Materials Science and Engineering C 31 (2011) 106–113

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

Near surface martensitic transformation and recrystallization in a Ti-24Nb-4Zr-7.9Sn alloy substrate after application of a HA coating by plasma spraying

G.L. Zhao [a], G. Wen [a,*], Y. Song [a], K. Wu [b]

[a] School of Materials Science and Engineering, Harbin Institute of Technology at Weihai, 2 Wenhuaxi Road, Weihai 264209, China
[b] School of Materials Science and Engineering, Harbin Institute of Technology, 92 West Da-Zhi Street, Harbin 150001, China

ARTICLE INFO

Article history:
Received 1 May 2010
Received in revised form 3 July 2010
Accepted 6 August 2010
Available online 13 August 2010

Keywords:
Martensitic transformation
Recrystallization
Mechanical properties
Plasma spraying
Titanium alloy

ABSTRACT

Plasma sprayed hydroxyapatite (HA) coatings on titanium alloy substrate have been used extensively due to their excellent biocompatibility and osteoconductivity. However, the influence of the high temperature process on substrates can not to be ignored, especially for metastable β type titanium alloy substrates. In this paper, martensitic transformation and recrystallization occurred in near surface of the low-modulus Ti-24Nb-4Zr-7.9Sn alloy substrate after application of a HA coating. Various analyses revealed that the martensitic transformation and recrystallization were mainly related to the high temperature and cooling process. The different microstructures can be attributed to inhomogeneous temperature and cooling rate distributions in the substrate. Corresponding to the microstructure, the Young's modulus and micro-hardness of the near surface of the alloy showed a similar graded distribution along the direction perpendicular to the coating/substrate interface. In addition, the martensitic transformation and recrystallization caused remarkable changes of the entire alloy.

1. Introduction

Recently, low modulus titanium alloys for biomedical implant applications have received significant attention due to intermateability between the implants and natural bones. Elastic matching of implants with surrounding bone favors both stress distribution and new bone formation [1,2]. Much effort has been made to attain lower modulus titanium alloys through the addition of β stabilizing elements, such as Nb, Zr, Ta, Sn, among others [3–5]. As a result, a new class of metastable β-type titanium alloys, such as Ti-35Nb-5Ta-7Zr [6], Ti-29Nb-13Ta-4.6Zr [7], Ti-24Nb-4Zr-7.6Sn [8] and Ti-24Nb-4Zr-7.9Sn (hereafter abbreviated as T2448) [9–11], have been developed. Of these titanium alloys, T2448, synthesized by Y.L. Hao et al. [9], is the most promising, due to the combination of an ultra-low elastic modulus and a satisfactory strength.

However, the T2448 alloy, similar to other titanium alloys, is only one kind of bio-inert material. Accordingly, the surface of the alloy should be modified before being used in the body [10]. Plasma spraying is a well established process for preparing bioactive coatings, as it can provide the required microstructure and bonding strength to the coatings by control of the process parameters. Furthermore, titanium and its alloys, coated with plasma sprayed HA, have been widely used in clinical studies [12,13], as the material combines the bioactivity of HA with the favorable mechanical properties of titanium alloys. Therefore, preparing HA coatings on the low modulus β-type T2448 alloy by plasma spraying should be a promising approach to fabricating more ideal biomedical materials for load-bearing applications. However, surface modification and high temperature post-treatment processes could have an impact on the microstructure, phase composition and mechanical properties of metastable β-type titanium alloys due to their poor thermal stability [14–16]. Li [17] reported the precipitation of some ω phase from the substrate and the formation of a hard $(\alpha+\beta)$ layer beneath the surface of Ti-29Nb-13Ta-4.6Zr due to the inward diffusion of oxygen during preparation of a bioactive glass-ceramic coating by a sintering treatment. Zheng et al. [18] found that a large amount of α phase precipitated in the alkali treated β-type Ti-24Nb-4Zr-7.6Sn alloy after a heat treatment at 600 °C to promote titanate growth. The martensite also appeared in T2448 alloy after heat treatment at 600 °C for 1 h or thermal plus hydrothermal treatment [19]. The Young's modulus of a multiphase alloy is mainly determined by the modulus of its constituent phases and their volume fractions [20,21]. Due to the precipitation of the α phase and the brittle ω phase, which have higher moduli than most phases in titanium alloys, the Young's modulus of the β-type titanium alloy must increase significantly. Although the formation of the new phases was regarded as beneficial to the tensile strength and fatigue resistance of the alloy as reported in [17], the significant increase in the Young's modulus, considered one of the most critical mechanical properties of β-type titanium alloys, must strongly influence their biomedical applications. Therefore, the influence of surface modifications on β-type titanium alloys should be examined concurrently with investigations of surface modification methods. To our knowledge,

