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Structure and Thermal Stability of Arc Evaporated $(\text{Ti}_{0.33}\text{Al}_{0.67})_{1-x}\text{Si}_x\text{N}$ Thin Films

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Abstract

$(\text{Ti}_{0.33}\text{Al}_{0.67})_{1-x}\text{Si}_x\text{N}$ ($0 \leq x \leq 0.29$) thin solid films were deposited onto cemented carbide substrates by arc evaporation and analyzed using analytical electron microscopy, X-ray diffraction, nanoindentation, and density functional theory. As-deposited films with $x \leq 0.02$ consisted mainly of a metastable c-(Ti,Al)N solid solution for which Si serves as a veritable grain refiner. Additional Si promoted growth of a hexagonal wurtzite (Al,Ti,Si)N solid solution, which dominated at $0.02 < x < 0.17$. For $x \geq 0.17$, the films were X-ray amorphous. Despite these widely different microstructures, all as-deposited films had nanoindentation hardness in the narrow range of 22-25 GPa. Isothermal annealing of the $x=0.01$ alloy film at a temperature of 900 °C, corresponding to that in turning operation, resulted in spinodal decomposition into c-AlN and TiN and precipitation of h-AlN. For $x=0.09$ films, annealing between 600 °C and 1000 °C yielded c-TiN precipitation from the h-(Al,Ti,Si)N-phase. Furthermore, the $x=0.01$ and $x=0.09$ films

exhibited substantial age hardening at 900 °C, to 34 GPa and 29 GPa due to spinodal decomposition and c-TiN precipitation, respectively. Films with a majority of c-(Ti,Al)N phase worked best in steel turning tests, while films with $x > 0.02$ developed cracks during such operation. We propose that the cracks are due to tensile strain which is caused by a decrease in molar volume during the phase transformation from hexagonal wurtzite (Al,Ti,Si)N into cubic TiN phase, which results in degradation in machining performance.

Introduction

Wear protective coatings for metal cutting applications have advanced considerably in the last decades. In the field of physical vapor deposition, the most used coatings are based on the ternary Ti-Al-N system. The thermal and mechanical properties of arc evaporated $\text{Ti}_{0.33}\text{Al}_{0.67}\text{N}$ films on WC-Co substrates have been thoroughly studied by Hörling *et al.* [1,2] and Mayrhofer *et al.* [3]. These films undergo spinodal decomposition of the cubic alloy into nm-size coherent domains of NaCl-structure AlN and TiN at 900-1400 °C. This secondary phase transformation yields coherency strain and effectively age hardens the structure. Above 950 °C, however, subsequent h-AlN precipitation takes place, which results in a moderate reduction of the film hardness.

More recently, the Ti-Si-N system has drawn attraction because of its excellent thermal and mechanical properties. We reported a compositional stability and retained hardness of 31-42 GPa up to 1000 °C due to the formation of a (semi)-coherent SiN_x tissue phase for arc evaporated film substrate with Si contents between 2-10 at.% [4,5].

The objective of this study is to combine the attractive properties of each of the Ti-Al-N and Ti-Si-N systems described above into a Ti-Al-Si-N thin film. Such a quaternary system adds microstructural complexity, but also creates corresponding design opportunities for functional properties of a coated tool. Similarly, Al-Cr-Si-N films were studied recently [6].

Ti-Al-Si-N coatings were grown previously using arc evaporation in [7-11] and magnetron sputtering in [12]. In terms of phase composition Veprek *et al.* reported the formation of a nanocomposite nc-(Ti_{0.4}Al_{0.6})N/a-Si₃N₄ [7]. Both (Ti_{0.38}Al_{0.62})_{0.82}Si_{0.18}N and (Ti_{0.61}Al_{0.39})_{0.96}Si_{0.04}N thin films were found to exhibit better oxidation resistance than (Ti_{0.49}Al_{0.51})N due to the formation of Al₂O₃ for the Ti-Al-Si-N films compared to mainly TiO₂ for the Ti-Al-N film [12]. The effects of a wider range of Si contents on the constitution and properties of Ti-Al-Si-N thin films and the potential for age hardening in coated tools were, however, not considered to date.

