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Titanium – Aluminium Thin Films Preparation By Oblique Angle Sputtering And Their Characterization

Sudheendra P[1]., A. O. Surendranathan[1], N. K. Udayashankar[2]

[1]Department of Metallurgical and Materials Engineering, [2]Department of Physics
National Institute of Technology Karnataka. P. O. Srinivasanagar, Surathkal, Mangalore-575025.

Abstract

Intermetallic titanium (Ti) aluminium (Al) films (Al content ranging from ~48 to ~53 at.%) were prepared on different substrates at 500˚C by unbalanced reactive magnetron sputtering in an Argon atmosphere of varying pressure. The chemical composition, microstructure, stress and microhardness properties of these films were systematically investigated by means of energy dispersive spectrometry (EDS), scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD) and microhardness measurements. Also heat treatment studies were carried out for the coated films. The XRD measurements reveal evolution of crystallite Ti-Al structure of the deposited films. The observed peak shows varying aluminium composition and their structures are in the form of Ti_{1-x} Al_x In order to understand the microstructure evolution, the XRD spectra and corresponding calculations of the Ti-Al films without substrate heating during deposition are also analyzed. The surface roughness of Ti-Al films also exhibits a nonlinear variation, which is due to the variation of grain size and the competitive growth of different size particles. The influences of microhardness of the films with various substrates were analysed. All the intermetallic Ti-Al films show enhanced mechanical properties when compared with the composite Ti-N films deposited under the same condition. The best microhardness is obtained for the Ti-Al film with 52 at.% Al.

Key Words: *Magnetron Sputtering, Intermetallic, Oblique angle, Microstructure, Heat-treatment*

1. Introduction

Oblique angle deposition is one of the methods used for deposition of thin films with columnar structure [1, 2]. This technique can be used to deposit metals, metal oxides [3-8]. It is well acknowledged that films deposited normal to the substrate have highly oriented structure [9, 10]. However, some times it was observed that the growth may occur the in the direction of vapour flux [11]. It has been also found that crystallographic orientation of the substrate greatly influences the growth orientation of the films.

This paper intends to investigate the growth mechanism of Ti-Al thin films prepared by the oblique angle deposition of individual Ti and Al targets in an unbalanced magnetron sputtering under variable conditions. There are a number of deposition parameters which may affect the properties of the films. The most important parameters are working pressure, target to substrate distance and DC power. Working pressure of the sputter gas along with the target power influences the deposition rate, film quality and crystallinity of the films. Also working pressure determines density of plasma bombarding the target and affects the mean free path of target atoms moving in the opposite direction. Whereas power determines the energy of atoms knocked out from the target, consequently influencing their mean free path and mobility before they hit the substrate. Good columnar grain structure growth observed when mobility is not high and deposition atoms are less scattered by Argon before they reach the substrate. Evidently, the deposition parameters counteract on the film properties and have to be balanced for the best crystallinity and the growth rate.

2. Experimental procedure

Ti-Al films were prepared by unbalanced DC magnetron sputtering from individual titanium and aluminium target onto corning glass, stainless steel (306) and copper substrates in argon atmosphere. Plasma was generated for 30 min. to clean the substrate before deposition. A sample holder with substrate heater is used for deposition. The target to substrate distance was varied in the range of 5 to 10 cm. The background pressure in the chamber was 2.67 x 10^{-4} Pa.

Two sets of samples were prepared. One set was prepared at the deposition angles 40° and 50°, at constant pressure of 0.27 Pa. Current for DC sputtering was set to 0.25 A with voltage of about 350 V, and the deposition time was 60 min along with substrate heating. For other set argon pressure was varied in the range of 0.67 to 2.67 Pa at deposition angle of 40°. Smaller current of 0.15 A was used for sputtering, however, the deposition time was increased to 90 min without substrate heating. The voltage values were different for different pressures to hold the same current: 260 V for 0.67 Pa, 240 V for 1.33 Pa and 220 V for 2.67 Pa.

Crystal structure and orientation of the obtained Ti – Al films were studied by an X-ray Diffractometer (XRD) with Cu K_α radiation. The tube voltage and current were 30 kV and 40 mA. The scan step size was 0.01°/s speed. Microstructure and the grain morphology analyses were performed using a JEOL Scanning Electron Microscope (SEM). SEM accelerating voltage was 15 kV.

