Advanced Powder Technology 26 (2015) 169–174

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Formation of face-centered cubic and tetragonal titanium oxynitride by low temperature annealing of ball milled titanium powder in air

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ARTICLE INFO

Article history:
Received 8 July 2014
Received in revised form 9 September 2014
Accepted 14 September 2014
Available online 26 September 2014

Keywords:
TiO_xN_y
$TiO_{2-x}N_x$
FCC
Ball-milling
Metastable

ABSTRACT

$TiO_{0.61}N_{0.29}$ was synthesized by annealing of ball milled Ti in air at 900 °C for 5 h. In addition, traces of rutile-type $TiO_{1.56}N_{0.56}$ phases were observed. The morphology of the synthesized powder displayed multiple interesting colours. Scanning electron microscopy, X-ray diffraction and Raman spectroscopy were used for characterization of the powders. Raman analyses showed a phase transformation upon annealing in air.

1. Introduction

For the past three decades, studies on ball milling (BM) or mechanical milling (MM) have aroused interest in the research field. The process induces deformations and grain refinement on elemental powders [1–3]. Although Ti shows allotropic phase transformation upon thermal stress, several authors reported on the intermediate metastable FCC phase using BM process [4–7].

However, the reaction of Ti with interstitial elements such as O, N, C, form stable compounds. The lattice parameters of the FCC phase reported after MM range from 4.24 to 4.40 Å [4–7]. The lattice parameters of titanium carbide (TiC), titanium nitride (TiN), and titanium monoxide (TiO_x) and titanium hydride (TiH_2) are found within this range. Literature shows that TiN can be synthesized on ball milled Ti powder at low temperatures [8]. In addition, the synthesis of nitride and oxynitride is feasible by milling Ti in air [9]. Lately, research shows a high interest in titanium oxynitride (TiO_xN_y) that is proposed as a material of choice for biomedical [10], and has electrical, optical, good thermal stability [11]. TiO_xN_y films provide a retarding diffusion barrier at the interface between a metal and silicon [9]. The preparation of TiO_xN_y involves sputtering [9,11–13] as well as MM [14]. It seems that hydroxyapatite (HA) implant material bond with TiO_xN_y due to its mixed-valence states on the Ti atoms surface by negative charge of oxygen thus promoting the adsorption of Ca^{2+} ions [10]. Therefore, in this current work, TiO_xN_y and $TiO_{2-x}N_y$ structures were prepared by milling in Ar and subsequent annealed in air due to the increasing interest in biomedical application. To study the surface morphology, element analysis and the phase composition of the obtained TiO_xN_y and $TiO_{2-x}N_y$, scanning electron microscopy, X-ray diffraction and Raman spectroscopy analyses were performed.

2. Experimental work

High purity titanium powder was subjected to high energy ball milling (BM). The powder was charged in a milling a 50 l stainless steel vial and 5 mm in diameter stainless steel balls filled with argon gas and charged inside a glove box. Ball milling (BM) was done for 30 h at 800 rpm and 20:1 ball-to-powder weight ratio. The two samples were annealed at 900 °C under air and nitrogen (N_2) atmosphere, respectively. Phase evolution was traced with a PANalytical X'pert PRO PW 3040/60 X-ray diffraction (XRD) machine fitted with a Cu Kα radiation source. The XRD peak broadening was calculated from the full width at half maximum (FWHM) of the most intense Bragg peak. Pure tungsten was used as a standard, while the average crystallite size was estimated using the Scherer formula [15].

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http://dx.doi.org/10.1016/j.apt.2014.09.004
0921-8831/

The surface morphology of the annealed and polished samples was studied using LEO 1525 field-emission scanning electron microscope (FE-SEM) coupled with a Robinson Backscatter Electron Detector (RBSD) and an Oxford Link Pentafet energy dispersive X-ray spectroscopy (EDS) detector. Raman spectra were collected using a Horiba Jobin–Yvon HR800 Raman microscopy equipped with an Olympus BX-41 microscope attachment. An Ar^+ laser (514.5 nm) with energy setting 1.2 mW from a Coherent Innova Model 308 was used as an excitation source. Optical images were captured by digital camera.

3. Results and discussions

3.1. Morphology and microstructures

Fig. 1 shows the SEM images of (a) unmilled and (b) 30 h ball-milled Ti powders. The unmilled Ti powder particles show a spherical shape morphology with a broad distribution of sizes ranging from 18 to 45 μm. Upon extensive and continuous milling for 30 h at 800 rpm, the spherical shape of the particles changes to thin flakes or pancakes. The two 30 h-milled Ti sample, has undergone annealing in nitrogen and air, respectively.