In this study, we deposited (Ti_{0.33}Al_{0.67})_{1-x}Si_xN films onto WC-Co substrates with a gradient in Si contents ranging from x=0 up to x=0.29 in order to investigate the role of Si in arc-evaporated (Ti_{0.33}Al_{0.67})N. It is found that Si serves as a grain refiner compared to pure (Ti_{0.33}Al_{0.67})N, even at as low content as x≈0.002. We also show that as-deposited (Ti_{0.33}Al_{0.67})_{1-x}Si_xN films with a small Si content of x=0.002 exhibits a two-phase structure of nanometer-size h-(Al,Ti)N precipitates in the dominating NaCl-structured (Ti,Al)N phase. The structure gradually changes for increasing Si-contents via hexagonal (0.04≤x<0.17) to amorphous for (x≥0.17). Annealing experiments reveal spinodal

decomposition for $x=0.01$ films into TiN and c-AlN, and precipitation of h-AlN after 2 h annealing at 900 °C. For $x=0.09$, c-TiN separates out of the h-(Al,Ti,Si)N phase in the form of nm-grains at 900-1000 °C. We report a substantial hardening for films with majority of both cubic and hexagonal phase. Films which consist of predominantly cubic phase had the longest life time in a cutting test application. Films with hexagonal phase cracked during turning because of the molar mismatch in the secondary phase transformation of h-(Al,Ti,Si)N into c-TiN induced by the high process temperature.

Experimental Details

$(\text{Ti}_{0.33}\text{Al}_{0.67})_{1-x}\text{Si}_x\text{N}$ films were deposited by arc evaporation in a commercial Metaplas MZR323 system with a base pressure of 5×10^{-6} mbar. Three 63 mm diameter cathodes of composition $\text{Ti}_{0.33}\text{Al}_{0.67}$, $\text{Ti}_{0.3}\text{Al}_{0.6}\text{Si}_{0.1}$, and $\text{Ti}_{0.23}\text{Al}_{0.47}\text{Si}_{0.30}$, respectively, were used in the same batch in order to produce films with close to $(\text{Ti}_{0.33}\text{Al}_{0.67})_{1-x}\text{Si}_x\text{N}$ composition with varying Si content depending on the substrate position in relation to the cathodes. The cathodes were produced by powder metallurgy. Cemented carbide (WC-Co with 6 wt.% Co) $12 \times 12 \times 4 \text{ mm}^3$ platelets were employed as substrates. Prior to deposition the substrates were ground and polished to a mirror-like surface with a surface roughness of $R_a \approx 0.01 \text{ }\mu\text{m}$, and cleaned in an ultrasonic alkaline degreasing agent. During deposition the substrates were held at a bias of -35 V and a temperature of $\sim 400 \text{ }^\circ\text{C}$ in an N_2 atmosphere. Some films were also deposited at $\sim 500 \text{ }^\circ\text{C}$ in order to assess the effect of substrate temperature on the film's mechanical properties.

The microstructure of the films was studied with X-ray diffraction (XRD), scanning electron microscopy (SEM), and analytical transmission electron microscopy (TEM). For the XRD, a Bruker AXS D8 Advance X-ray diffractometer with a line-focus Cu K_{α} X-ray source was used. θ - 2θ scans were conducted in the 2θ range from 30° to 70° . In order to minimize the substrate peak intensity due to overlap with film peaks, grazing incidence angle of $\omega=4^{\circ}$ was used for some measurements of the annealed films. The SEM investigation was carried out with a LEO 1550 FEG-SEM. Energy dispersive X-ray spectroscopy (EDX) was performed in the SEM using a Noran Si-detector. Industrial standards, supplied from the manufacturer of the instrument, and ZAF correction were used for the quantitative analysis. An FEI Tecnai G² TF 20 UT microscope operating at 200 kV was used for the TEM and scanning transmission electron microscopy (STEM) investigations as well as for the EDX mapping. For the STEM analysis, a high angle annular dark field detector was used and a camera length of 220 mm. The maps were recorded with a pixel size of 2 nm and a dwell time of 1 s. In order to minimize drift, the specimens were settled in the microscope for at least 12 h before analysis, and heated up by the electron beam by continuous scans across the area of interest. During the measurement, a drift correction utility from the manufacturer of the instrument was applied.

Turning tests were performed on the films with $x=0.002, 0.01, 0.02, 0.04, 0.09$, and 0.24 , deposited onto WC-Co inserts. The cutting speed was $v=240$ m/min, feed rate $f=0.03$ mm/rev, and cutting depth $a_p=2$ mm in continuous turning of steel (AISI4140) without

cooling. The inserts were taken out for inspection at 3, 6, 9, 12, and 13.5 min or until the measured flank wear was >0.2 mm.

