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Correlation of elastic modulus, hardness and density for sputtered TiAlBN thin films

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Abstract

This paper describes the correlation between the elastic modulus, hardness and density of mainly X-ray amorphous $TiAl_xB_yN_z$ ($0.29 \le x \le 1.32$; $1.15 \le y \le 2.07$; $0.37 \le z \le 2.19$) films, deposited by simultaneous reactive magnetron sputtering from TiAl and TiB_2 targets onto AISI 316 stainless steel and Si(100) substrates in Ar/N_2 mixtures at 150 °C. The elastic modulus, hardness and density were found to depend on chemical composition and the phases present, and an approximately linear correlation between elastic modulus and hardness could be established. The elastic modulus and hardness were also found to be a function of film density, except in films containing significant amounts of BN.

Keywords: Elastic properties; Hardness; Physical vapour deposition (PVD); Sputtering

1. Introduction

The elastic modulus, hardness and density of thin films often deviate from the theoretical bulk material values, due to effects relating to (for example) the microstructural, textural and compositional nature of the film. These are influenced by the deposition process used and the applied parameters. For example, electron-beam evaporation of a hot-pressed Ti–Al–B–N mixture resulted in films with elastic moduli of around 300 GPa [1], whilst the bulk hot-pressed material itself displayed an elastic modulus value of only 68 GPa [2]. Furthermore, for many recently-developed nanostructured/nanocomposite films (such as those from Ti–Al–B–N alloys with different compositions), bulk properties are not known – since such materials have never been produced in this form.

Compared to 'pseudo-binary' TiBN transition-metal boride/nitride thin films (i.e., TiN/TiB_2, TiN/BN), only a few papers have been published concerning the deposition and characterisation of physical vapour deposition (PVD) films within the Ti–Al–B-N quaternary system – using either magnetron sputtering [3–8] or electron-beam evaporation [1,9,10]. TiAlBN films can exhibit excellent wear resistance, with optimised film compositions demonstrating a substantial increase in lifetime in lubricated drilling tests [10], and lower observed contact temperatures during 'in situ' measurements at the cutting edge in unlubricated steel drilling [11] (both compared to standard TiAlN films). Depending on their composition and preparation method, elastic moduli of between 185 and 340 GPa for TiAlBN thin films with low amounts of Al (2–14 at.%) [1,9], 140 and 260 GPa with approximately 9 at.% Al [8], and 250±50 GPa [7] (composition not stated) have been reported. Hardness values of up to 37 GPa were observed for TiAlBN thin films [9]; however, no values for the densities of thin films produced within either of the above alloy systems are available in the literature. From other materials systems it is known that density variations can strongly affect the properties (e.g. the elastic modulus can be changed in both tetrahedral amorphous carbon [12] and amorphous boron suboxide films [13]).

In this work, the influence of the nitrogen content on two sets of sputtered TiAlBN thin films with boron to aluminium ratios

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Table 1
Elemental concentrations and stoichiometry for the TiAlBN thin films determined by GDOES

B/Al ratio	Elemental concentration (at.%)				Stoichiometry
	Ti	Al	B	N	
≈1	26.1	32.2	30.1	11.6	$TiAl_{1.23}B_{1.15}N_{0.44}$
≈1	21.7	28.6	29.0	20.7	$TiAl_{1.32}B_{1.34}N_{0.95}$
≈1	17.6	20.0	23.9	38.5	$TiAl_{1.14}B_{1.36}N_{2.19}$
≈5	27.4	10.4	52.1	10.1	$TiAl_{0.38}B_{1.90}N_{0.37}$
≈5	24.5	8.1	50.3	17.1	$TiAl_{0.33}B_{2.05}N_{0.70}$
≈5	19.4	5.7	40.2	34.7	$TiAl_{0.29}B_{2.07}N_{1.79}$

of ≈1 and ≈5, in terms of hardness, elastic modulus and density, is investigated using both nanoindentation and laser-induced surface acoustic wave (L-SAW) measurements. The present work was directed by a desire to identify possible correlations between elastic modulus, hardness and density in such films, thereby gaining a better understanding of how complex phase compositional changes influence the physical and mechanical properties of PVD thin films produced within the Ti–Al–B–N quaternary system.

