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Improved properties of Ti-Al-N coating by multilayer structure

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ABSTRACT

Multinary Ti-Al-N coatings are used for various applications where hard, wear and oxidation resistant materials are needed. Here, we prepare TiAlN/TiN nano-multilayer coatings with modulation period of ~20 nm in order to further improve the properties of Ti-Al-N coating. Annealing of both coatings up to 700 °C results in an increase in hardness due to the precipitation of cubic Al-rich domains by spinodal decomposition. Multilayer structure results in an increase in adhesion with substrates from ~72 N for Ti-Al-N single layer coating to 98 N for TiAlN/TiN nano-multilayer coating. Additionally, the interfaces of TiAlN/TiN nano-multilayer coating retard the outward diffusion of metal atoms (Al and Ti) and inward diffusion of O while exposing coatings in air atmosphere with elevated temperature, and thus improve its oxidation resistance. An improved machining performance regardless of continuous cutting and milling is obtained by TiAlN/TiN nano-multilayer coated inserts, which can be attributed to the combined effects of higher adhesion with substrates and better oxidation resistance.

1. Introduction

Metastable Ti-Al-N with cubic (c) NaCl structure, where Al substitutes for Ti in the TiN based structure, has become one of the most important wear resistant coatings for industrial applications due to their outstanding performance with respect to high hardness, high temperature oxidation resistance and age-hardening ability [1–4]. Among them, thermal stability and oxidation resistance are the key factors for their widely industrial applications. During annealing above 600 °C, the decomposition of metastable, aluminum-rich solid solution cubic (c) TiAlN into the c-TiN and c-AlN, and concomitant increase of the hardness occurs [5,6]. However, following phase transition of the c-AlN to stable h-AlN leads to a drop in hardness for a further elevated annealing temperature to above 900 °C [5,6]. Age-hardening of Ti-Al-N coating plays an essential role in industrial application in combination with the oxidation resistance. When exposed to air at elevated temperatures, Ti-Al-N coating forms a bilayer Al_2O_3/TiO_2 oxide scale [7–9]. The oxidation resistance of Ti-Al-N coating is based on the formation of dense Al_2O_3 scales, which retard the corresponding diffusion processes (simultaneous out-diffusion of Al and the inward diffusion of O) [7]. However, the increase of the TiO_2 sub-layer thickness during the oxidation process is accompanied by the development of compressive stress due to large differences of the molar volume between TiO_2 and TiN. These stresses might lead to cracking of the protective Al_2O_3 outer-layer and consequently accelerate the degradation of the oxidation behavior [7–9].

Improvement of the properties of Ti-Al-N coating can be obtained by an optimized Al content, microstructure (e.g., changing from single layer to multilayer and superlattice), and crystal orientation. Among them, multilayer coatings and superlattices are the most widely performed which provide a better alternative as these structures allow combining different materials selected to tailor the properties of the coating towards the application [10–14]. Additionally, an increased hardness compared to the corresponding monoliths is obtained due to the difference in elastic properties between the sublayers which hinders dislocation motion [10].

In this work, we deposited TiAlN/TiN nano-multilayer coating by magnetron sputtering in order to improve the properties of Ti-Al-N single layer coating. Consequently, we researched the microstructure, oxidation resistance, thermal stability and mechanical properties of Ti-Al-N single layer and TiAlN/TiN nano-multilayer coatings using a combination of electron probe microanalysis (EPMA), X-ray diffraction (XRD), scanning electron microscope (SEM), nano-indentation and cutting tests.

2. Experimental details

2.1. Coating deposition

Ti-Al-N single layer and TiN/TiAlN nano-multilayer coatings with a thickness of ~3 μm were deposited by magnetron sputtering with 4 cathodes. TiN/TiAlN nano-multilayer coating is achieved by sputtering of three TiAl and Ti targets, where the layered structure is realized simply by sequential exposure of the coated surfaces to the vapor fluxes

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emitted from the cathodes; the power for Ti target is switched off during deposition of single layer Ti-Al-N coating. Different substrates were used for the individual investigations: powder metallurgically prepared CNMG120408 style cemented carbide (WC-6 wt.% Co) and SEET12T3 style cemented carbide (WC-10 wt.% Co) for hardness measurements and cutting performance of as deposited coatings; low alloyed steel for DSC and X-ray diffraction measurements of as deposited and annealed coatings, and polycrystalline Al_2O_3 plates ($10 \times 10 \times 1$ mm^3) for oxidation resistance measurements. Before loading the deposition chamber, the substrates were ultra-sonically cleaned in acetone and ethylene.

2.2. Isothermal annealing and oxidation

Isothermal annealing of the coated cemented carbide substrates has been performed in vacuum furnace (COD533R) at 0.1 mPa. Heated from room temperature with a heating rate of (RT) 5 K/min, coated cemented carbide substrates were annealed at 700, 800, 900, and 1100 °C for 2 h. And then the annealing samples cooled down inside the furnace with the heater switched off. For isothermal oxidation experiments, coated polycrystalline Al_2O_3 substrates were isothermally oxidized at 800 °C for 24 h in a conventional tube furnace, respectively, and then the thickness of oxidized layer was observed by SEM.

