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High temperature wettability and oxidation behavior of TiN, Ti–Al–N and Ti–Si–N PVD film

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Abstract

In aluminium cutting and die casting, tools are exposed to Built UP Edge (BUE) and Built Up Layer (BUL) and erosion due to the frequent contact of the tool surface to the aluminum alloy, to oxidation due to high temperatures. For this reason, the susceptibility to reaction with liquid aluminum and stability of TiN, Ti–Al–N and Ti–Si–N films were investigated using wetting test, high temperature oxidation experiment and complementary differential scanning calorimetry. The results show that the type of chemical bond affects the surface tension, tool steel with metal bonds is most easily wetted, after being wetted and cooled by molten Al at 725 °C, the contact angle is approximately 0°. Because the maximum temperature of the experiment has reached the decomposition temperature of TiN film, therefore, the contact angle of TiN film with ionic bond is 35.3°, slightly larger than tool steel. However, there are complex ionic bond compounds Ti3AlN and covalent bond compounds Si3N4 in Ti–Al–N and Ti–Si–N films, which significantly reduce the wettability of the film with molten aluminum. The contact angles are 78° and 71°, respectively. During the oxidation process, due to Ti–Al–N and Ti–Si–N films contain Al and Si elements, the phase and morphology did not change until 800 °C, this indicates that the effects of different chemical bonds caused by alloying elements on oxidation resistance and wetting resistance have a similar relationship.

1. Introduction

When using metal cutting tools to process low-hardness metal workpieces such as stainless steel, aluminum alloy, and magnesium alloy, the 'Built UP Edge (BUE) and Built Up Layer (BUL)' is an adhesion phenomenon caused by the influence of cutting heat, which will reduce the tool life and the surface quality of the workpiece, and affect the fatigue strength of the tool. At the same time, it also destroys the dimensional accuracy and aesthetics of the workpiece. Although the use of metal working fluids can reduce BUE and BUL, it will also cause environmental pollution and corrode to the surface of the workpiece [1–4]. In addition, in the field of casting molding, metal molds are widely used. After contact with high-temperature liquid metal, the life of the mold will be reduced due to erosion, and it also affects the quality of castings [5]. The former is the adhesion produced when solids contact each other, and the latter is the erosion produced when the liquid contacts the solid surface. Adhesion and erosion seem to be two different phenomena, but they have the same essence from the perspective of thermodynamics [6]. This can be considered as a kind of wetting phenomenon caused when metal is heated to form a liquid on the surface of cutting tools and molds.

In recent years, the application of inorganic compounds as protective coatings can play a good role in solving these problems. AK Chattopadhyay et al [7] studied the wetting behavior of cemented carbide, TiC, TiN, Al2O3 and diamond coatings on pure aluminum, and found that the chemical stability of TiN is higher than TiC, which reasonably determined the wetting of TiN The angle is larger than the wetting angle of TiC. The wetting angle of Al2O3 to aluminum is slightly smaller than that of TiN, which may be caused by the reaction of Al2O3 and aluminum to form Al2O3, which leads to accelerated wetting [8, 9]. The research group of Chen Jian and Gu Ming

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1.1. Experimental materials and sample preparation
Films of TiN, Ti–Al–N and Ti–Si–N onto tool steel substrate were prepared for this study using hollow cathode assisted multi-arc ion plating technique (Shenzhen Nissin Vacuum Technology Co. China). The size of tool steel was 15 mm × 15 mm × 5 mm, the three kinds of films were pre-plated according to the parameters in table 1, and the targets were pure Ti, Ti/Al (50/50), and Ti/Si (82/18) alloy targets, respectively.

1.2. Wettability tests
The sessile drop method [2, 12, 13] was used to measure the wettability of Al and tool steel, TiN, Ti–Al–N and Ti–Si–N films at 25 °C to 725 °C. The pure aluminum was cut into small cylinders (φ3 mm × 5 mm) and polished, before placing the samples in the furnace, they were placed in acetone and alcohol and washed with ultrasonic wave to remove surface stains. The heating rate was 10 °C min⁻¹, and the temperature was kept at 725 °C that higher than the melting point of Al for 10 min to ensure that the molten aluminum was spread and stable on the surface of the tested sample. At the same time, a CCD digital camera was used to take pictures, and then the samples were cooled to room temperature and taken out.