Isothermal annealing of the films with $x=0.01$ and $x=0.09$ were performed in a vacuum system in conjunction with a Philips X'pert MPD X-ray diffractometer at $\sim 3 \times 10^{-7}$ mbar base pressure. Continuous recording from 30 - $50^\circ 2\theta$ with a step size of $0.05^\circ/\text{step}$ and a dwell time of 5 s/step were used. Prior to each θ - 2θ scan, optimization of the peak intensity of the 002 substrate peak using 2θ and ω scans was done. The samples were placed and resistively heated in vacuum on a Ta filament providing a chemically inert atmosphere. Two annealing procedures were done; the first was conducted at 600°C , 700°C , and 800°C , with two θ - 2θ scans being recorded at each temperature, giving an annealing time of ~ 90 min per temperature. The second procedure was performed at 900°C and 1000°C , respectively. Here, three θ - 2θ scans were recorded during the total annealing time of ~ 130 min for each temperature.

The hardness measurements were carried out on polished taper sections using an UMIS nanoindenter equipped with a Berkovich diamond tip. The indentation load P_{max} was tested between 7 mN and 29 mN in order to find optimal P_{max} . The indentation sequence was as follows: 1) load segment to P_{max} , 2) hold for 10 s, 3) unload to 10% of P_{max} , 4) unload. Prior to the test the samples were mounted in the environmental enclosure for a couple of hours until thermal equilibrium was established. The actual indent procedure lasted ~ 45 s, which is short enough to ensure that no thermal drift affected the measurement. The average hardness and its standard deviation were determined from at

least 20 indents in each sample following the method described by Oliver and Pharr [13]. The average hardness was measured on the reference fused silica sample, SiO_2 , giving reasonable values of 9.5 GPa.

Computational Details

First-principles density functional theory (DFT) calculations were performed for hexagonal (wurtzite) random alloys of $(\text{Al}_{1-y}\text{Ti}_y)\text{N}$ with $y=0.000, 0.125, 0.250$, and 0.375 as well as for $(\text{Al}_{1-z}\text{Si}_z)\text{N}$ with $z=0.125$. The projector augmented wave method [14] as implemented in the Vienna ab-initio simulation package (VASP) [15,16] was used in conjunction with the generalized gradient approximation (GGA) [17] for exchange-correlation energy. Supercells of 128 atoms (64 metal and 64 N atoms per cell) were created following the strategy laid out in Ref. [18]. In these supercells, the environments of the metal atoms mimic the situation in a true random alloy, at least for the first seven metallic neighbor shells. For each concentration, the lattice parameters that minimize the total energy were found. All internal atomic positions were allowed to relax. A test of the effect of magnetization of Ti atoms were performed in the case of $\text{h}-(\text{Al}_{0.875}\text{Ti}_{0.125})\text{N}$. Although small moments (maximum of $0.59 \mu_B$) were found on some of the Ti atoms, the magnetization energy was very small, 16 meV per Ti atom or 2 meV per formula unit, which is a factor of 40 times smaller compared to the reported values for the related system $\text{c}-(\text{Cr}_{0.125}\text{Al}_{0.875})\text{N}$ [19] in which magnetization was shown to be important. The effects of magnetization on the lattice parameters were negligible. Since the magnetization is believed to be even smaller, or zero, for higher Ti concentrations, the results of non-magnetic calculations are presented here.

Results and Discussion

Chemical composition of as-deposited films

The chemical composition of the as-deposited $(\text{Ti,Al})_{1-x}\text{Si}_x\text{N}$ films as analyzed by EDX is presented in Table I. The Si content in the different films varied between $0 \leq x \leq 0.29$. The N content was not quantified in this study. However, our previous combined EDX and elastic recoil detection analysis study on the Ti-Si-N system showed that increased Si content yields a higher N content in the films [5]. We chose to use the notation $(\text{Ti}_{0.33}\text{Al}_{0.67})_{1-x}\text{Si}_x\text{N}$ for the films to reflect the nominal Ti and Al fractions from the deposition although the metal composition varies slightly between films, see Table I for exact compositions.

From Table I it is apparent that there is a reduction by a few at.% of Al content in the films compared to the target composition. This can be explained by the different average ionization for Ti and Al at the target during arc evaporation [20]. Using a substrate bias (-35 V here), the Ti ions having the higher average ionization will impinge on the sample surface with a correspondingly higher energy and thus penetrate deeper into the film compared to the Al. This will cause sub-plantation of Ti and preferential resputtering of the surface-near Al. Hence, the film will suffer a reduced concentration of Al.

