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Microstructure evolution and age hardening in (Ti,Si)(C,N) thin films deposited by cathodic arc evaporation

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ABSTRACT

$Ti_{1-x}Si_xC_yN_{1-y}$ films have been deposited by reactive cathodic arc evaporation onto cemented carbide substrates. The films were characterized by X-ray diffraction, elastic recoil detection analysis, transmission electron microscopy, energy-dispersive X-ray spectroscopy, electron-energy loss spectroscopy and nanoindentation. Reactive arc evaporation in a mixed CH_4 and N_2 gas gave films with $0 \le x \le 0.13$ and $0 \le y \le 0.27$. All films had the NaCl-structure with a dense columnar microstructure, containing a featherlike pattern of nanocrystalline grains for high Si and C contents. The film hardness was 32–40 GPa. Films with $x>0$ and $y>0$ exhibited age-hardening up to 35–44 GPa when isothermally annealed up to 900 °C. The temperature threshold for over-ageing was decreased to 700 °C with increasing C and Si content, due to migration of Co, W and Cr from the substrate to the film, and loss of Si. The diffusion pathway was tied to grain boundaries provided by the featherlike substructure.

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1. Introduction

Transition metal ceramics are commonly used as coatings on metal cutting tools. The tool performance relies on the wear resistance of the coating, which depends on properties such as hardness and oxidation resistance. To that end the family of titanium nitride based coatings, which share the basic NaCl structure and have a high hardness (typically 20–30 GPa [1–6], are particularly useful. Commercially available coatings in this family are, for example, TiN, TiC, TiCN, CrN, CrCN, TiAlN and TiSiN. Demand for ever better coatings drives interest towards more complex multinary films. One candidate for such coatings is the Ti–Si–C–N system, which is surprisingly unexplored given that its components have been investigated in depth [2,7–10].

By using physical vapour deposition techniques it is possible to synthesize metastable compounds, the most well know example is cubic-(Ti,Al)N which is widely used for cutting tools today [11]. In that case the miscibility gap is utilized to provide a driving force for phase separation at elevated temperatures [12]. This in turn leads to improved mechanical properties by mechanisms which involve spinodal decomposition on the metal sublattice and particle precipitation with resultant age hardening [13–15]. Another example is Ti(B,N) that exhibits separation on the nitrogen sublattice [16]. For (Ti,Si)N solid solution films synthesized by cathodic arc evaporation [17], a high hardness is attained in the as-deposited state, but only with limited age-hardening. These films are limited in high-temperature applications by interdiffusion of substrate species and loss of Si by diffusion into the substrate.

The Ti–Si–N system is of interest due to reports of extreme hardness of nanocomposite films consisting of nanocrystalline TiN grains embedded in a SiN_x ($1 \le x \le 1.33$) matrix [7,18]. This structure is formed when depositing a film without kinetic limitations due to the miscibility gap in the TiN–Si_3N_4 system, which gives a driving force for phase separation [19]. In all but one (see below) of the few reports [20–22] on Ti–Si–C–N films the reported microstructure is similar to one of the Ti–Si–N nanocomposites. These coatings exhibit similar high hardness as the Ti–Si–N system and a reduced friction coefficient in comparison to TiCN. Shtansky et al. [20] reported on solid solution Ti–Si–C–N films deposited by magnetron sputtering. These transformed to a nanocomposite structure for moderate silicon contents (>5 at.%). There was unfortunately only a rudimentary characterization of the mechanical properties of these films and no data on their thermal stability.

Here, we report the synthesis and characterization of Ti–Si–C–N solid solution thin films grown by reactive arc evaporation from Ti–Si cathodes. The evolution of microstructure, composition and mechanical properties of the films has been investigated as a function of Si and C contents, as well as temperature of post deposition annealing.

