Thermal stability and mechanical properties of amorphous arc evaporated Ti-B-Si-N and Ti-B-Si-Al-N coatings grown by cathodic arc evaporation from TiB₂, Ti₃₃Al₆₇, and Ti₈₅Si₁₅ cathodes

Hanna Fager, J.M. Andersson, Jens Jensen, Jun Lu and Lars Hultman

Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:

Hanna Fager, J.M. Andersson, Jens Jensen, Jun Lu and Lars Hultman, Thermal stability and mechanical properties of amorphous arc evaporated Ti-B-Si-N and Ti-B-Si-Al-N coatings grown by cathodic arc evaporation from TiB₂, Ti₃₃Al₆₇, and Ti₈₅Si₁₅ cathodes, 2014, Journal of Vacuum Science & Technology. A. Vacuum, Surfaces, and Films, (32), 6, 061508.

<http://dx.doi.org/10.1116/1.4897170>

Copyright: American Vacuum Society

<http://www.avs.org/>

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-106573>

Thermal stability and mechanical properties of amorphous coatings in the Ti-B-Si-Al-N system grown by cathodic arc evaporation from TiB_2 , $\text{Ti}_{33}\text{Al}_{67}$, and $\text{Ti}_{85}\text{Si}_{15}$ cathodes

H. Fager,^{1, a)} J.M. Andersson,² J. Jensen,¹ J. Lu,¹ and L. Hultman¹

¹⁾Thin Film Physics Division, Department of Physics, Chemistry, and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden

²⁾Seco Tools AB, SE-737 82 Fagersta, Sweden

(Dated: 25 August 2014)

Ti-B-Si-Al-N coatings were grown on cemented carbide substrates in an industrial scale cathodic arc evaporation system using $\text{Ti}_{33}\text{Al}_{67}$, $\text{Ti}_{85}\text{Si}_{15}$, and TiB_2 cathodes in a reactive N_2 atmosphere. The microstructure of the as-deposited coatings changes from nanocrystalline to amorphous with addition of (B+Si+Al), or high amounts of (B+Si) to TiN. In the as-deposited state, the 4 μm -thick amorphous coatings are dense and homogenous, besides slight compositional modulation with Ti-rich layers induced by rotation of the substrate holder fixture during deposition, and have unusually few macroparticles. Annealing at temperatures ranging from 700 °C to 1100 °C results in that the coatings crystallize by clustering of TiN grains. The hardness of as-deposited amorphous coatings is 17-18 GPa, and increases to 21 GPa following annealing at 800 °C. At annealing temperatures of 1000 °C and above the hardness decreases due to inter-diffusion of Co from the substrate to the coating.

I. INTRODUCTION

Transition metal (TM) nitrides are used in a wide range of applications, including wear protective coatings on cutting tools. This is due to their high hardness,¹ mechanical wear resistance,² high thermal stability,³ and good oxidation resistance.⁴⁻⁷

A problem with these materials is that since they are hard, they are also brittle. They often exhibit a characteristic columnar structure, where the grain boundaries perpendicular to the surface represent short crack paths that deteriorate toughness properties.⁸ One way to achieve column-free structures is to grow equiaxed nanocrystalline coatings, where much of the research interest has been focused over the past decades.

Another option is to grow amorphous coatings, but despite the extensive technological and academic research interest in glass, very little is known about amorphous transition metal nitrides. In analogy to metallic glasses,⁹ the formation of amorphous multicomponent transition metal nitrides should be based on alloying elements, where (1) the heat of mixing is strongly negative, hence in systems with strong tendency for compound formation, (2) there is a large difference (>10%) in atomic size, and (3) deep eutectic points exists.^{10,11}

Stable, refractory, hard transition metal (TM) nitrides (where TM=Ti, Zr, Hf, V, Nb, Ta or Cr), in combination with a p-element like Si, which can either bond to the metal or to nitrogen, is a well-studied route for formation of nanocrystalline or even amorphous nitrides. Silicon nitride grows amorphous at temperatures as high as 1100 °C¹² and possesses structural flexibility thanks

to the fourfold coordination of nitrogen. B has been suggested to be an even better choice for the formation of an amorphous phase since it can be both three- and four-fold coordinated. Also, B-N bonds are stronger than Si-N ones,^{13,14} which is beneficial for hard coating applications.

We previously showed that addition of Al to the Ti-Si-N system distorts nanocrystalline growth and promotes renucleation and an x-ray amorphous structure in cathodic arc evaporation.¹⁵

Currently, a systematic study pinpointing the composition window, where hard amorphous multicomponent nitrides can be produced by cathodic arc evaporation is lacking. Cathodic arc deposition offers, by virtue of the high metal ionization and thus energetic deposition conditions that promotes recoil mixing in the coatings, the possibility to grow dense, well-adherent, and mixed-alloy nitrides suitable for cutting tool applications.

The effects of multiple alloying in the Ti-B-Si-Al-N system is furthermore lacking. We have limited the number of nitride forming elements to four, thus exploring a window of alloys with potential to form amorphous alloys. Adding more elements adds entropy to the system such that high-entropy alloys (HEA) form that are apt to crystallize in the more simple crystal structures such as face centered cubic.¹⁶

In this study, we present the microstructural changes and thermal stability in arc-evaporated multicomponent Ti-B-Si-Al-N over a wide range of compositions for coatings grown from commercially available TiB_2 , $\text{Ti}_{33}\text{Al}_{67}$, and $\text{Ti}_{85}\text{Si}_{15}$ cathodes, with focus on the synthesis of hard amorphous coatings. It is found that addition of (B+Si+Al) or high amounts of (B+Si) to TiN is needed for the formation of amorphous structures. In the as-deposited state the Ti-B-Si-Al-N sample is mainly amorphous with only a few nanocrystalline grains, while the x-ray amorphous Ti-B-Si-N contains a larger number of

^{a)} hanfa@ifm.liu.se

nanocrystals. The hardness of as-deposited amorphous samples are ~ 17 GPa, which increases only slightly with annealing temperatures up to 800°C , and decreases at temperatures of 1000°C and above due to inter-diffusion of Co from the substrate to the coating. The mechanical properties of amorphous does not seem to be dependent on composition, yielding the same values for both Ti-B-Si-N and Ti-B-Si-Al-N coatings.

