Characterization of TiAlV Films Prepared by Vacuum Arc Deposition: Effect of Substrate Temperature

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Three TiAlV films have been prepared by vacuum arc discharge technique at different substrate temperatures (50, 300, and 400 °C). The depositions were carried out from aluminum, vanadium and titanium elemental targets. The temperature effects on the crystalline quality and texture have been investigated by means of X-ray diffraction. Two phases have been identified and the grain size has been found to increase with temperature. The composition of the films has been determined by proton induced X-ray emission technique. The Ti ratio was found to increase with temperature. The microhardness, measured by the Vickers indentation method was found to decrease with temperature. X-ray photoelectron spectroscopy was used to study the chemical composition of the passive layer formed on the films by analyzing high resolution spectra of Al 2*p*, Ti 2*p* and V 2*p*. This layer was mainly composed of TiO_2 with a small participation of other oxidation and metallic states of Ti, Al and V.

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1. Introduction

Due to its interesting chemical and mechanical properties, titanium alloy is widely used in many applications [1–4]. One particular alloy, the Ti–6Al–4V, has the best performance among the different grades of titanium. The pure titanium is a monophase, physiologically inert, and non-toxic metal. Ternary titanium alloys containing Al and V or Nb exhibit α and β phases structure that has attractive mechanical properties, high wear resistance, hardness, tenacity, resistance to fatigue and high corrosion resistance [5–9] besides having a low density, which makes it a good candidate in the aeronautics industry. In addition, this alloy has an excellent biocompatibility permitting its use in the fabrication of medical implants [4, 10].

It is critical from the biocompatibility point of view to understand the surface properties of the alloy. The formation of passive oxide layer (TiO_2) has the potential to stop the corrosion by reducing the electronic exchange process. Moreover, this layer is chemically stable and can be renewed quickly after each degradation [11].

It is also important to study the microhardness of the films. Many factors could affect it such as TiO_2 phase, defect density, stoichiometry, preferred orientation, residual stress, α/β phases and grain size [12].

Titanium alloys can be produced by chemical vapor deposition (CVD) or physical vapor deposition (PVD) such as rf-dc sputtering [13–15] and flash evaporation [16]. Although it is not frequently used in this domain, the vacuum arc discharges is an attractive method owing to its high efficiency, control of composition and structure of the films, and high adhesion forces between film and its substrate. It can also produce ions of higher kinetic energies (up to 150 eV) [17, 18]. This results in the formation of a denser film and reducing surface defects, such as voids and columnar growth. While the vacuum arc discharge is normally employed to obtain nitride or oxide films, to our knowledge nobody prepared this alloy (TiAlV) using industrial vacuum arc. Therefore, we aimed to prepare TiAlV alloys starting from elemental targets and using this technique.

In this work, three TiAlV films have been deposited on Si substrates by vacuum arc discharge method with three different temperature conditions. The crystallographic properties of the films were studied by X-ray diffraction (XRD) technique. X-ray photoelectron spectroscopy (XPS) was used to investigate the passive layer formed at the surface. The microhardness was investigated using the Vickers method. In addition, the elemental composition of the films was obtained by proton induced X-ray emission (PIXE) and energy dispersive X-ray (EDX) analysis techniques.

2. Experimental details

The films were prepared by vacuum arc deposition using a V-1000 "U" system from pure aluminum, vanadium, and two titanium elemental targets used in four independent arc sources of metallic plasma (Fig. 1). The films were deposited on a Si (100) substrate within an argon discharge for 15 min. The residual pressure was lower than 3×10^{-6} Torr, and the working pressure was about 5×10^{-3} Torr. The substrate rotated continuously around the vertical central axis. The substrate was not biased (floating). During deposition, the arc current was maintained at 100 A, 80 A and 90 A for Ti, Al, and V targets, respectively. Three films were prepared under the same conditions but with different substrate temperatures (50 °C, 300 °C, and 400 °C).

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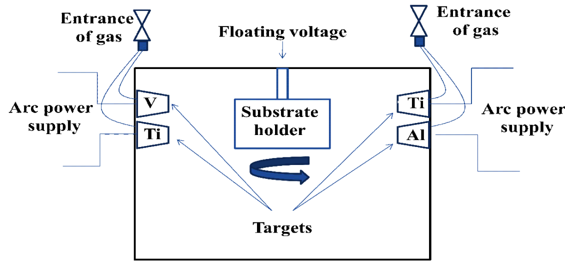

Fig. 1. The vacuum arc discharge system used in the deposition.

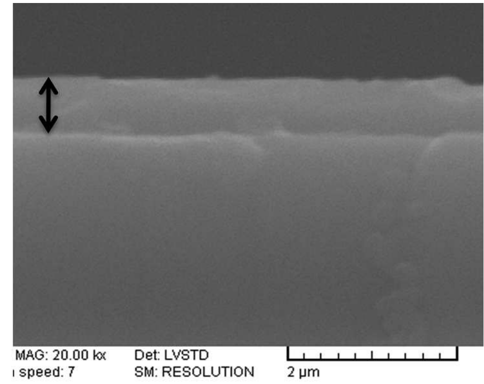

Fig. 2. SEM Cross-section image for film prepared at 50 °C.