Fig. 2 shows the XRD patterns of Ti powders (a) unmilled, (b) 30 h-milled and (c) 30 h-annealed at 900 °C. The unmilled and 30 h milled Ti retained the HCP crystal structure as shown in Fig. 3(a) and (b). Moreover, the crystallite size reduced from 110.27 nm to 47.21 nm after milling. Fig. 3(c) shows the XRD pattern of the 30 h milled Ti powder in flowing air at 900 °C. It is evident that new peaks have developed. The FCC and tetragonal phases

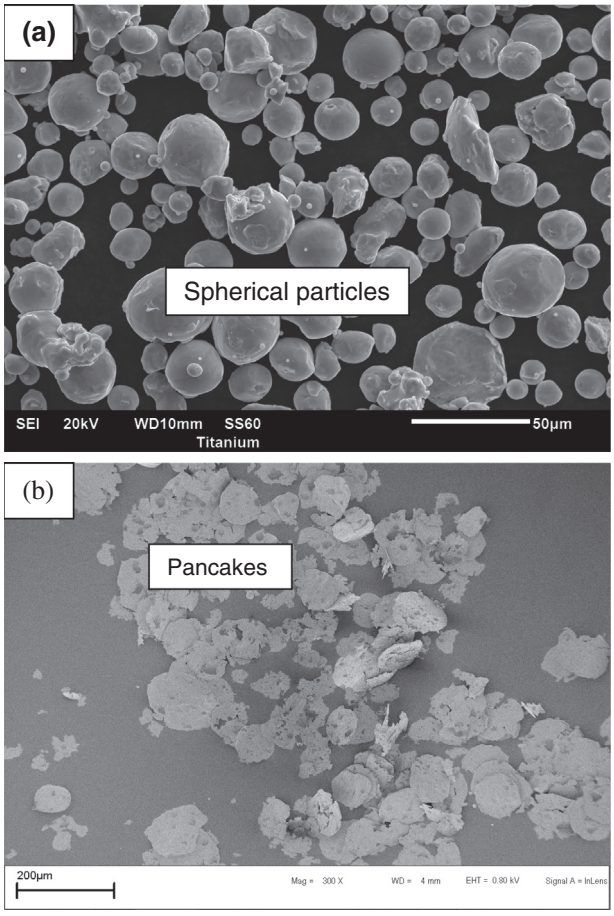

Fig. 1. SEM images of (a) 0 and (b) 30 h-milled Ti powders.

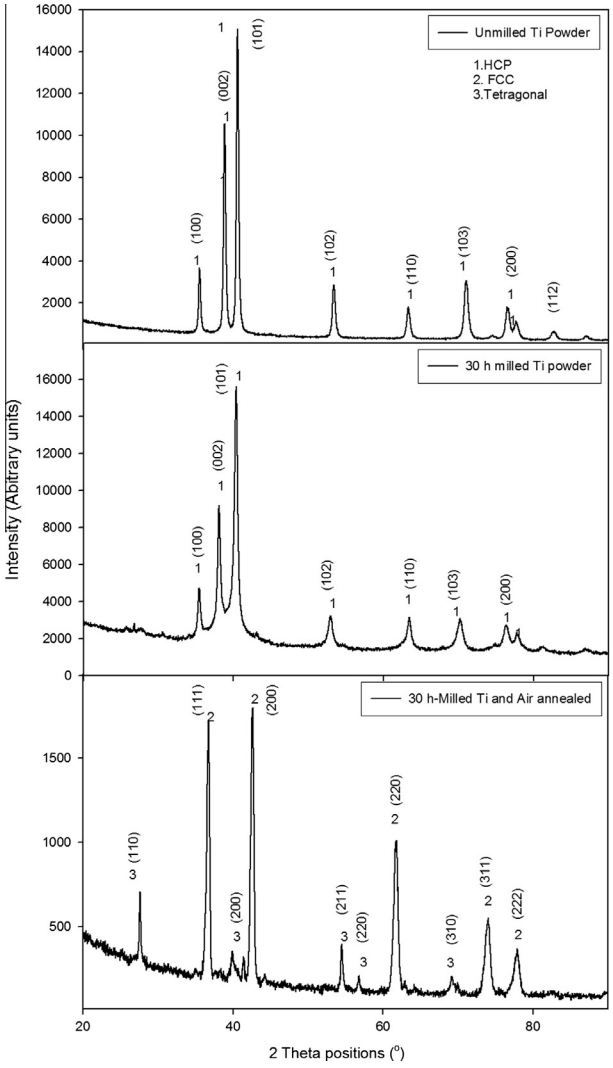

Fig. 2. XRD patterns of (a) unmilled, (b) 30 h-milled and (c) 30 h-annealed Ti powders in air.

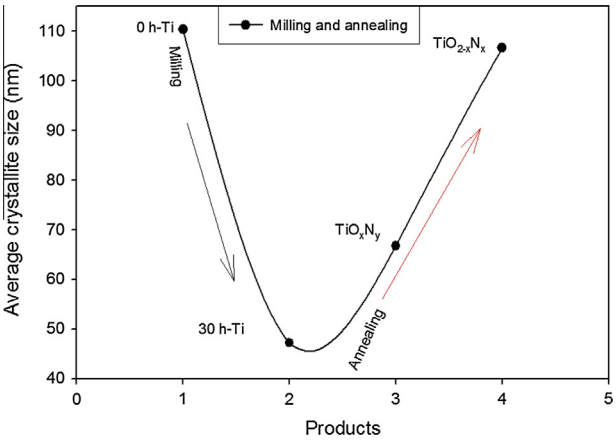

Fig. 3. Evolution of average crystallite sizes of Ti powders before and after annealing in air.

confirm the formations of titanium oxynitride phases; TiO_xN_y and rutile-type $TiO_{2-x}N_x$. The former has a lattice parameter a = 4.260 Å while the latter has a = 4.555 Å; c = 2.962 Å. The crystallite size of FCC TiO_xN_y is 66.72 nm while rutile type has a larger