Effects of substrate bias on structure and mechanical properties of AlCrTiWNbTa coatings

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AlCrTiWNbTa multielements high entropy alloy films have been synthesised by using magnetron co-sputtering of three binary alloy targets. Effects of substrate bias on the microstructure and mechanical properties of the films are studied. The composition and the crystallographic structure of the films are characterised by an electron probe microanalyser (EPMA) and an X-ray diffractometer respectively. The surface micrographs of the films are described by atomic force microscope (AFM). The microhardness and elastic modulus of the films are measured using a nanoindenter. It is found that the deposition rate of the AlTiWTaNbCr films decreases as the increase in the bias voltage. The microstructure of the deposited films is amorphous. The microhardness and elastic modulus of the films keep at about 12·5 and 180 GPa respectively. The surface roughness is in the range of 0·3–0·5 nm.

Keywords: Multicomponent alloys films, Hardness, Amorphous, Bias voltage

Introduction

High entropy (HE) alloy is defined by Yeh[1] as an alloy with at least five principal elements and equiatomic or nearequiatomic composition. The present researches show that high entropy alloys (HEAs) tend to form solid solution, mainly of face centred cubic (fcc) or body centred cubic (bcc), and nano or even amorphous structure. Because of high randomness and not easy diffusion of atoms, properties of HE alloys are obviously better than the traditional alloys.[2] Through appropriate composition design, HE alloys can exhibit high hardness,[3] excellent resistance to softening even at 800°C,[4] good high temperature oxidation,[1] better work hardening ability, and soft magnetic performance.[5]

Bulk HEAs are usually synthesised by metallurgy technique such as rapid solidification or spray forming. However, all kinds of casting defects including segregation are unavoidable due to a big feature difference between components. Therefore, we are convinced that filming should be an ideal solution to achieve HEAs on real significance. So far, different techniques have been employed to synthesise HEAs including magnetron sputtering, thermal spray deposition, laser cladding, and high energy ion plating, among which magnetron sputtering is easy to realize a mixture of elements on atomic level. The magnetron sputtering technique[6] allows deposition of HEA films in a wide range of chemical compositions. Stoichiometry can be easily controlled by varying the target powers and the relative surface fraction of each element on a mosaic target.

Selection of HEAs elements mainly focuses on subgroup B. Research works have been done on AlCrFeNiMn, AlCrCuFeCoNi, AlMoNbSiTaTiVZr, AlFeTiCrZnCu, etc. Some benefits in lightweight and performance should be brought by adding some non-metals (B, Si) or light metals (Al, Ti). In this study, magnetic elements (Fe, Co, and Ni) are not sedulously selected. AlCrTiWNbTa thin films have been synthesized by magnetron sputtering from three binary alloy targets, rather than from an alloyed target formed by melting or casting, which is difficult to adjusting the stoichiometry. Influence of bias voltage on the HEAs thin films has been investigated.

Experimental

HEAs thin films were deposited using a JGP-450 Type multi-target magnetron sputtering system manufactured by Shenyang Scientific Instrument Research Centre. Three targets are Al–Cr, W–Ti, and Nb–Ta alloys respectively with a purity of 99·99%, and focused onto rotating *p*-Si substrates, which are ultrasonically cleaned successively in acetone, ethanol, and deionised water for 10 min before being putted into the vacuum chamber. After the Si substrate is etched by Ar plasma for 10 min the deposition of multicomponent alloy thin films is carried out according to the parameters shown in Table 1.