1.3. Thermal analysis experiment
Using Complementary differential scanning calorimetry (DSC) method (Netzsch409PC), the temperature range was 25 °C−1000 °C to test the preparation of three kinds of films, and the chemical stability of the films under high temperature conditions was analyzed. First, the film sample was cut into thin slices and put into a 20% HCl solution to remove the tool steel matrix, and then about 30 mg of the film was taken into the crucible, and the heating and cooling speeds are set to 20 °C min⁻¹, and the flow rate was 20 ml min⁻¹. A mixture of argon and oxygen at a ratio of 2:1 was introduced, and the heat flow rate of the film sample from 25 °C to 1000 °C was recorded as the temperature increased.

| Variable                        | TiN | Ti–Al–N | Ti–Si–N |
|---------------------------------|-----|---------|---------|
| Hollow cathode cleaning current(A) | 120 | 120     | 120     |
| Argon gas pressure (Pa)         | 5 × 10⁻¹ | 5 × 10⁻¹ | 5 × 10⁻¹ |
| Pre-treatment voltage (V)       | 240 | 240     | 240     |
| Pre-treatment time(min)         | 30  | 30      | 30      |
| Temperature of substrate(°C)    | 300 | 300     | 300     |
| Cathode current(A)              | 80−100 | 90−120   | 80−100  |
| duty ratio                      | 80% | 80%     | 80%     |
| gas ratio (Ar/N₂)               | 30/270 | 40/260   | 50/250  |
| Working pressure (Pa)           | 1.5 | 1.5     | 1.5     |
| Deposition time(min)            | 60  | 60      | 60      |
1.4. High temperature oxidation experiment
Three samples with film layers were placed in a box-type electric furnace, heated to 600 °C, 700 °C, 800 °C, and 900 °C under air conditions, and kept for 1 h, then cooled to room temperature in the furnace. SEM was used to observe the surface morphology of the sample, and XRD was used to detect and identify the heated sample, and to analyze the high temperature oxidation resistance of the three film layers.

1.5. Phase analysis
The phases for the surface of the films prepared in light of table 1, molten aluminum wetted interface and the film after heat treatment at different temperatures were identified by x-ray diffraction using Cu Kα at 40 kV, 100 mA with the scanning rate 2° min⁻¹. (XRD, D-MAXIIA Rigaku, Japan).

2. Results and discussion
The organization structure and mechanical properties of the TiN, Ti–Al–N, and Ti–Si–N films prepared according to the process parameters presented in table 1 have been described in our previous work [14]. The XRD phase analysis results are illustrated in figure 6. Combined with the EDS analysis of the elements contained in the films (figure 1), it can be determined that the TiN film was obtained in the Ti–N binary system, Ti₅AlN + TiN film was obtained in the Ti–Al–N system (the mass fraction of Ti₅AlN is 61.8%), and TiN + Si₃N₄ film was obtained in the Ti–Si–N system (the mass fraction of Si₃N₄ is 13.62%).

The cross-sectional SEM photo of the film is exhibited in figure 2. The thickness of the three films of TiN, Ti–Al–N and Ti–Si–N are 596 nm, 495 nm and 645 nm, the TiN and Ti–Al–N films are in the form of columnar crystals, however, the Ti–Si–N film changes the original columnar crystal morphology of TiN due to the growth of the independent nucleation of Si₃N₄, refining the film structure.

2.1. Analysis of film wetting behavior
The change curve of the contact angle of metal Al on the substrate tool steel and three kinds of film surface with increasing temperature is illustrated in figure 3, and the CCD photos of the wetting state at different temperatures are presented in figure 4.