In the first set of samples pressure was fixed at 0.27 Pa. The films were deposited with distance from the target varied from 5 to 10 cm and fixed at 6 cm to get good homogeneous film. The mean free path (mfp) of Ti/Al atoms in argon (Ar) can be calculated as $l_{mfp} = \frac{1}{nA}$, where $A = \pi(R_t + r)^2$ is effective area of colliding target and gas atoms having radius R_t and r respectively, n is number of atoms per unit volume which can be determined from the Avagadro's number N_A and ideal gas law leading to equation

$$l_{mfp} \sim \frac{RT}{\sqrt{2\pi}(R_t + r)^2 N_A P}$$

Here R is the gas constant, T is absolute temperature, and P is pressure of working gas. As there is no experimental value of r for inert gas Ar, the theoretical value of 71 pm is used. For Titanium atoms R is 147 pm while for Aluminum atoms R is 143 pm. Then l_{mfp}, calculated for Titanium and Aluminium atoms was found to be 5.19 cm and 5.37 cm respectively at room temperature. These values are close to the fixed distance between the substrates and the target D = 6 cm.

3. Result and Discussion

3.1 Scanning Electron Microscopy and X – Ray Analysis

Some SEM pictures of the prepared samples are shown in Fig. 1. All of the samples have a columnar grain structure for Ti – Al films. It is seen that the films deposited at oblique angle 40˚, grow towards the direction perpendicular to the substrate. At deposition angle of 50° the grains grow at an angle to the surface. It is seen that the oblique columnar structure is not well defined because the columns consist of stacks of small grains and it is difficult to draw the exact angle of the growth.

SEM pictures clearly show that some of the grain structures have grown at an angle from the vertical to the substrate. The only explanation to this could be the oblique grain growth direction is not along the crystal orientation. Initially the crystals grow on the substrate from nuclei in all directions with the orientations vertical to the substrate until they reach the shadow from their neighbours. The vertical and sidewise growth will occur untill coloumns touch one another. Then a new layer of crystals grow on top of them retaining the original orientation but shifted as a whole towards the target. The resulting granular structure should have inclined columns shaped as a staircase where a single step represents a crystal with a orientation perpendicular to the substrate. Obviously, the crystal size in vertical direction and the voids between the grains will be determined by the oblique angle of deposition.

Fig. 2 shows XRD patterns of deposited Ti – Al films revealing (200) peak only a vertically oriented crystal structure typical for oblique angle deposition. Texture was studied by the XRD. Experimental values of the crystal size s (in vertical direction), calculated from the Scherrer's equation using the full width at half maximum (FWHM) values of (200) peaks. $s = \frac{0.9\lambda}{\left(B_m^2 - B_s^2\right)^{1/2} \cos\theta}$ and texture of the film was calculated using $t = \frac{I_{film}}{I_{Std.}}$ here λ is the X-ray wavelength; B_m and B_s are the experimental and instrumental FWHM's, respectively. The s value decreases with the deposition angle (longer grain shadows lead to smaller crystal size). The calculated crystallite sizes are of the order of 1200 – 1300 nm and are close to the size of small grains

observed in Fig. 1a as "bricks" of the oblique columns.

