana, G. B. Viswanathana, P. I. Goumab, K. V. Vasudevanc, Y.-W. Kimd, and M. J. Millsa, "Mechanisms and effect of microstructure on creep of TiAl-based alloys," *Materials Science and Engineering A*, vol. 329–331, pp. 621–630, 2002.

[9] H. A. Calderon, V. Garibay-Febles, M. Umemoto, and M. Yamaguchi, "Mechanical properties of nancrystalline Ti-Al-X alloys," *Materials Science and Engineering A*, vol. 329–331, pp. 196–205, 2002.

[10] Z. M. Sun and H. Hashimoto, "Fabrication of TiAl alloys by MA-PDS process and the mechanical properties," *Intermetallics*, vol. 11, no. 8, pp. 825–834, 2003.

[11] Y. D. Liu and W. Liu, "Mechanical alloying and spark plasma sintering of the intermetallic compound $Ti_{50}Al_{50}$," *Journal of Alloys and Compounds*, vol. 440, no. 1-2, pp. 154–157, 2007.

[12] T. Liu, T. Zhang, M. Zhu, and C. Qin, "Synthesis and structures of Al-Ti nanoparticles by hydrogen plasma-metal reaction," *Journal of Nanoparticle Research*, vol. 14, no. 3, pp. 738–745, 2012.

[13] S. Zinn and S. L. Semiatin, *Elements of Induction Heating, Design Control, and Applications*, ASM International, Materials Park, Ohio, USA, 1988.

[14] C. M. Li, H. Lei, Y. J. Tang, J. S. Luo, W. Liu, and Z. M. Chen, "Production of copper nanoparticles by the flow-levitation method," *Nanotechnology*, vol. 15, no. 12, pp. 1866–1869, 2004.

[15] A. Kermanpur, B. N. Rizi, M. Vaghayenegar, and H. Ghasemi Yazdabadi, "Bulk synthesis of monodisperse Fe nanoparticles by electromagnetic levitational gas condensation method," *Materials Letters*, vol. 63, no. 5, pp. 575–577, 2009.

[16] A. Kermanpur, M. R. Dadfar, B. Nekooei Rizi, and M. Eshraghi, "Synthesis of aluminum nanoparticles by electromagnetic levitational gas method condensation," *Journal of Nanoscience and Nanotechnology*, vol. 10, no. 9, pp. 6251–6255, 2010.

[17] M. Vaghayenegar, A. Kermanpur, and M. H. Abbasi, "Formation mechanism of ZnO nanorods produced by the electromagnetic levitational gas condensation method," *Scientia Iranica*, vol. 18, no. 6, pp. 1647–1651, 2011.

[18] D. Sivaprahasam, A. M. Sriramamurthy, M. Vijayakumar, G. Sundararajan, and K. Chattopadhyay, "Synthesis of FeCu nanopowder by levitational gas condensation process," *Metallurgical and Materials Transactions B*, vol. 41, no. 4, pp. 841–856, 2010.

[19] S. J. Chen, X. B. Li, G. Niu et al., "Synthesis and characterization of single-phase nanocrystalline Ag_2Al particles," *Transactions of Nonferrous Metals Society of China*, vol. 22, no. 1, pp. 134–138, 2012.

[20] S. J. Chen, Y. Chen, Y. J. Tang et al., "Synthesis and characterization of FeAl nanoparticles by flow-levitation method," *Journal of Central South University*, vol. 20, no. 4, pp. 845–850, 2013.

[21] S. J. Chen, Y. Chen, X. L. Kang et al., "Bulk synthesis of monodisperse magnetic $FeNi_3$ nanopowders by flow levitation method," *Journal of Nanoscience and Nanotechnology*, vol. 13, no. 10, pp. 6906–6909, 2013.

[22] PCPDFWIN X-ray database, version 2.2, JCPDS-ICDD, 2001.

[23] A. Guinier, *Theoriè et Technique de la Radiocristallographie*, Dunod, Paris, France, 1956.

[24] A. Khorsand Zak, W. H. Abd. Majid, M. E. Abrishami, and R. Yousefi, "X-ray analysis of ZnO nanoparticles by Williamson-Hall and size-strain plot methods," *Solid State Sciences*, vol. 13, no. 1, pp. 251–256, 2011.

[25] H. Hahn, "Gas phase synthesis of nanocrystalline materials," *Nanostructured Materials*, vol. 9, no. 1–8, pp. 3–12, 1997.

[26] D. E. Mencer, T. R. Hess, T. Mebrahtu et al., "Surface reactivity of titanium-aluminum alloys: Ti_3Al, TiAl, and $TiAl_3$," *Journal of Vacuum Science & Technology A*, vol. 9, no. 3, pp. 1610–11615, 1991.

[27] C. D. Wagner, A. V. Naumkin, A. Kraut-Vass, J. W. Allison, C. J. Powell, and J. R. Rumble, Eds., *NIST X-Ray Photoelectron Spectroscopy Database, Version 3.0*, National Institute of Standards and Technology, Gaithersburg, Md, USA, 2000.

[28] J. Chastain and R. C. King, *Handbook of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer, Eden Prairie, Minn, USA, 1995.

[29] B. V. Crist, *Handbook of Monochromatic XPS Spectra: The Elements and Native Oxides*, John Wiley & Sons, New York, NY, USA, 2000.