II. EXPERIMENTAL DETAILS

Ti-B-Si-N, Ti-B-Al-N, and Ti-B-Si-Al-N coatings were grown in an industrial arc evaporation system (Sulzer Metaplas MZR323). Three 100 mm diameter cathodes were aligned vertically, with compositions (top to bottom): $\text{Ti}_{85}\text{Si}_{15}$, TiB_2 , and $\text{Ti}_{33}\text{Al}_{67}$. This arrangement enabled variations in the coating compositions depending on the position of the substrates in relation to the cathodes. The cathodes were operated with an arc current of 120 A DC. Cemented carbide (WC-Co) $12 \times 12 \times 4 \text{ mm}^3$ were used as substrates, which were mounted on magnetic holders on a one-fold rotating drum fixture in the center of the deposition chamber, with a cathode-to-substrate distance of 16 cm.

Prior to mounting in the chamber, the substrates are polished to a mirror-like surface, and ultrasonically cleaned in a degreasing agent. After initial degassing of the chamber at $\sim 400^\circ\text{C}$, and plasma etching of the substrates, the depositions were carried out at approximately 300°C . A negative bias potential of -30 V was applied during deposition. Nitrogen (99.995 % purity) was introduced as the reactive gas at a total pressure of 4 Pa. The base pressure was $\sim 10^{-3}$ Pa and the total coating thickness was $\sim 4 \mu\text{m}$.

Post-deposition anneals of samples were performed in vacuum ($\sim 10^{-4}$ Pa) using a tube furnace with temperatures ranging from 700°C to 1100°C . The furnace was heated with a rate of $20^\circ\text{C}/\text{min}$ to the selected temperature, and held constant for 2 h. Following annealing, the samples were cooled at a rate of $20^\circ\text{C}/\text{min}$ to room temperature.

The elemental compositions of as-deposited coatings are determined by energy dispersive x-ray spectroscopy (EDX) in a LEO1550 field emission gun scanning electron microscope (SEM) equipped with AZtec X-max EDS, operated at 20 kV. For the quantitative analysis, industrial standards were used, and ZAF-correction (Z =atomic number, A =absorption, and F =fluorescence) was applied. Due to the poor detection limit of light elements in EDX, i.e. for elements with $Z < 11$, elastic recoil detection analysis with a time-of-flight and energy detector (TOF-E-ERDA) using a 36 MeV $^{127}\text{I}^{8+}$ beam incident at 67.5° relative to the sample surface normal with the detector at a 45° recoil scattering angle,¹⁷ and evaluated using the CONTES code,¹⁸ was used in addition to confirm the composition and to check for light elements and impurities in the coatings. The precision of

TOF-E-ERDA is typically better than $\pm 1 \text{ at.}\%$, while the precision of EDX is about $\pm 2 \text{ at.}\%$. For phase and structural analysis, a Philips Bragg-Brentano diffractometer with a line focus $\text{Cu K}\alpha$ x-ray source was used. θ - 2θ scans were conducted in the 2θ range from 10° to 110° .

A FEI Tecnai G2 TF 20 UT microscope operated at 200 kV was used for transmission electron microscopy (TEM), scanning TEM (STEM), and energy dispersive x-ray spectroscopy (EDX) elemental mapping investigations. Cross sectional TEM (XTEM) samples were prepared by mechanical polishing and ion milling. For the STEM analysis, a high angle annular dark field detector (HAADF) was used. Elemental mapping was carried out over $50 \times 100 \text{ nm}^2$ for a Ti-B-Si-Al-N coating annealed at 900°C .

Hardness measurements were performed on tapered cross sections using a Hysitron TI-950 TriboIndenter equipped with a Berkovich 142.3° diamond probe, calibrated using a fused silica standard. For each sample, a minimum of 50 indents were made at an indentation depth of $\sim 150 \text{ nm}$ (less than 10% of the coating thickness), corresponding to a maximum applied load of 12 mN. The indentation procedure consisted of three steps: 1) loading to P_{max} during 5 s, 2) hold for 2 s, and 3) unloading during 5 s. The average hardness and its standard deviation were determined using the method described by Oliver and Pharr¹⁹ by fitting 75% of the unloading curve.

III. RESULTS AND DISCUSSION

Coatings were grown with compositions chosen to achieve amorphous or highly-distorted nanostructured materials. We present here typical coating compositions for the pentanary Ti-B-Si-Al-N system. Films with high Ti content are more crystalline, which confirms the results from our previous study on addition of Si and Al to TiN.¹⁵

FIG. 1. Schematic of the setup during deposition showing the position of the samples in relation to the cathode positions.

TABLE I. Elemental composition of the as-deposited coatings on WC-Co substrates as determined by a combination of TOF-E-ERDA and EDX. The values have been normalized to 100 at.%.

Sample	Ti (at.%)	B (at.%)	Si (at.%)	Al (at.%)	N (at.%)	O (at.%)	Composition
A1 - Ti-B-Si-N	39.2	2.5	5.0	0.2	53.2	0.2	Ti _{0.84} B _{0.05} Si _{0.11} N _{1.14}
A2 - Ti-B-Si-N	31.8	9.9	4.1	0.5	53.7	1.1	Ti _{0.69} B _{0.21} Si _{0.09} N _{1.16}
A3 - Ti-B-Si-Al-N	29.9	11.5	3.5	1.7	53.4	1.3	Ti _{0.64} B _{0.25} Si _{0.07} Al _{0.04} N _{1.15}
A4 - Ti-B-Si-Al-N	21.2	17.4	1.0	9.5	50.9	1.0	Ti _{0.43} B _{0.35} Si _{0.02} Al _{0.20} N _{1.04}
A5 - Ti-B-Al-N	16.2	3.3	0.2	28.3	52.0	1.1	Ti _{0.34} B _{0.07} Al _{0.59} N _{1.09}
B4 - Ti-B-Si-N	21.6	23.6	1.5	0	53.3	0	Ti _{0.46} B _{0.51} Si _{0.03} N _{1.14}

Fig. 1 shows a schematic of the deposition system. During deposition of samples A1-A5, three cathodes were in use (top to bottom): Ti₈₅Si₁₅, TiB₂, and Ti₃₃Al₆₇. This enabled growth of coatings with various elemental compositions during one deposition by placing the substrates in different positions with respect to the cathodes. For comparison, one coating (B4) was deposited with the Ti₃₃Al₆₇-cathode switched off. Samples A4 and B4 were placed in the same position in the chamber.