The composition and phase structure of the deposited films are characterised by an electron microprobe analyser (EPMA-1600) and multifunctional X-ray diffraction (Bruker-D8, XRD) respectively. The film

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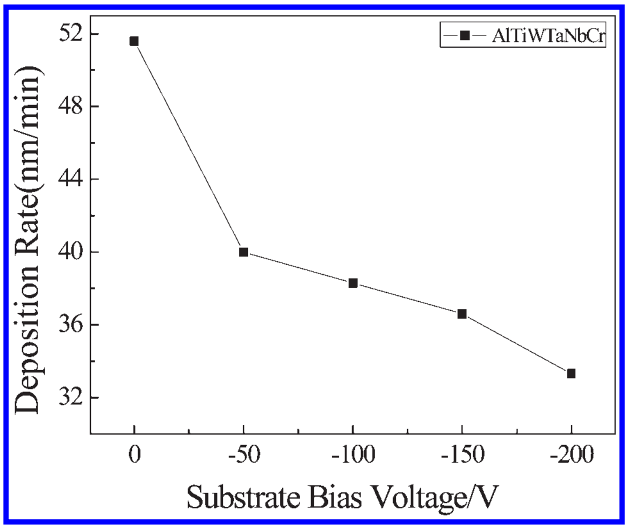
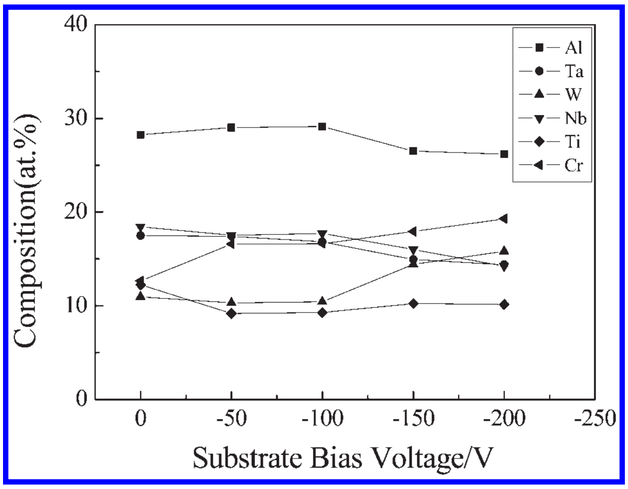


1 Deposition rate of AlTiWTaNbCr films under different substrate biases



2 Chemical composition and relative content of AlTiWTaNbCr films analysed by EPMA as function of substrate bias

thickness is measured in a ZYGO type surface profiler. The microstructure and thickness of the films are observed by SUPRA 55 SAPPHIRE (ZEISS, Germany). The microhardness and elastic modulus of the films are examined by nano-indentation (XP System MTS). AFM observations are performed in tapping mode (Nano-Instuments CSPM-5000).

Results and discussion

Relationship between the deposition rate with the bias voltage is shown in Fig. 1. It can be seen that the deposition rate decreases from 51·6 to 33·3 nm min^{-1} with the increase in bias voltage from 0 to -200 V. The decrease in deposition rate can be ascribed to an increase in the bombarding ion energy, which is expressed in a formula as following[8]

$$U_k \propto \frac{D_W V_s}{P_g^{0\cdot 5}}$$

where D_w is target power, P_g is chamber pressure and V_s is bias. It is obvious that there is a direct correlation between the ion energy and bias voltage. The bombardment of ions has a re-sputtering effect on the deposited film besides enhancing film densification.[9]

Figure 2 shows the chemical composition of the films deposited at various bias voltages. It can be seen that the atomic per cent of the components except for Cr has no significant change when the bias voltage is -100 V. The content of W and Cr increases and that of Al, Nb, and Ta decreases with the increasing bias voltage after over -100 V. Titanium content is not sensitive to the bias in the range of -50 to -200 V. It can be also found in Fig. 1 that the changing trend of the contents of the sputtered elements from the Nb–Ti target with the bias voltage is accordant, which is different from the other two targets. Generally, the atomic percent of each element in all the films changes from 10 to 30 at-%, which is in accord with HE definition, i.e. the concentration of each alloying elements is not less than 5 at-% and not more than 35 at-%. We believe that the atomic per cent of the films has a close relationship with the composition of alloying target, sputtering rate, and the kinetic energy and mass of the depositing metallic atoms. The kinetic energy of the metallic atoms depends on the argon pressure and the target to substrate distance in our experimental conditions. Bias effect is most evident in the kinetic energy and mass. Therefore, the design of the targets in the present study is reasonable. The films with the stoichiometry of HEAs can be achieved at various voltages, and, as is known to all, applying a bias is helpful to improve the adhesive strength and to obtain a more compact film.

