Effects of the ratio of Al/Ti target current on the chemical composition, structure, morphology, wettability and corrosion resistance of sputtered titanium aluminium films

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Abstract. Titanium aluminium (TiAl) alloy thin films were deposited on silicon wafer and stainless steel substrate by sputtering method. The effects of the Al/Ti target current ratio (R) on chemical composition, structure, surface morphology, wettability, and corrosion resistance of the deposited films were investigated using energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), contact angle measurement, and potentiostat, respectively. In the experiment, when the Al/Ti target current ratio increased from 0.375 to 1.5, the Al/Ti concentration ratio of the deposited films increased. When the Al/Ti target current ratios were 1.0 and 1.5, the deposited film structure exhibited γ-TiAl phase with tetragonal crystal structure. Moreover, the Al/Ti target current ratio of 1.5 provided the deposited film with the highest crystallinity, surface roughness, hydrophobicity, and corrosion resistance.

Keywords: TiAl alloy thin films; Al/Ti target current ratio; Sputtering

1. Introduction

Titanium aluminium or titanium aluminides (TiAl) are one of the most promising advanced alloys, have great potential for high temperature applications in the airspace and automobile industries due to their high strength, light weight, and good corrosion resistance [1-3]. Many methods have been widely used to produce TiAl alloys, such as rapid solidification [4], mechanical alloying [5], and sputtering [6-10]. Sputtering is an attractive method of physical vapor deposition (PVD) to deposit thin films on well-defined substrates. However, many studies indicate the effects of different parameters such as working gas pressure, substrate temperature, annealing temperature and duration, target composition of Al-Ti alloys and target current on the chemical composition, structure, morphology, and corrosion resistance of sputtered TiAl alloy thin films [6-11].

Al/Ti target current ratio is an alternative parameter to accomplish the required stoichiometry of sputtered TiAl alloy thin films by independently varying the current of the Ti and Al targets. In the present study, the TiAl alloy thin films were deposited by DC magnetron co-sputtering method with different Al/Ti target current ratios. The chemical composition, structure, morphology, wettability, and corrosion resistance of the deposited films were investigated as a function of the Al/Ti target current ratio (R).
2. Experimental details
The TiAl alloy thin films were deposited on silicon wafer and stainless steel substrates by DC magnetron co-sputtering system. The vacuum chamber had the diameter of 310 mm and the height of 370 mm, and the cathodes used in the experiment were 75 mm diameter magnetron cathodes, using targets of Ti with the purity of 99.995% and Al with the purity of 99.9995% (Kurt J Lesker Company). The working gas was argon with the purity of 99.999%, and the flow rate was controlled with a type 1605 flow controller (Edwards Corporation). Deposition procedures, the substrates were placed at 13 cm from the targets. The vacuum chamber was evacuated to a base pressure of about 5×10⁻⁵ mbar to decrease the contamination in the deposition process, and the working pressure was kept constant at 3.5×10⁻³ mbar with argon gas flow rate at 4.0 sccm. The Al/Ti target current ratios (R) were varied from 0.375 to 1.5, and the film thickness was fixed at 700 nm. Table 1 is a summation of the deposition parameters used in this study.

Table 1. Detailed parameters for the deposition of TiAl alloy thin films.

| Parameter                              | Condition                      |
|----------------------------------------|--------------------------------|
| Target                                 | Ti and Al                      |
| Substrate                              | silicon wafer and stainless steel |
| Distance between target and substrate  | 13 cm                          |
| Base pressure                          | 5×10⁻⁵ mbar                    |
| Working pressure                       | 3.5×10⁻³ mbar                  |
| Film thickness                         | ~ 700 nm                       |
| Al/Ti target current ratio (R)         | 0.375, 0.5, 1.0, 1.5           |

The chemical composition of deposited TiAl alloy thin films was characterized using energy dispersive X-ray spectroscopy (EDX, Leo 1450VP). The structure of films was examined by X-ray diffractometer (XRD, Bruker AXS D8 Discover). The morphology of films was investigated via scanning electron microscope (SEM, Leo 1450VP) and atomic force microscope (AFM, Veeco Nanoscope IV). The wettability of film surfaces was evaluated using the water contact angle measurements. The contact angle values measured with 20 µl of deionized water droplets at five different positions on each film surface.

