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# High temperature properties of the Cr – Nb – Al – N coatings with increasing Al contents

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ABSTRACT

Cr – Nb – Al – N coatings with Al content from 0 to 12 at.% were deposited by d.c. reactive magnetron sputtering. The coatings were annealed in protective atmosphere at 800 and 900 °C for 1 h and exposed to air at 800, 900 and 1200 °C for different times. The chemical composition, structure, microstructure, hardness and adhesive/cohesive strength of the coatings, in as-deposited and annealed conditions, were investigated and the oxidation resistance was evaluated. As expected, the Al content increased gradually in the coating with increasing power density in the Al target; nitrogen was kept approximately constant. All coatings exhibited columnar cross section morphology and fcc NaCl-type B1 phase structure. After thermal annealing, an increase in the grain size and a decrease in the lattice parameter were observed, which led to either a decrease in the hardness or lower adhesion/cohesion strength than the as-deposited coatings. The onset oxidation temperature was approx. 900 °C for all coatings. High Al content coatings showed minimum oxidation when exposed to 800 °C for 2 h and to 900 °C for 0.5 h in air. The Al-free and low Al coatings exhibited lower oxidation resistance; $Cr_2O_3$ and $CrNbO_4$ coexisting together although signs of the cubic nitride phase were still detected. The increase of Al was beneficial to the improvement of the thermal stability and oxidation resistance of the Cr – Nb – Al – N coatings.

## 1. Introduction

Recently, machining technology has been developed towards high precision, high speed, high efficiency and low emission, which has required cutting tools with higher hardness, lower wear-resistance, and higher thermal stability and oxidation resistance [1]. Due to suitable hardness, low friction coefficient and strong adhesion to metal substrates, Cr – N coatings have been widely used on cutting tools for several decades [2]. However, those increasing requirements are making binary Cr-based nitride coatings inadequate in many applications [2–4].

Alloying is an effective method to improve the properties of Cr-based coating. By using alloy elements, especially those with large atomic radius, e.g. Zr, Nb, Ta and W [5–8], ternary nitride coatings exhibit higher hardness and improved high temperature properties than the binary system. Furthermore, it was reported that NbN with high melting point, good mechanical properties and excellent corrosion resistance have also been used in many fields as protecting coatings [9–12]. Therefore, Cr – N coatings with Nb alloying were considered appropriate for the protection of cutting tools. However, Hsieh et al. [13] found that Cr-Nb-N coatings started to oxidize just over 500 °C independently of the Nb/Cr ratio and their wear rate was rather high even at the room temperature.

The addition of Al has often been reported to improve the mechanical properties and thermal stability of Cr-based and Ti-based nitride coatings [2,14]. Due to age hardening effect, the coating hardness can be enhanced ~30% after thermal annealing [15,16], and the onset oxidation temperature was increased about 100–200 °C with the introduction of Al into the coatings [17,18]. Moreover, Barshilia et al. [19] found that the addition of Al could also improve the thermal stability and oxidation resistance of Nb-based nitride coatings. Although Franz et al. [20] showed that the onset oxidation temperature markedly increased with the Al content in the Nb-based nitride coatings, they suggested that the mechanical properties would be weakened as high Al content was added. Thus, the influence of Al on the high temperature properties of these nitride coatings is still not understood. Till now research of the effects of Al on the properties of the Cr – Nb-based quaternary nitride coatings has not yet been reported. The thermal stability and oxidation resistance of such quaternary coatings are still unclear.

In this paper, Cr – Nb – Al – N coatings with different Al contents were deposited by d.c. reactive magnetron sputtering technology.

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**Table 1**
Chemical composition, thickness, $L_{c3}$ and designated name of the coatings.

| Al target power density ($W/cm^2$) | Chemical composition (at.%)* | | | | Thickness(μm) | $L_{c3}$ (N) | | Designated name |
|---|---|---|---|---|---|---|---|---|
| | Nb | Cr | Al | N | | As deposited | 900 °C annealing | |
| 0.0 | 10.3 | 38.0 | 0.0 | 51.7 | 1.70 | N/A | 29 | CrNb10N |
| 0.75 | 9.2 | 34.8 | 4.0 | 52.0 | 1.80 | N/A | 45 | CrNb9Al4N |
| 1.5 | 8.5 | 33.1 | 7.4 | 51.0 | 1.85 | N/A | 48 | CrNb9Al7N |
| 2.25 | 7.9 | 29.7 | 9.6 | 52.8 | 1.95 | N/A | 49 | CrNb8Al10N |
| 3.0 | 7.6 | 28.2 | 12.0 | 52.2 | 2.05 | N/A | 36 | CrNb8Al12N |

* All values ±0.2%.

The influence of Al on the structure and mechanical properties of the coatings before and after thermal annealing was investigated, and the oxidation resistance of the coatings was studied.