Changes of the roughness (Ra and RMS) with substrate bias are shown in Table 2. One can see that roughness average decreases with substrate bias until it reaches a minimum of about 0·3 nm at -150 V. Typical AFM micrographs of AlTiWTaNbCr thin films deposited at 0, -50, -100, -150 and -200 V are shown in Fig. 3*a–e* respectively. The decrease in surface roughness with bias is ascribed to an increase in the density and energy of the ions flux, leading to a denser structure. However, the surface roughness starts to increase with further increasing the bias. The increase in the roughness is attributed to re-sputtering or etching of the grown film by high energy particles.

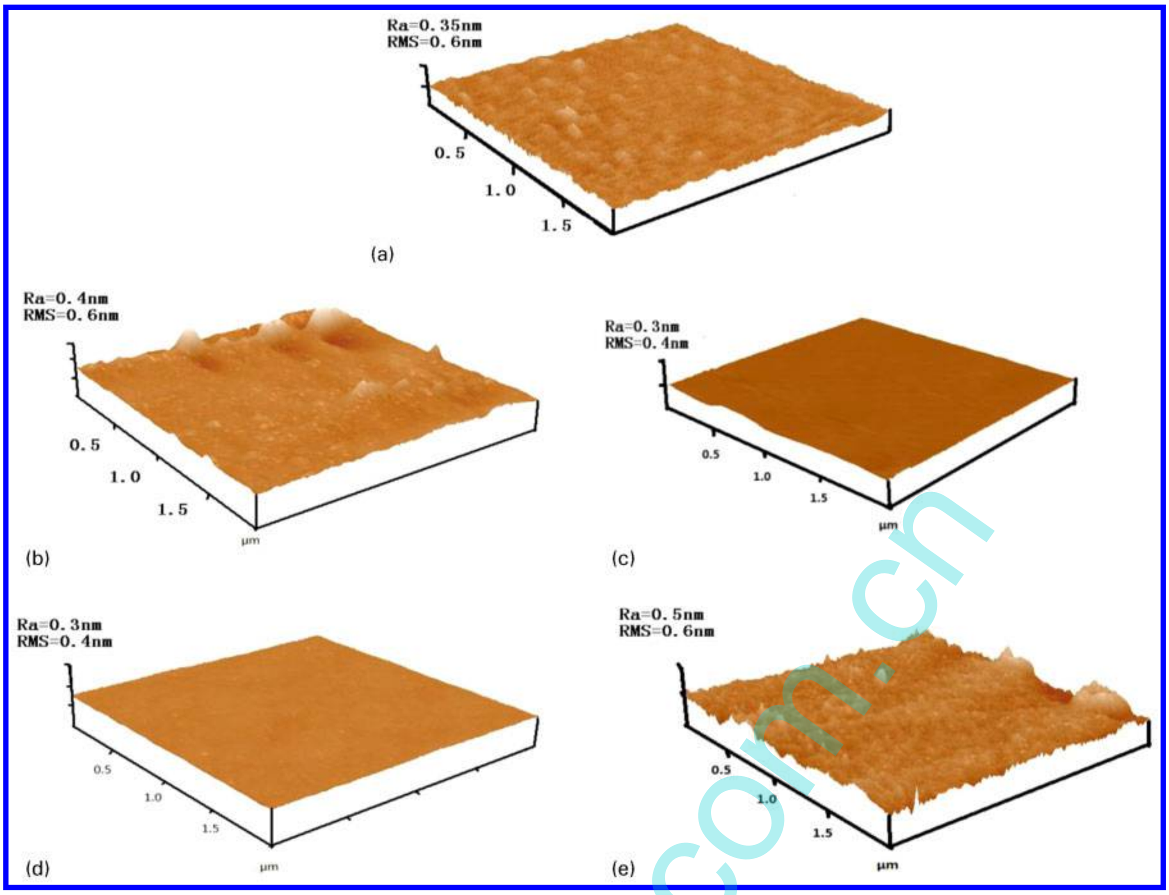
From XRD analysis shown in Fig. 4, it is found that all of the films deposited films at various bias voltages exhibit only substrate Si peaks and a broadened peak

