Study on Oxidation Resistance of TiAlN Films Deposited by Magnetron Sputtering

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Abstract. In this paper, TiAlN hard thin film is deposited on hard alloy surface by magnetron sputtering; at 400 ℃ to 825 ℃, oxidation experiment is performed for the samples; XRD is used for phase analysis of TiAlN hard thin film; Through the use of HVS-1000 digital micro-hardness tester and WS-2004 automatic scratching tester, microhardness of the samples and substrate-film adherence are analyzed. Results show: the microhardness and coherence of TiAlN thin film reduces with the rise of temperature; at 800 ℃, the microhardness and substrate-film adherence remain at 1603 HV and 48 N respectively; it is found through comprehensive judgment that TiAlN thin film can work under 800 ℃.

1. Introduction
The main forms of failure of parts in the working process are wear, corrosion and fatigue. Especially in high temperature, high speed, high pressure, working conditions, such as overloading, corrosion, parts often due to surface damage and the local failure, lead to equipment instability or even scrapped. Therefore, the use of various techniques to improve the surface performance of the parts is to increase the safety and reliability of the parts, and to prolong the service life. Surface membrane technology is in parts coated on the surface of a particular material to achieve important technology to improve the surface performance of the parts, the parts surface with very little material of high hardness, high temperature resistant, corrosion resistant, and special properties such as light, heat, electricity, magnetism, a need to use a large number of whole material to achieve or to meet the performance, thus get rapid development in recent years, has been widely used in machinery manufacturing, aerospace, optical engineering, computer engineering, electronic technology [1-2].

In modern industry, cutting tools are required to operate at higher and higher speed. And the frictional heat causes cutting blades to be in high temperature. Therefore, there are higher requirements on the red hardness, wearability, thermal stability and antioxidation of cutting tools. For its hardness, wearability and high oxidation resistance, TiAlN thin films are adopted by hard alloy cutters, so as to significantly promote cutter performance and service life [3-4]. There have been studies on high temperature oxidation property of TiAlN, which mostly focus on the influences of preparation methods, process and additional elements [5-7]. There have been no reports on the effects of oxidizing temperature on film hardness and binding force. In this paper, unbalanced magnetron sputtering is used for preparation of TiAlN thin film on the substrate of hard alloy; isothermal oxidation experiment is performed in different temperature, so as to analyze the effects of oxidation temperature on microhardness and substrate-film adherence.

2. Experiment
Hard alloy numbered with YG6 is used as the substrate in this experiment. To ensure the cleaness of the substrate surface, substrate needs pretreatment: clamping the substrate; add detergent solution into
ultrasonic machine, and heat the solution to about 60 °C; put the substrate in the ultrasonic machine and clean it for 10 minutes; dry the substrate with high pressure nitrogen and then put it into baker for 10 minutes; start the experiment when the substrate is completely dry.

Main instrument: JGP450 multi-functional magnetron sputtering machine. The sputtering target is made of titanium aluminum alloy—Ti:Al=7:3; the working gas is argon (with purity above 99.999%), and the reacting gas is nitrogen (with purity higher than 99.999%). Parameters pertaining to deposition process are as follows—base pressure: 5×10⁻³Pa; deposition pressure: 4×10⁻¹Pa; deposition current: 120 A; substrate bias voltage: -120 V; partial pressure of Ar: 1.3E⁻¹ Pa; nitrogen flow: 60mL/min; sputtering time: 120 min.

The isothermal oxidation experiment is performed in electric resistance furnace with static air, where the heating temperatures are set as 400 °C, 500 °C, 600 °C, 700 °C, 800 °C and 825 °C. Each time following the heating processes, which are numbered with 2 to 7, there is heat preservation of one hour; the unheated sample is numbered with 1.

X-ray diffractometer (XRD) is used for analysis of the samples; HVS-1000 digital micro-hardness tester is utilized to test the sample hardness; WS-2004 automatic scratching tester is employed to test the substrate-film adherence.

