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Age hardening in $(Ti_{1-x}Al_x)B_{2+\Delta}$ thin films

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ABSTRACT

Thin films of $(Ti_{0.71}Al_{0.29})B_{2+1.08}$ have been deposited by magnetron sputtering. Post-deposition annealing at 1000 °C for 1 h results in increased hardness and elastic modulus, from 32 to 37 GPa and from 436 to 461 GPa, respectively. In both as-deposited and annealed states the films adhere well to the substrate, indicating no considerable internal stress. The initial high hardness is attributed to a columnar microstructure consisting of crystalline (Ti,Al)B_2 columns separated by an amorphous B matrix. The observed age hardening corresponds to phase separation within the (Ti,Al)B_2 columns including the formation of Ti-deficient crystallites within the grain interior upon annealing.

TiB_2 is a ceramic material, particularly well-studied in bulk form, which exhibits attractive properties such as high chemical stability, high melting temperature, and high thermal and electric conductivity [1]. It crystallizes in a hexagonal AlB_2-type structure, where B atoms acquire interstitial positions between close-packed Ti(001) planes, resulting in alternating layers of Ti and B along the c-direction. Thin films of TiB_2 have primarily been deposited by non-reactive magnetron sputtering, see, e.g., Ref. [2–6], where a tendency towards overstoichiometric (001) textured films with a dense columnar microstructure has been observed [3]. A compressive residual stress in combination with excess B segregated to grain boundaries have resulted in superhardness of ~60 GPa [4]. Understoichiometric films, on the other hand, are obtained from vacuum arc evaporation from TiB_2 cathodes [7], however, no properties of such films have been reported to date.

TiB_2 coatings are crucial for machining aluminum, ubiquitous in the automobile, aerospace, and telecommunications industries. They also exhibit technological potential for, e.g., reducing wear and corrosion in engineering components, tribological applications, and as protective coatings for cutting tools. However, the high elastic modulus, ~560 GPa [8], constitute a poor match to the elastic modulus of the most common industrial substrates such as steel (~200 GPa [8]). This results in high thermally induced stresses, affecting coating adhesion and often leading to early failure; it is a main limitation for TiB_2 coating applications. Materials performance can typically be improved by synthesis of multicomponent systems, e.g., by using alloying as a method to tune properties, control the microstructure, and obtain overall enhanced functionality [9,10]. One example is the metastable ceramic alloy $Ti_{1-x}Al_xN$, one of the archetypes for hard-coating applications, in which isostructural clustering and the resulting age hardening has been a primary reason behind its success [11]. Moreover, incorporation of Al into TiN considerably improves the oxidation resistance [12]. In a most recent theoretical study, (Ti,Al)B_2 was identified as an alloy with a strong driving force for phase separation and with a suggested coherent isostructural, possibly spinodal, decomposition at elevated temperatures [13]. The potential for age hardening is therefore high, and promising for hard and wear-resistant coating applications. According to the equilibrium phase diagram, a combination of TiB_2, liquid Al, and AlB_{12} phases is predicted to be stable at 1000 °C [14].

Low-temperature growth of Ti-Al-B coatings has previously been performed by magnetron sputtering, though not targeting a metal diboride composition or structure [15,16]. The incorporation of Al was shown to significantly increase H/E ratio, which is related to improved impact and wear resistance. In the present study, we have investigated the effect of alloying TiB_2 with AlB_2, with a particular focus on structural and mechanical properties of as-deposited as well as post-annealed films. Through high resolution electron microscopy and spectroscopy, we show evidence for phase separation accompanied by an increase in hardness upon annealing.

Ti-Al-B thin films were deposited on Al_2O_3(0001) substrates by non-reactive dc magnetron sputtering in confocal geometry from 3″ sintered TiB_2 (99.5%) and AlB_2 (99.9%) targets. The targets were mounted opposite to each other at 39° tilt from the substrate normal. Prior to deposition the substrates were degassed in the vacuum chamber at the growth

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temperature of 400 °C for 60 min. The vacuum chamber had a base pressure of $1.03 \cdot 10^{-6}$ Pa, with 10.4 sccm Ar introduced up to a partial pressure of 0.133 Pa. The depositions were carried out at a substrate-target distance of 150 mm, in a power-controlled mode with closed magnetic field configuration, with 150 and 75 W on the TiB_2 and AlB_2 targets, respectively, corresponding to power densities of 3.29 and 0.0164 W/mm^2. A negative 50 V bias was applied to the substrates, and a deposition time of 2 h gave a film thickness of 410 nm. The substrates were stationary during the deposition. An as-deposited sample was cut in half and one half was annealed at 1000 °C for 1 h under high-vacuum conditions. The observed good film adhesion to the substrate was not affected by the annealing procedure. Henceforth, the studied samples are referred to as “as-deposited” and “annealed” throughout the text.

Theory predicts a driving force for isostructural phase separation even at high temperatures for almost the whole composition range [13], and we therefore chose a Ti-rich film composition with an estimated Ti:Al ratio of about 2. The elemental composition of the films was obtained by time-of-flight energy elastic recoil detection analysis (ToF-E ERDA) using the set-up at Uppsala University [17]. The measurements were performed with a 36 MeV $^{127}I^{8+}$ ion beam with an incident angle of 22.5° from the surface. Forward scattered recoil ions were detected at an angle of 45° relative to the incoming ion beam. The measured recoil ToF-E spectra were converted into relative atomic concentration profiles using the CONTES code [18]. Composition was also evaluated with X-ray photoelectron spectroscopy (XPS). Ti 2p, Al 2p, B 1s, O 1s, and C 1s scans were performed with an AXIS Ultra^{DLD} system from Kratos using monochromatic Al Kα radiation. Surface oxidation and carbon contamination were removed prior to XPS acquisition through 0.5 keV Ar^+ beam exposure for 180 s. Quantification was performed after background removal using a Shirley function.

