Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

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

A design of Ti-6Al-4V/ZrB_2 multilayers with good thermal stability to enhance mechanical properties of titanium alloy

Yuyao Nie[a,b,1], Lei Dong[a,b,1], Jie Wu[a,b], Dejun Li[a,b,*]

[a] College of Physics and Materials Science, Tianjin Normal University, Tianjin 300387, China
[b] Tianjin International Joint Research Centre of Surface Technology for Energy Storage Materials, Tianjin 300387, China

ARTICLE INFO

Keywords:
Ti-6Al-4V/ZrB_2 multilayers
Thermal properties
Grain growth
Diffusion

ABSTRACT

The inserting a ZrB_2 modulation layer into TC4 (Ti-6Al-4V) film to form TC4/ZrB_2 multilayers was developed to improve the performance of TC4 film. The enhanced crystallinity of ZrB_2 not only enhanced mechanical properties of multilayers with the modulation ratio decreases, but also restricted the propagation of shear bands and promoted the nucleation of new shear bands, which was of help for the plasticity enhancement of TC4 layer. Moreover, the highest hardness (22.54 GPa) and elastic modulus (262.25 GPa) values were reached at l_{TC4}:l_{ZrB2} of 1:5, and the law of variation was like that simulated by the rule of mixture. The highest critical fracture load (L_{max} = 57.6 mN). With the stability of the mixed interface, the multilayers also exhibited excellent thermal stability. High temperature annealing experiments proved that the multilayers maintain good microstructure and the hardness increased about 3 GPa after annealed.

1. Introduction

Alloy films are known for their good electrical conductivity and soft magnetic properties. However, the plastic deformation of the alloy film at room temperature or lower temperature is usually accomplished by the initiation and expansion of the shear bands [1,2], which makes alloy films prone to plastic failure. In our previous studies about TC4 (Ti-6Al-4V) alloy film, we found that the hardness and elastic modulus of TC4 monolayer film are not excellent enough. How to improve the plasticity of TC4 film should been paid great attention. Up to now, however, the study of TC4 modification is rarely reported.

Multilayers is a typical artificial structural material that exhibits many excellent properties over monolayers, such as the increased hardness in mechanical properties [3–5]. Pan and other research groups have also found that by inserting the second phase material in the alloy film can improve the film plasticity. ZrB_2 has been widely studied because of its high hardness, high melting point and other characteristics [6,7]. Therefore, the periodic insertion of the ZrB_2 layers into the TC4 film to enhance its plasticity has become a consideration for improving the mechanical properties of TC4 film.

For multilayer films, the modulation period and the modulation ratio are two important factors for the growth process [8–10]. In the previous experiments, we found that the multilayer film exhibited better mechanical properties at a modulation period of approximately 30 nm (Λ = 30 nm). In this work, we mainly discuss the influence of the modulation ratio on the microstructure and mechanical properties of the TC4/ZrB_2 multilayers. The $(001)_{ZrB2}$ and $(002)_{TC4}$ have larger mismatch. The mismatch has a great influence on the epitaxial heterogeneous interface, while the interface plays an important role in crystal growth. Pan et al. used a lower mismatch to produce VN/TiB_2 multilayers of coherent growth [4]. In addition, the Zr ($r_{Zr}/r_{Ti} \approx 1.10$) and B ($r_B/r_{Ti} \approx 0.65$) atoms can permeate the Ti lattice forming lattice distortion, which may form a diffusion layer and improve the high temperature performance of the film.

2. Experimental details

The TC4, ZrB_2 monolayers, and a series of TC4/ZrB_2 multilayers at the same modulation period (Λ = 30 nm) and different modulation ratios (l_{TC4}:l_{ZrB2}) ranging from 1:1 to 1:5 were synthesized by the balanced multi-target magnetron sputtering system (FJL560CI2, Chinese Academy of Science). High-purity ZrB_2 (99.99%) and TC4 (Ti-6Al-4V) targets in diameter of 2 in. were mounted at the bottom of the chamber. This deposition system can be found in our previous work [4,5]. The silicon wafer (100) substrates were ultrasonically cleaned in acetone and ethanol sequentially for 15 min and later dried before being mounted on a rotatable substrate holder. The substrate rotation speed was 3 rpm during the deposition process. The substrate temperature