Table 1 Parameters of magnetron sputtering

Parameters	Value
Substrate material	Si
Gas flow/Ar	20sccm
Base pressure/Pa	$8\cdot 0\times 10^{-3}$
Working pressure/Pa	0·67
Deposition time/h	1
Sputtering power/W	100
Substrate temperature	RT
Substrate bias/V	0, −50, −100, −150, −200

Table 2 Surface roughness of thin films deposited at different substrate negative biases

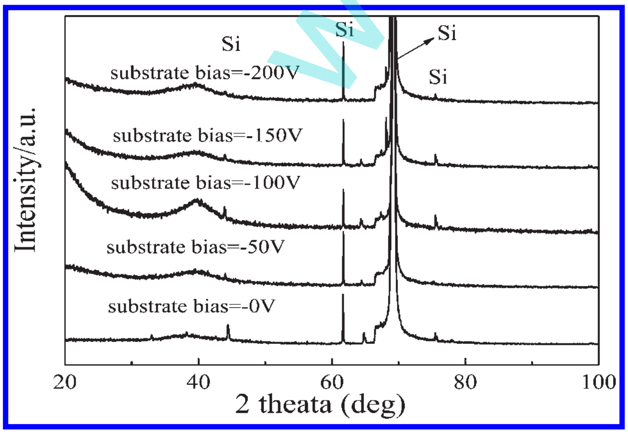
Surface roughness	0 V	50 V	100 V	150 V	200 V
R_a (roughness average)/nm	0·35	0·4	0·3	0·3	0·5
RMS (root mean square)/nm	0·6	0·6	0·4	0·4	0·6



3 **AFM Micrographs of AlTiWTaNbCr thin films deposited at *a* 0 V, *b* −50 V, *c* −100 V, *d* −150 V and *e* −200 V**

centred at 35–45° which is evidenced that the structure is amorphous or nanocrystalline phase. Along with the increase in bias voltage, the diffraction peak has a tendency toward becoming strong and sharp.

Results from the bulk HEAs show that a complex relationship exists between crystalline structure and composition. It has been found that the presence of Cu, Co, or Ni promotes the formation of a FCC solid solution, whereas, Cr or Fe induces the formation of a BCC solid solution. Yeh *et al.*[9] have even shown that the BCC structure is stabilised when the atomic percentage of Al with FCC structure is higher than about 15%. The films in the present study, however, have an amorphous structure in spite of the atomic percentage of Al over