## 2. Experimental procedure

Cr–Nb–Al–)N coatings were deposited by d.c. reactive magnetron sputtering in unbalanced mode. The configuration of the deposition chamber can be found in a previous paper [21]. Polished M2 (AISI) steel coupons (for mechanical properties measurement), Fecralloy (for oxidation test; chemical composition $Fe_{72.8}Cr_{22}Al_5Y_{0.1}Zr_{0.1}$), polycrystalline alumina slices (for TGA analysis) and (111) silicon wafers (for chemical composition and thickness measurements, and microstructural observation) were used as substrate materials. Before loading into the chamber, the substrates were ultrasonically cleaned in acetone and alcohol each for 15 min, respectively. After the chamber was evacuated to less than $1.5 \times 10^{-4}$ Pa, an $Ar+$ ion sputter-etching was carried out for 20 min with a negative substrate bias of 400 V to remove the surface contamination. In order to enhance the coating's adhesion, a ~200 nm thick Cr interlayer was first deposited in Ar atmosphere. The Cr–Nb– (Al–)N coatings were deposited at −70 V bias under a mixed gas flow of Ar 35 sccm and $N_2$ 48 sccm. During deposition, the power densities for pure Nb and pure Cr targets were fixed as 1.5 $W/cm^2$ and 2.25 $W/cm^2$ respectively, and the Al target's power density was set as 0, 0.75, 1.5, 2.25 and 3.0 $W/cm^2$, respectively. The deposition time was 150 min.

The samples were annealed at 800 and 900 °C for 1 h in Ar + 5% $H_2$ atmosphere. Thermogravimetric analyses (TGA) were performed

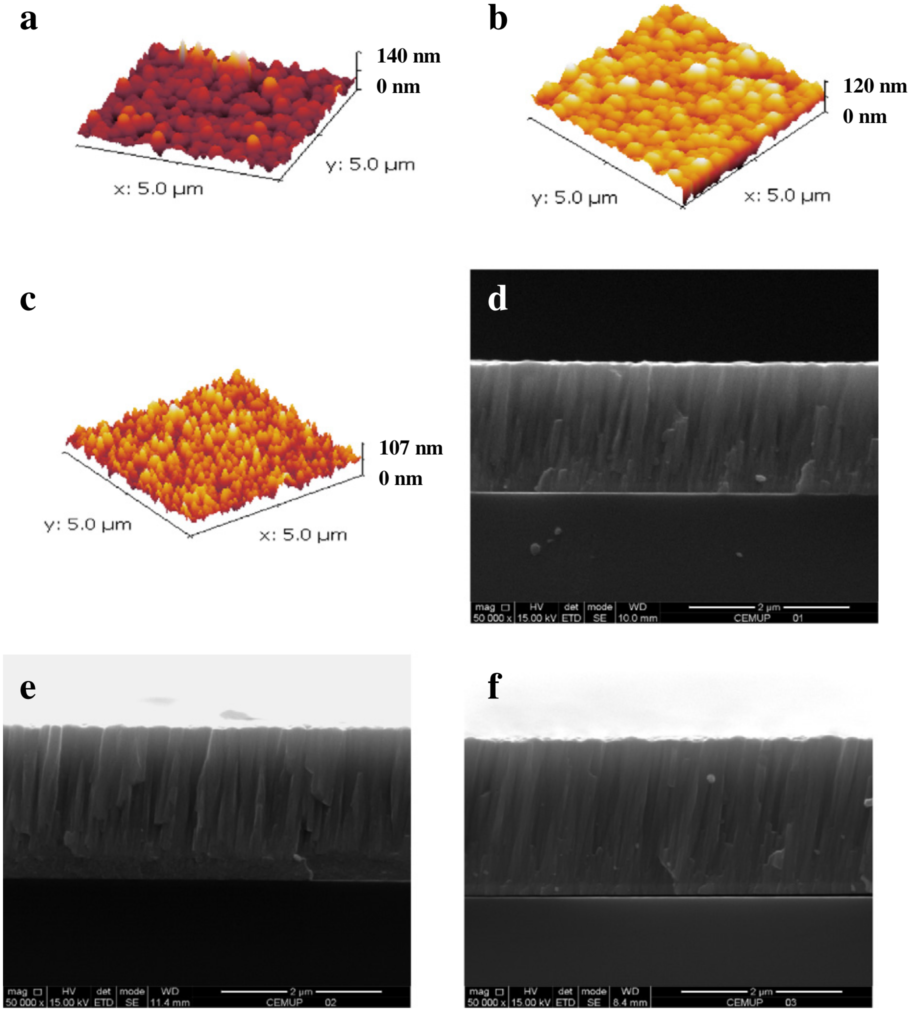

**Fig. 1.** AFM (a–b) and fracture cross-sectional SEM (d–f) morphologies of as-deposited CrNb10N (a, d), CrNb9Al4N (b, e) and CrNb8Al10N (c, f) coatings.