---

[*] Corresponding author.
E-mail address: wgw@hitwh.edu.cn (G. Wen).

0928-4931/$ – see front matter © 2010 Published by Elsevier B.V.
doi:10.1016/j.msec.2010.08.003

few systematic studies on the influence of plasma spraying on substrates of β-type titanium alloys have been reported. Because the microstructure of the plasma-sprayed HA coatings has been studied in our previous work [22], this paper mainly focuses on changes in the microstructure and phase compositions of the substrate, the formation of new phases, and the influence of the microstructure on the mechanical properties of the alloy.

2. Materials and experimental

2.1. Materials and fabrication of samples

T2448 alloy plates of 5 mm thickness (fabricated by Institute of Metal Research Chinese Academy Sciences) were used as substrates of plasma spraying in this study. The chemical composition of the alloy can be found in Table 1. HA coatings were prepared on the alloy by an air plasma spray technique with parameters shown in Table 2. The temperatures of the substrates were measured immediately after plasma spraying. Before plasma spraying, the substrate surface was blasted with alumina particles, ultrasonically washed with acetone, and dried at 40 °C. The alloy modified by HA coatings is hereafter abbreviated as T2448M. The T2448 and T2448M plates were sectioned along thickness into chips with size of 10 mm × 10 mm. The surfaces of the T2448 chips and the cross-sections of T2448M chips were ground with 800#, 1000# and 1500# abrasive papers, then soaked in 2% HF solution for 40 s. After taken out from the HF solution the specimens were washed with deionized water, and dried at room temperature. For preparation of nanoindentations, one of the T2448M chips was embedded in urea formaldehyde, and the cross-section of the sample was ground and polished by a grinder–polisher machine (Buehler, USA). Specimens for tensile tests were prepared with linear cutting, and ground with 800# and 1000# abrasive papers. The shape and size are shown in Fig. 1. Before machining with linear cutting, the HA coatings were removed by abrasive papers. Three specimens were used for the tensile tests.

2.2. Characterization

Phase compositions were examined by X-ray diffraction (XRD; D8 Advance, Germany) using Cu Kα irradiation at an accelerating voltage of 40 kv and a current of 250 mA. The microstructure and fracture surfaces of tensile specimens were observed using a scanning electron microscope (SEM; Tescan Vega α, the Czech Republic). Chemical compositions were analyzed by an energy-dispersive X-ray spectrometer (EDS; EDAX-Genesis, USA) attached to the SEM system. Transmission electron microscopy (TEM; Tecnai 20, Holland) was performed to characterize the microstructure of the alloys. A nanoindenter (Nano Indenter SA2, USA), with systemic load resolution of 50 nN and distance resolution of 0.01 nm, was utilized to evaluate the Young's modulus and the micro-hardness in the cross-section of T2448M. Berkovich tip was used for the tests. Tensile tests were conducted at room temperature at a cross-head speed of 0.5 mm/min using an Instron load frame (Instron 5569, USA). For the determination of thermal expansion of the T2448 alloy the bar specimens with the dimension of $5 \times 5 \times 4\ \mathrm{mm}^3$ were tested using Shimadzu dilatometry (model TMA60) with a heating rate of 10 °C min^{-1} in ambient atmosphere.

