# Preparation of hard film on 7A04 aluminium alloy by magnetron sputtering

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## Abstract

**Titanium nitride thin films were prepared on 7A04 aluminium alloy by unbalanced magnetic field magnetron sputtering. The phase composition of the films was analyzed by X-ray diffraction (XRD), and the surface morphology of the films was observed by scanning electron microscopy (SEM). The hardness and film-base bonding force of each sample under different sputtering process and time were analyzed by HVS-10 digital display Vickers hardness tester. The effect of sputtering time and process on corrosion resistance of 7A04 aluminium alloy was discussed by electrochemical polarization curve, and its corrosion behavior was analyzed.The experimental results show that TiN thin films with uniform and compact surface can be prepared on aluminium alloy by magnetron sputtering. The hardness of the coating is higher than that of the aluminum alloy substrate. The test of bonding force shows that the film-substrate bonding force is better than that of the film sputtered for 6 hours after 2 hours and 4 hours. A new phase Ti2N is formed by X-ray diffraction (XRD), which improves the hardness of the film. The electrochemical polarization curves show that the corrosion resistance of the film after coating is better than that of the aluminum alloy. The best corrosion resistance is the sample sputtered for 4 hours after heat treatment, which has higher corrosion resistance than the film treated by other processes.**

## Keywords

**Magnetron Sputtering, TiN Thin Films, Hardness, Adhesion, Corrosion Resistance.**

## 1. Introduction

Aluminum alloys are widely used in many industrial fields because of their own advantages. It has the advantages of small density, high stiffness and specific strength, good conductivity and thermal conductivity, and easy processing to form [1]. However, when aluminium alloys are used in many fields, some shortcomings are unavoidable, such as low hardness and poor corrosion resistance. When they are used in friction systems, especially in rotating and slipping parts, when the surface is not lubricated, wear failure will easily occur, which is unfavorable. These factors make it difficult for aluminum alloy to meet the high requirement of [2] for application in some fields. When a hard film is coated on the surface of aluminium alloy, these disadvantages will be weakened. On the one hand, the advantages of aluminium alloy can be maintained, such as light weight, on the other hand, the advantages of hard film can be brought into full play. Among the many hard coatings that have been applied, the most commonly used coatings are titanium nitride and other coatings. However, up to now, most of the hard wear-resistant coatings only show good properties on hard materials and high-speed steel substrates [3, 4]. However, the preparation of high quality hard wear-resistant coatings on materials with lower hardness, such as aluminium alloys, is still in its infancy, and many scholars are still studying them. Titanium nitride thin films were prepared on 7A04 aluminium alloy by magnetron sputtering. The mechanical properties and corrosion resistance of the samples under different sputtering time and process were discussed. It provides a research direction and theoretical basis for the future application of this technology on light alloy matrix, and provides a reference and direction for the future application of 7A04 aluminium alloy in more fields.

## 2. Experimental part

### 2.1 Experimental materials.

The material used in this experiment is aluminum alloy bar with diameter of 45mm. The composition of aluminum alloy is shown in Table 1.

The sputtering target TiN used in this experiment is a nearly black powder solid with a melting point of 2950℃and a density of 5.43 g/cm$^3$. The detailed chemical composition is shown in Table 2.

Table 1 Chemical composition of 7A04 aluminum alloy (wt.%)

| Material | Zn | Mg | Cu | Cr | Fe | Si | Mn | Al |
|---|---|---|---|---|---|---|---|---|
| Content (wt%) | 6.24 | 2.29 | 1.41 | 0.11 | 0.10 | 0.10 | 0.20 | Bal. |

Table2 The chemical composition about TiN

| Brand name | Ti | N | O | C | Si | Fe | Ca | P | S | FSSS(μm) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | ≥ | | | | ≤ | | | | |
| TiN | 75 | 18 | 0.8 | 0.05 | 0.05 | 0.05 | 0.1 | 0.02 | 0.05 | 2.0 |

### 2.2 Preparation of thin films.

In this experiment, a non-equilibrium magnetic field magnetron sputtering device (SP60/50) was used to prepare thin films. The device is shown in Figure 1.

Fig. 1 The picture of magnetron sputtering equipment

Titanium nitride powder is selected as target material in the experiment. Its advantages are good corrosion resistance, chemical stability, oxidation resistance, and chemical reaction with metal is not easy. It is an inert film. The technological process of thin film preparation is as follows: external cleaning, sample setting, vacuum pumping, working gas entering, pre-sputtering (only once), internal cleaning, formal sputtering, cooling, sample setting and target cleaning. When the sputtering power is the same, the change of sputtering time will also affect the properties of the films. This paper discusses the properties of the films when the sputtering time (2, 4, 6 hours) is changed at the same power of 300W. The specific parameters of the experiment are as follows.