A. Elemental composition of as-deposited coatings

Tab. I and Fig. 2 show the composition of the as-deposited coatings. Sample A1-A4 is a compositional series where the Ti and Si contents are decreased, while the Al and B contents increase. Sample A5 is an Al-rich Ti-B-Al-N coating. Sample B4 is a B-rich Ti-B-Si-N coating.

Sample A1 is a Ti-B-Si-N coating with a high Ti content (39.2 at.%). A1 was positioned in front of the Ti₈₅Si₁₅ cathode. Due to overlap of the plasma from the TiB₂ cathode, this coating also contains some B (2.5 at.%). The Si content in the as-deposited coating is slightly lower than the cathode composition, but in line with previous reports on arc evaporation from Ti-Si cathodes.^{15,20} The Al content in sample A1 is negligible.

FIG. 2. (Color online) Relative amount of each element in the coatings.

Sample A2 is also a Ti-B-Si-N coating with slightly lower Ti content (31.8 at.%) than sample A1. Since sample A2 was positioned closer to the TiB₂ cathode, the B content is higher (9.9 at.%) while the Si content is slightly lower (4.1 at.%). The Al content is negligible also in this sample. Sample A3 contains almost the same amount of Ti (29.9 at.%) as sample A2, but the B and Si content are slightly lower, while the Al content is increased to 1.7 at.%.

Sample A4 contains a mixture of all element. The sample was positioned slightly below the TiB₂ cathode, and plasmas from all three cathodes have been contributing to the total coating composition. Sample A4 is especially rich in Ti and B (21.2 and 17.4 at.%, respectively), but also contain 9.5 at.% Al. At this position only minor contributions come from the Ti₈₅Si₁₅ cathode. Sample A5, that was positioned slightly above the Ti₃₃Al₆₇ cathode contains less Ti than all other coatings (16.2 at.%), but its Al content is high (28.3 at.%). B is present with 3.3 at.%, whereas the Si content is negligible. Sample B4 was horizontally positioned in line with sample A4, see Fig. 1, but in this deposition the Ti₃₃Al₆₇-cathode was switched off. In comparison with sample A4, sample B4 contains almost the same amount of Ti, which indicates that the major Ti contribution comes from the TiB₂ cathode in both cases. Both samples A4 and B4 contain a high amount of B, slightly higher for sample B4 (23.6 at.% compared to 17.4 at.%). The Si content is almost the same for both samples (1.0 and 1.5 at.% for A4 and B4, respectively), which is attributed to contributions from the Ti₈₅Si₁₅ cathode. The major difference between samples A4 and B4 is the Al content. Sample B4 contains no Al since the Al-containing cathode was switched off during deposition.

From Tab. I it is obvious that there is a few at.% reduction in both Si and Al and a quite drastic reduction in B in the coatings compared to cathode composition. In sample A1 and A2, B has been substituting for mainly Si, and for sample A5, B has substituted for Al. Both in sample A1 and A5, the Ti contents are nearly exact the same in the coatings as in the cathodes.

For samples A3 and A4, the trends are not as clear, since the samples have contributions from all three cathodes. Regarding the fact that sample A4 has been closely facing the TiB₂ cathode the obtained composition of Ti_{0.43}B_{0.35}Si_{0.02}Al_{0.19}N_{1.04} is remarkable, especially with respect to the reduction in B. The same reduction in B

FIG. 3. (Color online) X-ray diffraction patterns from as-deposited coatings. A typical XRD pattern for an uncoated WCCo substrate is added at the bottom for clarity. Substrate peaks are indicated by S, c-TiN with circles and dotted lines, h-AlN with squares and small dotted lines, and h-TiB₂ with triangles and dashed lines.

is observed for sample B4. The total impurity level is <2 at.% in all coatings, where the major impurity is O, as reported in Tab. I. The reported oxygen levels are in line with previously reported values for arc evaporated nitride coatings deposited in industrial systems, see e.g., Ti-Al-N by Hörling et al.³ and Ti-Si-C-N by Eriksson et al.²¹.

B. Microstructure of as-deposited coatings

Fig. 3 shows the x-ray diffraction patterns for the as-deposited coatings within the 2θ ranges 30-55° and 75-100°. No coating diffraction peaks were visible outside this region. A typical XRD pattern for an uncoated WC-Co substrate is added at the bottom for clarity. Substrate peak positions are indicated by S, and high intensity peak positions for c-TiN,²² h-AlN,²³ and h-TiB₂.²⁴ Sample A1 has a strong intensity peak corresponding to TiN(200) at $2\theta \approx 42.6^\circ$. Also, a broader peak corresponding to TiN(400) is visible at $2\theta \approx 93.2^\circ$. Sample A2 is characterized by a TiN(200) peak with weaker intensity than for sample A1, which is well in agreement with the reduced Ti content in sample A2. At $2\theta \approx 44.2^\circ$, a peak corresponding to the Co(111)²⁵ substrate metal is visible. For sample A3, the TiN(200) peak intensity is further reduced, and sample A4 shows no indications of coating diffraction peaks, and is considered to be x-ray amorphous. Sample A5 has a broad peak between $2\theta = 30-42^\circ$, with its central position $\sim 35^\circ$. Due to the width of the peak it is difficult to

determine an exact peak position, while this peak could include a number of possible phases: h-TiB₂(10 $\bar{1}$ 0) ($2\theta = 34.133^\circ$ ²⁴), h-AlB₂(10 $\bar{1}$ 0) ($2\theta = 34.414^\circ$ ²⁶), h-AlN(0002) ($2\theta = 36.041^\circ$ ²³), c-TiN(111) ($2\theta = 36.663^\circ$ ²²), and r-BN(104) ($2\theta = 34.878^\circ$ ²⁷). However, sample A5 contains only 3 at.% B, which makes the B-containing phases less likely. Considering the high Al content (28 at.%), the most likely phase is h-(Al,Ti)N with corresponding shift in peak position to lower diffraction angles, due to solid solution of Ti in the hexagonal lattice. Similar results have been reported for high Al-content arc evaporated Ti_{1-x}Al_xN coatings.^{28,29}

Sample B4 has a similar structure as sample A4, and appears to be x-ray amorphous. However, there is an unidentified peak at $2\theta \sim 44.7^\circ$, also visible in the diffractogram for sample A3, located at a slightly higher diffraction angle than the Co(111) peak stemming from the substrate. This peak is unlikely from coating diffraction considering its shape and intensity, which is of the same order of magnitude as the peaks stemming from the substrate. We infer that it is a peak from an unidentified substrate phase or an artefact of the x-ray diffraction measurement.

