Journal of Alloys and Compounds 557 (2013) 67–72

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

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

In situ formation of Ti alloy/TiC porous composites by rapid microwave sintering of Ti6Al4V/MWCNTs powder

C.Y. Tang [a,*], C.T. Wong [a,*], L.N. Zhang [a], M.T. Choy [a], T.W. Chow [b], K.C. Chan [a], T.M. Yue [a], Q. Chen [a]

[a] *Department of Industrial and Systems Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, PR China*
[b] *Faculty of Dentistry, The University of Hong Kong, Pokfulam Road, Hong Kong, PR China*

A R T I C L E I N F O

Article history:
Received 9 May 2012
Received in revised form 22 December 2012
Accepted 28 December 2012
Available online 3 January 2013

Keywords:
Microwave sintering
Titanium alloy
Carbon nanotubes
Microstructure
Mechanical properties

A B S T R A C T

The rapid *in situ* formation of a Ti alloy/TiC porous composite was achieved using the powder metallurgy approach. Ti6Al4V powders were mixed with 14.5 vol.% of multiwalled carbon nanotubes (MWCNTs) and the particle size of Ti6Al4V was reduced to ~5 μm by ball milling. The MWCNTs acted as microwave susceptors as well as reactants for the rapid sintering of Ti alloys. The green compact of the Ti6Al4V/MWCNTs powder was sintered in a 1.4 kW, 2.45 GHz bi-directional microwave emission furnace without using any protective gas environment. The microwave sintering was completed within 2 min. The surface temperature of the sample reached 1620 °C during sintering, as measured by a pyrometer. Titanium carbide was formed after the sintering as confirmed by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The composite has a porosity of approximately 25%, compressive strength of 270.41 ± 24.97 MPa, compressive yield stress of 145.48 ± 27.28 MPa, compressive Young's modulus of 10.87 ± 2.46 GPa and compressive strain of 3.75 ± 1.11%. The Vickers hardness value in the TiC region (545.4 ± 13.9 HV) is significant higher than that in the Ti alloy region (435.9 ± 12.9 HV). An overall Rockwell hardness of 47 HRA was measured.

1. Introduction

Titanium alloys have a wide variety of applications in the aerospace, automotive and biomedical industries. Ti6Al4V alloy, with 6 wt.% aluminum and 4 wt.% vanadium, has been used in aircraft, turbines and surgical implants due to its heat treatment ability, adequate mechanical strength, good corrosion resistance and biocompatibility. The powder metallurgy (P/M) technique has been utilized to produce titanium alloys and their composites [1–3], offering advantages such as low cost, near net-shape fabrication, increase in material yield, and variation of composition. The possibility of reinforcement in metal matrix composites can change the properties of the composites so that their applications can be broadened. The *in situ* formation technique offers the advantages of better control of size and level of reinforcement so that the properties of the composites can be modified. Titanium carbide (TiC) has been used for reinforcement of titanium alloy matrices due to its compatibility [4–6].

Traditional P/M processing of titanium alloys and their composites requires a long sintering time, of the order of hours. Although a prolonged heating time can ensure complete sintering, it also increases the chance of impurities formation, such as oxides. In such cases, the sintering needs to be performed in either a protective gas atmosphere or in a vacuum [7].

Microwave heating has been used for the processing of materials such as ceramics, metals and composites, taking advantage of time and energy saving, reduced processing cost, decreased sintering temperature, better production quality, and lower environmental hazards [8]. The transfer of microwaves to the materials directly can result in a faster generation of heat, thereby achieving rapid and uniform heating. Roy et al. [9] firstly obtained a fully sintered dense metal in a single-mode microwave cavity, after which microwave assisted P/M methods were developed for the sintering of metal alloys and their composites [10–13].

In this study, a Ti alloy/TiC porous composite was fabricated by the *in situ* formation of TiC from the reaction between multiwalled carbon nanotubes (MWCNTs) and Ti alloy powders, using the microwave sintering technique. This composite was designed to be used as a dental implant material, possessing a porous structure to favor bone interlocking, and a Young's modulus closer to that of cortical bone to avoid the stress shielding effect and bone resorption. A pure titanium matrix composite reinforced with MWCNTs was reported using spark plasma sintered MWCNTs and partially *in situ* formed TiC was obtained [14]. With reference to the use of carbon material as a microwave susceptor material [15–17], it is hypothesized that the absorption of microwave energy by MWCNTs can cause a vigorous reaction with Ti and form TiC,

* Corresponding authors. Tel.: +852 2766 6608; fax: +852 2362 5276.
E-mail addresses: mfcytang@polyu.edu.hk (C.Y. Tang), jackywct@hotmail.com (C.T. Wong).