The corrosion behaviors of films were determined in 3.5 wt.% NaCl solution at room temperature. Electrochemical potentiodynamic polarization were carried out on potentiostat (Autolab PGSTAT 302N) to evaluate the corrosion resistance. A three-electrode cell was composed of a working electrode (film), a platinum sheet counter electrode and an Ag/AgCl electrode as reference electrode. Open circuit potential (OCP) measurements were recorded as a function of time about 10 min. The potentiodynamic polarization behaviors of films were performed from -1.2 V to 1.4 V from OCP, with a scanning rate of 2.25 mV/s.

3. Results and discussion
Figure 1 reveals the EDX spectra of the elements present in the TiAl alloy films, all the films deposited at different Al/Ti target current ratios reveal a similar spectrum confirming the fact that Ti and Al elements are present in the films. The Ti and Al concentrations of the films deposition as a function of Al/Ti target current ratio are shown in table 2. When the Al/Ti target current ratio increased from 0.375 to 1.5, the Al concentration increased from 41.17 at.% to 76.60 at.%, while the Ti concentration decreased from 58.83 at.% to 23.40 at.% and the Al/Ti concentration ratio increased from 0.70 to 3.27. The increasing of Al/Ti concentration ratio of deposited films related to the increased Al/Ti target current ratio. The increasing of Al/Ti target current ratio with independently
varying the current of the Al and Ti targets, leading to decrease the number of sputtered Ti atoms and increase the number of sputtered Al atoms [8].

Figure 1. EDX spectra of TiAl alloy thin films deposited at different Al/Ti target current ratios: (a) 0.375, (b) 0.5, (c) 1.0 and (d) 1.5

Table 2. Chemical composition of TiAl alloy thin films deposited at different Al/Ti target current ratios (R).

| R     | Elements (at.%) | Al/Ti concentration ratio |
|-------|-----------------|---------------------------|
| 0.375 | 41.17           | 58.83                     | 0.70 |
| 0.5   | 49.34           | 50.66                     | 0.97 |
| 1.0   | 70.13           | 29.87                     | 2.35 |
| 1.5   | 76.60           | 23.40                     | 3.27 |

Figure 2 shows the XRD patterns of the TiAl alloy deposited as a function of Al/Ti target current ratio. At the Al/Ti target current ratio of 0.375 and 0.5, the broad XRD peak is present in the 2θ range of 35° to 45°, indicating that the deposited films are amorphous phase [12, 13]. For the Al/Ti target current ratio of 1.0 and 1.5, the XRD patterns of film exhibited γ-TiAl phase with tetragonal crystal structure and the orientation of TiAl structure corresponded to (111) plane (JCPDS card no.65-5414). The transformation of the deposited TiAl alloy films from amorphous phase to crystalline phase related to the Al/Ti target current ratio. When increasing the Al/Ti target current ratio, the atoms of Ti sputtered from Ti target can bond with atoms of Al sputtered from Al target due to their high kinetic energy and momentum, leads to the formation of γ-TiAl phase [9].
Figure 2. XRD patterns of TiAl alloy thin films deposited as a function of Al/Ti target current ratio (R).

Figure 3. SEM images of surface morphology of TiAl alloy thin films deposited at different Al/Ti target current ratios: (a) 0.375, (b) 0.5, (c) 1.0 and (d) 1.5

Figures 3 and 4 show the SEM and AFM images of surface morphology of TiAl alloy thin films deposited at different Al/Ti target current ratios. The results indicated that the surface morphology of films deposited at the Al/Ti target current ratio of 0.375 and 0.5 is smooth. At the Al/Ti target current ratio of 1.0 and 1.5, the surface morphology of deposited films is large grains. The grain size of films deposited at the Al/Ti target current ratio of 1.5 is bigger than that of films deposited at the Al/Ti target current ratio of 1.0. Table 3 presents the root mean square (RMS) roughness of films deposited as a function of Al/Ti target current ratio which determined from the AFM results. The RMS roughness of films deposited at the Al/Ti target current ratio of 0.375 and 0.5 are 2.12 nm and 1.86 nm, respectively. The RMS roughness of film slightly decreased at the Al/Ti target current ratio of 0.5 due to the Ti target current at the Al/Ti target current ratio of 0.375 is lower than that at the Al/Ti target current ratio of 0.375. The decreasing of Ti target current results in the lower energy of sputtered Ti atoms, leads to the surface of deposited films is smoother [9]. For the Al/Ti target current ratios of 1.0
and 1.5, the RMS roughness of deposited films has a high value of 18.67 nm and 27.61 nm, respectively. The surface morphology of deposited films from the SEM and AFM results corresponded to the film structure of the XRD results.