The amorphous state of sample A4 is explained by the difference in size ($r_N = 0.065$ nm, $r_{Si} = 0.110$ nm, $r_{Al} = 0.125$ nm, $r_B = 0.085$ nm, and $r_{Ti} = 0.140$ nm³⁰) between the constituent elements, in combination with the different bond coordination, and preferred crystallographic structure of the parent compounds. Bonding in NaCl-structure transition metal nitrides such as TiN involves a combination of metallic, covalent, and ionic contributions³¹, where the atoms are octahedrally coordinated and have a preferred 1:1 stoichiometry. AlN and SiN are both tetrahedrally coordinated; Si₃N₄ with hexagonal, trigonal or amorphous structure, and AlN with hexagonal structure. Both consist of a mixture of covalent and ionic bonding.³² B can be both three- and fourfold coordinated, form hexagonal structures with both Al and Ti, and orthorhombic, rhombohedral, hexagonal or amorphous BN. B is a much smaller atom than the other metals and metalloids in this system, and in size it is more similar to N. At the same time, it is more similar to Al in terms of valence electrons. We conclude that the amorphous state of the coatings in our case is due to a synergistic effect of adding both Si, Al, and B to TiN, which hinders crystalline growth. For sample B4, which does not contain any Al, the combination of large amounts of B and a few at.% Si is enough to distort the structure into an amorphous one. Both samples A4 and B4 have a Ti content <0.5. Sample A5 has an even lower Ti content, 0.34, but the Al content is high, 0.59, and the coating is characterized by its h-(Al,Ti)N phase. For samples A4 and B4 the mixture of almost equal amounts of competing cubic (i.e. TiN) and hexagonal phases (TiB₂ and AlN), with additions of Si, that is known to act as a grain refiner and has been shown in numerous studies to effectively distort crystalline structures even at low concentrations, is an effective route for

FIG. 4. a) BF-XTEM image, with b) corresponding SAED pattern, and c) HR-TEM image with larger grains indicated by white circles, from the Ti-B-Si-Al-N sample A4.

synthesis of, at least, x-ray amorphous coatings.

To further examine the microstructure in the as-deposited state, TEM investigations were performed on samples A4 and B4. Fig. 4a) is a BF-XTEM micrograph of sample A4 showing a 4 μm thick homogeneous and featureless coating, without droplets or other common process-related artefacts. Fig. 4b) shows the corresponding selected area electron diffraction (SAED) pattern, with weak diffraction rings corresponding to TiN(111) and TiN(002). The outer ring is likely from TiN(220) or TiB₂(11 $\bar{2}$ 0). The HR-TEM image in Fig. 4c) shows that the coating consists of extremely small nanocrystalline grains (1-2 nm) as revealed by their lattice fringes. A few larger grains of the size 3-5 nm are also present, as marked with white circles.

Fig. 5 shows the corresponding images for sample B4, which is without Al. The BF-XTEM image in Fig. 5a) is also completely featureless, and the corresponding SAED pattern inset shows the same diffraction rings, with the addition of an outer ring that could correspond to TiN(222) or TiB₂(20 $\bar{2}$ 1). Fig. 5b) shows an area of the sample at higher magnification, where a clear layering is visible. This type of layering has previously been reported for arc evaporated coating growth using the same type of rotating sample fixture as applied here.^{3,33} Eriksson et al.³⁴ presented a detailed description of this phenomena for Ti-Si-C coatings, where it was shown that compositional layering is induced in the coatings during deposition. In a rotating sample fixture configuration the arc plasma processing infers self-sputtering on the substrates, with increasing efficiency at higher ion inci-

FIG. 5. a) BF-XTEM image with corresponding SAED pattern as inset, b) BF-XTEM image showing compositional layering resulting from rotation of the sample fixture during deposition, and c) corresponding HR-TEM image, where the layers are indicated by white lines, from the Ti-B-Si-N sample B4.

dence angles. The difference in sputter yield between normal and high incidence angles is larger for lighter elements, thus resputtering of lighter elements will occur in sections leading up to and away from the position directly facing the cathode. The implications of this for the present study is that heavier Ti ions causes resputtering of lighter Al, Si, B, and N, and even though the coatings appear to be homogeneous in the as-deposited state, they contain alternating Ti-rich and Ti-poor layers which, as shown later, will affect their crystallization. Characteristically, the layering follows the roughness of the substrate, moving like surging waves through the coating. At some positions, like the one presented in Fig. 5b) layered fronts that have formed around particulates (e.g., droplets) meet, and interruptions of the layers occur. Here, the layers consist of about 100 nm long sections, with areas free from layering in-between. Fig. 5c) shows a HR-TEM image covering two periods. It is obvious that this sample is nanocrystalline with 3-5 nm grains throughout. The two thinner layers that appear as a double line with a bottom dark line and a brighter thin line on top in Fig. 5b) are visible here as well. The brighter parts of the two lines are marked with white lines in the figure. Any compositional differences between the layers are, however, much limited as they were not possible to distinguish using EDX.

The major difference between samples A4 and B4 is the Al addition in sample A4. This addition distorts the

FIG. 6. (Color online) X-ray diffraction patterns following annealing between 700 °C and 1100 °C for samples A1 (black - bottom six curves) and A2 (green - top six curves) between 30-100° 2 θ .

crystalline structure and promotes amorphous growth. Previous studies on arc evaporated Ti-Si-N^{20,35,36} have shown that an addition of 7-10 at.% Si to TiN distorts the nanocrystalline structure, but is not enough to form a fully amorphous one. Ti-B-N has been grown in several

FIG. 7. (Color online) X-ray diffraction patterns following annealing between 700 °C and 1100 °C for samples A3 (light blue - bottom six curves) and A5 (dark blue - top six curves) between 30-100° 2 θ . The red line indicate the shift of the (Ti,Al)N peak with increasing annealing temperature.

