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Effects of Ti alloying of AlCrN coatings on thermal stability and oxidation resistance

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ABSTRACT

Quaternary cubic $(Ti_xCr_{1-x}Al_{\sim 0.60})_1 N_1$ coatings with $0 < x < 0.33$ have been grown using reactive cathodic arc evaporation. When adding Ti the hardness was retained after annealing up to 1100 °C which is a dramatic improvement compared to CrAlN coatings. The coatings showed an age hardening process caused by spinodal decomposition into coherent TiCr- and Al-rich cubic TiCrAlN domains and the formation of hexagonal AlN precipitates and cubic TiCrN domains in the vicinity of the grain boundaries. The improved hardness was attributed to the stabilization of the cubic structure suppressing the formation and growth of hexagonal AlN. Furthermore, the presence of Ti atoms generated incoherent nanometer-sized crystallites within the hexagonal AlN precipitates disrupting the hexagonal lattice during the coarsening process.
The addition of Ti promoted the formation of a TiO_2 layer over Al_2O_3 resulting in a lower oxidation resistance. However, by tuning the composition it is possible to design coatings to have both good oxidation resistance and good high temperature mechanical stability.

1. Introduction

In metal forming and plastic molding operations CrN coatings are widely used to protect the working tools from corrosion and oxidation [1]. However, the abrasive wear resistance and the hardness of CrN coatings are low in comparison to other transition metal nitrides and therefore not suited for protection of tools used for metal machining. One way to improve the mechanical properties is to add Al forming a ternary system [2]. It is possible to deposit metastable cubic (*c*)-CrAlN coatings with up to 60–70 at. % of Al-content [3,4]. If the amount of Al is higher hexagonal (*h*)-AlN will form during deposition and the hardness decreases [4]. Since *h*-AlN is a more stable phase there is always a driving force for transformation of the cubic phase into the hexagonal phase. Thus, at elevated temperatures where there is sufficient energy for diffusion the mechanical properties will deteriorate fast. The cubic phase and a high hardness can be retained up to 2 hours of annealing at 900 °C [4]. Results from $Cr_{0.32}Al_{0.68}$ N coatings [5] show a weak age hardening process [6,7] due to *h*-AlN precipitation at ~700 °C but at higher temperatures the mechanical properties deteriorate.

The performance of coatings for cutting tools depends highly on the hardness and the oxidation resistance at elevated temperatures. Because of temperatures reaching above 1000 °C at the edge of a cutting tool during metal machining [8], CrAlN coatings are usually inadequate for high-temperature and high-abrasive applications. On the contrary, TiAlN coatings are widely used for metal machining because of its superior mechanical properties at elevated temperatures. However, in terms of corrosion and oxidation resistance CrAlN coatings are superior [9]. In short, there is an opening for functional coatings having both high hardness and good oxidation resistance at elevated temperatures. It has been pointed out, that improving thermal stability and oxidation resistance by fine-tuning the composition is a necessity for further advances in hard coating development [10]. Here we aim to do so through a multicomponent alloying concept. In this paper the influence of Ti additions to *c*-$Cr_{0.4}Al_{0.6}$ N is investigated and coupled to the phase and microstructure evolution, the high temperature mechanical properties and the oxidation resistance. The results are obtained with scanning transmission electron microscopy (STEM and TEM), nanoindentation, x-ray diffraction (XRD), differential scanning calorimetry (DSC) and thermogravimetric analysis.

2. Experimental details

The coatings were deposited by an industrial Sulzer/Metaplas MZR-323 reactive cathodic arc evaporation system using a combination of different compound cathodes in a 4.5 Pa N_2 atmosphere onto polished WC–Co substrates and Fe foils at ~500 °C with a substrate bias of −40 V. The WC–Co substrates and the Fe foils were mounted on a rotating sample fixture inside the deposition system. The aim was to have an Al content close to 60 at. % therefore cathodes containing $Ti_{29}Cr_5Al_{66}$, $Cr_{33}Al_{67}$, $Ti_{33}Cr_{33}Al_{34}$ and $Ti_{33}Al_{67}$ were mounted at different heights inside the chamber, yielding different compositions depending on where the substrate is placed in front of the cathodes. After evacuating the chamber to a base pressure of 1 mPa the substrates were sputter cleaned through Ar bombardment. Deposition for about

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2 hours yielded coatings with a thickness of ~3 μm. See Ref. [11] for more details.