Table3 The parameters table of experimental technique

| Powder Name | Sputtering Power (W) | Sputtering Pressure (Pa) | Vacuum (Pa) | Protection Gas | Sputtering Time (h) |
|---|---|---|---|---|---|
| TiN | 300 | $2.0\times10^{-1}$ | 2.0×10-3 | Ar | 2 |
| TiN | 300 | $2.0\times10^{-1}$ | 2.0×10-3 | Ar | 4 |
| TiN | 300 | $2.0\times10^{-1}$ | $2.0\times10^{-3}$ | Ar | 6 |

### 2.3 Detection of thin film properties.

The surface morphology of TiN thin films was observed by scanning electron microscopy (SEM). The phase composition of the films was analyzed by X-ray diffraction (XRD), and the hardness and film-base adhesion of the samples were analyzed by HVS-10 digital display Vickers hardness tester under different sputtering processes and time. The effect of sputtering time and process on corrosion resistance of 7A04 aluminum alloy was discussed by electrochemical polarization curve using three-electrode system, and its corrosion behavior was analyzed.

## 3. Results and discussion

### 3.1 Surface morphology of thin films.

Fig. 2 is the surface topography of TiN thin films obtained by SEM for ten thousand times and twenty thousand times. From the scanned images, it can be seen that there are scratches and defects on the surface of the matrix, but the overall morphology, defects and scratches in the field of vision still account for a relatively small proportion. The reason for this morphology may be that the cleaning of the matrix is not thorough enough, and a small amount of irregular impurities remain attached to the surface. In the sputtering process, if the surface of the substrate is not uniform, the titanium nitride particles will encounter the surface bulging impurities when sliding along the surface, thus sliding along the external surface of the impurities will eventually result in the accumulation of particles, thus forming defects. As can be seen from the following figure magnified by 20,000 times, the titanium nitride particles on the film surface are basically round, and the grain size and distribution are relatively uniform. Although there are overlapping particles in some areas, the overall surface is basically flat. Therefore, if the state is ideal, it can be considered that a uniform TiN film can be prepared by unbalanced magnetron sputtering.

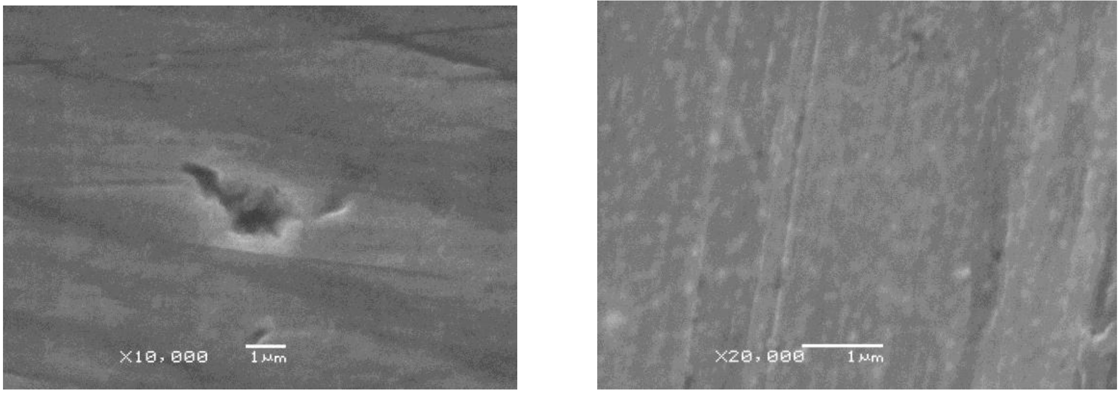


Fig. 2 The surface morphology of titanium nitride films

### 3.2 Hardness testing of thin films under different sputtering time.

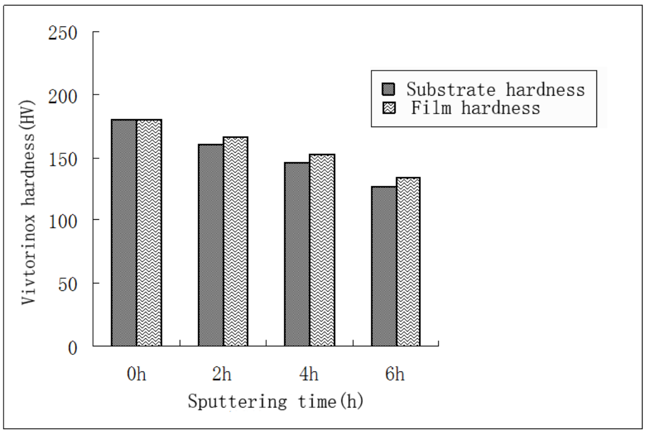


Fig. 3 The hardness contrast between the film and substrate under the different sputtering time