FIG. 8. (Color online) X-ray diffraction patterns following annealing between 700 °C and 1100 °C for samples A4 (red - bottom six curves) and B4 (yellow - top six curves) between 30-100° 2 θ .

studies using arc evaporation³⁷⁻⁴¹ with B contents ranging from a few atomic per cent up to ~25-26 at.% without yielding an amorphous structure. A study on reactively sputtered Ti-B-N films grown with different nitrogen flow rates, claims that all N-containing films grown with nitrogen flow rates from 2-8 sccm are amorphous.⁸

The elemental compositions of above mentioned films vary greatly from Ti:B:N (21:57:2) with a flow rate of 2 sccm to Ti:B:N (10:28:22) with a flow rate of 8 sccm. The lack of HR-TEM characterization, however, makes it impossible to know whether the films are fully electron diffraction amorphous, or if they are x-ray amorphous with the presence of few nanocrystalline grains.

In our previous study¹⁵ we added both Si and Al to TiN and concluded that the addition of high amounts of both elements were needed for formation of fully amorphous structures using the similar deposition parameters as in this study. For the Ti_{1-x-y}Al_xSi_yN_z coatings to be amorphous, the Ti content had to be <0.34. In the present study, both samples A4 and B4 contain more Ti, and the small amount of Si in sample B4 is not sufficient to distort the structure to a fully electron-diffraction amorphous state. Despite the low Si content in sample A4, it forms an almost fully amorphous structure. The Si concentration in sample A4 is almost equal to that of sample B4 (1.0 at.% in A4 compared to 1.5 at.% in B4). Since the B content is higher in sample B4, we conclude that it cannot be the high B content in sample A4 alone that yields the amorphous structure, but a combination of a high Al and a high B content.

To summarize the microstructure of the as-deposited coatings, we show that decreasing the Ti and Si con-

tents in the coatings, while the Al and B contents are increased, yields a transition from cubic Ti-B-Si-N coatings to hexagonal Ti-B-Al-N coatings, via the formation of amorphous Ti-B-Si-Al-N coatings for Ti contents <0.5 . Ti-B-Si-N coatings can be deposited in an x-ray amorphous state with Ti contents <0.5 .

C. Structure evolution with annealing temperature

The thermal stability following ex-situ isothermal annealing experiments were studied for all six samples between temperatures 700 °C and 1100 °C. The XRD patterns are presented from 30-100° 2θ in Fig. 6 for samples A1 and A2, Fig. 7 for samples A3 and A5, and in Fig. 8 for samples A4 and B4. Outside these regions, no coating diffraction peaks were found.

Fig. 6 shows the result for the Ti-B-Si-N samples A1 (black curves) and A2 (green curves). It is obvious that the already strong TiN(200) peak is increasing in intensity with increasing annealing temperature. The weaker TiN(400) peak is also increasing in intensity with annealing temperature. At 900 °C the Co-peaks positioned at 44.2° and 51.5° 2θ are growing. At 1000 °C the peaks are sharp and indicate that Co has started to diffuse into the coating. At 1100 °C, an additional peak shows up at $\sim 41.7^\circ$, which corresponds to a CoTa_2 phase.⁴² This is the result of the Ta-containing holder in the annealing furnace that at 1100 °C reacted with the Co-containing substrates. This caused Co diffusion, and could also explain why the Co(200) peak vanishes at 1100 °C. This behavior could be realized after optical inspection of the samples after annealing at 1100 °C.

The same type of behavior is observed for sample A2, where the TiN(200) peak is drastically increasing in intensity for increased annealing temperature. Here, the peak is diffuse in the as-deposited state, with a full width at half maximum (FWHM) corrected for instrument broadening going from $\sim 1.37^\circ$ for the as-deposited state to 0.55 following annealing at 1000 °C. For sample A1, corresponding FWHM value at 1000 °C is ~ 0.45 , indicating a slightly higher crystallinity in the A1 sample. The Co substrate metal peak at $\sim 44.2^\circ$ is visible after annealing at 1000 °C, but vanishes at 1100 °C, due to the formation of the CoTa_2 -phase.

Fig. 7 shows the results for the Ti-B-Si-Al-N sample A3 (light blue) and the Ti-B-Al-N sample A5 (dark blue). For sample A3, the TiN(200) peak evolves during annealing, and increases in intensity with corresponding decrease in FWHM to ~ 0.39 after annealing at 1000 °C, indicating an even higher crystallinity for this sample than for samples A1 and A2. At 1000 °C the TiN (111) and (220) peaks also appear. At $2\theta \approx 91.4^\circ$, the $\text{TiB}_2(0003)$ peak is visible at 700 °C and 800 °C. The peak then vanishes at 900 °C. This can be explained by a transformation of the coatings into a cubic structure, indicated by the increased intensity of the TiN peaks which leads to a decreased h- TiB_2 grain size, or even segrega-

tion of the Ti to TiN grains and formations of a BN_x grain boundary phase. The Co (111) substrate peak follow the same behavior as for previous samples, where the intensity increases with annealing temperatures up to 1000 °C, followed by a intensity decreases or complete evanescence, upon formation of the CoTa_2 phase at 1100 °C. At 1100 °C there is an additional peak positioned at slightly higher diffraction angles than the substrate peak at $\sim 36^\circ 2\theta$. This peak could correspond to AlN, but due to the low Al content in sample A3 (1.7 at%), the peak is more likely CoTa_2 .

The most interesting feature for sample A5 is the broad peak around 35° that shifts to higher diffraction angles with increasing annealing temperature. This is marked with a red line in the figure. In the as-deposited state, this peak most likely corresponds to h-(Al,Ti)N with Ti in solid solution, due to the high Al content in the coating. With increasing annealing temperature, Ti segregates out of the hexagonal lattice, causing a shift of the h-AlN peak towards higher diffraction angles. At 1100 °C peaks corresponding to TiN(111), TiN(200), and TiN(220) are well developed. Co(111) substrate peaks are visible at 700 and 800 °C. At 900 °C, also the Co(200) peaks is present.

