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Preparation of TiAlN/ZrN and TiCrN/ZrN multilayers by RF magnetron sputtering

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Abstract: Titanium-based nitride coatings on cutting tools, press molds and dies can be used to prolong their life cycle because of their superior corrosion and oxidation resistance. TiAlN/ZrN and TiCrN/ZrN multilayer coatings were prepared by RF magnetron sputtering, and their microstructural evolution and corrosion resistance during heat treatment were investigated. The TiAlN/ZrN and TiCrN/ZrN multilayer coatings are degraded by heating up to 600 ℃ with the formation of oxides particles on the surface. During the heat treatment, the TiCrN/ZrN and TiAlN/ZrN multilayer coatings show the lowest corrosion current density and the highest polarization resistance at temperature range of 400−500 ℃. Consequently, the TiAlN/ZrN and TiCrN/ZrN multilayer coatings show good corrosion resistance at temperature range of 400−500 ℃ during heating.

Key words: TiCrN/ZrN; TiAlN/ZrN; multilayer coating; RF magnetron sputtering

1 Introduction

Titanium nitride(TiN) coating on materials has some excellent properties, such as high hardness, good wear resistance, chemical stability and corrosion resistance, which is widely used in industry of cutting tools, press dies, and decoration parts, etc[1−2]. However, TiN coating is degraded by oxidation at high temperature during working. So, it is very important to enhance its oxidation resistance for successful utilization. Recently, nanolayered, or multilayered coatings are known to exhibit superior oxidation resistance as compared with single layer coatings[3−4]. TiN and CrN coatings are reported to be stable up to 500 and 600 ℃, but TiAlN and TiCrN coatings show the stability up to 750 ℃ [5−10]. On the other hand, ZrN-based coatings have attraction for its superior corrosion and wear resistance, good hardness, low resistivity, and golden color[11−14]. In previous works, the preparation and characterization of TiN/ZrN and TiCN/ZrCN super lattice coatings were reported[15−17], but the TiAlN/ZrN and TiCrN/ZrN multilayer coatings has not yet been studied in detail.

In this study, the TiAlN/ZrN and TiCrN/ZrN multilayer coatings were prepared by RF magnetron sputtering, and the microstructural evolution and their corrosion resistance during heating was investigated.

2 Experimental

2.1 Preparation of multilayer coatings by RF sputtering

The commercially obtained press mold steel (SKD11) was used as a substrate after annealing at 1 030 ℃ for 1 h and then tempering at 520 ℃ for 1 h. All substrates were finely polished to 1 μm, and then ultrasonically cleaned in acetone for 10 min. TiAlN/ZrN coating was obtained by coating TiAlN onto SKD11 plates, followed by deposition of ZrN with RF magnetron sputtering. TiCrN/ZrN coatings were also deposited by the same method. The experimental parameters of the deposition process are shown in Table 1. The as-prepared TiAlN/ZrN and TiCrN/ZrN coating layers were heat- treated at different temperatures in tube furnace from 400 to 800 ℃ in flowing N_2 gas.

2.2 Analysis of microstructure, phase and oxidation resistance

The microstructure of the coated layers was observed by FE-SEM and their crystalline phases were

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Table 1 Operating parameters of RF magnetron sputtering

Parameter	Value
Base pressure/Pa	2.0×10^{-5}
Working pressure/Pa	9.5
Substrate	SKD11, Si
Rotational speed of substrate/ ($r\cdot min^{-1}$)	10
Target (d50.8 mm×6.35 mm)	TiAl, TiCr (50%:50%) Zr(99.95%)
Gas mixture/($cm^3\cdot min^{-1}$)	Ar:20 (99.999%), N_2:30 (99.999%)
RF power/W	80
Distance of cathode to substrate/ mm	50

determined by X-ray diffraction. The glancing incidence angle was 1° and the scanning speed was 1−2 (°)/min. The corrosion tests were performed in 0.9% NaCl solution from −2.0 to 3.0 V of transmission volt under free air condition at room temperature. Prior to corrosion test, all samples were cleaned with distilled water before loading the sample to the Tafel sample holder. The Tafel plot was obtained after the electrochemical measurements. The φ_{corr} (corrosion potential) and J_{corr} (corrosion current density) were deduced from the Tafel plot:

$$J_{corr}=\left[\frac{b_a b_c}{2.303(b_a+b_c)}\right]\frac{1}{R_p} \quad (1)$$

where b_a and b_c are the Tafel slopes or the Tafel constants, expressed in V/decade, and R_p is the polarization resistance expressed in $\Omega\cdot cm^2$. The polarization resistance is calculated using the following equation:

$$R_p=(\Delta\varphi/\Delta I)|_{\Delta\varphi\to0} \quad (2)$$

where $\Delta\varphi$ is the polarization potential and ΔI is the polarization current. If the polarization resistance increases the corrosion current decreases[18].