The crystallographic properties of the prepared films were studied by XRD (Stoe StadiP Transmission X-ray diffractometer). Although that transmission electron microscopy (TEM) measurements could provide a more clear insight of the grain size, but it is fair enough to use Scherrer's formula to follow the variation of the averaged grain size with the substrate temperature. Films thicknesses were obtained with a Tescan Vega II XMU scanning electron microscope (SEM). EDX was used for determining the elemental composition of the prepared samples.

The elemental composition of the films was measured using the PIXE technique. The measurements were performed using 2 MeV proton beam produced from the 3 MV HVEETM tandem accelerator [19]. Pure Ti, Al, V and Si reference materials have been used to validate and calibrate the PIXE measurements.

The microhardness has been measured using the Vickers technique with a pyramidal diamond indenter and under a loading force varied from 15 to 75 gram force (gF). The loading time was fixed at 15 s. The load values were chosen carefully after a series of experiences and the values were close to that found in literatures applied on similar hard alloys. SEM was used to determine the dimensions of the indentation. The microhardness values are the average of three measurements.

The XPS analyses were performed using the SPECS UHV/XPS/AES system with a hemispherical energy analyzer. The monochromated Al K_α X-ray (1486.6 eV) is used as the excitation source and is operated at 250 W. High resolution spectra of the Al 2p, Ti 2p and V 2p peaks are treated and deconvoluted, with CasaXPS version 2.3.16 Dev52, using a non-linear least-squares method with a Gaussian/Lorentzian peak shape GL(30) and the background was subtracted using the Shirley method [20, 21].

3. Results and discussion

3.1. Structural characterization (SEM + XRD)

The thickness of the films was found to be less than 1 μm. Figure 2 shows the SEM cross-section image for film prepared at 50 °C. This thickness was about 700 nm.

Figure 3 shows the XRD patterns of the TiAlV films. Two small peaks can be identified and associated to α-phase of Ti(100) at 35.2° and α-phase of Ti(101) at 40.15°. The highest intensity peak is asymmetric and can be assigned to α-phase of Ti(002) and β-phase of Ti(110) at 38.2° and 38.4°, respectively. The α/β peak was deconvoluted by Gaussian/Lorentzian peak shape and the FWHM of the α-phase of Ti(002) peak was calculated. The grain size was then calculated using Scherrer's formula [22] for the three films.

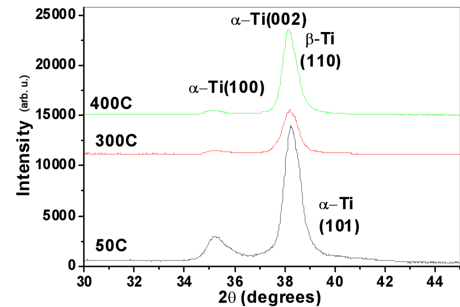

Fig. 3. XRD pattern of the TiAlV films deposited at temperatures 50 °C, 300 °C and 400 °C.

Table I shows that the grain size increased from 13.4 nm to 17.5 nm when the substrate temperature increased from 50 °C to 400 °C. Similar results have been obtained for cubic ZrN thin film [23] and for TiN_xO_y films [24]. This indicates an improvement of the crystalline quality with the temperature.

TABLE I

Grain size (nm) as a function of substrate temperatures.

Temperature [°C]	50	300	400
Grain size [nm]	13.4	15.5	17.5

3.2. Micro-hardness measurement

Table II shows the result of the microhardness measurements for the three films with different loading force

values. Since the thickness of the films is less than 1 μm, only the measurements corresponding to smaller loads (15 gF and 25 gF) are representative of the proper microhardness of the films. Measurements taken with larger load values could be influenced by the substrate hardness. Thus, in the following the measurements corresponding to smaller loads are discussed.

TABLE II

Vickers microhardness as a function of the loading force for TiAlV films prepared at different temperatures. The results presented here are the mean value of three measurements ($\pm$ standard deviation).

Load force	Micro-hardness [GPa]		
[gF]	50 °C	300 °C	400 °C
15	18.1 ± 0.3	16.2 ± 0.1	15.2 ± 0.2
25	17.2 ± 0.6	14.8 ± 0.2	13 ± 0.1
50	12.3 ± 0.4	16 ± 0.4	14 ± 0.2
75	12.1 ± 0.4	15 ± 0.6	13.6 ± 0.5

The microhardness shows a clear decrease with increasing the temperature. This could be attributed to the increase of oxygen content in the films as follows. It was previously reported [24] that oxygen content in the films prepared by vacuum arc technique decreased with increasing the temperature. On the other hand, the works of Leng et al. [25] on TiO_x and Lui et al. [26] on wollastonite/TiO_2 composite coating suggest an increase of the microhardness with increasing the oxygen content.

