



Influence of ZrN on oxidation resistance of Ti–Al–N coating



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ABSTRACT

Ti_{1-x}Al_xN coatings are today used as wear protection for cutting tools due to their outstanding oxidation resistance and thermal stability as well as good mechanical properties. Improvement of the mechanical and thermal properties by incorporation of the fourth alloy element receives great attentions. Here, the effect of ZrN on the structure and oxidation resistance of Ti–Al–N is investigated. Alloying with ZrN results in a slight structural transition from single phase cubic structure for Ti–Al–N into a mixed cubic–hexagonal structure. The Ti–Al–Zr–N coating shows a lower oxidation resistance in the temperature range from 700 to 800 °C than the Zr-free Ti–Al–N coating, due to the higher affinity of Zr to oxygen and the Zr-promoted formation of small hexagonal phase fractions already in the as-deposited state. However, further increasing the oxidation temperature shows a better oxidation resistance for Zr-containing coating. After thermal exposure for 10 h in air at 850 °C, the Ti–Al–Zr–N coating only exhibits a ~0.61 μm oxide scale, whereas Ti–Al–N coating is fully oxidized. It is attributed to the retarded transformation of anatase-rutile TiO₂. Only a slight increase in oxide scale to ~0.70 μm is obtained after oxidation at 900 °C.

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1. Introduction

Ti_{1-x}Al_xN coatings with a substitutional solid solution of Al for Ti in the TiN based face centered cubic (c) lattice, which exhibits excellent mechanical and thermal properties, are widely used as protection for cutting tools [1–5]. The mechanical and thermal properties of Ti_{1-x}Al_xN coatings as well as the preferred crystal structure are strongly depending on their Al content [6–8]. Increasing Al content within the cubic solid solubility limitation leads to an enhanced mechanical properties and oxidation resistance [6–10]. For Al contents exceeding the maximum cubic solubility (x_{\max} , ~0.7), a mixed c–NaCl and hexagonal–ZnS (w–AlN) structure is formed, which exhibits poor mechanical properties and oxidation resistance [6–10]. During machining applications, especially for dry machining, tools are always exposed to air at elevated temperature. This raises a rigorous claim for the high temperature oxidation resistance of protective coating. The Ti_{1-x}Al_xN coatings exhibit a dense Al₂O₃ scale during the initial oxidation stage, which retards the oxidation diffusion process and has a beneficial effect on the oxidation resistance [8–10]. A bilayer Al₂O₃/TiO₂ oxide scale is formed with the ongoing oxidation process (prolonging oxidation time or elevating oxidation temperature) [8–10]. The growth of porous TiO₂ scale leads to the crack formation, and propagates to the dense and protective Al₂O₃ out-scale [8–10]. Consequently, break away oxidation occurs. Therefore, increasing Al content within cubic structure promotes

the formation of Al₂O₃ out-scale, and finally results in the improvement of the oxidation resistance [8–10].

Numerous studies indicate that the thermal oxidation temperature of cubic Ti_{1-x}Al_xN coatings is below 850 °C [8–12]. However, the application temperature of cutting tools for machining of high strength materials, e.g. titanium- and nickel-based alloys exceeds the limits of Ti_{1-x}Al_xN coatings. An improvement in mechanical and thermal properties can be obtained by incorporation of a fourth alloying elements, such as Si, Zr, Hf, or Ta [13–18]. Alloying with ZrN, as a congener element with TiN, retards the formation of w–AlN during thermal annealing, resulting in an increased thermal stability as well as improved mechanical properties [14]. The positive effect of ZrN on the oxidation resistance is also reported [14,15,19]. However, a detailed investigation on the oxidation resistance of Ti–Al–Zr–N coating has not yet been explored. In this paper, the effect of ZrN on the structure and oxidation resistance of Ti–Al–N is presented. According to our previous work, the Ti–Al–Zr–N coating with 5 at.% Zr (Ti_{0.40}Al_{0.55}Zr_{0.05}N) exhibits the best mechanical and thermal properties [14]. Consequently, the Ti–Al–N and Ti–Al–Zr–N coatings with similar Al content are deposited targets by cathodic arc evaporation using Ti_{0.50}Al_{0.50} and Ti_{0.40}Al_{0.55}Zr_{0.05} targets.