2. Experimental details

The films were grown by reactive cathodic arc evaporation in an industrial scale deposition system (Metaplas MZR323). In all

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depositions three cathodes aligned vertically were used, with compositions (top to bottom) of $T_{i0.8}S_{i0.2}$, $T_{i0.9}S_{i0.1}$ and pure Ti. The substrates were mounted on a rotating drum in rows opposite the cathodes. As reactive gases a mixture of N_2 and CH_4 was used at a constant total pressure of 2 Pa. To vary the C-content in the films the flow ratio between the gases (ratios of 0, 10, 20 and 50% CH_4) was changed between depositions. A heating filament was used to achieve a temperature of the substrates of approximately 400 °C and a bias potential of −30 V was applied to the substrate fixture. Polished cemented carbide WC–(Co,Cr) plates $12\times12\times4$ mm^3 were used as substrates. Post deposition anneals of selected films were performed in an inert Ar atmosphere for 2 h at 700, 800, 900, 1000 and 1100 °C, respectively.

The microstructure of the as-deposited and annealed films was investigated using surface and cross sectional scanning electron microscopy (LEO 1550 Gemini equipped with Oxford Link EDX operated at 20 kV), X-ray diffractometry (XRD; Philips PW 1820 using Cu-K_α radiation) and cross sectional transmission electron microscopy (TEM; FEI Technai G2 operated at 200 kV). The chemical composition was investigated using energy dispersive X-ray spectroscopy (EDX) on all samples for Ti/Si ratio determination and elastic recoil detection analysis (ERDA, Tandem Accelerator at Uppsala University) on selected samples for C, N and trace element quantification as well as validation of the EDX measurements.

The residual stress was determined by the $\sin^2\psi$-method using the 422 peak, using a elastic modulus of $E=450$ GPa and a Poisson's ratio of $\nu=0.22$ [23]. The thermal component of the residual stress was calculated through $\sigma=\Delta\alpha\Delta TE/(1-\nu)$, where $\Delta\alpha$ is the difference in thermal coefficients and ΔT the difference in temperature. For the substrate, thermal coefficients of $\alpha=5.1*10^{-6}$ and $\alpha=5.8*10^{-6}$ K^{-1} were used for 400 and 1000 °C, respectively [24]. As there is no study of the thermal coefficients of TiSiCN, an approximate value was calculated from the room temperature value of TiC ($7.4*10^{-6}$ K^{-1}) and TiN ($9.35*10^{-6}$ K^{-1}) [25]. The rule of mixtures was applied to obtain α for different C-contents. An UMIS nanoindenter (UMIS-2000, Fischer-Cripps Laboratories) was used to probe the mechanical response of as deposited and heat treated films. Indentations were made on tapered cross sections prepared by mechanical polishing. The maximum load was 25 mN and a minimum of 20 indents for each sample were used to determine the average hardness, here reported with 90% confidence intervals. The hardness values were extracted from the indentation data by Oliver and Pharr's method [26].

3. Results and discussion

3.1. Microstructure of as-deposited samples

The compositions of selected films are given in Table 1, reported as $(Ti_{1-x}Si_x)(C_yN_{1-y})_z$ with titanium nitride as the prototype. The Si content (x) ranges from $x=0.01$ for the sample facing the Ti cathode to $x=0.14$ for the sample facing the $Ti_{0.8}Si_{0.2}$ cathode. The Ti:Si ratio is seen to be independent of the CH_4:N_2 gas mixture for all samples. Gas flow mixtures of 10, 20 and 50% CH_4 resulted in an atomic fraction of 8, 12 and 27% of C against N in the deposited films, respectively. The films are close to stoichiometric with z between 0.85 and 1.04, although the measurement underestimates z due to the presence of metallic macroparticles from the arc process in the films. Assuming that the ideal gas law holds, then the volume fraction of molecules in the mixtures is the same as their flow fractions given above. The atomic fraction of C (C/(C + N)) in the gas mixtures is determined by $u/(2-u)$ where u is the CH_4 fraction, which yields 0, 5, 11 and 33% C for the used parameters (0, 10, 20 and 50% CH_4), which should be compared with the C to N fraction (y) in the films (~1, 8, 12 and 27%). The measured uptake of carbon is higher than the assumed for a gas

Table 1
Composition of as-deposited $(Ti_{1-x}Si_x)(C_yN_{1-y})_z$ films as determined by ERDA.