It can be observed that wetting does not occur from 660 °C (lower than the melting point of Al) to room temperature. The surface of the sample begins to exhibit a change in contact angle when Al melts into a molten state, and the change rate and size of the contact angle vary with different samples and films. According to observation and testing, the trend of the change rate and size of the contact angle is in correspondence with the
relationship of tool steel ($20.4^\circ$) $>$ TiN($35.3^\circ$) $>$ Ti–Si–N($71^\circ$) $>$ Ti–Al–N($78^\circ$), the data in parentheses are the contact angles of each sample detected at 725 °C after wetting with Al, meanwhile, Al is almost completely spread on the surface of the substrate tool steel; after cooling to room temperature, the contact angle is measured close to 0°, which is the smallest. The SEM photos of four different samples at room temperature after the wetting test are provided in figure 5.

It can be indicated from figures 3–5 that the contact angle of the sample coated with TiN film is second only to that of the tool steel sample, demonstrating that the TiN film has been damaged under the temperature of 725 °C and the wetting of molten Al, hence, making it unable to protect the matrix tool steel. At lower temperatures, there have been many reports and studies on the formation of iron-aluminum intermetallic compounds after the wetting of molten Al on the steel surface [15]. In this study, only the changes in three different films under molten Al are analyzed. Additionally, the XRD diffraction patterns of the surface of TiN, Ti–Al–N, and Ti–Si–N samples (without wetting and with wetting to remove the molten aluminum) are displayed in figure 6. Comparative analysis reveals that the decomposition temperature of TiN (600 °C) [16, 17] has been exceeded when the temperature reaches 725 °C, after the film is damaged, Al atoms diffuse to the substrate and meet Fe atoms to form a new phase Fe$_2$Al$_5$ (figure 5(a)). Regarding Ti–Al–N and Ti–Si–N films, their thermal stability is higher than that of TiN due to the existence of Ti$_3$AlN and Si$_3$N$_4$ phases in the film, their contact angles have changed at the test temperature, detected as 78° and 71°, respectively. However, the
diffraction peaks of the new phase did not appear according to figures 5(b) and (c), suggesting that the film did not decompose and still had a protective effect on the substrate.

