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Full Length Article

The structural characterizations of Ti-17 alloy films prepared by magnetron sputtering

Gang Liu, Yanqing Yang*, Na Jin, Xian Luo, Bin Huang, Pengtao Li, Zongde Kou

State Key Lab of Solidification Processing, Northwestern Polytechnical University, Xian 710072, PR China

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ABSTRACT

One of the most attractive structural features of titanium (Ti) alloys is its α + β dual-phase growth. Previous work focused on α- or β-Ti phase films, but dual-phase growth in films has not yet been studied. This paper investigates the magnetron-sputtered structures of Ti-5Al-2Sn-2Zr-4Mo-4Cr alloy as a function of substrate temperature from 125 °C to 530 °C. The film shows a phase transformation from single β to α + β growth as substrate temperature rises. We discuss the morphology and texture evolutions that arise in sputtering deposition in reference to the structure zone model. We use nanoindentation to assess the mechanical properties of the films. The phase evolution, zone 1–zone T transition, and texture growth with the increasing substrate temperature all contribute to mechanical property improvements of the films.

1. Introduction

Titanium (Ti) alloy films have been studied extensively for use as aerospace materials and biomedical implants. The structure, phase and chemical composition, and related physical or functional properties of these films have been investigated systematically. Physical vapor deposition (PVD) methods mostly are used to produce these films in different coating systems, such as magnetron sputtering [1–8], arc ion plating [9], plasma immersion ion implantation and deposition [10], cold spraying [11], and pulsed laser deposition [12]. Magnetron sputtering is a suitable choice for Ti alloy films because of its ability to produce cohesive, uniform, and fine coating structures. Controlling the deposition parameters, such as substrate temperature (T_s), working pressure, sputtering power, and substrate bias, is the basic way to study the film's structure. The relationships among parameter, structure, and film properties are of fundamental importance because understanding these correlations helps to control the structure and related properties of the film.

The two allotropic forms of Ti are low-temperature hexagonal closed packed (hcp), known as α-Ti, and high-temperature body-centered cubic (bcc), known as β-Ti. Both forms have advantages: α-Ti is characterized by a high degree of anisotropy and high strength, and β-Ti has enhanced biocompatibility, lower modulus, and better ductility. Until recently, the current focus was on single α- or β-Ti films (without regard for intermetallic compounds, such as TiAl [13] or $TiAl_3$ [14]). Ma et al. [15] studied the as-sputtered Ti6Al4 V coatings at different working pressure and sputtering powers on silicon carbide (SiC) fibers and found that the coatings developed columnar crystallites with the α (002) texture. Zhang et al. [14] investigated the structure of Ti51Al8.3 V (atomic ratio [at%]) alloy coatings on SiC fibers in the sputtering process and found that an amorphous phase forms first and α-Ti(Al) and that $TiAl_3$ forms later. Liu et al. [7] studied the structural evolution of Ti6Al4 V alloy films as the T_s rises, suggesting a transition from columnar to equiaxial crystallites with the texture from α (002) to random. Musil et al. [16] reported that the α (002) texture in Ti6Al4 V alloy film can be weakened by increasing substrate bias and pointed out that alloy elements strongly inhibit the crystalline and texture growth compared with pure Ti films. Wang et al. [17] investigated the relationship between texture and mechanical properties of co-sputtered α-type titanium-zirconium (TiZr) alloy films by controlling T_s and proposed that texture strengthening contributes to mechanical property improvements of the films. Recently, for biomedical applications, Tallarico et al. [3] studied the growth and surface characterizations of β-titanium-niobium-zirconium (β-TiNbZr) alloy films. Similarly, Gonzalez et al. [6] investigated the composition, morphology, and microstructures of biomedical β-titanium-niobium (β-TiNb) alloy films.

The α + β dual-phase growth is a topic of primary importance in conventional bulk Ti alloy materials because it combines the strength of α-Ti and the ductility of β-Ti. Mechanical properties

* Corresponding author.
E-mail address: yangyanqingdaoshi@163.com (Y. Yang).

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of the alloy strongly depend on morphology and volume fractions of these two phases, which in turn are determined by parameters of the manufacturing process. Lots of effort has been devoted to the α + β dual-phase structures of Ti alloys in the last decades [18,19]. From the perspective of current surface science, to form a film with a composite structure has become an effective way to seek new physical or functional properties of the film, such as the development of hard nanocomposite coatings [20–23], or multilayer coatings [24–26]. These coatings not only combine the advantages of each phase or component, but also utilize the strengthening effect from the grain and phase boundaries which have a substantial volume fraction in the nanomaterials. Therefore, the α + β dual-phase Ti alloy films have completely different structural and physical properties compared to α- or β-Ti films, and deserve to be developed. In spite of these, to the best of our knowledges, the α + β dual-phase growth in Ti alloy films have not been studied.

Theoretically, the α + β dual-phase growth of the film can be formed by the cooling process following the deposition above the T_β (β transus temperature), whereas in real depositions, the T_s often cannot reach the T_β to reduce the interfacial reaction between the film and substrate. Because of the energy delivered to the growing surface of the film by particle bombarding, Musil et al. [27] found that the metastable β-Ti growth can be obtained in Ti–10 wt.% chromium (Cr) and Ti–10 wt.% iron (Fe) films below 100 °C ($T_{\beta,Ti\text{-}Cr} \geq 667$ °C [27], $T_{\beta,Ti\text{-}Fe} \geq 595$ °C [28]). This result not only shows a promising route to form β-Ti film at a low T_s ($T_s < T_\beta$) by controlling bombardment conditions, but also suggests that a sufficiently low T_s ($T_s < T_\beta$) is needed for the stability of metastable β-Ti film. Moreover, these conditions give rise to an issue about the relationship between the higher T_s ($T_s < T_\beta$) and the phase in the film. Until now, no work has reported the phase evolution in Ti alloy film at the low T_s range ($T_s < T_\beta$). Some work has been devoted to magnetron sputtering the α + β-type Ti alloy sources at different conditions, such as the Ti6Al4 V [7,15,16,29] or Ti6Al7Nb [30], but no α + β dual-phase growth of the film has been observed.