Fig. 3 shows the hardness of the coating and the substrate prepared by magnetron sputtering TiN (2 hours, 4 hours and 6 hours) on 7A04 aluminum alloy at 300W power. It can be seen from the column diagram that the hardness of the coated part is higher than that of the uncoated substrate, but with the increase of sputtering time, the hardness of the TiN film matrix is lower than that of the aluminium alloy matrix. This is because, firstly, aluminium is a low melting point metal. The melting point of pure aluminium is 660 C. The melting point of aluminium alloy is slightly lower than that of pure aluminium. Although magnetron sputtering is low temperature sputtering, the temperature of the matrix will increase with sputtering time because of the impact of titanium nitride on the surface of the matrix at high speed when the machine works. As a result, the internal structure of the aluminium matrix changes, and the matrix softens and the hardness decreases. Secondly, although the load used in hardness testing is the minimum load, due to the sputtering time limitation, the film is still very thin and penetrates the surface film completely under the minimum load, which results in the hardness of the tested hardness affected by the hardness of the aluminum alloy matrix itself. However, experiments have shown that the hardness of TiN films prepared by magnetron sputtering will increase with the prolongation of sputtering time, on the premise that the substrate has no significant influence on the heating temperature. Combined with the experimental results in this part, the hardness of the coated part is higher than that of the uncoated substrate. It is reasonable to believe that the hardness of the film will increase with the prolongation of sputtering time. In fact, the incremental difference between the hardness of the coated part and the hardness of the substrate with time proves this point.

### 3.3 Adhesion test of thin films.

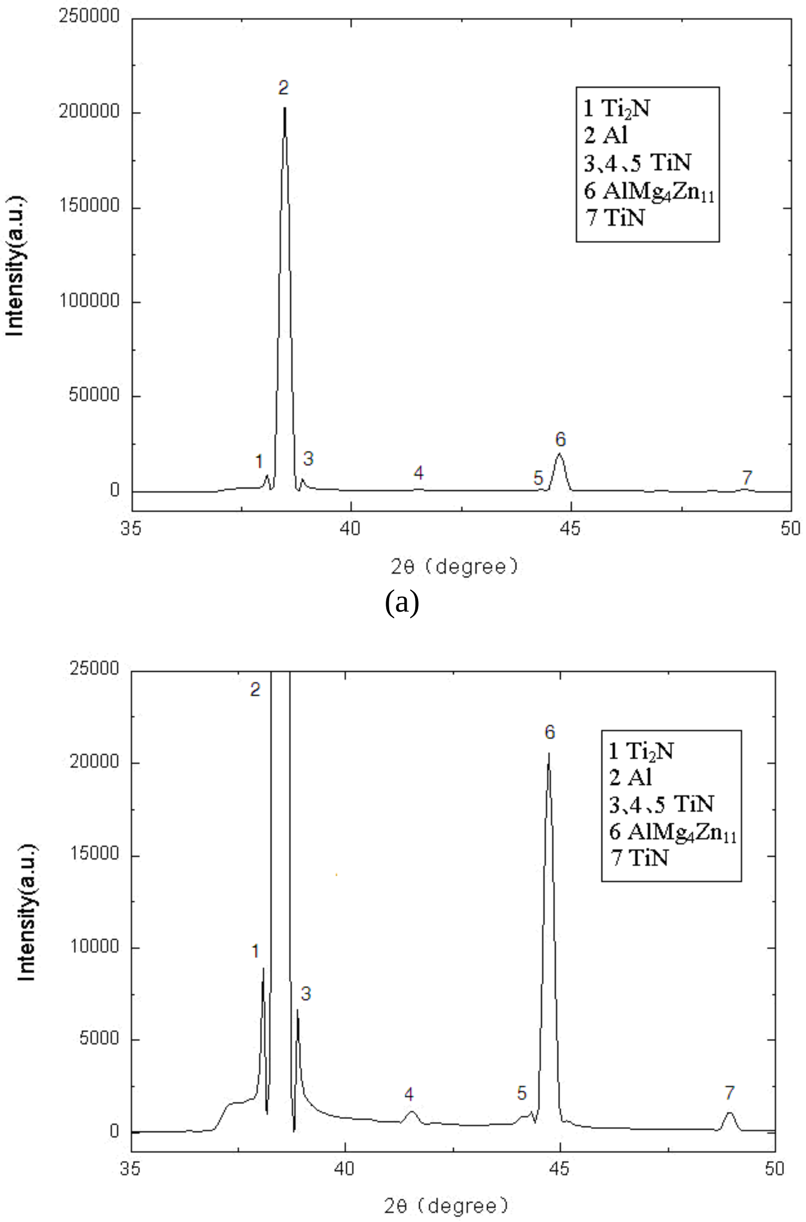
Table.4 The morphology under different sputtering time(2,4,6 hous)of TiN film