3. Results and analyses

3.1 Results and analysis of TiAlN film oxidation

The quality before and after oxidation the sample of 2~7 was measured respectively, which were measured by the FA1104 electronic precision scales produced by Shanghai balance factory, and accuracy was 0.1mg. Sample number and oxidation parameters are shown in Table 1. The experimental results are shown in Table 2.

The table 2 shows, the samples were not nodal increment at 400 °C and 500 °C and insulation 30 min. even aerobic element diffusion under 500 °C, the amount is very small, under one over ten thousand g orders of magnitude. the sample is 0.2 mg of weight gain at 600 °C, weight gain is not obvious, so oxidation resistance of film is still very good. The quality of the sample was larger increase( 4.4 mg) at 700 °C Compared to at 600 °C. When the oxidation temperature up to 800 °C, oxidation is more serious, sample weight to 23 mg. When the oxidation temperature of 825 °C, the sample weight is 30.9 mg.

Temperature will be above 600 °C oxide with quadratic polynomial fitting quality weight, quality weight gain and the relation between the oxidation temperature:

\[ Y=0.0008X^2-0.9488X+295.75 \]  \( (3.1) \)

Correlation coefficients R² = 0.9995.

The formula for the rate of sample oxidation of the 2.1 derivation:

\[ Y'=0.0016X-0.9488 \]  \( (3.2) \)

As the oxidation temperature increases, the oxidation rate also increases.

### Table 1 The technology parameters of oxidation experiment

| Number | Oxidation temperature /°C | Holding time /min | Cooling way        |
|--------|---------------------------|-------------------|--------------------|
| 1#     | Room temperature          | —                 | furnace cooling    |
| 2#     | 400                       | 30                | furnace cooling    |
| 3#     | 500                       | 30                | furnace cooling    |
| 4#     | 600                       | 30                | furnace cooling    |
| Number | 1#     | 2#     | 3#     | 4#     | 5#     | 6#     | 7#     |
|--------|--------|--------|--------|--------|--------|--------|--------|
| Before oxidation /g | 5.1677 | 5.2179 | 5.1567 | 5.1434 | 5.1434 | 5.1707 | 5.1628 |
| After oxidation /g  | 5.1677 | 5.2179 | 5.1567 | 5.1436 | 5.1436 | 5.1937 | 5.1937 |
| Weight increment /mg | 0      | 0      | 0      | 0.2    | 4.4    | 23     | 30.9   |

**Table 2** The results of oxidation experiment

3.2 TiAlN thin-film phase analysis

Figure 1 represents the XRD spectrogram for film preparation, which shows the two phases of the samples: WC and Ti₃AlN— the former is the major constituent of the hard alloy and the latter the component of Ti₃AlN. The spectrogram shows no other phases. It’s known that there are 4\(^{[8]}\) Ti-Al-N phases: Ti₅.₅Al₀.₅N, Ti₂AlN, Ti₃AlN and Ti₁.₅AlN, among which Ti₃AlN is a common phase. From figure 2-5, the oxidation temperature is below 600 ℃, there is no change in the phase composition of the sample. Ti₆O₁₁ from 600 ℃ to a new phase, the phase at 700 ℃ still exist, but contrast method was 600 ℃, 700 ℃ Ti₆O₁₁ phase characteristic peak of map has been obviously reduced, and at 800 ℃ Ti₆O₁₁ disappear. The literature\(^{[9]}\) considers that the oxidation of TiAlN films is divided into two processes. The first is the diffusion process of O atoms to the inside of the film, while Ti atom and Al atom are diffused at low temperature. With oxidation temperature rise, Al, Ti atoms to the film surface diffusion, by contrast, Al atoms to the film surface diffusion speed is higher than that of Ti atom diffusion velocity, thus rich Al poor Ti in film surface, accordingly, the inner rich Ti poor Al. Therefore, first of all, on the surface of the membrane, the Al atom combined with O atoms to form the oxide layered Al₂O₃, and a small amount of oxygen formed TiO by reaction with Ti through the Al₂O₃ oxide layer, forming the Al₂O₃ / TiO₂ two oxide layered structure.