2. Experimental details

TiAlBN films were deposited onto polished AISI 316 stainless steel (R_a=0.05 μm) and Si(100) wafer substrates by simultaneous sputtering from TiAl (3.7 W/cm^2) and TiB_2 (11.1 W/cm^2) targets of 200 mm×88 mm×5 mm, in Ar/N_2 gas mixtures at 150 °C, using a CemeCon CC800 system with a base pressure of $<5\times10^{-4}$ Pa and deposition pressure of 0.45–0.5 Pa, depending on nitrogen flow rate. Ultrasonic cleaning of the substrates was performed in acetone and isopropanol prior to film deposition. The deposition equipment, sequence, process parameters and substrate arrangements are described in detail elsewhere [5].

Film composition and chemical bonding were determined with a Leco GDS-750 QDP glow discharge optical emission spectrometer (GDOES) and a Surface Science Instruments M-Probe X-ray photoelectron spectroscopy (XPS) instrument with a 50 eV pass energy and monochromatic Al Kα X-rays. A TiB_2 standard and control samples of $(Ti_{0.5}Al_{0.5})N_{1.0}$ (thin film), TiBN and TiAlBN (both commercially available evaporation boats from Sintec Keramik GmbH and Co. KG, Halblech, Germany [2]) of known composition were used for instrument calibration. X-ray diffraction data were obtained using a Siemens D5000 X-ray diffractometer with a thin film attachment using an unmonochromated copper source at an incident angle of 0.5°, a current setting of 40 mA, a generator voltage of 40 kV, step-angle size of 0.02° and step time of 5 s; the scans were acquired over a range between 20° and 85° of 2θ. Fracture cross-sections of coated AISI 316 samples were prepared for morphology and topography studies by scanning electron microscopy (SEM). Transmission electron microscopy (TEM) studies were performed using a Philips CM200 instrument operated at 200 keV, employing a LaB_6 filament. Specimen preparation involved grinding and polishing the AISI 316 stainless steel substrate, followed by dimpling and ion beam thinning. Film thickness was measured using a Veeco DEKTAK^{3ST} profilometer with a vertical resolution of 50 nm and verified by SEM cross-sectional measurements.

Nanoindentation experiments were performed using an MTS Nano Instruments 'Nanoindenter XP' system (equipped with a Berkovich indenter) on TiAlBN coated Si(100), to obtain hardness and elastic moduli data. The loading curve was obtained by keeping the indentation rate constant (3 nm/s) and measuring the displacement until a depth of 200 nm was reached (i.e. <10% of film thickness in all cases). The load frame compliance and tip correction function were estimated using sapphire and fused silica control samples [14]; ten measurements were averaged for each sample.

The laser-induced surface acoustic wave (L-SAW) technique [15,16] was used to obtain thin film elastic modulus and density values from TiAlBN coated Si(100) samples. The L-SAW technique uses the frequency-dependent dispersion effects of a laser-induced shock wave to yield dispersion spectra, which have specific shapes depending on the elastic properties (E) and density (ρ) of both film and substrate – as well as on film thickness [15,16]. A Poisson's ratio (V) value of 0.2 was assumed for the coatings (as used previously in nanoindentation

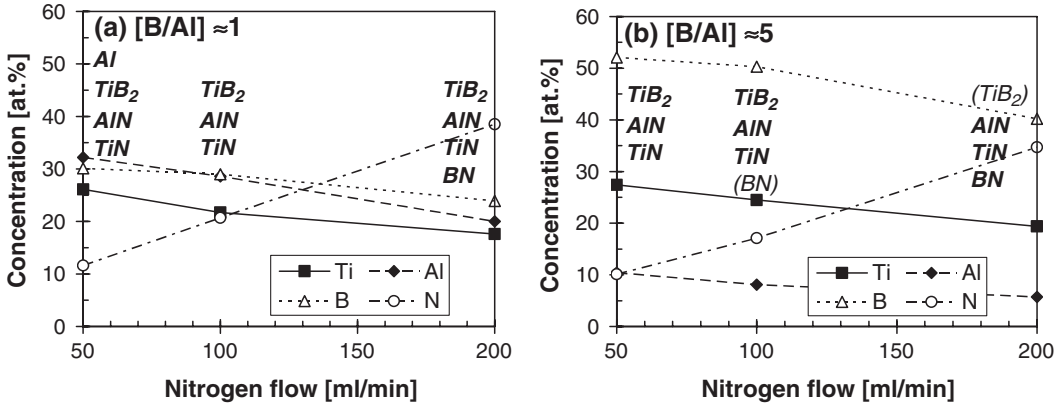

Fig. 1. Elemental composition (determined by GDOES; reproduced as data points in graphs) and phases in films observed (determined by XPS analysis, comparing binding energies in films with standards; indicated on top of data points) for two sets of TiAlBN thin films with B/Al ratios ≈1 (a) and ≈5 (b), vs. nitrogen flow.