| Sputtering Time (h) | 2. 94（0.3Kgf） | 4. 9N(0.5Kgf) | 9. 8N(1Kgf) |
|---|---|---|---|
| 2 | Diamond indentation | Diamondindentation | Diamond indentation |
| 4 | Diamond indentation | Diamond indentation | Diamond indentation |
| 6 | Diamond indentation | Parallel marks around the indentation. | A rash mark around the diamond shaped indentation. |

Observation Table 4 shows that the indentation morphology of TiN films after sputtering time of 2 hours and 4 hours is intact diamond-shaped under three different loads. The morphology of the diamond-shaped indenter in the field of vision is observed under a microscope, which shows that the film has good adhesion with the matrix. Combining with the surface morphology before sputtering, it is shown that TiN thin films with uniform and compact surface can be formed on the Al alloy substrate after sputtering. However, after 6 hours of magnetron sputtering, there are nearly parallel marks around the indentation under the two different loads. Especially under heavy load, disordered marks were observed around the indentation by microscopy. The main reason for the formation of imprinting marks was that there was no uniform and compact film between TiN particles sputtered on the surface of aluminium alloy, which resulted in the rupture of the film under heavy pressure. It is concluded that the bonding force between TiN film and Al alloy substrate after sputtering for 6 hours is general. The reason is that the thickness of TiN film will gradually deepen with the prolongation of sputtering time, and the plastic deformation ability and thermal expansion coefficient of TiN film and TiN film are quite different. When the external stress or thermal stress occurs, there is no good transition and coordination between the membrane and the matrix, which reduces the binding force of the membrane.

### 3.4 XRD analysis of tin nitride films.

Fig. 4 (a) is a complete peak pattern. Fig. 4 (b) is the peak pattern after amplification. It can be seen from Fig. 4 (a) that two very strong peaks 2 and 6 are the peaks of aluminum alloy matrix. The comparison card shows that 2 is Al, 6 is AlMg4Zn11, and its crystal face index is (114). On the left side of the strongest peak, there is a smaller peak of 1 ($Ti_2N$) (112). It shows that new phase Ti2N is formed in magnetron sputtered TiN film, which is a common Ti-N interstitial compound. In this structure, titanium metal is arranged in close hexagonal lattice, and nitrogen atoms are located in its interstitial position. In TiN structure, titanium atoms are arranged in a face-centered cubic lattice. Nitrogen atoms form a typical B1-Nacl structure in the octahedron gap. Its stability and hardness are better than titanium nitride. However, in this experiment, $Ti_2N$ thin films prepared by magnetron sputtering are relatively thin, so only small Ti2N peaks can be seen from the XRD spectrum. The peaks 3, 4, 5 and 7 are TiN peaks. The lower peaks 5 are TiN (111) diffraction peaks, and the higher peaks 4 and 7 are TiN (200) diffraction peaks. This indicates that the preferred orientation of TiN films deposited by magnetron sputtering is mainly (200) crystal plane. With this preferred orientation peak, it is more conducive to refine the grain and strengthen the crystal boundary, thus comprehensively strengthening the base material and improving the surface hardness.