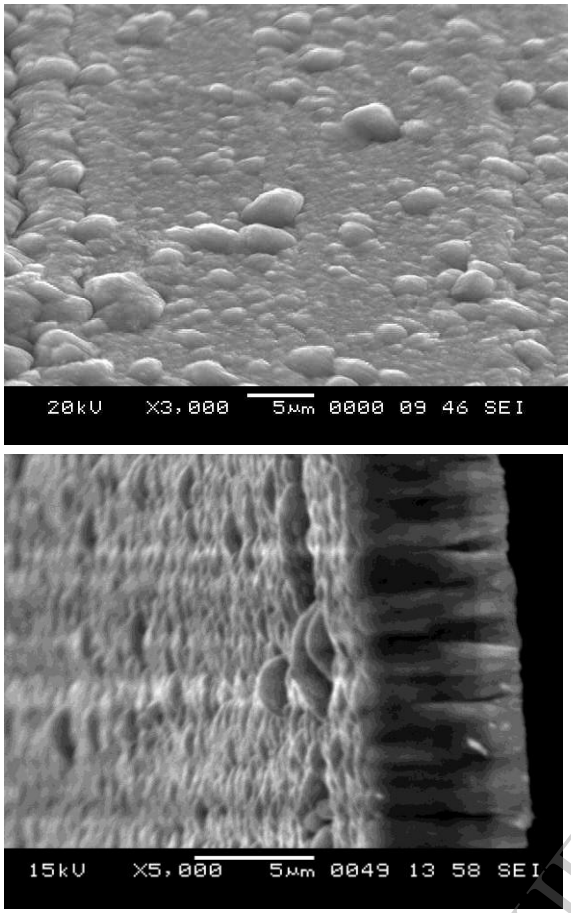

Fig. 1 SEM pictures of the free standing Ti – Al films samples – Top view and side view.

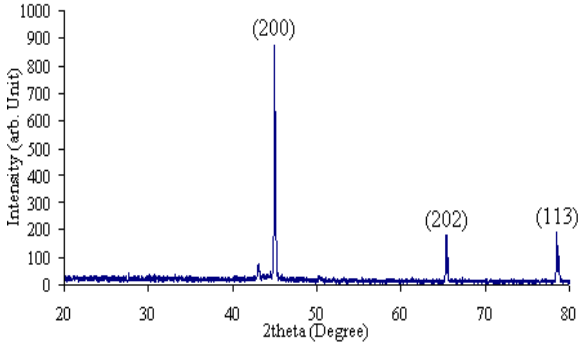

Fig. 2 X-ray diffractogram of TiAl thin film coated

Table 1. Texture coefficients of the XRD peaks of the TiAl thin films

Sl. No.	Peak Position (degree)	(hkl)	Texture coefficient (T)
1	44.99	(200)	0.832
2	65.56	(202)	0.079
3	78.89	(113)	0.088

It is known that Ti – Al columnar grains develop a significant compressive stress in the direction parallel to the surface as a result of growing closely parallel. It leads to the (200) peak shift to higher d- spacing values from the unstressed value of d and it decreases with the deposition angle. Obviously, it is because of long grain shadows during the deposition and big voids between the crystals.

3.2. Deposition pressure

In the second set of experiments, the oblique angle was fixed at 40°, and the pressure was increased to 0.67, 1.33 and 2.67 Pa in order to increase plasma density. This allowed to reduce the values of applied voltage and to decrease the energy of depositing atoms. The applied DC current was also reduced down to 0.15 A.

Fig. 3 shows the obtained film thickness as a function of pressure and distance from the target. The film growth gradually decreases with distance for all pressures. It is seen that for small distances the most optimal deposition pressure was 0.7 Pa when the balance between plasma density, mean free path and energy of Ti – Al atoms is achieved. If the distance to the target is above 7 cm dissipation becomes dominating parameter and reducing the growth rate. While the growth rate tends to decrease with pressure, the crystallite size increased significantly. It is also seen that the 0.7 Pa value is the most optimal pressure for the Ti – Al film growth. At higher pressure the crystal size is very sensitive to the distance between the target and the substrate. When the distance is shortest, the biggest crystallites of 1400 nm are grown.

It is interesting to note that the texture measured as a function of FWHM of (200) peaks, deteriorates gradually with pressure and distance. The optimum aligned crystals are grown at 0.70 Pa pressure.

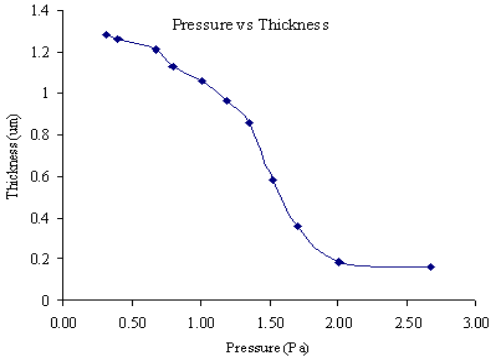

Fig. 3 Variation of film thickness as a function of working pressure

3.3 Microhardness

The microhardness characterization of the thin films coated on different substrates with coating thickness of 1.2 μm was carried out using Clemex microhardness tester. A Vickers indenter was impressed into the material at loads of a few grams. The impression length was measured microscopically, and the test loads were used to calculate the hardness value. Microhardness average values were as listed in the table 2 below and are in agreement with the literature values. It was observed that the substrates are influencing the microhardness values of the coated TiAl films largely.