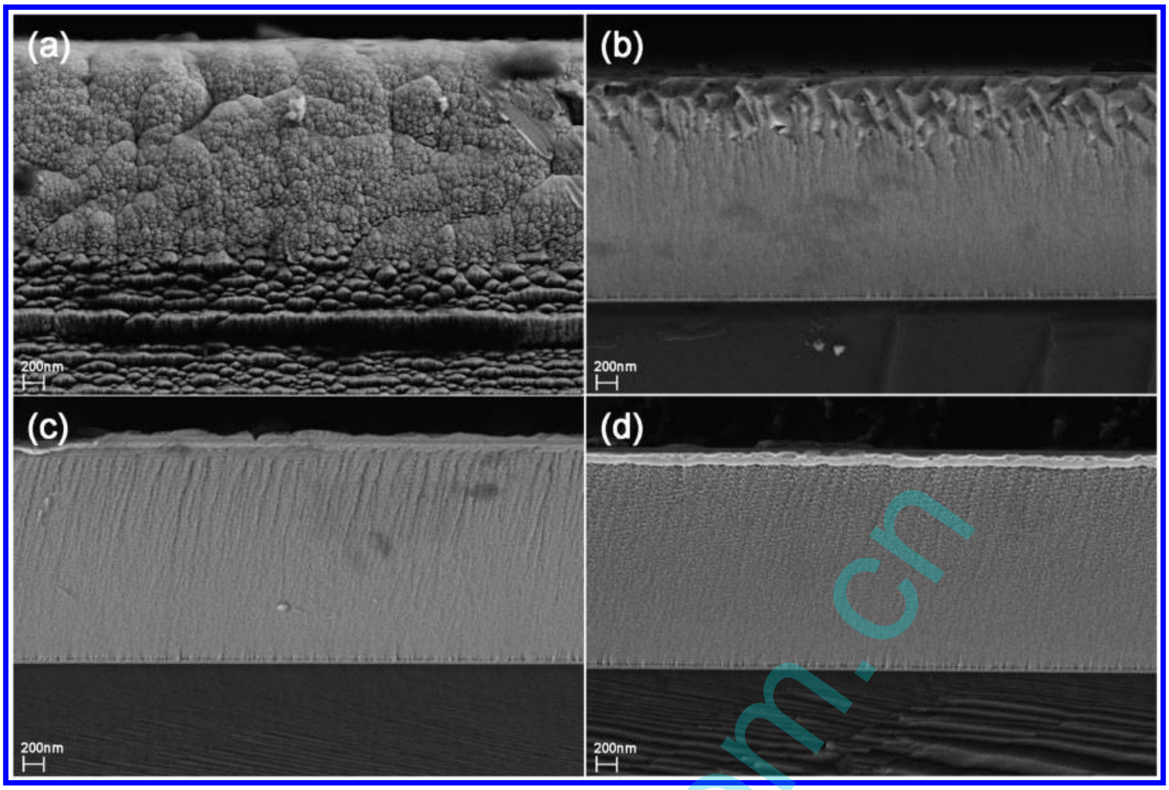


4 **X-ray diffraction patterns of multicomponent alloy films as function of substrate bias**

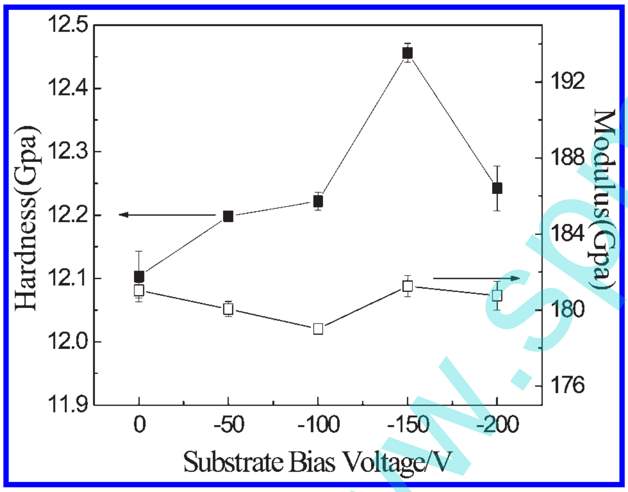
25%. Possible reasons are that the atomic percentage of other components except for Al corresponds to the theoretical composition for an equimolar HEA of six elements, and that low substrate surface temperature can also play a role, in this case, it remains below 100°C. The surface diffusion of the energetic species impacted on the substrate rarely occurs in such temperature.

Figure 5 shows the SEM cross-sectional morphology of the deposited films at different biases. Figure 5*a–d* represents deposited at 0, −50, −100 and −150 V respectively. The particles and layer of the film can be clearly seen in Fig. 5*a*. The cross-section of Fig. 5*b* and *c* present apparent column structures, and the view of Fig. 5*d* displays very fine striation lines with interspacing. These are the amorphous grain boundaries as described by literatures. The thickness of the films deposited under a series of bias voltages is in agreement with the results measured by surface profiler.