Microstructure of the as-deposited films

Fig. 1 shows θ -2 θ X-ray diffractograms of the as-deposited films. The $\text{Ti}_{0.33}\text{Al}_{0.67}\text{N}$ film consists of a saturated metastable NaCl-structure $(\text{Ti,Al})\text{N}$ solid solution phase. A

comparison between the $x=0$ and $x=0.002$ films in Fig. 1(b) reveals that even minute amounts of Si trigger the formation of hexagonal phase. The films with lowest Si content, $0.002 \leq x \leq 0.02$, consist of two phases; the majority phase is a cubic NaCl structure (Ti,Al)N solid solution, and the minority one is an hexagonal wurtzite (h) phase, with slightly larger a- and c-lattice parameters than h-AlN. Both phases exhibit more or less random crystallographic orientation. The fraction of hexagonal phase gradually increases in exchange of the cubic phase with increasing Si content. The transformation is complete at $x \geq 0.04$. For $x \geq 0.17$, however, also the hexagonal peaks disappear and only a very broad low-intensity hump, ranging from ~ 31.5 to $38.5^\circ 2\theta$ remains, which indicates an amorphous structure.

Table I. Chemical composition of the $(\text{TiAl})_{1-x}\text{Si}_x\text{N}$ films. Ti+Al+Si content is normalized to 1.

Sample	as-deposited			Composition
	Ti (at.%)	Al (at.%)	Si (at.%)	
1	38.9	60.9	0.2	$(\text{Ti}_{0.39}\text{Al}_{0.61})_{0.998}\text{Si}_{0.002}\text{N}$
2	37.6	61.7	0.6	$(\text{Ti}_{0.38}\text{Al}_{0.62})_{0.99}\text{Si}_{0.01}\text{N}$
3	36.7	61	2.3	$(\text{Ti}_{0.38}\text{Al}_{0.62})_{0.98}\text{Si}_{0.02}\text{N}$
4	38.8	56.9	4.3	$(\text{Ti}_{0.41}\text{Al}_{0.59})_{0.96}\text{Si}_{0.04}\text{N}$
5	35.7	57.6	6.7	$(\text{Ti}_{0.38}\text{Al}_{0.62})_{0.93}\text{Si}_{0.07}\text{N}$
6	35.5	55.2	9.3	$(\text{Ti}_{0.39}\text{Al}_{0.61})_{0.91}\text{Si}_{0.09}\text{N}$
7	34.5	54.5	11	$(\text{Ti}_{0.39}\text{Al}_{0.61})_{0.89}\text{Si}_{0.11}\text{N}$
8	32.8	50.1	17.1	$(\text{Ti}_{0.40}\text{Al}_{0.60})_{0.83}\text{Si}_{0.17}\text{N}$
9	30.8	45.3	23.9	$(\text{Ti}_{0.40}\text{Al}_{0.60})_{0.76}\text{Si}_{0.24}\text{N}$
10	28.1	43.3	28.6	$(\text{Ti}_{0.39}\text{Al}_{0.61})_{0.71}\text{Si}_{0.29}\text{N}$

The position of the 002-peak for the cubic (Ti,Al)N-phase is at $\sim 43.5^\circ 2\theta$ for $x \leq 0.02$, which corresponds to an out-of-plane lattice parameter of $\sim 4.16 \text{ \AA}$. For comparison, the

Fig. 1. X-ray diffractograms of as-deposited $(\text{Ti}_{0.33}\text{Al}_{0.67})_{1-x}\text{Si}_x\text{N}$ and reference $\text{Ti}_{0.33}\text{Al}_{0.67}\text{N}$ films on WC-Co substrates in (a) overview for all studied compositions and (b) X-ray diffractograms with higher magnification of the intensity scale for compositions $x=0$, $x=0.002$, $x=0.01$ and nominal peak positions for stoichiometric c-TiN and h-AlN are indicated in the figure by solid lines and trace of the $11\bar{2}0$ -peak is indicated by a dashed line.

lattice parameter of TiN is 4.24 Å [21]. A similar shift has been reported previously for Al substituting for Ti atoms in the TiN lattice, see e.g., [22,23].

The X-ray diffractograms in Fig. 1 show that the positions of the peaks from the h-AlN based phase are at substantially lower 2θ angles compared to the nominal ones for h-AlN. For increasing Si content, however, the peak positions change anisotropically. Specifically, the 0002 peak shifts from $\sim 34.7^\circ 2\theta$ for $x=0.01$ to $\sim 34.3^\circ 2\theta$ for $x=0.09$, while $11\bar{2}0$ shifts from $\sim 57.5^\circ 2\theta$ for $x=0.01$ to $\sim 58.2^\circ 2\theta$ for $x=0.09$. Note that angles are approximate due to the difficulty in determining exact peak positions for low-intensity and broad peaks. In [24-26], peak shifts of the h-AlN were attributed to Ti dissolved into the h-(Al_{1-y}Ti_y)N lattice up to $y=0.20$.