3 Results and discussion

The cross-sectional FE-SEM micrographs of TiAlN/ZrN and TiCrN/ZrN coatings are shown in Fig.1, respectively. However, their coating thickness is unclear at the SEM micorgraph. By previous TEM investigation, most of TiN-based multilayer coatings show a dense columnar structure with the mixture of two kinds of nano scaled nitrides.

In case of coatings on SKD11, the peaks corresponding to the coatings can be hardly detectable because the peaks attributed to SKD11 are too strong.

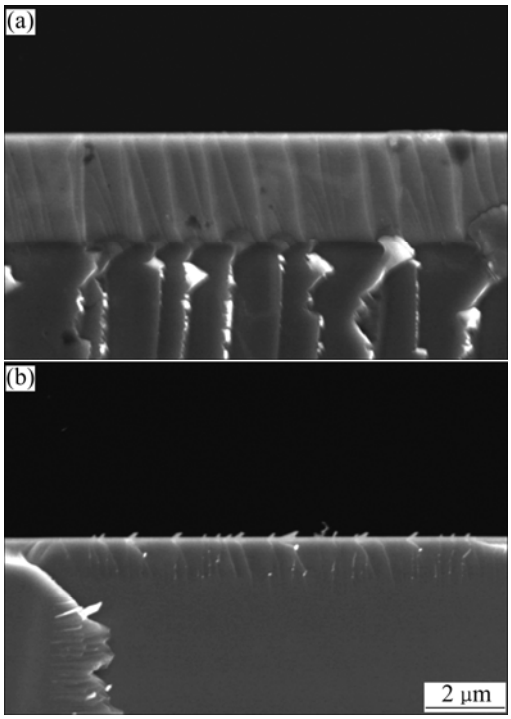

Fig.1 Cross-sectional FE-SEM micrographs of TiAlN/ZrN (a) and TiCrN/ZrN (b) coatings

Therefore, TiAlN/ZrN and TiCrN/ZrN are coated on Si substrates for the analysis of the crystalline phases. In both cases, higher fraction of ZrN phase in (111) plane is found in the coating from XRD patterns of the as deposited films.

The XRD patterns for phase change by the oxidation on the surface of the multilayer coatings are shown in Fig.2 in temperature range of 400−700 ℃. In case of the TiAlN/ZrN coating, there is no change in the XRD patterns below 500 ℃; however, some peaks for oxides (γ-Ti_3O_5, rutile TiO_2, Ti_2ZrO_6) formed by corrosion are observed above 600 ℃. In the case of TiCrN/ZrN coating, the oxides peaks for Cr_3O_8, rutile TiO_2, Ti_2ZrO_6 and TiO phases are observed above 500 ℃. The oxidation for TiAlN/ZrN or TiCrN/ZrN multilayer coatings may result from the residual oxygen in the furnace or oxygen impurity of N_2 gas.

Fig.3 and Fig.4 demonstrate the microstructural change on the surface of TiAlN/ZrN and TiCrN/ZrN coatings during heating, respectively. Smooth surface is observed both on the surface in as-deposited film or heat-treated specimen at 400 ℃. However, many of spherical particles with approximately 100−200 nm diameter are found on the surface heated above 500 ℃ and their particle size increases with heating temperature increasing. On thinking the relation between XRD patterns and microstructural change during heating, most of spherical particles are oxides particles of γ-Ti_3O_5, TiO, TiO_2, Ti_2ZrO_6, and Cr_3O_8, which may be formed by