2. Experimental details

Ti–Al–N and Ti–Al–Zr–N coatings were deposited by a commercial cathodic arc evaporation system (Balzers Oerlikon Rapid Cooling System, RCS) from Ti_{0.5}Al_{0.5} and Ti_{0.40}Al_{0.55}Zr_{0.05} targets (99.99% purity). The working gas pressure of N₂ (99.99% purity) atmosphere was ~2 Pa,

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the substrate bias was -100 V, the target current was 180 A, and the deposition temperature was 550 °C. Prior to the deposition, the substrates were cleaned with an Argon-ion-etching process at 0.3 Pa Ar pressure, -150 V DC substrate bias for 20 min. Low-alloy steel was used for differential scanning calorimetry (DSC), thermo gravimetric analyzer (TGA) and X-ray diffraction (XRD) measurements, and polycrystalline Al_2O_3 plates were used for oxidation resistance measurements.

DSC with TGA was performed in a Netzch-STA 409C from room temperature to 1500 °C with a heating rate of 10 K/min and a cooling rate of 50 K/min in synthetic air (79% N_2 , 21% O_2 , 20 sccm flow rate). Thermal annealing was also performed in Netzch-STA 409C from room temperature to annealing temperature (T_a) of 800, 950, 1000, 1100 and 1450 °C with the same conditions as the DSC test. Prior to these measurements, the Ti–Al–N and Ti–Al–Zr–N coatings were removed from their low-alloy steel substrates by chemical etching in 10 mol% nitric acid. Phase identification and structure investigations of the layers (after removal from their low-alloy steel substrates) in their as-deposited state and after thermal annealing in the synthetic air were conducted by XRD with $\text{CuK}\alpha$ radiation using a Bruker D8 diffractometer in Bragg/Brentano mode at 40 mA and 40 kV. Coated polycrystalline Al_2O_3 substrates were isothermally oxidized from 700 to 950 °C for 10 h in the DSC equipment with a heating rate of 10 K/min and a cooling rate 50 K/min in synthetic air with flow rate of 20 sccm, and then investigated by the fracture cross-sectional SEM (LEO1525, Germany). The chemical compositions of the coatings in their as-deposited state and after the oxidation experiments were determined using energy dispersive X-ray analysis (EDX) with an Oxford Instruments INCA EDX unit attached to a SEM operated with 25 kV.

3. Results and discussion

Elemental analysis by EDX reveals that the Ti–Al–N and Ti–Al–Zr–N coatings are stoichiometric with N/metal ratios of 1 ± 0.02 and compositions of $\text{Ti}_{0.52}\text{Al}_{0.48}\text{N}$ and $\text{Ti}_{0.45}\text{Al}_{0.49}\text{Zr}_{0.06}\text{N}$. Fig. 1 shows the XRD patterns of powdered freestanding coating samples. Analysis of the XRD results indicates that the Ti–Al–N coating has a single phase cubic structure. Alloying ZrN into Ti–Al–N results in a slight structure transition into mixed cubic–hexagonal structure, which is indicated by the weak peak of w-AlN at $\sim 33.2^\circ$. A broadening in diffraction peaks can be observed with addition of ZrN, which indicates a reduction in grain size due to its binary phase structure. Fig. 2a shows the dynamic DSC experiments of powdered Ti–Al–N and Ti–Al–Zr–N freestanding coating samples up to 1500 °C in synthetic air. Both coatings exhibit the

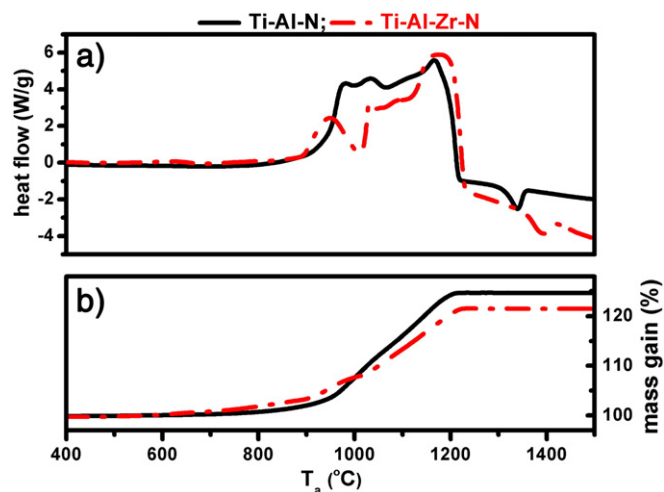


Fig. 2. DSC (a) and TGA (b) results of Ti–Al–N and Ti–Al–Zr–N freestanding coatings in synthetic air.

exothermic reactions consisting of several exothermic peaks due to the oxidation. The Ti–Al–Zr–N coating shows a lower onset temperature of exothermic heat flow, and an additional pre-reaction in the temperature range of 900–1010 °C. Alloying with ZrN leads to a shift of the peak temperature of rapid oxidation from ~ 980 to 947 °C. However, the Ti–Al–N coating exhibits a higher exothermic heat flow while exceeding ~ 955 °C. This dovetails well with the TG result, see Fig. 2b. A higher mass gaining is obtained for the Ti–Al–Zr–N before 955 °C, whereas further elevating temperature leads to a lower mass gaining. Additionally, the ending temperature of mass gaining slightly shifts to lower temperature with the ZrN-incorporation, which is corresponding to the maximum exothermic peak value.