* Corresponding author at: College of Physics and Materials Science, Tianjin Normal University, Tianjin 300387, China.
E-mail address: dejunli@mail.tjnu.edu.cn (D. Li).
[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.ceramint.2017.12.052
Received 2 November 2017; Received in revised form 6 December 2017; Accepted 7 December 2017
0272-8842/

was approximately kept at room temperature (≈ 20 °C). The substrate was positioned on top of the chamber, 6 cm away from each of the target surfaces. The base pressure was less than 3.8×10^{-4} Pa, and then high-purity Ar gas (99.999%) was introduced into the chamber, whose pressure was kept at 2.0 Pa. All substrates were cleaned by ion etching for 15 min prior to deposition at −300 V. The deposition process was carried out in RF mode, with constant powers of 60 W and 120 W at a constant Ar gas flow of 40 sccm and a constant substrate bias of −40 V. The working pressure was 0.5 Pa. The deposition rates of the TC4 layer and ZrB_2 layer were approximately 3.9 nm/min and 7.2 nm/min under the constant parameters mentioned above, respectively. To obtain different l_{TC4}:l_{ZrB2}, the sputtering times of TC4 and ZrB_2 sources were adjusted accurately via programming the coating systems. The thickness of each sample was approximately 600 nm (Λ~30 nm). The top layers of all samples are TC4 layers. The prepared film samples were packed at 3.8×10^{-4} Pa in vacuum and then heated to 600 °C. At this temperature, the samples were remained for 1.5 h. Then the samples were cooled naturally to room temperature (≈ 20 °C), and the TC4/ZrB_2 multilayers were obtained.

The microstructure of the multilayers was characterized using X-ray diffraction (XRD, D8A, Bruker, Germany) with Cu-Kα (40 kV, 20 mA, λ = 1.54056 Å) radiation. The interface and modulation structure of the films were examined with high resolution transmission electron microscopy (HRTEM, JEM-2100F, JEOL, Japan). A Nanoindenter XP system with a continuous stiffness measurement was employed to characterize the hardness and elastic modulus. The maximum indention depth for all samples was kept at 15% of the coating thickness to minimize the substrate effects. This system was also used to perform a nano-scratch test. In this test, the maximum load was set to 80 mN to measure the fracture resistance. All the tests were performed at ambient temperature.

3. Results and discussion

Fig. 1 shows the XRR pattern of TC4/ZrB_2 multilayer at l_{TC4}:l_{ZrB2} = 1:1 (l_{TC4} = 15 nm, l_{ZrB2} = 15 nm). We can clearly observe the multi-stage diminished diffraction peak with the highest number of stages up to 6. This indicates that sharp, flat interfaces and a distinct modulation structure exist in the TC4/ZrB_2 multilayers. The value of modulation period can be calculated according to the diffraction peaks (six orders) located at 2θ = 3.136°, 3.680°, 4.221°, 4.781°, 5.301° and 5.824° using the modified Bragg's law [11], given by:

$$\sin^2\theta = \left(\frac{n\lambda}{2\Lambda}\right)^2 + 2\delta \quad (1)$$

Where Λ is the modulation period, n is the integer reflection order number, λ = 1.54056 Å and δ is the average deviation of the refractive index form unity. The graph in Fig. 1 shows the plot of $\sin^2\theta_n$ versus n^2. Λ = 32.1 nm is obtained from this linear regression of $\sin^2\theta_n$ versus n^2 plot and it is like the modulation period we designed.

To further simulate the low-angle XRD curves to quantify the interface and modulation period, we use the relationship of X-ray intensity and incidence angle 2θ [12]:

$$I \sim I_0 \frac{\sin^2\left(\frac{N\Lambda\sin\theta}{2\lambda}\right)}{\sin^2\left(\frac{\Lambda\sin\theta}{2\lambda}\right)} A(\theta) \quad (2)$$

Where $A(\theta)$ represents structure factor of electronic system in primitive cell [11,13]. For left part of Eq. (2), it is easily derived from the perspective of periodic reflection of X-ray in multi-interface. N represents the number of layers involved in the reflection. I_0 is taken as 1, because we only imitate the periodicity of curves. As for $A(\theta)$, related to the density of charge, superlattice structure, interface roughness and so on, is too complicated to define, we use $e^{-b\theta}$ ($0 < b < 1$) instead of $A(\theta)$ to fit our experiments' curves [12]. Based on the above theoretical analysis, we simulated the XRR curves of multilayers by MATLAB. The result is shown in Fig. 1. We find that as Λ is chosen to be 31.6 nm, the simulated curves reach an agreement with the experimented curves in the diffraction peaks' position.