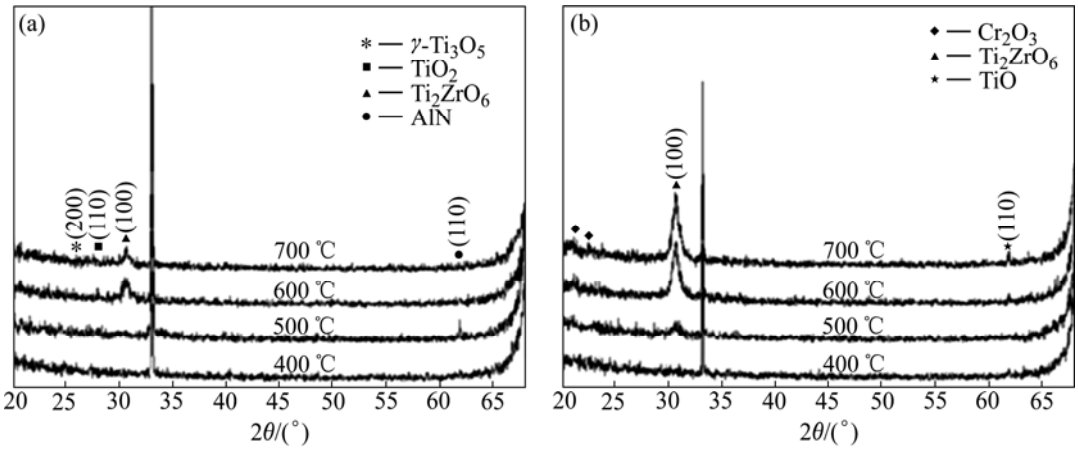

Fig.2 XRD patterns of TiAlN/ZrN (a) and TiCrN/ZrN (b) coatings heat-treated at 400−700 ℃

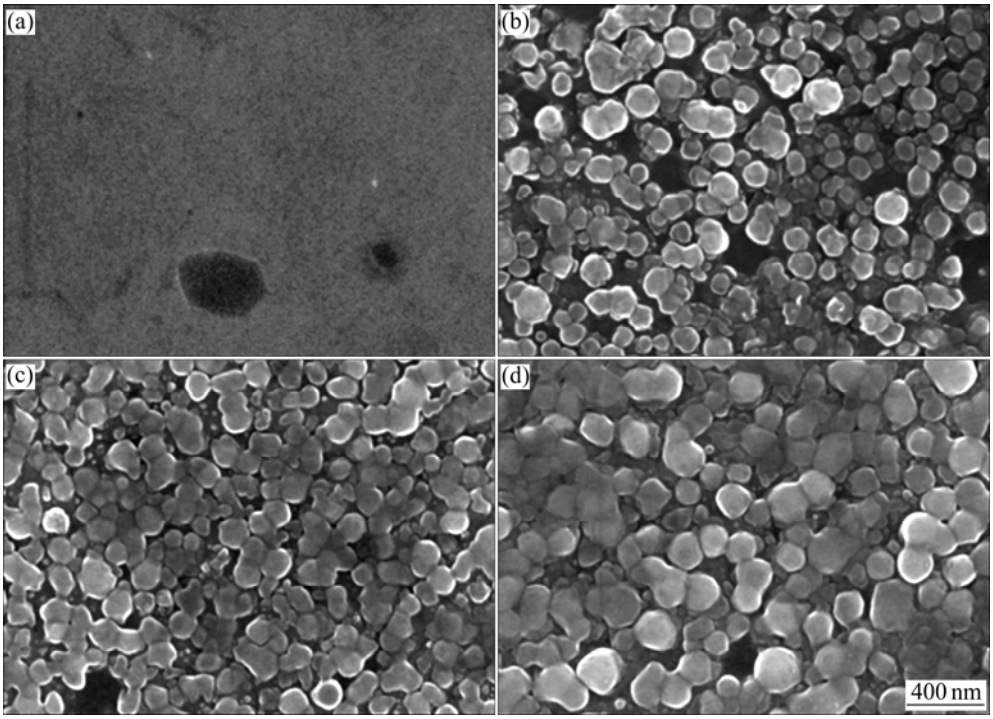

Fig.3 Microstructures of TiAlN/ZrN coatings heat-treated at 400 ℃ (a), 500 ℃ (b), 600 ℃ (c) and 700 ℃ (d)

oxidation of TiAlN, TiCrN and ZrN.

The Tafel plots obtained from multilayer coatings of TiAlN/ZrN and TiCrN/ZrN in 0.9% NaCl solution are shown in Fig.5 and Fig.6, respectively. The TiAlN/ZrN and TiCrN/ZrN coatings heat-treated at 600 ℃ to 700 ℃ show lowest passivation. On the other hand, the TiAlN/ZrN and TiCrN/ZrN coatings heat-treated at 400 ℃ to 500 ℃ show the highest passivation.

The corrosion potential(φ_{corr}) and corrosion current (J_{corr}) for TiAlN/CrN and TiAlN/CrN coatings with different heat treatment temperatures are given in Fig.7. It can be seen that the corrosion resistance at 400−500 ℃ of TiAlN/ZrN and TiCrN/ZrN coatings is good by the ability to form a passive layer over the surface, however, above 600 ℃, the multilayer coatings of TiAlN/ZrN and TiCrN/ZrN are degraded by oxidation.