(a)

(b)

Fig. 4 The XRD patterns about the surface of TiN film

### 3.5 Analysis of polarization curves of TiN thin films at different sputtering time.

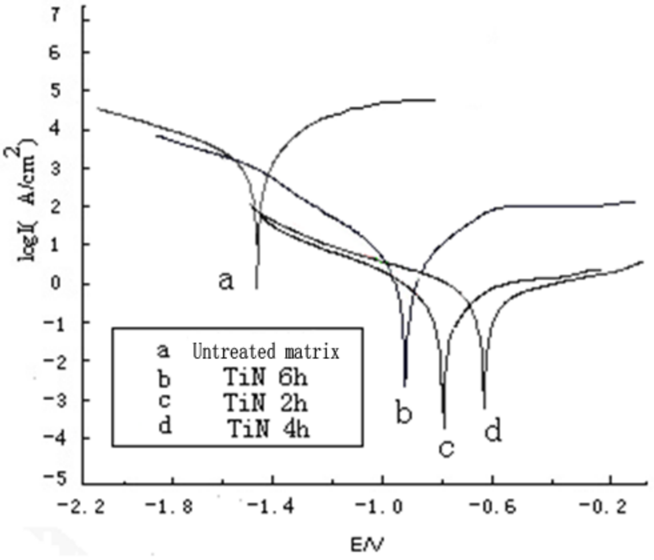


Fig.5 The tafel curves in 3.5%NaCl solution

Fig. 5 shows the anodic polarization curves of TiN films in 3.5% NaCl solution at different sputtering time (2, 4, 6 hours). The four polarization curves show that the corrosion potential of TiN films prepared at three different sputtering times is more positive than that of aluminium alloy matrix (curve a) and the corrosion current is lower than that of matrix. Therefore, it shows that the Cl-in solution is not easy to penetrate the film layer, and the TiN films prepared by magnetron sputtering are not easy to penetrate. TiN film has a good protective effect on 7A04 aluminium alloy matrix, and TiN film effectively improves the corrosion resistance of aluminium alloy matrix. When the sputtering time is 6 hours (curve b), the corrosion potential of TiN film shifts to about 0.6548V and the corrosion current density decreases. It shows that the corrosion resistance of TiN film after 6 hours sputtering is better than that of substrate, while the corrosion potential of TiN film after 2 hours sputtering is 0.1544V higher than that of 6 hours sputtering. The best corrosion resistance of these curves is the TiN film sputtered for 4 hours (curve d). Its corrosion resistance is better than that of the potential corrected for 2 hours, which indicates that the corrosion resistance of TiN film is better. These curves show that the corrosion resistance of TiN film on 7A04 aluminium alloy surface is affected by the thickness of the film on the one hand, and the thicker the film, the better the corrosion resistance. On the other hand, when the thickness of the film exceeds a certain value, the corrosion resistance does not rise or fall, which has the opposite effect on the results. Combining with the analysis of bonding force test before, this may be because there are some micro-cracks on the surface of the film. The larger internal stress in the film of the sample sputtered for 6 hours makes the micro-cracks on the surface of the film easy to extend and extend to the inside of the film, which makes the corrosion resistance of the film of the sample sputtered for 6 hours worse than that of the sample sputtered for 2 hours and 4 hours.

## 4. Conclusion

(1) Magnetron sputtering can produce certain thickness, uniform and compact titanium nitride thin films.

(2) The phase composition of the film was analyzed by X-ray diffraction (XRD) instrument, and a new phase formation ($Ti_2N$) was obtained. Moreover, the hardness of the film was higher than that of titanium nitride, so the hardness of the film was improved by the new phase formation.

(3) The hardness of aluminium alloy matrix decreases with the prolongation of sputtering time, but the hardness after coating is higher than that of aluminium alloy matrix. The bonding force between the film and the substrate after sputtering for 2 hours and 4 hours is better than that of the film and the

substrate after sputtering for 6 hours. The sputtering time will affect the bonding force between the film and the substrate. When the sputtering time is 6 hours, the bonding force between the film and the substrate becomes worse. This is because the long sputtering time of the film will cause the internal stress and micro-cracks between the film and the substrate, resulting in the decrease of the adhesion between the film and the substrate.

(4) TiN films with excellent corrosion resistance can be obtained on 7A04 aluminium alloy by magnetron sputtering. The corrosion resistance of the substrate is different in each state. The corrosion resistance of the coated film is better than that of the aluminium alloy. The corrosion resistance of the film is different under different sputtering time and different sputtering process. The best corrosion resistance is the film sample sputtered for 4 hours after heat treatment, followed by direct sputtering for 2 hours and 6 hours. The thin film specimen is finally treated without any treatment on the aluminum alloy substrate.

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