$CH_4/(CH_4+N_2)$ %	Facing cathode	Si/(Si + Ti) % (x)	C/(C + N) % (y)	(C + N)/(Ti + Si) (z)
0	$Ti_{0.8}Si_{0.2}$	13.7	1	0.97
0	$Ti_{0.9}Si_{0.1}$	7.3	0.8	0.91
0	Ti	1	4	0.92
10	$Ti_{0.8}Si_{0.2}$	13.8	8.1	1.04
10	$Ti_{0.9}Si_{0.1}$	6.7	n/a	n/a
20	$Ti_{0.8}Si_{0.2}$	13.7	12.3	0.99
20	$Ti_{0.9}Si_{0.1}$	6.52	11.8	0.85
20	Ti	0.5	11.8	0.92
50	$Ti_{0.8}Si_{0.2}$	13.9	27.8	0.87
50	$Ti_{0.9}Si_{0.1}$	7.1	27.2	0.91
50	Ti	1.4	23.4	0.90

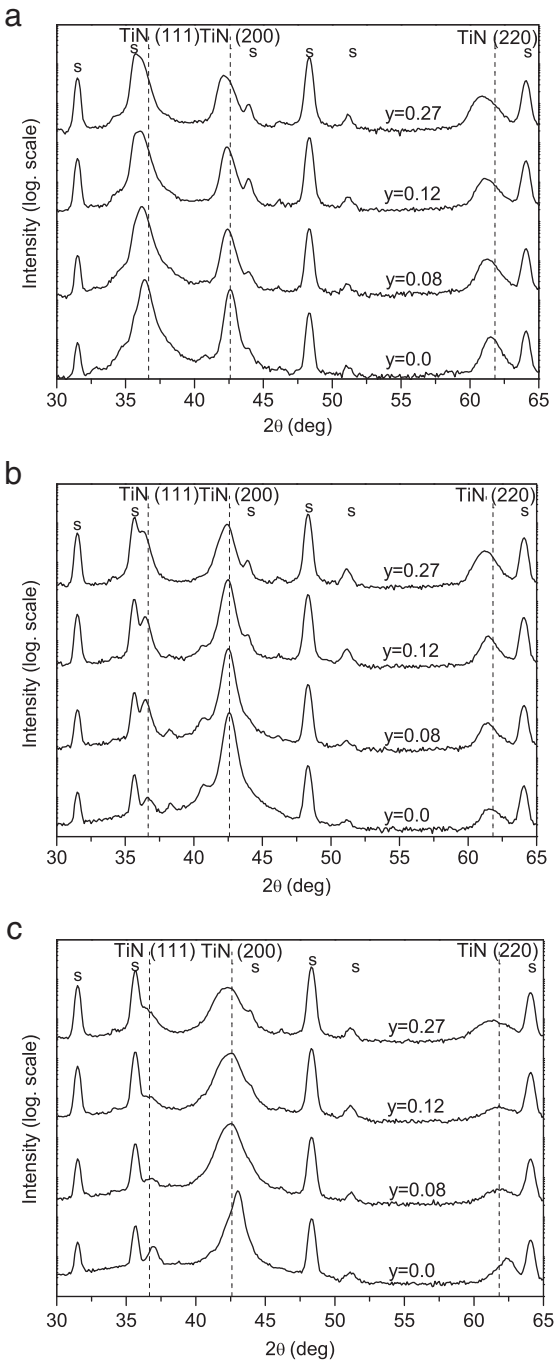

Fig. 1. X-ray θ–2θ diffractograms of films with different C-content (y) and different Si-content (x): (a) $x=0.01$, (b) $x=0.07$ and (c) $x=0.13$.

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