To correlate lattice parameters and/or phase compositions from peak shifts deduced in θ - 2θ diffractograms of a polycrystalline hexagonal wurtzite AlN-based phase is not a straight forward task. First, only the planes parallel to the surface are probed, hence any stress would yield anisotropic strain for differently oriented grains due to the difference in Young' modulus of ~ 280 GPa and ~ 330 GPa along the $\langle 10\bar{1}0 \rangle$ and $\langle 0001 \rangle$ directions, respectively [27]. A compressive stress state is expected for our arc evaporated films, which would yield an extension of the plane distances for the planes parallel to the surface, as probed with the Bragg-Brentano geometry. Second, the anisotropic strain and different termination may yield different solid solution limits for each grain orientation. In [26] Kimura *et al.* found the shift to be anisotropic for the a-

axis and c-axis for Ti substituted for Al in h-AlN. In [28,29] Si dissolved in $(\text{Al}_{1-z}\text{Si}_z)\text{N}$ up to $z=0.12$, resulted in a decrease for both the a- and c-axes.

Since it showed to be difficult to determine the effects of Ti and Si occupying Al sites in the h-AlN lattice, we performed *ab initio* calculations on the $\text{h}-(\text{Al}_{1-y}\text{Ti}_y)\text{N}$ and $\text{h}-(\text{Al}_{1-z}\text{Si}_z)\text{N}$ structures, respectively. It is important to be aware of that these calculations are performed in the absence of external forces, e.g., residual stresses. The results from the calculations are presented in Table II. While the size of the c-axis is more or less unaffected, the a-axis shifts gradually to a larger lattice parameter for a larger amount of Ti atoms substituted for Al, which also results in a volume increase. These results agree relatively well with the experimental observations of an anisotropical lattice change for substituting up to $y=0.20$ in $(\text{Al}_{1-y}\text{Ti}_y)\text{N}$ [26]. Moreover, the substitution of Si for Al results in a minute increase for both the a- and c-axes.

Table II. DFT calculated lattice parameters of hexagonal wurtzite $\text{h}-(\text{Al}_{1-y}\text{Ti}_y)\text{N}$ and $\text{h}-(\text{Al}_{1-z}\text{Si}_z)\text{N}$. The volumes are given per unit cell.

y	a (Å)	c (Å)	V (Å ³)	z	a (Å)	c (Å)	V (Å ³)
0	3.13	5.02	42.6	0	3.13	5.02	42.6
0.125	3.16	5.04	43.7	0.125	3.13	5.06	42.7
0.25	3.20	5.02	44.6	-	-	-	-
0.375	3.24	4.97	45.2	-	-	-	-

Fig. 2 shows fracture-section scanning electron micrographs from the as-deposited films. Already for the lowest Si content of $x=0.002$, the films have a fine-grained structure with substantially smaller grains compared to pure $(\text{Ti}_{0.33}\text{Al}_{0.67})\text{N}$. A similar grain-refining effect of Si was observed in Al-Cr-Si-N films [6]. For higher Si contents, the grain size

decreases further until the structure appears amorphous except for some micro particles (present in all films), which originate from the arc process at the target side. The film thickness was 4-6 μm for all films.

Fig. 2. Fractured cross-section scanning electron micrographs of as-deposited $(\text{Ti}_{0.33}\text{Al}_{0.67})_{1-x}\text{Si}_x\text{N}$ films on WC-Co substrates (a) $x=0$, (b) $x=0.002$, (c) $x=0.01$, (d) $x=0.09$, and (e) $x=0.29$.

Fig. 3 shows a cross-sectional TEM micrograph and the selected area diffraction (SAED) pattern of the as-deposited $(\text{Ti}_{0.33}\text{Al}_{0.67})_{0.99}\text{Si}_{0.01}\text{N}$ film. The grains are elongated in the growth direction with a grain width between ~50-200 nm and length between ~200-1500 nm. The SAED pattern confirms the presence of randomly oriented c-(Ti,Al)N and h-(Al,Ti)N. Elemental maps in STEM over areas of $100 \times 100 \text{ nm}^2$ with a pixel resolution of 2 nm (not shown here) did not reveal any segregation of Ti or Al. This agrees with the results from XRD that Ti and Al are dissolved in solid solution nitride phases for the as-deposited $(\text{Ti}_{0.33}\text{Al}_{0.67})_{0.99}\text{Si}_{0.01}\text{N}$ film.