Table 2. Microhardness values of the TiAl thin films coated on different substrates

Sl. No.	Substrate	Microhardness (HV)
1	Copper plate	1897
2	Alumina (Al2O3)	1903
3	Mild steel	1878
4	Corning glass	1898

3.4 Heat-treatment

The oxidation behavior and the structural evolution of the coatings were studied by carrying out heat treatment at elevated temperatures of 400 °C to 1100 °C in the steps of 100 °C for 1 hr. Above 900 °C the films started to crack in regular patterns. This may be due to release of the stresses present inside the coatings at the time of deposition. Also it was observed that the formation of TiO_2 and Al_2O_3 on the film surface. The formation of TiO_2 and Al_2O_3 above 900 ˚C was confirmed by XRD analysis. After the heat treatment there is a decrease in the crystallite size of the coating along with the increase microstrain of the coatings (Fig. 4).

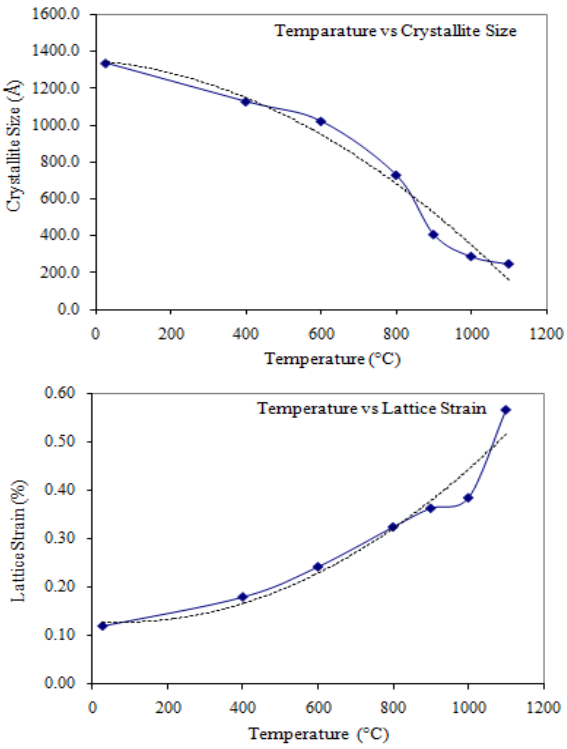

Fig. 4 Variation of crystallite size and lattice strain as a function of temperature

4. Conclusion

Microstructure of Ti – Al films deposited at different oblique angles of 40° and 50°, under different pressures of 0.27, 0.67, 1.33 and 2.67 Pa and DC currents of 0.15 and 0.25 A at a distances of 5 to 8 cm from the target were studied. The results showed that the grains start to grow on to the substrate when the deposition angle is 40°. It was observed that the grains consisted of a number of crystals growing with the crystal orientation along the grain growth perpendicular to the substrate. It was found that the crystal size decreased with the deposition time, as a result of grain shadows, and they become less aligned. Internal stress, decreases with the deposition angle. It was found that the film growth rate decreased with Ar pressure but had a local maximum at 0.70 Pa when the distance to the substrate to target was fixed for 6 cm. Films deposited at 1.33 Pa had the biggest crystal size and high texture coefficient. However, crystal spatial orientation deteriorated gradually with pressure. Also the microhardness of the Ti – Al film was in accordance with the literature values within experimental errors. It was also observed that at the time of heat treatment in the range of 400 ˚C to 1100 ˚C there was formation of TiO_2 and Al_2O_3 on the film surface above 900 ˚C. After the heat treatment there is a decrease in the crystallite size of the coating along with the increase microstrain of the coatings.

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