Red curves in Fig. 8, shows the XRD data for the x-ray amorphous Ti-B-Si-Al-N sample A4, and yellow curves correspond to the x-ray amorphous Ti-B-Si-N sample B4. For sample A4, a low intensity peak appears at 91.4° at 700 °C, which is h- $\text{TiB}_2(0003)$. This peak vanishes for

FIG. 9. a) BF-TEM overview image, with corresponding SAED as inset, b) layering around a droplet and corresponding superlattice reflections as inset, and c) corresponding HR-TEM showing the layering from a Ti-B-Si-Al-N sample A4 annealed at 900 °C.

higher annealing temperatures, which follow the explanation above for sample A3, where a transformation to a cubic structure occur at higher annealing temperatures. At 900 °C, a broad peak corresponding to TiN(200) at 42.6° is developing, and at 1000 °C the peak is very clear with $\text{FWHM} \approx 0.92$. Also TiN(111) is forming at 36.7° , and the Co(111)-peak intensity increases. In addition, there is a peak at $61.6^\circ 2\theta$ that appears at 1000 °C and above, which corresponds to TiN(220) or $\text{h-AlB}_2(11\bar{2}0)$ peak, indicated in the figure by a vertical line. However, the same peak shows up in sample B2, which does not contain Al, leading to the conclusion that this most likely is TiN(220). At 1100 °C there is a peak at $\sim 42.3^\circ$ with high intensity. This peak can correspond to either the TiN(200), shifted to slightly lower diffraction angles, or it can be the CoTa_2 peak that has been observed in the crystalline samples. However, all other samples have shown indications of decreasing Co-peak intensities, combined with several CoTa_2 peaks following annealing at 1100 °C. No such indications are present in sample A4, and we therefore conclude that the peak at $\sim 42.3^\circ$ most likely is TiN(200).

Fig. 8 shows the diffraction data for the x-ray amorphous Ti-B-Si-N B4 sample in yellow. For annealing temperatures of 700 °C and above, a very low intensity peak

FIG. 10. (Color online) Cross-sectional STEM/HAADF image and Ti, Al, and Si EDX elemental mapping shown as insets from a Ti-B-Si-Al-N sample A4 annealed at 900 °C.

FIG. 11. a) BF-XTEM image with corresponding SAED pattern as inset, b) BF-XTEM image showing compositional layering resulting from rotation of the sample fixture during deposition, and c) corresponding HR-TEM image where the layers are indicated by white lines, from a Ti-B-Si-N sample B4 annealed at 900 °C.

is seen around 91.4° , which can be concluded to be TiB_2 . The Co(111) peak appears already at 700 °C. At 1000 °C and above TiN(111) and (200) peaks are fully developed, where the (200) peak has a FWHM value of ~ 1.07 . It should, however, be noted that the film peaks for both sample A4 and B4 are very broad and the exact peak position and width of the peaks are difficult to determine. At peak corresponding to TiN(220) develops at 1000 °C and above.

The x-ray amorphous samples A4 and B4 show no tendencies of reaction with Ta upon annealing at 1100 °C, in contrary to the crystalline coatings. The diffraction patterns clearly show Co peaks in sample A4 and B4, with increasing intensity with increasing annealing temperature, which indicate that Co is present in the films. Nevertheless, the amorphous structures seem to slow down the Co-diffusion and hinder Co from diffusing through the whole thickness of the coating, in contrary to the nanocrystalline structures where grain boundaries present fast diffusion paths. This effectively prevents the formation of a CoTa_2 -phase at the surface of the amorphous coatings.

Fig. 9a) is a BF-XTEM micrograph showing an A4 sample after annealing at 900 °C. The layering is visible already at this magnification, especially in the thin top part in an area close to the SAED pattern. The corresponding SAED pattern shows diffraction rings typical of a nanocrystalline sample. Fig. 9b) is a higher magnification

FIG. 12. a) Nanoindentation hardness and b) reduced elastic modulus for as-deposited coatings.

cation BF-XTEM micrograph showing the layering more clearly around a droplet in the coating with the corresponding diffraction pattern showing the superlattice reflections. The HR-TEM shows one of the thin darker layers. These layers are Ti-rich, as evidenced by EDX elemental mapping presented in Fig. 10, and consist of ~ 5 nm large crystallites that are positioned next to each other like beads on a string, indicated by white rings in the HR-TEM image. The Ti-poor areas in between the layers contain randomly oriented nanocrystalline grains. The elemental mapping in Fig. 10 shows that Ti has segregated, forming clearly visible layers following annealing at 900 °C. In addition, there is a tendency for Al segregation, but not as clear as for Ti. Si is uniformly distributed over the mapped area.

Fig. 11 is the corresponding TEM images for the B4 sample after annealing at 900 °C. The BF-XTEM image in Fig. 11a) shows the layering clearly throughout the thickness of the coating. The SAED inset shows the same diffraction rings as in the as-deposited state, but with stronger intensity. Fig. 11b) shows a higher-magnification BF-TEM image with well-defined layering, and corresponding SAED pattern as inset. Two thin dark-contrast lines corresponding to TiN-rich domains are visible in the HR-TEM image, and they are indicated with white lines. The area in between the TiN-rich layers appears to be more crystallized, indicated by a greater number density of nanograins, compared with the corresponding areas in sample A4.

The compositional layering is most likely an artefact that is introduced in the coatings already during deposition, due to resputtering of the lighter elements (Al, Si, and B), leading to alternate Ti-rich and Ti-poor layers, even though it is not as pronounced in sample A4 as in sample B4, and not possible to distinguish using EDX. Annealing amplifies the layering through recrystallization and growth of TiN nanograins in the Ti-rich regions, and possible segregation of Ti and B into TiN and BN_x -phases.