Figure 4. AFM images of surface morphology of TiAl alloy thin films deposited at different Al/Ti target current ratios: (a) 0.375, (b) 0.5, (c) 1.0 and (d) 1.5

Table 3. Surface roughness of TiAl alloy thin films deposited as a function of Al/Ti target current ratio (R).

| R     | RMS roughness (nm) |
|-------|--------------------|
| 0.375 | 2.12               |
| 0.5   | 1.86               |
| 1.0   | 18.67              |
| 1.5   | 27.61              |

Figure 5 shows the images of water drop on surfaces of TiAl alloy thin film deposited at different Al/Ti target current ratios. At the Al/Ti target current ratio of 0.375 and 0.5, the water contact angle on surface of deposited films is 76.4° and 74.2°, respectively, showing a hydrophilicity. While at the Al/Ti target current ratios of 1.0 and 1.5, the water contact angle on surface of deposited films is 111.3° and 116.3°, respectively, showing a hydrophobicity. The water contact angle depended on the surface roughness of deposited films. The surface roughness of film increased, leading to decrease the contact area between the water droplet and the surface of film, increasing the water contact angle [14].

Figure 6 reveals the potentiodynamic polarization curves of the stainless steel and TiAl alloy thin films deposited at different Al/Ti target current ratios (R) in 3.5 wt% NaCl solution. The corrosion parameters are potential ($E_{corr}$), corrosion current density ($I_{corr}$), and corrosion rate (CR) obtained from Tafel extrapolation of the stainless steel and deposited films, are shown in table 4. At the Al/Ti target current ratio of 0.375 and 0.5, the corrosion rate of deposited films is 0.043280 mm/year and 0.048640 mm/year, respectively. When the Al/Ti target current ratios of 1.0 and 1.5, the corrosion rate of deposited films is 0.007773 mm/year and 0.005379 mm/year, respectively. The corrosion rate of the
films deposited at the Al/Ti target current ratios of 1.0 and 1.5 which is less than of the stainless steel at 0.026265 mm/year, indicating the good corrosion resistance of films. The corrosion resistance of TiAl alloy films depended on the hydrophobic property. As the hydrophobicity of films increased, the films has an increased corrosion resistance. The film surface with hydrophobicity owns an ability to trap air and can form a layer of air film which protect the film surface from coming into contact with the chloride ions in the NaCl solution [14].

![Figure 5](image_url)  
**Figure 5.** Images of water drop on surfaces of TiAl alloy thin film deposited at different Al/Ti target current ratios: (a) 0.375, (b) 0.5, (c) 1.0 and (d) 1.5

![Figure 6](image_url)  
**Figure 6.** Potentiodynamic polarization curves of stainless steel and TiAl alloy thin film deposited at different Al/Ti target current ratios (R) in 3.5 wt.% NaCl solution.
Table 4. Corrosion parameters obtained from Tafel extrapolation of stainless steel and TiAl alloy thin films deposited at various Al/Ti target current ratios (R).

| Sample       | $E_{\text{corr}}$ (V) | $I_{\text{corr}}$ (mA/cm$^2$) | CR (mm/year) |
|--------------|-----------------------|-------------------------------|--------------|
| Substrate    | -0.32176              | 2.26×10$^{-3}$                | 0.026265     |
| TiAl, R = 0.375 | -0.30553              | 3.77×10$^{-3}$                | 0.043280     |
| TiAl, R = 0.5 | -0.36406              | 4.19×10$^{-3}$                | 0.048640     |
| TiAl, R = 1.0 | -0.41164              | 6.69×10$^{-4}$                | 0.007773     |
| TiAl, R = 1.5 | 0.02660               | 4.63×10$^{-4}$                | 0.005379     |

4. Conclusions
The effects of the Al/Ti target current ratio on chemical composition, structure, morphology, wettability and corrosion resistance of TiAl alloy thin films deposited by DC magnetron co-sputtering were investigated. When the Al/Ti target current ratios increased from 0.375 to 1.5, the Al concentration increased from 41.17 at.% to 76.60 at.%, while the Ti concentration decreased from 58.83 at.% to 23.40 at.% and the Al/Ti concentration ratio increased from 0.70 to 3.27. For the Al/Ti target current ratios of 1.0 and 1.5, the deposited film structure exhibited $\gamma$-TiAl phase with tetragonal crystal structure. Moreover, the Al/Ti target current ratios of 1.5 provided the deposited film with the highest crystallinity, surface roughness, hydrophobicity, and corrosion resistance.

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