At above 800 ℃, O(oxygen) begins to reacts with the hard alloy substrate, generating CoWO₄. This indicates that TiAlN thin film has been seriously damaged, and there is weakened or no separation between external oxygen and the substrate. Meanwhile, it can be seen from Figure 6 that the characteristic peak pertaining to Ti₃AlN is still noticeable, which indicates that the thin film has not been totally oxidized or dropped— it is still functioning.
3.3 Analysis of the effects of oxidation temperature on TiAlN film hardness

In this experiment, HVS-1000 digital micro-hardness tester is adopted, with the indenter loaded with 100 gf. The test results are shown in Table 3. It can be seen from the table that the film hardness undergoes no significant changes below 400 °C. This is because the TiO\textsubscript{2} generated at low temperature is not enough to have effects on the overall hardness. With the oxidation temperature rising, the film hardness decreases obviously; when the oxidation temperature reaches 825 °C, the microhardness of the sample is close that of hard alloy substrate. The oxidation causes the reduction in film densification; the phase changes and increased stress in the film, etc. can lead to reduction of film microhardness.
Many data show that the microhardness of TiAlN film in more than 3000 hv. However, because of the thin film thickness low, this paper’s microhardness of thin film is low. For a thin film with very low thickness, the hardness of the film is difficult to avoid without the influence of the substrate, and the microhardness value measured is the compound hardness of the film and the matrix. The thickness of the film thickness, the smaller the influence of the substrate, the closer the hardness of the measured microhardness is. On the contrary, the thickness of the film is thinner, and the larger the influence of the substrate, the closer the measured microhardness is to the hardness of the substrate. The thinness of the TiAlN film is the cause of low hardness.

| Temperature/℃ | Room temperature | 400  | 500  | 600  | 700  | 800  | 825  |
|----------------|------------------|------|------|------|------|------|------|
| Micro-hardness /Hv | 2580.0 | 2168.3 | 1778.6 | 1752.6 | 1672.2 | 1603.0 | 1509.0 |

3.4 Analysis of the effects of oxidation temperature on TiAlN film adherence
Substrate-film adherence is a very important film indicator. Currently, scratching is mostly used for test of film adherence[11]. In this experiment, WS--2004 automatic scratching tester is utilized for test of substrate-film adherence in the samples. Table 4 demonstrates the adherence under different oxidation temperature. It can be seen from it that oxidation temperature has significant effects on the adherence. Below 800℃, the adherence declines gently— this is due to the differences between thermal expansion coefficients of the substrate and thin film. Accordingly, the stress between them increases, which results in the deduction of substrate-film adherence. Above 800℃, the adherence undergoes dramatic changes, when thermal expansion coefficients are no longer the major factors causing adherence reduction; with oxidation temperature rising, new phases emerge in the film, changing the film's thermal expansion coefficient, which has effects on the substrate-film adherence. Through XRD analysis, it can be seen that the composition of thin film has changed significantly; large amounts of TiO$_2$ have been generated under the temperatures; the reduction of TiN and increase of TiO$_2$ are the major factors in adherence reduction.

| Temperature/℃ | Room temperature | 400  | 500  | 600  | 700  | 800  | 825  |
|----------------|------------------|------|------|------|------|------|------|
| Adhesion strength /N | 64   | 58   | 57   | 55   | 50   | 48   | 38   |

4. Conclusion
(1). TiAlN thin film has been prepared using unbalanced magnetron sputtering; the film hardness reaches 2580 HV, and the coherence 64 N.
(2). The microhardness and coherence of TiAlN thin film reduces with the rise of temperature; at 800 ℃, the microhardness and substrate-film adherence remain at 1603 HV and 48 N respectively; it can be found through comprehensive judgment that TiAlN thin film can work under 800 ℃.

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