Nanohardness measurements reflect the hardness and Young's modulus of AlTiWTaNbCr films deposited at varying bias. The penetration depth should be less of 10% of the films thickness to avoid substrate effects. Each sample was taken 9 points during the test and hardness and Young's modulus values of every sample were determined from the mean value. The microhardness and modulus is shown in Fig. 6 as a function of substrate bias. It can be seen that the hardness increases with substrate bias until it reaches a maximum of about 12·5 GPa at −150 V, beyond which it decreases. The modulus is observed to initially decrease, but then increase and maintain an approximately constant value for a bias over −150 V. The mechanical properties of the selected target elements are shown in Table 3.[10]



5 Images (SEM) of AlTiWTaNbCr films deposited at *a* 0 V, *b* −50 V, *c* −100 V and *d* −150 V



6 Hardness and elastic modulus of AlTiWTaNbCr films analysed by Nano indenter as function of substrate bias

Clearly, the microhardness of multielements high entropy alloy films is greatly improved, which is credited to solid solution strengthening, i.e. the components in the films are not just a simple mixture in physics. The decrease in hardness at a lower and higher substrate bias should be attributed to the densification and residual internal stress of the deposited films.

Tribological property of films depends mainly on their thickness, surface roughness, hardness and elastic modulus. From Ref. 11 it can be known that H/E and H^3/E^2 can better reflect the frictional characteristics, where H and E are the hardness and the elastic modulus of the film respectively. It means the greater the ratio of H/E, the better toughness, thus superior frictional behaviour. Accordingly, the higher H^3/E^2, the larger load can be born on the film without yield, and hence the better resistance.

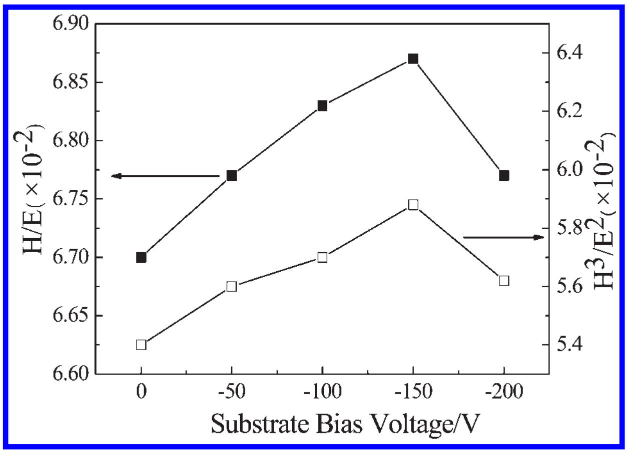
Relationship between the ratios of H to E and H^3 to E^2 and the substrate bias are shown in Fig. 7. It is clear that there is a maximum value attained at −150 V, which is similar to the change trend shown in Fig. 6, i.e. the film deposited at −150 V bias has a best mechanical property.

Conclusions

In this study AlCrTiWNbTa HEA thin films have been successfully deposited by magnetron co-sputtering of three binary alloy targets at a range of applied substrate biases. The chemical composition, microstructure, and properties of the films have been investigated. It has been found that the atomic fraction of all the elements in

Table 3 Characters of selected elements' mechanical properties

Element	Hardness/HBS or HV	Elastic modulus E/GPa	Tensile strength σ_b/MPa	Yield strength $\sigma_{0\cdot2}$/MPa
Al	20–35	62	40–50	15–20
Cr	110	102	300	150
W	450 (HV)	405–410	1000–1200	750
Ti	60–74	106	235	140
Nb	80 (HV)	103	275	207
Ta	120 (HV)	186	392	362



7 ***H/E* and H^3/E^2 of HEA films deposited at various substrate biases**

the films deposited in this experimental conditions is in the range of 10–30%, in accordance with the definition of high entropy alloy, that the deposition rate decreases with increasing substrate bias due to re-sputtering and densification, that the films deposited at an applied bias of −150 V have the highest hardness and elastic modulus as a result of ion-induced defects, and that the surface roughness is in the range of 0·3–0·5 nm.

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