The values of the microhardness of the TiAlV films found in the literature varied from 4 GPa to 11 GPa [25, 27–29]. Our measurements are higher than these reported values of about few GPa. This difference could be due, as we believe, to the difference in synthesis techniques. In vacuum arc deposition (we are using), the energy of ionic bombardment is higher (< 150 eV) than the sputtering bombardment energy (< 50 eV).

It is noteworthy to mention that the larger value of the microhardness corresponds to the smaller grain size (at 50 °C). This correlation is in good agreement with a previous study [12] in which authors suggest a relation between the grain size and the microhardness.

3.3. Composition measurement (EDX + PIXE + XPS)

The elemental composition of the films has been obtained by means of the PIXE technique. The Ti ratio in the film was calculated as Ti/(Ti+Al+V). Table III demonstrates the values of Ti ratio for the three films. It is clear that the Ti content increased with the temperature.

TABLE III

The evaluation of Ti ratio as a function of the substrate temperature.

	50 °C	300 °C	400 °C
Ti ratio	0.814	0.822	0.841

The stoichiometry of films was found to be sensitive to the substrate temperature. The EDX analysis of the film prepared at 50 °C showed that the Ti ratio was about 0.81. This value is in good agreement with that found by PIXE technique.

The ratio at 0.841 is close to that found by Alfonso et al. whose films were prepared by RF sputtering method starting from a Ti6Al4V target [30].

XPS probes only the very first layers of the surface (< 10 nm) while both PIXE and EDX probe deeper depths (order of microns). For this reason, the stoichiometry is generally obtained using PIXE or EDX.

The chemical composition of the passive layer formed by the exposure of the deposited films to air was studied by means of XPS. No significant change regarding the chemical composition has been observed between the samples. Therefore, we present in Fig. 4 high resolution spectra of Ti 2p, V 2p, and Al 2p for one sample.

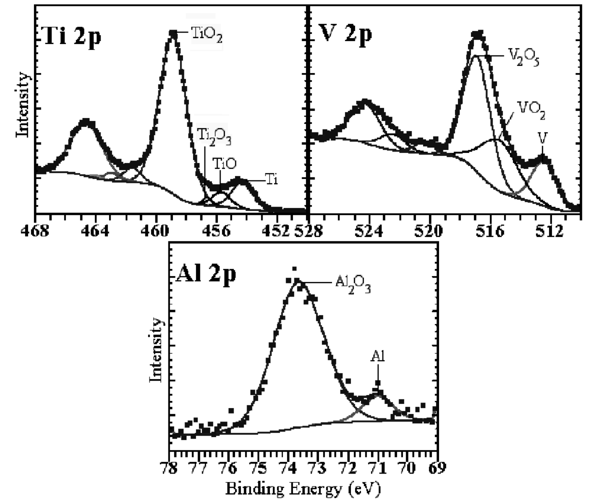

Fig. 4. Deconvolution of high resolution spectra of Ti $2p_{3/2}$, V $2p_{3/2}$, and Al $2p_{3/2}$.

The deconvolution of Ti $2p_{3/2}$ spectrum gives four components that correspond to TiO_2 (BE = 459.2 eV, 83%) [31], Ti_2O_3 (BE = 456.5 eV, 1%) [30, 32], TiO (BE = 455.4 eV, 5%) [33–35] and Ti (BE = 454.2 eV, 11%) [35–37]. This result is in good agreement with previously reported studies, where TiO_2 was also the major component.

V $2p_{3/2}$ spectrum has been deconvoluted into three components; V_2O_5 (BE = 516.4 eV, 51%) [38–40], VO_2 (BE = 515.4 eV, 31%) [30, 38] and metallic vanadium (BE = 512.2 eV, 18%) [41, 42].

This finding is different from Alfonso et al. [30], where vanadium was mainly composed of the VO_2 component and a smaller V_2O_5 component; and also different from Milosev et al. [35], where only metallic vanadium was observed on the passive layer surface. In both studies a non-monochromatized Al K_α X-ray source has been used. The disagreement in this result is probably due, as we believe, to difference in synthesis techniques.

Al $2p_{3/2}$ spectrum shows a major contribution of Al_2O_3 (BE = 73.6 eV, 91%) and a small part of metallic alu-

minum (BE = 71.0 eV, 9%) [30]. Similar behavior was reported in both studies [30, 35].

4. Conclusion

In this work, we showed that TiAlV films can be successfully prepared by vacuum arc discharge technique starting from Ti, Al, and V elemental targets. The effect of temperature on the composition and crystalline quality has been investigated. The films composition is found to be getting to the standard Ti6Al4V alloy. Increasing the temperature permitted to increase the Ti ratio and to enhance the texture of the films. The microhardness of the films was found to decrease with the temperature and to be slightly larger than literature values. XPS study proved that the thin passive layer is composed mainly of TiO_2. The investigation of corrosion in such films is necessary and it will be the subject of a future work.

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