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Effect of CrN addition on the structure, mechanical and thermal properties of Ti-Al-N coating

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ABSTRACT

Optimization of Ti–Al–N coating by incorporation of fourth substantially alloying elements attracts extensive attention in order to meet the severe application requirements at elevated temperature. Here, we investigate the effect of CrN addition on structure, mechanical and thermal properties of Ti–Al–N coating with cubic structure. Alloying with CrN promotes the spinodal decomposition of Ti–Al–N to form Al-depleted and Al-enriched domains and also the formation of hexagonal AlN during thermal annealing. Cr-containing coating has an increase in hardness from the as-deposited value of ~34.4 GPa to the maximum value of ~38.7 GPa with $T_a = 900$ °C, whereas the hardness of Ti–Al–N coating only increases from ~31.2 GPa to ~34.1 GPa. Thermal annealing of Ti–Al–Cr–N coating results in the N-loss to form h-Cr_2N with $T_a = 1000$ °C and finally Cr with $T_a = 1200$ °C. Also addition of CrN into Ti–Al–N coating retards the transformation of metastable an-TiO_2 into stable r-TiO_2 and thereby the growth of porous Ti-oxide rich sublayer, which is beneficial to its oxidation resistance. Only a thin scale of ~0.55 μm for Cr-containing coating is shown after annealing in air at $T_a = 850$ °C for 10 h, whereas Ti–Al–N coating is already completely oxidized. Consequently, Ti–Al–Cr–N coated inserts have a better machining performance than Ti–Al–N coated inserts during continuous turning.

1. Introduction

Metastable Ti–Al–N coatings have been well acknowledged as a protective layer for industrial applications due to their excellent mechanical, chemical and thermal properties. Especially the age-hardening ability of Ti–Al–N, which involves the isostructural spinodal decomposition to form cubic Al-rich and Ti-rich domains during thermal load up to ~900 °C and thus leads to an increased hardness, makes it extremely valuable for high temperature application (e.g. cutting tools) [1–4]. However, their mechanical and thermal properties quickly decline above 900 °C due to its transformation into stable wurtzite (w-) AlN following the spinodal decomposition [1,5]. Additionally, the oxidation resistance of Ti–Al–N coatings also plays a very important role in their industrial application, where a bi-layered oxide scale with dense Al_2O_3 outer-layer and porous TiO_2 sub-layer can be formed while exposed to temperature ~850 °C [6]. Further increasing oxidation temperature up to 900 °C results in a complete oxidation with the fast growth of TiO_2 layer.

Nevertheless, with the development of the machining technology (high-speed and dry cutting), the working temperature often exceeds that of Ti–Al–N coatings. In order to meet these requirements, multilayer and multicomponent Ti–Al–N coatings have been used to optimize their properties [7,8]. Multilayer coatings have higher mechanical and thermal properties as well as combining the advantages of different materials selected. A positive effect on the mechanical and thermal properties can also be obtained by the incorporation of fourth substantially alloying element X into Ti–Al–N. For instance, alloying with larger atomic radius than Ti (e.g. Y, Zr, Nb, Ta and Hf) results in an increased hardness, thermal stability and oxidation resistance [9–13]. Most of them indicate that the $Ti_{1-x-y}Al_xX_yN$ coatings for X mole fractions $y < 0.1$ have the most positive effect on the mechanical and thermal properties [9–13]. Ti–Al–V–N coatings have lower friction and wear due to the formation of self-lubricating phases during machining [14]. A considerable amount of attention has been paid to the effect of CrN on Ti–Al–N as a strengthening, wear and corrosion resistant element [15–20]. Alloying with CrN into Ti–Al–N coating leads to a higher onset temperature for oxidation by ~200 °C [21]. Recently, theoretical prediction and experimental verification by Lind et al. [8] and Forsén et al. [22] indicate that the addition of CrN into Ti–Al–N delays the formation of w-AlN formation during thermal annealing in vacuum. Elevating Cr content results in an increased hardness, and retards the formation of w-AlN during annealing. However, a detailed investigation on the effect of CrN on the thermal decomposition of Ti–Al–N, especially with respect to the high temperature above 1100 °C, has not yet been explored.

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In this paper, we studied the influence of 6 at.% CrN on the structure, mechanical and thermal properties of Ti–Al–N coating. Especially, the structural evolution of Ti–Al–Cr–N coating during annealing in Ar and air was investigated in detail.

2. Experimental and calculation details

2.1. Coating deposition

Ti–Al–N and Ti–Al–Cr–N coatings were prepared by a commercial cathodic arc system (Balzers Oerlikon Rapid Cooling System, RCS) with a two fold substrate-rotation fixture using $Ti_{0.50}Al_{0.50}$ and $Ti_{0.40}Al_{0.55}Cr_{0.05}$ targets (99.99% purity), respectively. The working gas pressure of N_2 (99.99% purity) atmosphere was ~2 Pa, 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 an Ar pressure of 0.3 Pa, and −150 V DC substrate bias for 20 min. Different substrates were used for the individual investigations: powder metallurgically prepared cemented carbide (WC–6 wt.% Co) for hardness measurements of as-deposited and annealed coatings; low-alloy steel for differential scanning calorimetry (DSC), thermo gravimetric analyzer (TGA) and X-ray diffraction (XRD) measurements of as-deposited and annealed coatings; and polycrystalline Al_2O_3 plates for oxidation resistance measurements, and CNMG120408 style cemented carbide (WC–6 wt.% Co) inserts for cutting tests. Before being loaded into the deposition chamber, the substrates were ultra-sonically cleaned in acetone and ethylene. The coating thickness of CNMG120408 style cemented carbide was kept constant at around 3 μm according to the previous deposition rates.