Regarding the wetting of ceramics by liquid metal, researchers have performed several meaningful works [18–20]. The two famous formulas [12, 21] used are: (1) the relationship between the contact angle $\theta$ and the surface tension $V$ of each phase: $\cos \theta = (V_{\text{sg}} - V_{\text{sl}})/V_{\text{lg}}$ (2) the relationship between the adhesion power $W$ of the liquid phase on the solid phase and the contact angle $\theta$: $W = V_{\text{lg}}(1 + \cos \theta)$. The former indicates that the larger the solid-liquid surface tension $V_{\text{sl}}$, the smaller the contact angle, that is, the easier it is for the liquid to wet the solid surface; the latter suggests that the greater the adhesion power $W$ between the liquid and the solid, the smaller the contact angle $\theta$, and the easier it is for the liquid to adhere to the solid surface. This is related to the energy required to break chemical bonds to create a new surface, according to the definition of surface tension; some scholars [22] expressed it as: surface tension = (the number of chemical bonds destroyed/surface per unit area formed) • (Energy/each bound). It can be concluded after the comprehensive analysis of the above-mentioned formulas that the more the number of chemical bonds destroyed on the solid surface, the higher the surface tension; the smaller the contact angle, the easier it is to be wetted. Based on this theory, the results of the
wetting of the four different solid surfaces by liquid Al in this experiment can be explained as follows. First, the surface tension of the tool steel is the largest; the reason is that its atoms are combined by metal bonds, and when they are in contact with liquid Al that is also a metal, their electron clouds would overlap if two atoms are moved closer (according to the distribution of electrons in molecules or atoms in compliance with the laws of quantum mechanics) [23]; at this time, the metal Fe already has more broken chemical bonds, making it easiest to be wetted. On the contrary, the chemical bonds of TiN, Ti3AlN and Si3N4 in the film are ionic bonds or covalent bonds, their bonding strength is much higher compared to Fe atoms bonded by metal bonds (according to the definition of chemical bonds). Particularly, the covalent bond Si3N4 is structurally more stable than the ionic bond TiN and Ti3AlN. From the perspective that the number of broken chemical bonds is less than that of the base tool steel, the contact angles of the three film samples wetted by liquid Al are significantly larger than those of the tool steel (figures 4 and 5). As revealed from comparing TiN and Ti–Al–N films, the latter is more difficult to be wetted by liquid Al compared to the former, which may be caused by the formation of a more complex compound Ti3AlN in the Ti–Al–N film. The combination of the composite anion and the cations in Ti3AlN that has a stronger binding force compared to simple compounds [24], with higher chemical stability; consequently, the broken chemical bonds are reduced, and low surface tension and adhesion power are exhibited on the surface of Ti–Al–N film. Therefore, the Ti–Si–N film in the test sample should be the least likely to be wetted by liquid Al. However, its contact angle of 71° is slightly smaller than the contact angle of 78° for the Ti–Al–N film, as illustrated in figures 4 and 5. The phenomenon may be related to the amount of Si3N4 contained in the Ti–Si–N film. As illustrated by the results of the EDS analysis in figure 1(c), the mass fraction of Si3N4 in the Ti–Si–N film is 13.62%, and the rest is TiN; meanwhile, the structural characteristics of TiN make its stability lower than that of Ti3AlN, resulting in the contact angle of the Ti–Si–N film being smaller than that of the Ti–Al–N film. Even though the mass fraction of Si3N4 in the Ti–Si–N film is only 13.62%, its contact angle is much higher than that of the TiN film, indicating that the ternary film Ti–Si–N prepared by adding element Si to the TiN system can significantly improve the ability of the film to resist the wetting of liquid Al. The experimental results demonstrate that if the third element is added in the preparation process of the binary TiN film, the ability of the film against the wetting of low-melting-point metals can be significantly improved when the composition phase contains complex ionic compounds or covalent compounds. Besides, ceramic film, as a protective coating, can effectively weaken the ‘BUE and BUL’ and the erosion of the mold surface by liquid metal.

2.2. Analysis of high-temperature oxidation resistance

DSC experiments and temperature resistance experiments with the range of 600 °C–900 °C were performed on the TiN, Ti–Al–N, and Ti–Si–N films to test the high-temperature resistance properties of the three films. The DSC curves of the samples are presented in figure 7. It can be observed from the figure that the curves of the three different films have inflection points in the area around 620 °C; with changes in the slope of the curve, the TiN film has the largest change, followed by the Ti–Si–N film and the Ti–Al–N film. This change may be caused by the decomposition of TiN. From 750 °C to the highest heating temperature in the test of 1000 °C, TiN is apparently oxidized and exothermic; however, Ti–Al–N and T–Si–N do not exhibit obvious ‘inflection point’, demonstrating that Ti3AlN and Si3N4 in the Ti–Al–N and Ti–Si–N films do not undergo violent oxidation.
The three different films were heated in a box-type electric furnace to further research the changes of the film under the influence of temperature; the temperature was selected as 600 °C, 700 °C, 800 °C, and 900 °C. The sample was heated to the selected temperature with 1-hour heat preservation and then cooled with the furnace; next, the surface morphology of the sample was observed using SEM, as illustrated in figure 8.