Identification of the major contributions of these oxidation reactions is achieved by XRD analyses of samples annealed to 800, 950, 1000, 1100, 1250 and 1450 °C in synthetic air using the DSC equipment, as shown in Fig. 3. After annealing at $T_a = 800$ °C, no obvious change is observed for Ti–Al–N (Fig. 3a), whereas the Ti–Al–Zr–N exhibits small XRD peaks as well as its matrix, signifying the formation of stable phase rutile (r) TiO_2 , see Fig. 3b. This indicates that alloying with ZrN promotes the oxidation reaction of Ti–Al–N due to the higher affinity of Zr to oxygen. As the Gibbs free energy for ZrO_2 with $\Delta G_{\text{ZrO}_2}^0 = -1039.7$ kJ/mol is more negative than for TiO_2 with $\Delta G_{\alpha\text{-TiO}_2}^0 = -889.4$ kJ/mol and $\Delta G_{\gamma\text{-TiO}_2}^0 = -883.3$ kJ/mol [20], the Zr atoms of the Ti–Al–Zr–N coating are easier oxidized than the Ti atoms. The formation of metastable phase (α) TiO_2 as well as r- TiO_2 for Ti–Al–N can be observed as T_a increases to 950 °C. In general, the metastable phase α - TiO_2 transforms into its stable phase r- TiO_2 with elevating temperature [21]. Additionally, the XRD patterns show a presence of the left-hand shoulder for the (111) peak, suggesting the spinodal decomposition of Ti–Al–N into Al-depleted and Al-enriched domains [5]. For annealed Zr-containing coating at $T_a = 950$ °C, a slight diffraction peak at $2\theta = 35.2^\circ$ suggests the formation of α - Al_2O_3 in addition to the oxidation products of α - and r- TiO_2 , see Fig. 3b. This indicates that ZrN-incorporation promotes the formation of α - Al_2O_3 . The XRD peaks of as-deposited coatings can be still detected after oxidation at $T_a = 1000$ °C. Here, the diffraction peaks of α - Al_2O_3 as well as the increased peak intensities of α - and r- TiO_2 are also observed for Ti–Al–N. The Ti–Al–Zr–N only exhibits an increased intensity of α - TiO_2 with increasing T_a from 950 to 1000 °C, see Fig. 3b, whereas the intensity of diffraction peaks for r- TiO_2 and α - Al_2O_3 almost keeps constant. Zr-based oxides, which probably exist above the detection limit of XRD, have not been observed. Another possibility is a solid solution of Zr in the α - TiO_2 lattice, which can be verified by its shift to the low angle relative to its standard peak positions as shown in Fig. 3b. Additionally,

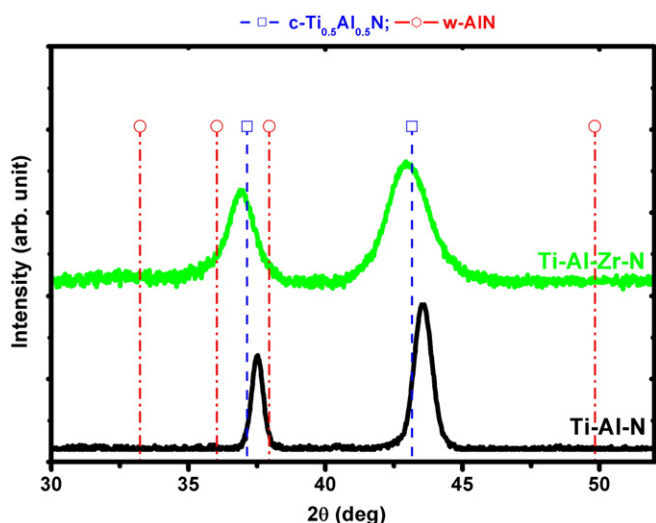


Fig. 1. XRD patterns of as-deposited Ti–Al–N and Ti–Al–Zr–N coating powder removed from their substrates.

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