Fig. 2 shows XRR image of TC4/ZrB_2 films with different modulation ratio (l_{TC4}:l_{ZrB2}). All multilayers show the obvious multistage diffraction peak, and the diffraction peak was weakened significantly as modulation ratio was 1:3. The main reason may be that interfacial diffusion occurs between the two layers, which leads to interface disappeared at modulation ratio of 1:3. As the thickness of ZrB_2 layer increases, the ZrB_2 grains grow and the effect of interface distortion weakens. The modulation structure becomes clear again at l_{TC4}:l_{ZrB2} to 1:4 and 1:5.

Fig. 3(a) shows the XRD patterns of TC4/ZrB_2 multilayers with different l_{TC4}:l_{ZrB2} and TC4 and ZrB_2 monolayers, respectively. The TC4 layer presents a strong (002) texture of α-Ti, and the ZrB_2 layer exists (001) preferred orientation. In multilayers, we can found that the $(002)_{TC4}$ and weakened $(001)_{ZrB2}$ appears at l_{TC4}:l_{ZrB2} of 1:1 and 1:2. Both of the diffraction peaks show a diffusion state, indicating that the film has formed an amorphous and nanocrystalline structure. With the increase of the thickness of ZrB_2 layer, the $(001)_{ZrB2}$ slightly strengthens, and the $(002)_{TC4}$ weakens, indicating that TC4 shows obvious amorphous when l_{TC4}:l_{ZrB2} = 1:3. At l_{TC4}: l_{ZrB2} = 1:5, the $(002)_{ZrB2}$ diffraction peak became stronger, and the crystallinity of the film is up to the best.

Lattice mismatch has an important effect on the interface [14,15]. The δ (mismatch degree) between $(002)_{\alpha\text{-Ti}}$ and $(001)_{ZrB2}$ can be

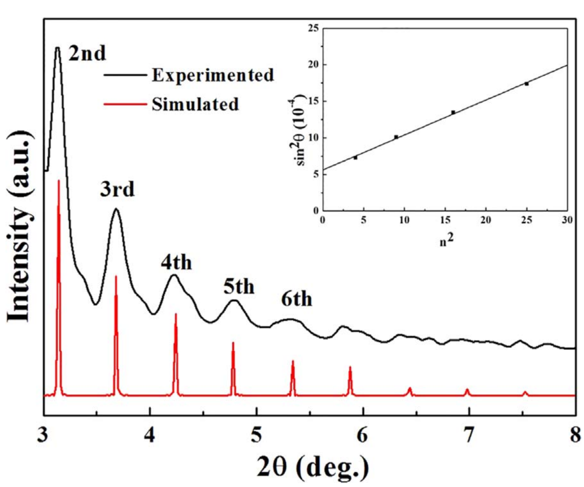

Fig. 1. XRR pattern and simulated curves for TC4/ZrB_2 film with l_{TC4}:l_{ZrB2} = 1:1.

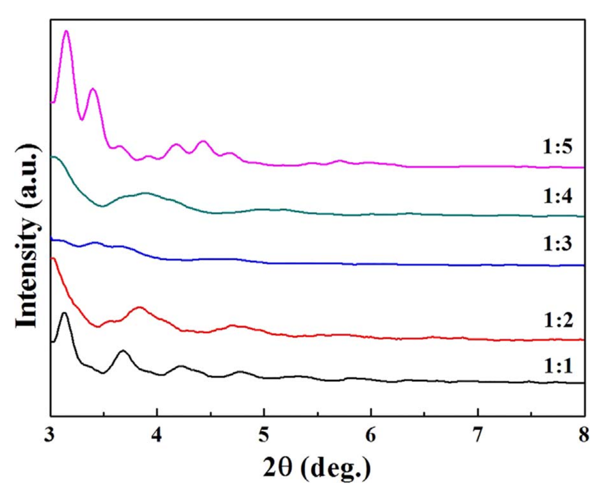

Fig. 2. XRR pattern of TC4/ZrB_2 film with l_{TC4}:l_{ZrB2} = 1:1, 1:2, 1:3, 1:4, 1:5.