D. Mechanical properties

Fig. 12 shows the nanoindentation hardness H , and reduced elastic modulus E_r for the as-deposited samples A1-A5, and B4. The hardness is highest for the Ti-B-Si-N sample A1 with $H=36.8 \pm 1.5$ GPa, followed by $H=34.2 \pm 1$ GPa for sample A2. The Ti-B-Si-Al-N sample A3 has a hardness of 20.5 ± 1 . For the Ti-B-Al-N sample A5, the hardness is $H=20.2 \pm 0.5$ GPa. The two x-ray amorphous samples have a hardness $17.1\text{--}17.9 \pm 0.5$ GPa. The reduced elastic modulus follows the same trend with the highest value, $E_r=316 \pm 8$ GPa for sample A1. For sample A2 it is slightly decreased to 297 ± 4 GPa, and for samples A3-A5, E_r is almost constant at $213\text{--}219 \pm 4$ GPa. For sample B2 E_r is slightly lower, 198 ± 5 GPa.

To be able to compare hardness values between nanocrystalline and amorphous samples, we must establish that the deformation mechanism is the same in both type of samples, and account for, or rule out, the presence of pile-up around indents in the amorphous samples. A number of indentations were thus performed at different loads in both nanocrystalline and amorphous samples. The indents were studied in SEM. Fig. 13 shows SEM images of resulting indents after 50 mN indentations with a standard Berkovich diamond probe for sample A1, which is nanocrystalline and A4 that is amorphous. It is obvious that the indents are identical both in shape and size. Also, there is no pile-up around the edges of the indent, so the deformation is the same in both samples and hardness and elastic modulus values can be compared between samples.

Fig. 14 shows hardness and reduced elastic modulus values for samples A4 and B4 after annealing between 700 °C and 1000 °C. The values for annealing at 1100 °C are omitted due to large scattering of the data. For sample A4, the hardness initially increases to 21.0 ± 0.3 GPa after annealing at 700 °C, but then decreases for higher annealing temperatures. Sample B4 shows an initial decrease in hardness to 15.8 ± 1.3 GPa after annealing at 700 °C, increases again to 18.0 ± 0.4 GPa at 800 °C, but then decreases almost linearly with increasing annealing

FIG. 13. SEM image showing the resulting indents following indentation in a nanocrystalline sample (A1), and an amorphous sample (A4) using a Berkovich diamond probe with a load of 50 mN.

FIG. 14. a) Nanoindentation hardness and b) reduced elastic modulus for annealed Ti-B-Si-Al-N (A4) and Ti-B-Si-N (B4) coatings with respect to annealing temperature. The values for as-deposited coatings are added for reference.

temperature. The reduced elastic modulus values follow the same trend as the hardness values for both samples. E_r for sample A4 is 183 ± 6 to 219 ± 3 , and for B4 152 ± 4 to 198 ± 5 .

The overall low hardness values can be explained by the relatively complex amorphous structures. Amorphous structures can be seen as statistically distributed aggregations of tetrahedrons. In between and around the tetrahedrons voids are present, that can be filled with small metalloids. The packing factor is low for TiB_2 (0.45⁸), which is positive for formation of amorphous structures, but a drawback is the high porosity and low density, which leads to decreased hardness. In the present study, the coatings are dense and featureless, without any indications of porosity, let alone vacancy-like voids as mentioned above.

The characteristic difference between the two deposition techniques is that high fractions of the arc evaporated material is ionized, while in conventional dc magnetron sputtering, the sputtered species are almost exclusively neutral. Kinetically limited growth using sputtering enables growth of amorphous structures, but they suffer from porosity. The energetic ionized particles involved in arc evaporation give an increased momentum transfer to the growing coatings, providing sub-plantation and recoil mixing, which favors densification and growth of the present hard and dense amorphous-structure coatings.

Mechanical properties of amorphous coatings cannot be explained following the theoretical and empirical framework that has been established for nanocrystalline coatings. Effects like the Hall-Petch relation and its inverse counterpart, grain boundary sliding, and hindering of dislocation motion is obviously not relevant in amorphous structures without grains. Rather, the limiting factor for the hardness is the stiffness of the amorphous network, which ultimately is dependent on the strength and density of the bonds in the system. In a study on

amorphous SiC it was suggested that the hardness of the samples is directly related to the density of Si-C bonds in the films, and independent on the actual composition of the films⁴³. A similar explanation could hold for why the two amorphous samples here, A4 and B2, with different composition, exhibit the same hardness behavior.

The complexity of the multicomponent system and its relatively large number of possible binary components make it difficult to determine what bond, or what set on bonds, are decisive for the hardness of the samples. The small variations in hardness with increasing annealing temperatures up to 800 °C can be related to simultaneous densification and stress relaxation, and the large decrease in hardness at 1000 °C and above is likely due to inter-diffusion of Co from the substrate. Yet it is noteworthy how small variations there are for the amorphous coatings in their mechanical properties around a level corresponding to bulk TiN (20-21 GPa^{44,45}) over a wide range of annealing temperatures. This is certainly due to their unusually homogeneous and dense structure, as realized herein.

IV. CONCLUSIONS

Hard amorphous Ti-B-Si-N and Ti-B-Si-Al-N coatings were grown by cathodic arc evaporation. The as-deposited Ti-B-Si-Al-N coatings contain greatly dispersed 2-3 nm crystallites, much more isolated than those in Ti-B-Si-N coatings, as determined by x-ray diffraction and transmission electron microscopy. The amorphous phase is otherwise homogeneous at atomic resolution in HR-TEM, and dense. The coatings crystallize by coarsening of nanocrystallites, preferentially in Ti-rich layers induced during deposition by substrate rotation and preferential resputtering of lighter elements. The amorphous nitrides have a hardness of 17-18 GPa in the as-deposited state, but can age harden to ~21 GPa with retained reduced elastic modulus up to 800 °C. At 1000 °C and above in-diffusion of Co from the substrate causes a decrease in hardness.

V. ACKNOWLEDGMENTS

This work was supported by the Swedish Research Council. H.F. would also like to acknowledge the SSF-project Designed Multicomponent Coatings, MultiFilms, for financial support. Uppsala University is acknowledged for access to the Tandem Laboratory for ERDA-measurements.