Ti-17 (Ti-5Al-2Sn-2Zr-4Mo-4Cr, wt.%), which belongs to the α + β group, is the most common Ti alloy for the aero-engine industry [31,32]. This paper studies the effects of T_s on Ti-17 alloy films. This study is significant for two reasons: (a) it shows a phase evolution in Ti alloy films by magnetron sputtering, and the α + β dual-phase film is obtained by controlling the T_s; and (b) currently, Ti-17 alloy has become a potential alternative material for use as a matrix coating in Ti matrix composites [14,15,33–36], so the relationship between the magnetron-sputtered structure and the deposition parameter needs to be investigated. In addition, we study typical structural features of the magnetron-sputtered films, such as morphology, residual stress, and crystalline orientation, because they are the main factors influencing film properties.

2. Experimental details

We deposited the Ti-17 alloy films on silicon (Si) (100) substrates by direct current magnetron sputtering from a Ti-17 alloy target with a diameter of 90 mm and a thickness of 4 mm. The target composition (wt.%) was 5.02Al, 3.93Cr, 3.90Mo, 2.40Sn, 1.92Zr, 0.04Fe, 0.01C, 0.01N, 0.003H, 0.12O, and balance Ti. We used high-purity (99.999%) argon as the sputtering gas. The base pressure was 2.0×10^{-4} Pa and the sputtering pressure was 0.5 Pa. Before starting the actual deposition, we presputtered the target for 30 min with a shutter covering the substrate. The actual deposition time was 60 min. The target-substrate separation was kept at 40 mm. The sputtering power was 180 W. The substrate temperatures were 125 °C, 200 °C, 300 °C, 400 °C, 450 °C, and 530 °C. Five samples were prepared for each substrate temperature. After each deposition, we kept the T_s for 20 min and then we cooled the films to room temperature in the vacuum.

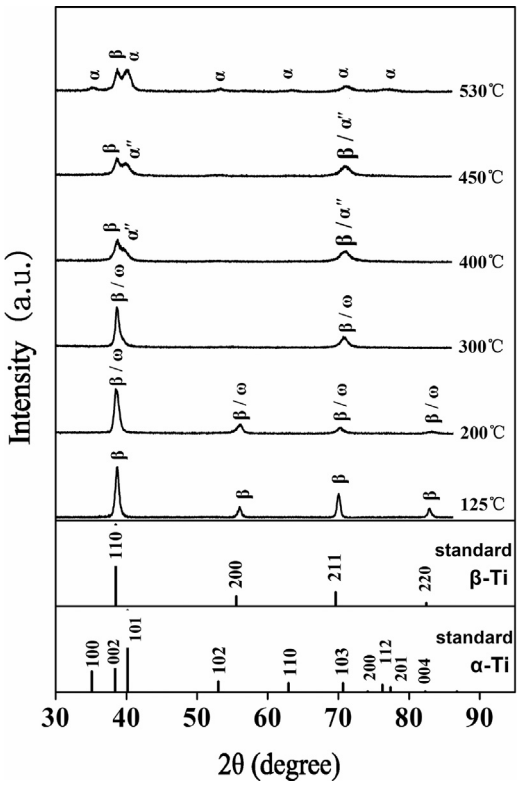

Fig. 1. The XRD patterns of Ti-17 alloy films at different temperatures.

We analyzed the phase, texture, and morphologies of the films using X-ray diffraction (XRD) operated on a PANAlytical X'Pert PRo MPD instrument (Almelo, Netherlands), Tescan MIRA3 XMU scanning electron microscope (SEM; Brno, Czech Republic), Shimadzu SPM-9600 atomic force microscope (AFM; Kyoto, Japan), and FEI Tecnai^{TM} F30 G^2 transmission electron microscope (TEM; Hillsboro, OR) with accelerating voltage of 300 kV. We measured residual stress using a substrate curvature method based on the Stoney's equation [37]:

$$\sigma_s = \frac{E_s}{6(1-\upsilon_s)} \frac{t_s^2}{t_c} \left(\frac{1}{R} - \frac{1}{R_0} \right), \quad (1)$$

where E_s, υ_s, t_s, and t_c denote the Young's modulus, Poisson's ratio, thickness of the substrate, and thickness of the films, respectively; R_0 is the curvature radius of bare substrate, and R is the curvature radius of film-substrate composite. For Si (100), the Young's modulus and Poisson's ratio can be described as $E_s/(1\text{-}\upsilon_s) = 180$ Gpa [38]. The values of t_s and R_0 for bare substrate are 400 μm and 400 m, respectively. Film thickness was determined by cross-sectional SEM observations. Deposition rate was obtained through dividing the thickness by deposition time. We performed nanoindentation tests on an Agilent Nano Indenter G200 (Santa Clara, CA) using a diamond Berkovich indenter probe. Less than one-tenth of the film thickness was taken into consideration to minimize the substrate influence. We averaged a total of eight indents to determine the mean hardness value for each sample.

3. Result and discussions

3.1. Phase evolution

Fig. 1(a) shows the typical XRD patterns of the Ti-17 alloy films from 30° to 90° at different T_s, with the standard reflections of bcc