2.2. Isothermal annealing and oxidation

Thermal annealing was performed in DSC (Netzsch-STA 409C, Germany) from room temperature (RT) to $T_a = 800$, 900, 1000, 1100, 1200, 1300, 1450 and 1550 °C with a heating rate of 10 K/min and a cooling rate of 50 K/min in flowing Ar (99.9% purity, 20 sccm flow rate). Prior to these measurements, the coatings were removed from their low-alloy steel substrates by chemical etching in 10 mol% nitric acid, in order to avoid substrate interference. Additionally, isothermal annealing of the coated CNMG120408 style cemented carbide (WC–6 wt.% Co) has been performed in a vacuum furnace (COD533R) at 0.1 mPa for hardness investigations of annealed coatings. Heated from RT with a heating rate of 5 K/min, each sample was annealed at 700, 900, 1000 and 1100 °C for 2 h and then cooled down with a rate of ~1 K/min [4]. For isothermal oxidation experiments, DSC with TGA was performed in a Netzsch-STA 409C from RT to 1500 °C with a heating rate of 10 K/min and a cooling rate of 50 K/min in flowing synthetic air (79% N_2, 21% O_2 and 20 sccm flow rate). Coated polycrystalline Al_2O_3 substrates were isothermally oxidized at 800 and 850 °C for 10 h in the DSC equipment 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, and 20 sccm flow rate), respectively, and then investigated by the fracture cross-sectional scanning electron microscopy (SEM) (LEO1525, Germany).

2.3. Characterization

The elemental compositions of the coatings were determined using electron probe microanalysis (EPMA) (JXA-8800R, JEOL). The morphologies and thickness of the coatings were studied using SEM. Structural

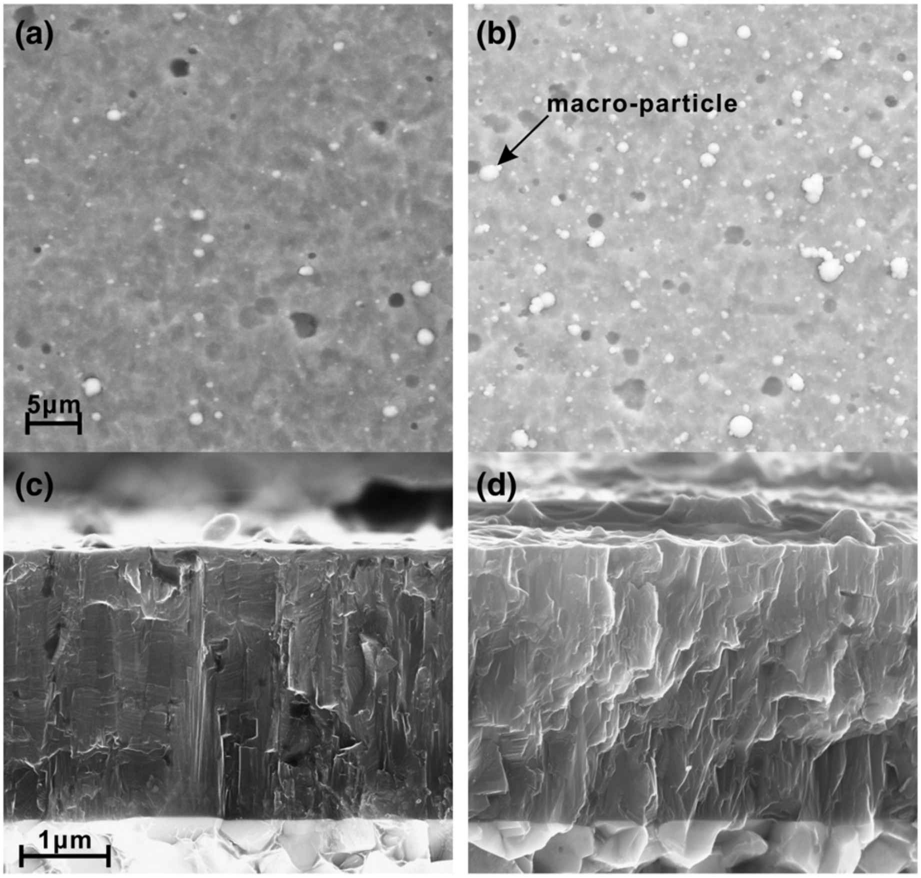

Fig. 1. SEM surface morphologies and fracture cross-section of Ti–Al–N (a and c) and Ti–Al–Cr–N (b and d) coatings at as-deposited state.