To establish the composition of the coatings a combination of elastic recoil detection analysis (ERDA) and energy-dispersive X-ray spectroscopy EDX was used. ERDA measurements utilized an $^{127}I^{9+}$ ion beam with incidence angle of 22.5º and accelerated to 40 MeV. A time-of-flight and energy detector (TOF-E ERDA) was used for detection of the ejected species. The concentration ratios between nitrogen, aluminum and the sum of titanium and chromium, N:Al:Ti + Cr, was obtained with ERDA. To establish the Ti:Cr ratio EDX was used instead of ERDA due to the similar mass of titanium and chromium.

The thermal response from the coatings was measured using a Netzsch STA 410 differential scanning calorimeter (DSC). DSC samples were prepared by removal of coated Fe foils through mechanical grinding and subsequent dissolution in concentrated HCl (37%). The remaining coating was filtered cleaned with acetone and crushed to a fine powder and approximately 50 mg powder was put in an Al_2O_3 crucible used for the measurement. The measurement was conducted by heating the powder up to 1400 °C at a rate of 20 °C/min under a He flow of 50 ml/min. At 1400 °C the sample was cooled down to room temperature and the heating was repeated. The second heating cycle was used for a base line correction of the thermal response in the first cycle.

The oxidation tests were conducted by heating the powder up to 1100 °C at a rate of 5 °C/min and 20 °C/min in air at atmospheric pressure while measuring the sample mass.

Post deposition anneals were performed of the coated WC–Co substrates at T_{max} = 700, 800, 900, 950, 1000, 1050 and 1100 °C in an argon atmosphere at atmospheric pressure using a Sintervac furnace from GCA Vacuum Industries. The samples were annealed with a heating rate of 7 °C/min up to 40 °C below the final annealing temperature, T_{max}, and then decreased to a rate of 5 °C/min. T_{max} was kept constant for 2 hours and thereafter the samples were cooled down to 500 °C during 1.5 hours and to 100 °C in 4 hours. This annealing procedure is the basis of the hardness measurements in Fig. 1. The WC–Co substrates did not withstand annealing temperatures above 1100 °C without reacting with the coating. Additionally, there are many overlaps in the XRD reflections from substrate and coating making interpretation more difficult. Therefore powder samples obtained from coated foils were heated in vacuum (~10^{-2} Pa) at steps up to T_{max} = 700, 800, 900, 950, 1000, 1050 and 1100, 1200, 1300, 1350 and 1400 °C with a rate of 20 °C/min. In this annealing series the same powder sample was repeatedly heated, cooled to room temperature, measured with XRD and then heated again to the next higher temperature (Fig. 3).

X-Ray θ-2θ diffractograms with a 2θ range from 20º to 80º were obtained with a Panalytical X'Pert PRO MRD X-ray diffractometer using Cu K_α radiation.

Scanning transmission electron microscopy, transmission electron microscopy, and X-ray energy dispersive spectroscopy were performed with a FEI Tecnai G^2 TF 20 UT microscope operating at 200 kV. For the STEM analysis a high angular annular dark field detector using a camera length of 170 mm was used. Cross sectional TEM samples were prepared by mechanical grinding and polishing followed by Ar-ion beam milling.

The hardness of the coatings was obtained using an UMIS nanoindenter equipped with a Berkovich diamond tip. Fused silica was used as a reference material to determine the tip shape. Indentation was performed on mechanically polished tapered cross sections of the coatings. The average hardness ± 1 standard deviation was calculated [12] from approximately 25 indents on each sample using a maximum load of 45 mN with an indentation depth of around 200 nm.