0925-8388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jallcom.2012.12.147

achieving rapid sintering of the Ti6Al4V powders as well. The sintering of Ti6Al4V can be performed without a protective atmosphere due to the rapid reaction and heating by microwaves. Complete *in situ* formation of TiC will eliminate the residue MWCNTs inside the composite which could otherwise pose a problem in biocompatibility. The microstructure and mechanical properties of the microwave sintered Ti alloy/TiC porous composites were studied.

2. Experimental procedures

2.1. Raw materials and sintering process

Titanium alloy (Ti6Al4V) powders (Xi'an Baode Powder Metallurgy Co. Ltd.) and multi-walled carbon nanotubes (MWCNTs) (Nanotech Port Co. Ltd.) were used as raw materials. Ti6Al4V powders have particle sizes of ~44 μm, and MWCNTs have lengths < 2 μm and diameters of 10–20 nm (with purity > 98%). Ti6Al4V powders and MWCNTs were weighed to give a composition of Ti6Al4V:MWCNTs = 100:17 -vol.%. The powders were blended in a planetary ball mill (QM-3SP2, Nanjing University Instrument Plant) at a speed of 200 rpm for 12 h in order to reduce their sizes and increase their homogeneity for microwave absorption. The powder to ball ratio was 1:4 by weight. The mixed powders were pressed into a rigid die by applying a uniaxial pressure of 200 MPa for 200 s to form a cylindrical green compact (15 mm diameter and 22 mm height).

Microwave sintering of the green compact was undertaken using a bi-directional microwave emission sintering furnace designed by the research team, as shown in Fig. 1. The green compact was placed on top of an inverted crucible to align the sample in the middle of the chamber for even microwave absorption. One magnetron was aligned to emit microwaves in the horizontal direction and another was aligned to emit microwaves in the vertical direction. Maximum output power (i.e., 2 × 700 W = 1400 W; 2.45 GHz) was used for microwave sintering of the Ti6Al4V/MWCNTs green compact. The Ti6Al4V/MWCNTs green compact was sintered for 2 min in air. The temperature of the sample surface was measured by a digital infrared pyrometer (Sentry 677 pyrometer). The product (Ti alloy/TiC porous composite) was cooled to room temperature, after which the surface layer was removed by polishing.

2.2. Characterization

Images of the Ti alloy/TiC porous composite were captured and observed by optical microscopy (Leica DM 4000M). The pore features of the Ti alloy/TiC composite were characterized through image analysis. The average value of porosity was measured by using six optical micrographs taken from different cross sections of the Ti alloy/TiC porous composites. The porosity was confirmed by Archimedes' method as well. The phase composition of the Ti alloy/TiC composite was identified by X-ray diffraction (XRD) with Cu Kα radiation (Rigaku SmartLab 9KW XRD). To observe the microstructure in the optical and electron microscopes, the Ti alloy/TiC composite was polished and then etched in a 10% HF + 40% HNO_3 + 50% H_2O solution for 180 s. The microstructure was characterized using scanning electron microscopy (SEM, JEOL JSM-6490) equipped with an energy dispersive X-ray spectroscope (EDX) detector for compositional analysis. SEM was also used to observe the powders after being blended in the planetary ball mill. X-ray photoelectron spectroscopy (XPS) was used to characterize the surface properties of the sintered Ti alloy/TiC composite and the raw Ti6Al4V powder. XPS measurements of the Ti 2p and C 1s core levels were performed using an Axis Ultra DLD (Kratos) photoelectron spectrometer with a Al Kα X-ray source. The surface of the composite was etched by the sputtering of Ar at 2 kV for 800 s prior to measurement.