For the formation of (pure) a- Si_3N_4 phase, as suggested by [7] in the nc-($\text{Ti}_{0.4}\text{Al}_{0.6}$)N/a- Si_3N_4 nanocomposites, the above analysis did not reveal any in the crystalline films. A segregated monolayer-thick crystalline SiN_z tissue phase, however, may exist as was shown to be the case for related TiSiN films [5]. Also, for the films with amorphous phase, a- Si_3N_4 is a likely possibility.

Fig. 3. Transmission electron micrograph and selected area electron diffraction pattern from an as-deposited $(\text{Ti}_{0.33}\text{Al}_{0.67})_{0.99}\text{Si}_{0.01}\text{N}$ film on WC-Co substrate.

Mechanical properties of the as-deposited films

Fig. 4 shows the hardness of the as-deposited films as measured with nanoindentation.

All films regardless of the Si content exhibit hardness on a moderate level of 22-25 GPa.

In other related ternary (pseudo-binary) systems Ti-Si-N [4], Zr-Si-N [9], and Cr-Si-N

[30] systems, the Si-concentration has a strong positive influence on the hardness, also for low to moderate concentrations (<20 at.%). However, this Si-related hardening effect was absent for the as-deposited films in the present study. Furthermore, the hardness of the films with low Si content is considerably lower than the reported hardness of 35 GPa for $(\text{Ti}_{0.33}\text{Al}_{0.67})\text{N}$ films grown at slightly higher temperature, $\sim 500^\circ\text{C}$ [1]. In order to investigate if the deposition temperature is crucial for achieving hard films, we measured the hardness of $(\text{Ti}_{0.33}\text{Al}_{0.67})_{1-x}\text{Si}_x\text{N}$ films deposited films at 500°C . The result is included in Fig. 4 and shows that the hardness is indeed higher (25-29 GPa) for $x \leq 0.07$ films. These films exhibit retained predominant cubic phase, but since the temperature increase would rather reduce the effect of defect hardening, the present phenomenon may be explained by an increased bond density at the grain boundaries. For $x \geq 0.09$ films, however, the hardness decreases to 22-25 GPa, i.e., similar to films grown at $\sim 400^\circ\text{C}$. We attribute this Si-related hardness reduction to the observed formation of hexagonal and amorphous phases, which have a lower density and strength compared to the cubic alloy phase.

Influence of Si in the films on cutting performance

Turning tests were performed on films with $x=0.002, 0.01, 0.02, 0.04, 0.09$, and 0.24 , deposited onto WC-Co inserts. Fig. 5 shows the resulting flank wear for the different coatings as a function of cutting time. The films with $x \leq 0.02$ perform well while the performance deteriorates with increasing amount of Si. The measured hardness between 22-25 GPa for all as-deposited coatings, cannot explain the differences in tool life. Instead, we note that the films with the (NaCl-structure) c-(Ti,Al)N majority phase,

$x \leq 0.02$, works better in machining than the films where h-(Al,Ti,Si)N or amorphous phases dominate the structure, i.e., for $x > 0.02$. SEM investigation after the turning test revealed that the films with Si content $x > 0.02$ formed cracks during the turning test; see Fig. 6(a). These cracks were larger and more numerous for higher Si contents and could thus be a reason for the diminishing performance of the tools as will be discussed more below.

Fig. 4. Nanoindentation hardness of as-deposited $(Ti_{0.33}Al_{0.67})_{1-x}Si_xN$ films on WC-Co substrates deposited at 400 °C and as a function of the Si content, x .

Fig. 5. Tool life versus cutting time in a turning test for six different $(\text{Ti}_{0.33}\text{Al}_{0.67})_{1-x}\text{Si}_x\text{N}$ films on WC-Co inserts.

Thermal stability of the films

In order to investigate the thermal properties of the films and help explaining the cutting results, isothermal annealing was performed on two samples, $(\text{Ti}_{0.33}\text{Al}_{0.67})_{0.99}\text{Si}_{0.01}\text{N}$ and $(\text{Ti}_{0.33}\text{Al}_{0.67})_{0.91}\text{Si}_{0.09}\text{N}$. The annealing temperature T_a was between 600 and 1000 °C.

In situ X-ray diffractograms were recorded during the annealing; these are presented in Fig. 7(a) for the $(\text{Ti}_{0.33}\text{Al}_{0.67})_{0.99}\text{Si}_{0.01}\text{N}$ sample. The scans were recorded from 30-50 °2θ in order to focus on the development of the cubic 002 peak during any phase separation.