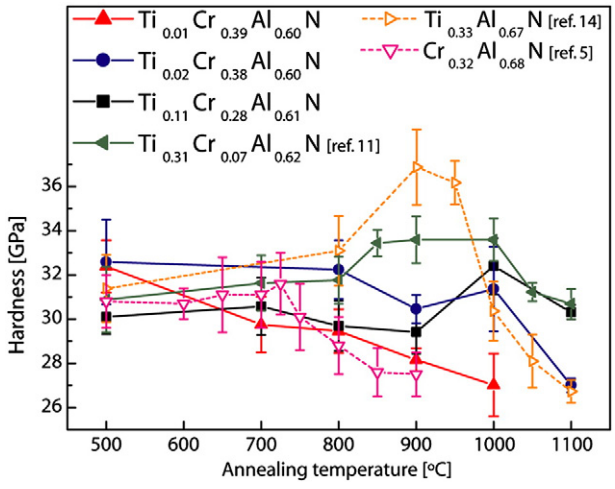

Fig. 1. Hardness results versus annealing temperature obtained with nanoindentation from $Ti_{0.01}Cr_{0.39}Al_{0.60}$ N, $Ti_{0.02}Cr_{0.38}Al_{0.60}$ N, $Ti_{0.11}Cr_{0.28}Al_{0.61}$ N, $Ti_{0.31}Cr_{0.07}Al_{0.62}$ N, $Ti_{0.33}Al_{0.67}$ N and $Cr_{0.32}Al_{0.68}$ N.

3. Results

The results presented here originates from $(Ti_xCr_yAl_z)_1$ N_1 coatings covering a metal composition range of 1 < x < 33 at. % and z = ~60 at. % where all samples contain 50 ± 1 at. % nitrogen in their as-deposited state. Different compositions are presented in order to present the influence of Ti alloying of CrAlN coatings.

3.1. Mechanical properties

Fig. 1 shows the hardness versus annealing temperature obtained with nanoindentation. For $Ti_{0.01}Cr_{0.39}Al_{0.60}$ N coating the hardness decreases with increasing annealing temperature. $Ti_{0.02}Cr_{0.38}Al_{0.60}$ N has a constant hardness up to 800 °C and at 900 °C the hardness decreases by ~1 GPa. The hardness is retained at 1000 °C and decreases significantly at 1100 °C. For $Ti_{0.11}Cr_{0.28}Al_{0.61}$ N the hardness in the as-deposited state is lower compared to the two compositions mentioned above and stays roughly constant up to 900 °C of annealing. In the 1000 °C annealed state the hardness increases ~10 % (~3 GPa) compared to the as-deposited state. At 1100 °C the hardness decreases to the same level as its as-deposited state, i.e. this composition retains its hardness to considerably higher temperatures compared to the 1 and 2 at. % Ti-containing coatings. Our previous studies show that with 31 at. % Ti-content the age hardening initiates at a lower temperature of 850 °C and is retained over a wider temperature range up to 1000 °C [11,13]. Surprisingly, both the 31 and 11 at. % Ti-containing coatings show similar high hardness at 1100 °C.

As references the hardness values of $Ti_{0.33}Al_{0.67}$ N [14] and $Cr_{0.32}Al_{0.68}$ N [5] coatings grown under similar conditions are also shown in Fig. 1. The age hardening is more pronounced for $Ti_{0.33}Al_{0.67}$ N compared to the other coatings, but the hardness between 1000 and 1100 °C is significantly lower compared to the 31 and 11 at. % Ti-containing coatings.

3.2. Phase evolution and thermal stability

Fig. 2 shows the *in-situ* DSC measurements of the thermal response of $Ti_{0.11}Cr_{0.28}Al_{0.61}$ N, $Ti_{0.02}Cr_{0.38}Al_{0.60}$ N and $Ti_{0.01}Cr_{0.39}Al_{0.60}$ N during heating up to 1400 °C with a heating rate of 20 °C/min. The right axis shows the relative mass change of the coatings during the heating process. Observed peaks in the thermal response have been numbered and marked on the temperature axis corresponding to the maximum slope of the thermal response. The exothermic peak located at T_1 = ~600 °C is observed for $Ti_{0.01}Cr_{0.39}Al_{0.60}$ N and $Ti_{0.02}Cr_{0.38}Al_{0.60}$ N. A peak at T_2 = ~800 °C is only observed for $Ti_{0.01}Cr_{0.39}Al_{0.60}$ N. There is an