The composition analysis of the as-deposited and annealed films is presented in Table I; the results from both ERDA and XPS analyses agree very well. For the as-deposited film, ERDA gives a Ti:Al ratio of 0.71:0.29 and (Ti + Al):B ratio of 1:3.08, resulting in an alloy composition of $(Ti_{0.71}Al_{0.29})B_{3.08}$. The observed excess of B is in agreement with previous reports on $TiB_{2+\Delta}$ films magnetron sputtered from stoichiometric targets [3,4] and in contrast to the studies of the related Cr-B [19] and Nb-B [20] systems. Overstoichiometry in B originates from different mass and scattering cross sections of Ti and B which results in preferential emission of B along the target normal. The centered B flux in the vicinity of the targets leads to a pronounced deficiency in Ti. An in-depth study of pressure, target-substrate distance, and deposition angle influence on the composition of coatings deposited from stoichiometric TiB2 targets has been performed by Neidhardt et al. [21]. The composition remains unchanged after annealing. The higher O and C content measured in XPS are due to the surface sensitivity of the technique. To reduce the tendency for element-selective etching of the sample material, the Ar^+ beam angle was selected to be only 25° relative to the surface plane.

The structural properties of the films were investigated by X-ray diffraction (XRD) using a Panalytical Empyrean MRD system equipped with a Cu Kα source (λ = 1.54 Å). Fig. 1(a) shows XRD θ-2θ scans of the as-deposited and thermally annealed samples, exhibiting a pronounced (001) texture. For the annealed Ti-Al-B film, an increase in the (00n) peak intensity along with a decrease in full width at half-maximum (FWHM) is observed, indicating an improved crystalline quality compared to the as-deposited sample. In addition, the peak slightly shifts towards higher 2θ angles (+0.2° for the (001) peak), corresponding to a decrease in the *c*-lattice parameter from 3.26 to 3.24 Å. The expected TiB_2 and AlB_2 phases both crystallize in the *P*6/*mmm* (191) crystal structure with reported *c*-lattice constants of 3.24 and 3.26 Å [22], respectively. From theory, calculated *c*-value corresponding to the synthesized Ti:Al ratio is 3.25 Å [13]. Due to the similar lattice parameters of TiB_2, AlB_2, and their alloys in-between [13], no conclusion can be made with respect to phase decomposition.

A Hysitron TI-950 Triboindenter with a Berkovich diamond indenter was employed to determine hardness and elastic modulus of the films. Loading-unloading curves for twelve indents, at 10 μm distances in between, were recorded in load-controlled mode. Prior to analysis the indenter was calibrated using a fused silica reference. In all measurements, the penetration depth was always kept lower than 12% of the film thickness to avoid substrate influence [23]. Fig. 1(b) shows loading-unloading curves recorded during nanoindentation of the as-deposited and annealed samples. A high elastic recovery is observed, which further increases upon annealing from 85 to 92% after a load of 2800 μN. The mechanical properties in the as-deposited and annealed states are summarized in Table I. Annealing of the film results in an increase from the initial hardness and elastic modulus of 32 and 436 GPa by ~5 GPa (+15%) and ~25 GPa (+6%), respectively. The hardness is in the same range as previously reported values for Ti-Al-B coatings of comparable composition deposited at 150–170 °C, while the elastic modulus is about 100 GPa higher [15,16]. The higher elastic modulus correlates with a better crystallinity and bonding that we obtained at higher deposition temperature. For (001) textured $TiB_{2+\Delta}$ coatings, hardness values above 45 GPa are generally observed [2,5,6]. The increase in H/E and H^3/E^2 ratio after annealing indicates an improved toughness and resistance to plastic deformation [24]. The coating remained well adherent to the substrate upon annealing, indicating no considerable internal stresses accumulated in the film.

To explore the structural evolution upon annealing and the origin of the increase in hardness, high-resolution transmission electron microscopy (HRTEM) as well as energy-dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS) were performed. Cross-sectional specimens for TEM were prepared from the samples using a traditional approach, which includes mechanical, mounting in a grid, gluing, and polishing to ~50 μm thickness. Specimen's electron-transparency was achieved by Ar^+ ion milling at 5 keV and 5° milling angle from both sides. Plan-view specimens were prepared by cutting 3 mm diameter discs from the samples using an ultrasonic cutter, mechanical polishing to ~70 μm thickness followed by Ar^+ ion milling from the substrate side. For both type of specimens, the Ar^+ ion energy was gradually reduced to 2 keV during the final step of milling to minimize surface

Table I
Film composition, hardness (H), elastic modulus (E), H/E ratio, and H^3/E^2 ratio for the as-deposited sample and after annealing under high vacuum at 1000 °C for 1 h.

Sample	Composition (at.%)			H (GPa)	E (GPa)	H/E	H^3/E^2 (GPa)	Elastic recovery (%)	Micro-structure
		ERDA	XPS						
As-deposited	Ti	17	17	32.1 ± 0.4	436 ± 3	0.074	0.18	85	Columnar voids-free
	Al	7	5						
	B	74	71						
	O	1	4						
	C	1	3						
Annealed	Ti	–	16	37.0 ± 0.8	461 ± 3	0.080	0.24	92	Columnar voids-free
	Al	–	5						
	B	–	71						
	O	–	4						
	C	–	4						