Fig. 6. Plan-view scanning electron micrographs from a $(\text{Ti}_{0.33}\text{Al}_{0.67})_{0.91}\text{Si}_{0.09}\text{N}$ film on WC-Co substrate (a) from the rake face after 13.5 min in turning test and (b) after annealing at 900 °C for 130 min.

At 900 °C, the 002-peak broadens and shifts from 43.5° to 42.7°, which matches the 002 peak position for TiN. At 1000 °C, the width of the peak decreases. In order to detect any peak shift for the hexagonal phase and to increase the signal-to-noise ratio compared to the *in situ* measurements, room temperature *ex situ* X-ray diffraction of the samples was performed in both θ -2 θ and grazing incidence angle modes up to 70 °2 θ . Fig. 7(b) shows that those measurements can differentiate between film and substrate peaks. Specifically

Fig. 7. X-ray diffractograms of annealed $(\text{Ti}_{0.33}\text{Al}_{0.67})_{0.99}\text{Si}_{0.01}\text{N}$ films on WC-Co substrates (a) in situ measurement performed at the respective indicated temperature and (b) room temperature measurement with both θ - 2θ geometry and grazing incidence angle of 4° of the post annealed samples.

there is a peak shift for the 002 c-TiN from $\sim 43.5^\circ$ to 42.7° . The broadening of the same peak at 900°C also looks similar to what was obtained in [2,3] for Si-less films, which indicates that a phase separation takes place initially into c-AlN and TiN components by spinodal decomposition followed by h-AlN precipitation from the as-formed c-AlN domains. Note that the c-AlN 002 peak is labeled with an area instead of a line, which denotes the range of reported lattice parameters between $4.045\text{ \AA}$ [31] and $4.12\text{ \AA}$ [32]. Alling *et al.* calculated the lattice parameter of c-AlN to be $4.10\text{ \AA}$ by the exact muffin tin orbital method (EMTO), and $4.07\text{ \AA}$ using projected augment waves (PAW) [18]. It should be noted that the used generalized gradient approximation (GGA) usually renders a small overestimation of the lattice parameter. For comparison, the correspondingly calculated lattice parameter of TiN is $4.29\text{ \AA}$ with EMTO and $4.26\text{ \AA}$ with PAW [18]. Hence, the calculations suggest that the correct lattice parameter for an unstrained c-AlN is $4.045\text{ \AA}$. The larger reported lattice parameter of $4.12\text{ \AA}$, may stem from the coherency strain from the spinodal (Ti,Al)N matrix with its larger lattice parameter.

The h-AlN based phase also exhibits XRD peak shifts during annealing as seen Fig. 7(b). This shift is attributed the decomposition of the h-(Al,Ti)N phase into c-TiN and residual h-(Al,TiN).

Room-temperature X-ray diffractograms of the annealed $(\text{Ti}_{0.33}\text{Al}_{0.67})_{0.91}\text{Si}_{0.09}\text{N}$ films are presented in Fig. 8. All hexagonal peaks gradually shift toward higher 2θ -angle with annealing temperature. More specifically, the as-deposited film consists of a h-(Al,Ti,Si)N phase with 0002 peak position at 34.3° and $11\bar{2}0$ at 58.0° , which after

annealing at 1000 °C shifts to 34.8° and 59.0°, respectively. Furthermore, randomly oriented cubic TiN peaks appear in the diffractogram at 800 °C with increasing intensity for higher annealing temperatures. From the shift of the h-(Al,Ti,Si)N and the nucleation of c-TiN, we infer that there is a gradual phase transformation of h-(Al,Ti,Si)N into c-TiN and remaining h-(Al,Ti,Si)N by nucleation and growth.

Fig. 8. X-ray diffractograms measured at room temperature of annealed $(\text{Ti}_{0.33}\text{Al}_{0.67})_{0.91}\text{Si}_{0.09}\text{N}$ films on WC-Co substrates.

The annealed films were further investigated in SEM. Interestingly, Fig. 6(b) reveals that the film with Si content $x=0.09$ develops cracks after annealing at 900 and 1000 °C, respectively, similar to those formed in the turning test, c.f., Fig. 6(a). We propose that

the cracks stem from tensile strain caused by the decrease in molar volume induced by the decomposition of h-(Al,Ti,Si)N into c-TiN and remaining h-(Al,Ti,Si)N that form in the film during annealing/turning and not from the wear itself. As an illustration, our calculations yield a volume decrease of ~3.0% when a h-(Al_{0.875}Ti_{0.125})N phase decomposes into c-TiN and pure h-AlN and a decrease of ~9.2% when a h-(Al_{0.625}Ti_{0.375})N phase decomposes into c-TiN and h-AlN. Furthermore, a compositional EDX analysis shows that the annealed films exhibit the same composition with respect to Ti, Al, and Si as the as-deposited films.