It indicates that the surface of the TiN film has changed after being heated at 700 °C. XRD analysis of the sample (figure 9(a)) reveals that the TiN film has been decomposed after being heated at 700 °C, and the peak of the TiO2 phase appears in the diffraction spectrum. This is consistent with the results of the DSC analysis in figure 7, as well as the related research reports [25]. The surface of the sample changes more significantly when the heating temperature rises to 800 °C, as exhibited in figure 8(d). The results of diffraction analysis are provided in figure 9(a). Besides, the oxygen atoms in the furnace diffuse into the film, and the film was thinner (<1 µm); therefore, Fe3O4 and Fe2O3 are formed when meeting with the iron atoms, consequently, the film was destroyed. However, regarding Ti–Al–N and Ti–Si–N films, the composition phase of the original TiN film is changed due to the introduction of Al and Si antioxidant elements during the film deposition process, leading to the significant improvement of its oxidation resistance. It is observed from figure 8(g) that the surface of the film changes after being heated at 800 °C. Diffraction analysis results in figure 9(b) suggests that a small amount of Fe2O3 diffraction peaks appear, and the number of Fe2O3 diffraction peaks increases significantly after being heated at 900 °C; meanwhile, the film surface morphology also dramatically varies. Different from the related research reported in [26], there is no Al2O3 phase in Ti–Al–N after being heated at 900 °C, demonstrating that the Ti3AlN phase in the film does not decompose, consistent with the DSC detection result (figure 7). Figure 8(k) illustrates that the surface of the Ti–Si–N film also begins to change after being heated at 800 °C while the degree of change is slightly weaker than that of the Ti–Al–N film. Figure 9(c) presents the XRD diffraction spectrum analysis results before and after the film is heated. After being heated at 800 °C, SiO2 phase appears in the film, and Si3N4 does not decompose at this temperature, indicating that there may be monatomic silicon in the original film. Besides, the absence of Si diffraction peaks in the XRD diffraction lines of the film may be caused by the low content of Si. Studies have reported [27, 28] that, in addition to TiN + Si3N4, monatomic silicon exists in Ti–Si–N films deposited by PVD. Although the number of SiO2 phases is small, the improvement of the oxidation resistance of the film is more significant. After the film is heated at 900 °C, its surface changes significantly (figure 8(l)), and the film is damaged. XRD diffraction line analysis results (figure 9(c)) reveals that
there are more Fe$_2$O$_3$ diffraction peaks; this accredits to the diffusion of oxygen atoms into the film and react with substrate at high temperature, as mentioned above.

From the analysis of the above experimental results, TiN, Ti–Al–N, and Ti–Si–N films not only have acceptable effects in anti-adhesion and molten metal wetting but also have resistance to high-temperature oxidation. Particularly, the produced Ti–Al–N and Ti–Si–N films have significantly improved high-temperature oxidation resistance when the components of the TiN film are added with Al and Si elements. This is caused by the different phases of the film composition and the formation of high-temperature-resistant phases under the action of temperature. Furthermore, the oxidation resistance of the film will be further improved if the thickness of the film is appropriately increased, the diffusion and penetration of oxygen atoms at high temperatures are blocked, and it is avoided to prematurely encounter with the matrix Fe atoms to generate iron oxide [26].

3. Conclusions

In order to study TiN ceramic film as a protective coating on the surface of tools and molds, the hollow cathode assisted multi-arc ion plating technology was used to prepare TiN, Ti–Al–N and Ti–Si–N coatings on the surface of tool steel. After the film is wetted by molten Al and oxidized at different temperatures of 600 °C∼900 °C, the wetting behavior and high temperature oxidation ability of different films are analyzed.

The spreading speed of molten aluminum on the surface of uncoated tool steel and ceramic film samples is: tool steel > TiN > Ti–Si–N > Ti–Al–N. This phenomenon is related to the constituent elements of the film layer and is also affected by the types of chemical bonds. Among them, the tool steel with metal bond has the smallest wetting angle, followed by the wetting angle of TiN film with ionic bond. Although Si$_3$N$_4$ in the Ti–Si–N film is covalently bonded, its mass fraction is only 13.62%, and the main component is TiN. Therefore, the wetting angle of Ti–Al–N and Ti–Si–N films is close and the highest. TiN film begins to decompose in the range of 600 °C∼700 °C, the appearance of TiO$_2$ in the film reduces the high temperature resistance of the film. Ti$_3$AlN and Si$_3$N$_4$ in Ti–Al–N and Ti–Si–N films and the product SiO$_2$ can improve the resistance. High temperature oxidation, so the high temperature oxidation resistance temperature of the two films can reach about 800 °C.
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