Table 1
The chemical composition of T2448 (wt.% [21].

Ti	Nb	Zr	Sn	O	N	H
Balance	24.1	3.92	7.85	0.11	0.008	0.006

Table 2
Main parameters of the plasma spraying.

Parameters	Values
Arc current (A)	600
Arc voltage (V)	45
Main gas flow rate (L/min)	45
Stand-off (mm)	80
Average diameter of feedstock (μm)	75–125

3. Results and discussion

3.1. Near surface martensitic transformation and recrystallization

3.1.1. Microstructure of T2448 and T2448M

A HA coating has been prepared on the T2448 alloy substrate, and the cross-section of the HA coating and the substrate is shown in Fig. 2. The HA coating with dense structure and few pores tightly binds to the substrate, indicating a high binding strength between the coating and the substrate.

Fig. 3 shows the microstructure and phase composition of the T2448 alloy. It is clear from SEM image (Fig. 3(a)) and XRD profile (Fig. 3(b)) that the T2448 alloy consists of equiaxed β grains with an average grain size of about 20 μm. The SEM image also shows a lot of dislocation-etch pits dispersed in the matrix [24], which may be caused by heavy deformation [25]. Fig 3(c)–(e) are TEM images of the T2448 alloy, and Fig. 3(f) is the selected-area diffraction (SAD) pattern from Fig. 3(c). Fig. 3(c) and (d) show butterfly-like or octopus-like strips distributed in the β matrix, confirming a large amount of tangled dislocations originating from the hot rolling process [26]. In addition, a great number of ultra-fine sub-grains with size ranges from several nanometers to several tens of nanometers can be seen in Fig. 3(e). The SAD pattern indicates the existence of only the single β phase in the T2448 alloy.

The metallographic structure in the cross-section of the T2448M is shown in Fig. 4. The obviously inhomogeneous features and variations in the metallographic structures from the coating/substrate interface to the interior can be observed. According to the microstructure, the cross-section of the substrate can be divided into three zones: A, B and C, as labeled in Fig. 4(a). The sizes of zone A and zone B are about 10 μm and 90 μm, respectively. Magnified images (Fig. 4(b) and (c)) of the structures in the three zones show significant differences between one another. Zone A consists of very fine grains and a large number of acicular structures. Typical plate-like structures are present in zone B, and the size of the plate-like structures increases with increasing distance from the coating/substrate interface. In contrast with zone A and zone B, zone C is composed of almost equiaxed grains. However, there are still plate-structures dispersed in a few of the equiaxed grains.

In order to further investigate the phase compositions of the three zones, a group of surfaces were selected from each zone to represent it approximately. The surfaces at 0 μm and 5 μm from the coating/substrate interface represent zone A, the surfaces at 10 μm, 20 μm, 40 μm, 60 μm, 80 μm and 100 μm represent zone B, and the surfaces at 120 μm, 140 μm and 200 μm represent zone C. Every surface was obtained by removing the above materials carefully for XRD. Fig. 5 shows XRD profiles of these surfaces. It can be seen clearly that the phase composition of the T2448M alloy has dramatically changed into three phases ($\beta + \alpha + \alpha''$) from a

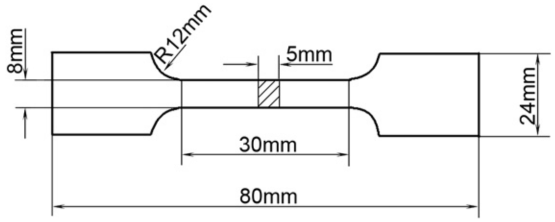

Fig. 1. Schematic of the samples for tensile tests.