Fig. 9 shows a cross-sectional transmission electron micrograph with corresponding SAED pattern from the (Ti_{0.33}Al_{0.67})_{0.99}Si_{0.01}N film after annealing at 900 °C. The microstructure is characterized by nanometer-size grains slightly elongated in the growth direction. Compared to the as-deposited state, the annealed film has slightly smaller, but better defined grains, c.f., Fig. 3. The SAED pattern shows that the grains are randomly oriented and confirms the presence of both cubic and hexagonal phases. STEM images and elemental maps conducted by EDX from the same film are presented in Fig. 10. The maps show that Al and Ti are separated into ~10-15 nm wide domains, which corresponds to the above described secondary phase transformation products.

Mechanical properties of annealed films

Fig. 11 shows the measured hardness of the annealed films. The film with x=0.01 exhibits a substantial hardness increase with maximum hardness of 34.4±2.8 GPa at 900 °C. At 1000 °C the hardness decreases to 31.3±2.8 GPa, which still is distinctly higher

Fig. 9. Transmission electron micrograph and selected area electron diffraction pattern from a $(\text{Ti}_{0.33}\text{Al}_{0.67})_{0.99}\text{Si}_{0.01}\text{N}$ film on WC-Co substrate annealed at 900 °C for 2 h.

Fig. 10. Overview scanning transmission electron micrograph and elemental EDX maps in magnified views from the white box of $(\text{Ti}_{0.33}\text{Al}_{0.67})_{0.99}\text{Si}_{0.01}\text{N}$ film on WC-Co substrate annealed at 900 °C for 2 h.

Fig. 11. Nanoindentation hardness of annealed $(\text{Ti}_{0.33}\text{Al}_{0.67})_{0.99}\text{Si}_{0.01}\text{N}$ and $(\text{Ti}_{0.33}\text{Al}_{0.67})_{0.91}\text{Si}_{0.09}\text{N}$ films deposited on WC-Co substrates at 400 °C as a function of annealing temperature.

than for the as-deposited state of 23.6 ± 1.1 GPa. The film with $x=0.09$ also exhibits hardening with 30.1 ± 2.7 GPa at 900 °C and 28.7 ± 2.4 GPa at 1000 °C. Both films, thus, exhibit age hardening at temperatures similar to process temperatures at the rake face of the cutting insert during cutting application.

Conclusions

Arc deposited $(\text{Ti}_{0.33}\text{Al}_{0.67})_{1-x}\text{Si}_x\text{N}$ films exhibit three different states of phase compositions depending on the Si content in the range $0 \leq x \leq 0.29$. For Si-depleted

conditions ($x \leq 0.02$), a cubic metastable (Ti,Al)N phase dominates. For $x \geq 0.04$ the films exhibit mainly a hexagonal wurtzite phase of (Al,Ti,Si)N solid solution. Higher Si contents ($x > 0.17$) render the films an X-ray amorphous structure. A drastic grain-refining effect of Si in (Ti_{0.33}Al_{0.67}N) was demonstrated for Si contents as low as $x = 0.002$. All as-deposited films exhibit nanoindentation hardness between 22 and 25 GPa. Isothermal annealing at 900 °C results in spinodal decomposition of c-(Ti,Al)N into TiN and c-AlN followed by h-AlN precipitation. The h-(Al,Ti,Si)N phase separates out c-TiN at 900 °C. Annealed $x = 0.01$ and $x = 0.09$ films increase in hardness by up to 50%, which is the largest age hardening effect among the transition metal nitride alloys reported to date. The films with the lowest Si content and mainly cubic phase performed best in a turning test. For $x \geq 0.04$ film, however, cracks appear during 13.5 min turning. Similar cracks as from the turning test appear also in $x = 0.09$ films after annealing at ≥ 900 °C for 130 min. We propose that the cracks formed under the two processing conditions stem from the tensile stress generated from a reduction in molar volume during phase transformation of h-(Al,Ti,Si)N into TiN and Ti depleted h-(Al,Ti,Si)N. The poor cutting performance of the Ti-Al-N based films with a majority of the hexagonal phase is thus explained.

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