According to ASTM E9-09 [18], cylindrical specimens with L/D of 1.5 and 2.0 are suitable for determination of the compressive strength of high-strength materials. Green compacts of the Ti alloy/TiC composite were prepared with length/diameter ratio (L/D) of about 1.5. After sintering, they were cut into specific dimensions for evaluation of the mechanical properties. Five samples for compression testing were machined into cylindrical shape of 3 mm diameter and 6 mm height (L/D = 2.0). Compression testing was performed by an MTS 810 material test system with extensometer (model: 632. 13F-20) at an initial strain rate of 0.001 s^{-1}. Samples (n = 5) for hardness determination were machined into discs of 15 mm diameter and 5 mm height. Hardness measurement was performed using a Matsuzawa DXT-1 digital hardness tester with a diamond indenter. Vickers hardness of the Ti alloy and TiC regions within the sintered Ti alloy/TiC composite were measured with a load of 10 kg. Five samples were tested to obtain an average value ± standard deviation. Rockwell hardness was measured at a load of 600 N. In order to check the difference in hardness inside the sample, three regions were selected (center: within 2.5 cm dia. from the center; mid.: within 2.5 cm to 5.0 cm dia. from the center; edge: within 5.0–7.5 cm dia. from the center).

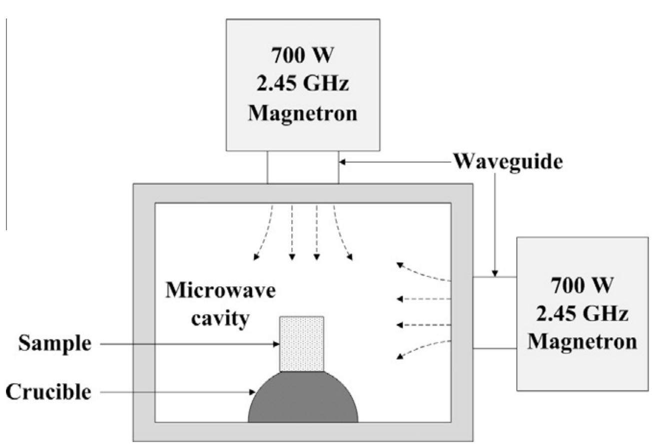

Fig. 1. Schematic diagram showing set-up of bi-directional microwave emission sintering of Ti6Al4V/MWCNTs sample.

3. Results and discussion

3.1. Rapid microwave sintering process

In order to achieve rapid microwave sintering, the powders should be able to absorb microwave energy and readily generate heat. Heating of metallic material by microwave absorption is related to the penetration depth (d), which is given by:

$$d = (\pi f \sigma \mu)^{-1/2} \tag{1}$$

where d is the penetration depth (m), f is the microwave frequency (Hz), σ is the electrical conductivity (Ω^{-1} m^{-1}) and μ is the magnetic permeability (N/A^2). For a particle to couple with the microwave radiation and achieve volumetric heating, at least one dimension of the particle should be less than or equal to the penetration depth [19]. Planetary ball milling was used to reduce the

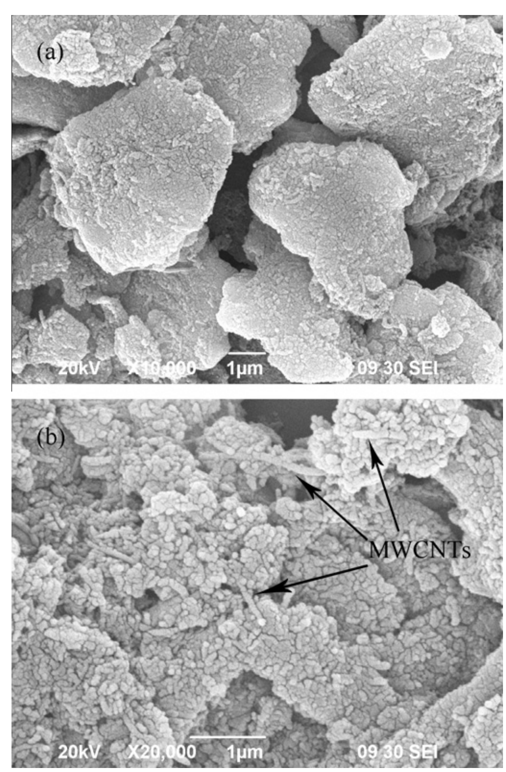

Fig. 2. SEM micrograph of (a) Ti6Al4V/MWCNTs powders after being blended in planetary ball mill; and (b) MWCNTs were attached on surface of Ti6Al4V particles.