4 Conclusions

The TiAlN/ZrN and TiCrN/ZrN multilayer coatings are degraded by heating up to 600 ℃ with the formation of oxides particles on the surface. During the heat treatment, TiAlN/ZrN and TiCrN/ZrN multilayer coatings show the lowest corrosion current density and the highest polarization resistance in temperature range of 400−500 ℃. TiAlN/ZrN multilayer coatings are better in oxidation resistance than TiCrN/ZrN coatings during heating. Both TiAlN/ZrN and TiCrN/ZrN multi-layer

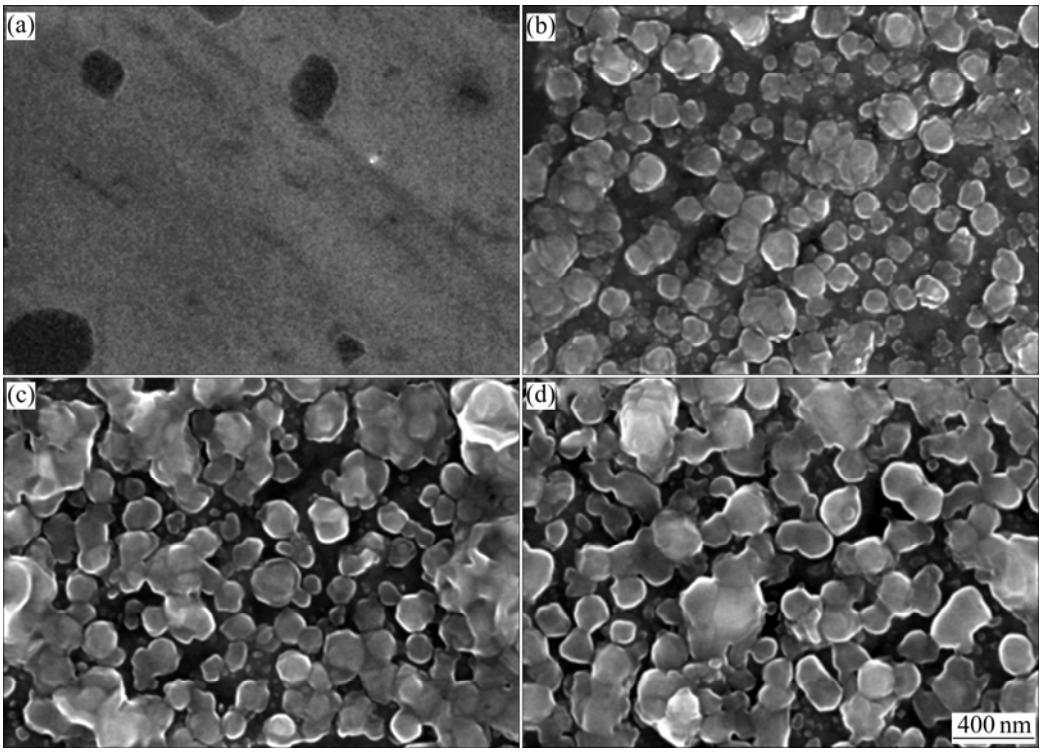

Fig.4 Microstructures of TiCrN/ZrN coatings heat-treated at 400 ℃ (a), 500 ℃ (b), 600 ℃ (c) and 700 ℃ (d)