2.3. Characterization

The elemental composition of the coatings was determined using EPMA (JXA-8800R, JEOL). The morphology of the coatings was studied using SEM (LEO1525, Germany). The polished coated substrate after chemical etching in mixed acid with 60 mol% nitric and 40 mol% hydrofluoric acid was observed in order to observe the multilayer structure of TiAlN/TiN coating. Phase identification and structural investigations of both coatings (after removal from their low alloy steel substrates) in their as deposited state and after thermal treatment with the DSC equipment in vacuum from room temperature (RT) to target temperature with a heating rate of 20 K/min in flowing Ar (99.9% purity, 40 sccm flow rate) were conducted by XRD with CuKα radiation using a Brucker D8 diffractometer in Bragg/Brentano mode at 40 mA and 40 kV. Prior to these measurements, both coatings were removed from their low alloyed steel substrates by chemical etching in 10 mol% nitric acid, in order to avoid substrate interference. The hardness of the coatings was obtained by nanoindentation with a Fischerscope H100VP after the Oliver and Pharr method [15]. According to the experimental results based on the large-load (30 mN) penetration test, a smaller penetration load of 8 mN was chosen to measure the mechanical properties of the coatings to keep the indentation depth below 10% of the film thickness.

2.4. Cutting tests

Continuous dry turning of stainless steel (1Cr18Ni9Ti) with CNMG120408-EM style cemented carbide inserts (WC-6 wt.% Co) was conducted with a cutting speed (v_c) of 160 and 200 m/min, a depth of cut (a_p) of 1.0 mm and a feed rate (f) of 0.2 millimeter per revolution (mm/r). Dry face milling of steel (42CrMo) with SEET12T3-DM style inserts (WC-10 wt.% Co) was performed with $v_c = 320$ m/s, $a_p = 2.0$ mm and $f = 0.15$ mm/r. The criterion for the tool life-time is when the flank wear lands exceed 0.3 mm.

3. Results and discussion

Elemental analysis by EPMA reveals that Ti-Al-N single layer coating are stoichiometric with N/metal ratio of 1 ± 0.02 and composition of $Ti_{0.50}Al_{0.50}N$. Fig. 1 shows the SEM fracture cross-section of Ti-Al-N single layer coating, which exhibits a pronounced columnar structure. Fig. 2 presents the SEM cross-section morphologies of TiN/TiAlN nano-multilayer coating (after etching in acid (a) and fracture (b)). Fig. 2a exhibits an evident lamellar structure composed of alternating TiAlN and TiN layers with modulation period of ~20 nm. Furthermore, a step cross section of fractional morphology is presented

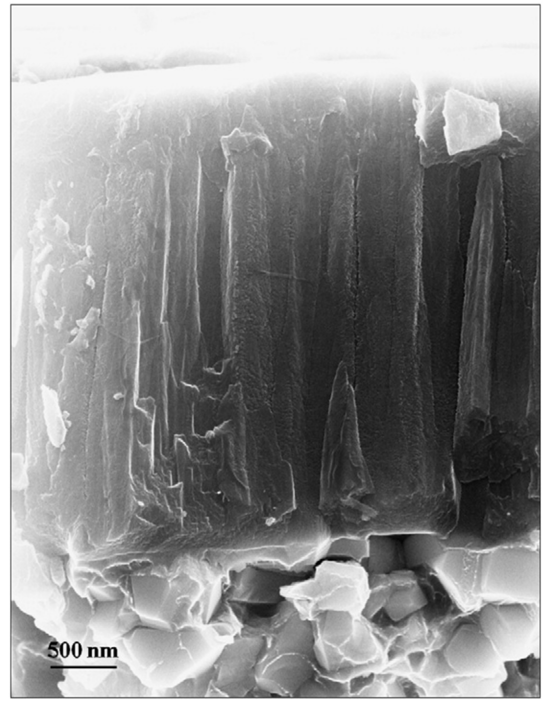

Fig. 1. SEM fracture cross-sectional image of Ti-Al-N single layer.

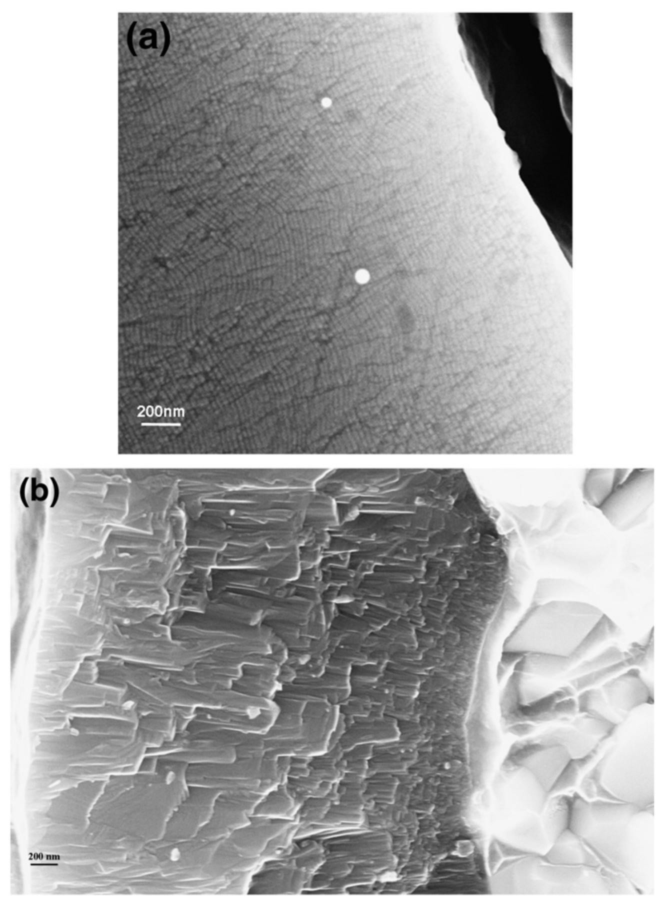

Fig. 2. SEM cross-section images of TiN/TiAlN nano-multilayer coating (after etching in acid (a) and fracture (b)).