Age hardening in $(\text{Ti}_{1-x}\text{Al}_x)\text{B}_{2+\Delta}$ thin films

A. Mockute,^{1,*} J. Palisaitis,¹ B. Alling,^{1,2} P. Berastegui,³ E. Broitman,¹ L.-Å. Näslund,¹ N. Nedfors,¹ J. Lu,¹ J. Jensen,¹ L. Hultman,¹ J. Patscheider,⁴ U. Jansson,³ P.O.Å. Persson,¹ J. Rosen¹

¹*Thin Film Physics Division, Department of Physics, Chemistry, and Biology (IFM), Linköping University, SE-58183 Linköping, Sweden*

²*Max-Planck-Institut für Eisenforschung GmbH, D-402 37 Düsseldorf, Germany*

³*Department of Materials Chemistry, The Ångström Laboratory, Uppsala University, P.O. Box 583 SE-751-21 Uppsala, Sweden*

⁴*Laboratory for Nanoscale Materials Science, EMPA, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland*

**Corresponding author; email: aurmo@ifm.liu.se*

Thin films of $(\text{Ti}_{0.71}\text{Al}_{0.29})\text{B}_{2+1.08}$ 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 $(\text{Ti,Al})\text{B}_2$ columns separated by an amorphous B matrix. The observed age hardening corresponds to phase separation within the $(\text{Ti,Al})\text{B}_2$ columns including the formation of Ti-deficient crystallites within the grain interior upon annealing.

Keywords: titanium diboride, thin films, mechanical properties, hardness

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 $\text{Ti}(001)$ 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 $\text{Ti}_{1-x}\text{Al}_x\text{N}$, 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, $(\text{Ti,Al})\text{B}_2$ 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 $\text{Al}_2\text{O}_3(0001)$ 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 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 $^{127}\text{I}^{8+}$ 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 K α 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 $(\text{Ti}_{0.71}\text{Al}_{0.29})\text{B}_{3.08}$. The observed excess of B is in agreement with previous reports on $\text{TiB}_{2+\Delta}$ 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 TiB_2 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.

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					
	Al	7	5					
	B	74	71	32.1 ± 0.4	436 ± 3	0.074	0.18	85
	O	1	4					
	C	1	3					
Annealed	Ti	-	16					
	Al	-	5					
	B	-	71	37.0 ± 0.8	461 ± 3	0.080	0.24	92
	O	-	4					
	C	-	4					

The structural properties of the films were investigated by X-ray diffraction (XRD) using a Panalytical Empyrean MRD system equipped with a $\text{Cu K}\alpha$ source ($\lambda = 1.54 \text{ \AA}$). Figure 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 ($+0.2^\circ$ for the (001) peak), corresponding to a decrease in the c -lattice parameter from 3.26 to $3.24 \text{ \AA}$. The expected TiB_2 and AlB_2 phases both crystallize in the $\text{P6}/\text{mmm}$ (191) crystal structure with reported c -lattice constants of 3.24 and $3.26 \text{ \AA}$ [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 TiB₂, AlB₂, 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]. Figure 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+Δ} coatings, hardness values above 45 GPa are generally observed [2, 5, 6]. The increase in H/E and H³/E² 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 damage. Scanning TEM (STEM) combined with high angle annular dark field (HAADF) imaging, STEM-EDX analysis as well as HRTEM imaging were performed in the double-corrected Linköping FEI Titan³ 60-300, operated at 300 kV. STEM-HAADF images were recorded using an optimized 30 mrad convergence semi-angle, which provided sub-Ångstrom resolution probes with ~ 0.1 nA beam current. STEM-EDX spectrum images of 252x252 pixels were acquired for 3 min using ~ 0.6 nA beam current. HRTEM images were recorded under negative spherical aberration imaging (NCSI) conditions.

There are no immediate differences in the cross-section projection between as-deposited and annealed samples, where the latter is shown in Figure 2. Both films exhibit a dense columnar microstructure with an average column diameter of ~ 20 nm, which is slightly increasing towards the surface as the growth process develops. The columns are inclined by 16° from the surface normal towards the higher incoming flux from the TiB_2 target. Lattice resolved images in Figures 2(b) and (c), acquired at the film/substrate interface and close to the surface, respectively, reveal that the columns consist of bundles of subcolumns

approximately 5 nm in diameter with (001) atomic planes parallel to the interface, in contrast to the tilted grain growth. The microstructure closely resembles previous observations of magnetron sputtered TiB_2 coatings [4]. The crystallographic orientation is not governed by the substrate, as the initial ~ 1 nm of the film exhibits an amorphous nature. This thin amorphous layer separates crystalline $(\text{Ti,Al})\text{B}_2$ from the Al_2O_3 and no considerable strain is introduced through lattice mismatch as can be concluded from homogeneous contrast of the Al_2O_3 substrate at the interface.

Elemental mapping of the film was performed by both STEM-EELS and -EDX. The elemental maps reveal that Ti is evenly distributed in the columns and not present in the boundaries between the columns, while Al shows less pronounced variations. The damped contrast in the Al map, compared to the stronger contrast of the Ti map in Figure 3 are most likely due to homogeneous Al-rich surface resputtering originating from the Al_2O_3 substrate during the Ar^+ ion milling in TEM sample preparation.