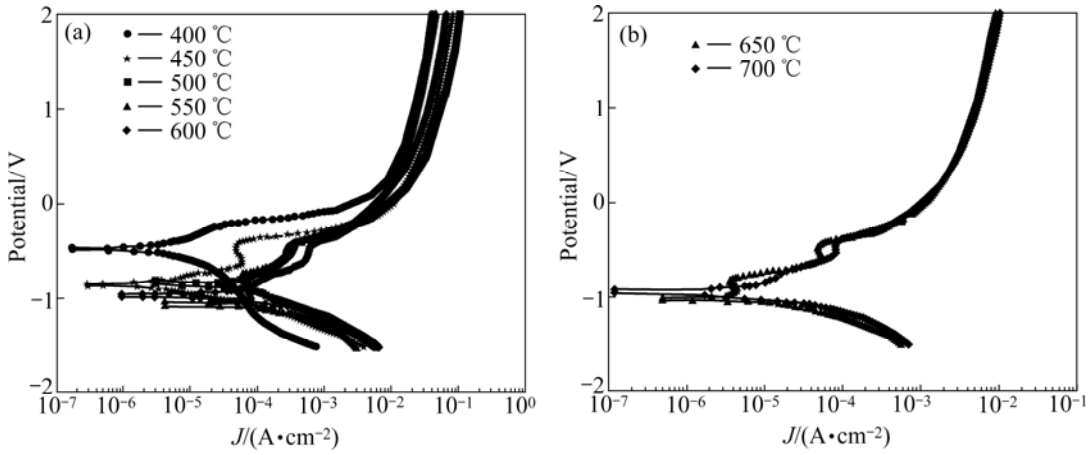

Fig.5 Potentiodynamic polarization curves of TiAlN/ZrN coatings with different heat treatment temperatures

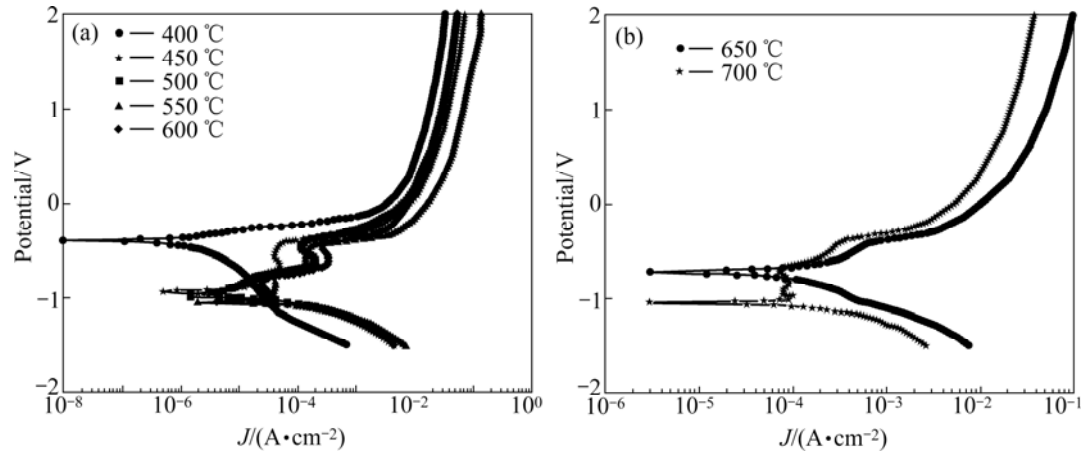

Fig.6 Potentiodynamic polarization curves of TiCrN/ZrN coatings with different heat treatment temperatures

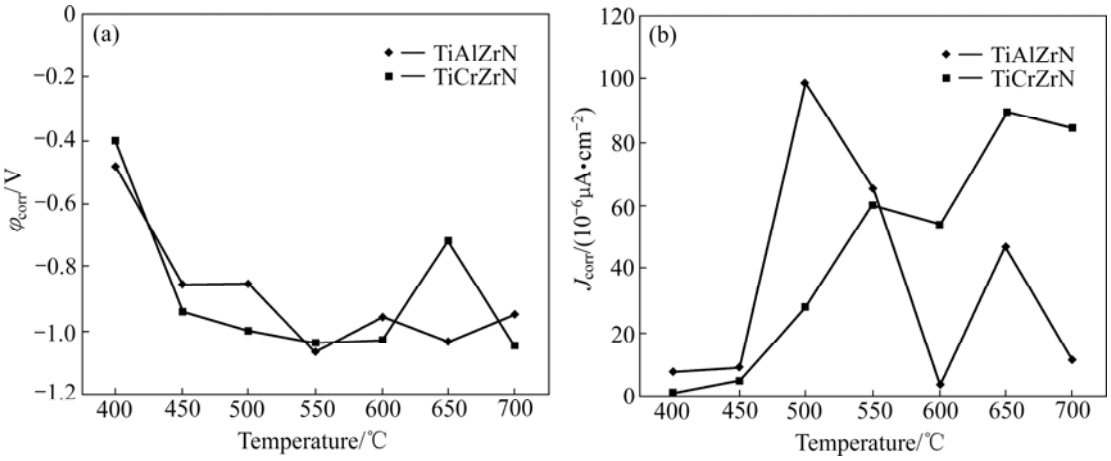

Fig.7 φ_{corr} (a) and J_{corr} (b) of coating layers with different heat treatment temperatures

coatings show good corrosion resistance in temperature range of 400−500 ℃. However, they are degraded above 600 ℃ by the formation of titanium oxide particles on the surface.

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