The effect of thermal-treatment on the microstructure is clearly visible in the plan-view images in Figure 4. Columns in the as-deposited state exhibit a fractal-like outlines, which assumes more well-defined shapes upon annealing. Selected area electron diffraction (SAED) patterns show that the films are constituted of the $(\text{Ti,Al})\text{B}_2$ phase in both as-deposited and annealed states. The embedding matrix also appears to grow in thickness with annealing. Additionally, phase segregation occurs in the grain interior, where Ti-deficient precipitates appear. In cross-section, the precipitates appear significantly more elongated (~ 20 nm) in the growth direction, as compared to the in-plane extension. STEM-EELS and -EDX composition mapping in combination with HRTEM reveal that the matrix consists of an amorphous B tissue phase, while the crystalline material consists of $(\text{Ti,Al})\text{B}_2$ phase as

supported by electron diffraction (ED) patterns acquired along the [001] zone axis. $(\text{Ti,Al})\text{B}_2$ also shows improved crystal order after annealing, in agreement with increased peak intensity and smaller FWHM in the corresponding XRD scan. Moreover, the development of Ti-depleted column interior is observed, which exhibits the same gray level as that of the intercolumnar tissue phase.

The observed changes in microstructure upon annealing are proposed to occur as a consequence of ripening of the segregated material. The original fractal grain structure holds excess B which segregates to boundaries or to precipitates as heat is applied. Extended annealing (not shown) further segregates the amorphous and crystalline phases. This is in agreement with calculations predicting B diffusion and segregation into grain boundaries in overstoichiometric TiB_2 thin films [25].

From the initial fractal crystal structure to the more ordered annealed appearance, the boundaries and precipitates assume an ordered structure on the nanoscale, which effectively hinders dislocation multiplication and movement. Thus, we propose that the 15 % increase in hardness is directly coupled to the development of the microstructure during high temperature annealing and resultant age hardening. Increased elastic modulus could be linked to higher crystal order after the thermal treatment. However, further investigations are needed to make conclusive statements regarding potential phase separation of coherent AlB_2 and TiB_2 rich domains within the hexagonal phase as predicted by calculations [13]. Such isostructural phase separation, in the form of spinodal decomposition, has been shown to give rise to a distinct age-hardening in the industrially important $\text{Ti}_{1-x}\text{Al}_x\text{N}$ system [11]. A difference in the present diboride case as compared to the nitrides, evident from the phase diagrams, is the existence of stable solid boron-rich phases at high temperature, such as

AlB₁₂ and pure B, which increases the challenge in understanding phase transitions between metastable and stable phases in the ternary Ti-Al-B system.

Additional annealing *in situ* TEM at 1000 °C for 12 h (not shown) resulted in only slightly more defined grain boundaries and no further significant structural or compositional changes, which would indicate a completed phase transformation. It is suggested that B overstoichiometry together with the low deposition temperature, i.e., low adatom mobility, results in segregation of excessive B to the grain boundaries obstructing further in-plane growth of (Ti,Al)B₂ grains. As a consequence of the limited dimensions, grain boundary diffusion and surface-directed decomposition are suggested to dominate the structural development at the applied annealing conditions. Hence, the observed microstructure transformation, more specifically, development of Ti deficient (Ti,Al)B₂ precipitates within the grain interior, is not attributed to spinodal decomposition, but rather nucleation and growth. It is expected that a (Ti+Al):B ratio closer to 1:2 (more suitable stoichiometry) combined with higher adatom mobility conditions would result in larger and more well defined columns, which would additionally facilitate bulk diffusion and isostructural clustering.

In conclusion, thin films of (Ti_{0.71}Al_{0.29})B_{3.08} were deposited on Al₂O₃ substrates by magnetron sputtering. The resulting microstructure of crystalline (Ti,Al)B₂ columns embedded into an amorphous B matrix gives rise to a high hardness of 32 GPa. An increase in hardness up to 37 GPa (+15 %) was achieved by annealing the film at 1000 °C for 1 h under high vacuum, accompanied by a microstructure transformation and development of Ti-deficient regions at the grain interior. Both as-deposited and annealed films remained well adherent to the substrate.

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Figure 1 (a) XRD θ - 2θ scans of the as-deposited and thermally annealed samples. Only peaks matching to $(\text{Ti,Al})\text{B}_2$ are observed. (b) Loading-unloading curves during nanoindentation of the studied samples.

Figure 2 Cross-sectional TEM of the annealed sample shows (a) dense columnar microstructure with ~ 20 nm columns inclined by 16° from the surface normal; HRTEM images at (b) the film/substrate interface and (c) near the surface reveal ~ 5 nm subcolumns (separated by white lines) with (001) atomic planes oriented parallel to the interface

Figure 3 Cross-sectional STEM-HAADF image of the annealed $(\text{Ti,Al})\text{B}_2$ sample and corresponding EDX elemental maps of Ti and Al.

Figure 4 Plan-view STEM-HAADF images and elemental maps with corresponding SAED patterns of (a) as-deposited and (b) annealed films clearly demonstrate the different microstructures of the two states.