- ¹L. Shizhi, S. Yulong, and P. Hongrui, Plasma Chem. Plasma P. **12**, 287 (1992).
- ²P. Hedenqvist, M. Bromark, M. Olsson, S. Högmark, and E. Bergmann, Surf. Coat. Tech. **63**, 115 (1994).
- ³A. Hörling, L. Hultman, M. Odén, J. Sjölen, and L. Karlsson, J. of Vac. Sci. Technol. A **20**, 1815 (2002).
- ⁴D. McIntyre, J. E. Greene, G. Håkansson, J.-E. Sundgren, and W.-D. Münz, J. Appl. Phys. **67**, 1542 (1990).
- ⁵L. A. Donohue, I. J. Smith, W.-D. Münz, I. Petrov, and J. E. Greene, Surf. Coat. Tech. **94-95**, 226 (1997).
- ⁶A. Ingason, F. Magnus, J. Agustsson, S. Olafsson, and J. Gudmundsson, Thin Solid Films **517**, 6731 (2009).
- ⁷P. Holubář, M. Jílek, and M. Šíma, Surf. Coat. Tech. **120-121**, 184 (1999).
- ⁸R. Wiedemann, V. Weihnacht, and H. Oettel, Surf. Coat. Tech. **116-119** (1999).
- ⁹J. P. Chu, J. Jang, J. Huang, H. Chou, Y. Yang, J. Ye, Y. Wang, J. Lee, F. Liu, P. Liaw, Y. Chen, C. Lee, C. Li, and C. Rullyani, Thin Solid Films **520**, 5097 (2012).
- ¹⁰C. Michaelsen, C. Gente, and R. Bormann, J. Appl. Phys. **81**, 6024 (1997).
- ¹¹H. Hecht, G. Weigang, S. Eickert, and U. Geyer, Z. Phys. B Con. Mat. **100**, 47 (1996).
- ¹²S. Veprek, J. Vac. Sci. Technol. A **17**, 2401 (1999).
- ¹³B. deB. Darwent, National Standard Reference Data Series, National Bureau of Standards, No. 31 (1970).
- ¹⁴T. L. Cottrell, *The Strengths of Chemical Bonds* (Butterworths Publications Ltd., London, 1958).
- ¹⁵H. Fager, J. M. Andersson, J. Lu, M. P. Johansson Jöesaar, M. Odén and L. Hultman, Surf. Coat. Tech. **235**, 376 (2013).
- ¹⁶T. K. Chen, T. T. Shun, J. W. Yeh, and M. S. Wong, Surf. Coat. Tech. **188**, 193 (2004).
- ¹⁷J. Jensen, D. Martin, A. Surpi, and T. Kubart, Nucl. Instrum. Meth. B **268**, 1893 (2010).
- ¹⁸M. Janson, "CONTES conversion of time-energy spectra - a program for ERDA data analysis," Internal Report, Uppsala University (2004).
- ¹⁹W. Oliver and G. Pharr, J. Mater. Res. **7**, 1564 (1992).
- ²⁰A. Flink, T. Larsson, J. Sjölen, L. Karlsson, and L. Hultman, Surf. Coat. Tech. **200**, 1535 (2005).
- ²¹A. Eriksson, N. Ghafoor, J. Jensen, L.-Å. Näslund, M. Johansson, J. Sjölen, M. Odén, L. Hultman, and J. Rosen, Surf. Coat. Tech. **213**, 145 (2012).
- ²²TiN, "Powder Diffraction File: 00-038-1420," JCPDS International Centre for Diffraction Data (2010).
- ²³AlN, "Powder Diffraction File: 00-025-1133," JCPDS International Centre for Diffraction Data (2010).
- ²⁴TiB₂, "Powder Diffraction File: 00-035-0741," JCPDS International Centre for Diffraction Data (2010).
- ²⁵Co, "Powder Diffraction File: 00-015-0806," JCPDS International Centre for Diffraction Data (2010).
- ²⁶AlB₂, "Powder Diffraction File: 00-039-1483," JCPDS International Centre for Diffraction Data (2010).
- ²⁷BN, "Powder Diffraction File: 00-060-0209," JCPDS International Centre for Diffraction Data (2010).
- ²⁸J. Andersson, J. Vetter, J. Müller, and J. Sjölen, Surf. Coat. Tech. **240**, 211 (2014).
- ²⁹A. Flink, J. M. Andersson, B. Alling, R. Daniel, J. Sjölen, L. Karlsson, and L. Hultman, Thin Solid Films **517**, 714 (2008).
- ³⁰J. C. Slater, J. Chem. Phys. **41**, 3199 (1964).
- ³¹J.-E. Sundgren, B. Johansson, A. Rockett, S. Barnett, and J. Greene, American Institute of Physics Series 149 Physics and Chemistry of Protective Coatings, edited by J.E. Greene and W.D. Sproul and J.A. Thornton (1986).
- ³²P. H. Mayrhofer, C. Mitterer, and H. Clemens, Adv. Eng. Mater. **7**, 1071 (2005).
- ³³J. Sjölen, L. Karlsson, S. Braun, R. Murdey, A. Hörling, and L. Hultman, Surf. Coat. Tech. **201**, 6392 (2007).
- ³⁴A. Eriksson, J. Zhu, N. Ghafoor, M. Johansson, J. Sjölen, J. Jensen, M. Odén, L. Hultman, and J. Rosén, Surf. Coat. Tech. **205**, 3923 (2011).
- ³⁵C.-L. Chang, C.-T. Lin, P.-C. Tsai, W.-Y. Ho, and D.-Y. Wang, Thin Solid Films **516**, 5324 (2008).
- ³⁶S.-M. Yang, Y.-Y. Chang, D.-Y. Lin, D.-Y. Wang, and W. Wu, Surf. Coat. Tech. **202**, 2176 (2008).
- ³⁷M. Balzer, H. Karrl, H. Jehn, and V. Güther, Surf. Coat. Tech. **116-119**, 766 (1999).
- ³⁸P. Karvankova, M. Veprek-Heijman, O. Zindulka, A. Bergmaier, and S. Veprek, Surf. Coat. Tech. **163-164**, 149 (2003).
- ³⁹J. Neidhardt, Z. Czigány, B. Sartory, R. Tessadri, M. O'Sullivan, and C. Mitterer, Acta Mater. **54**, 4193 (2006).
- ⁴⁰J. Neidhardt, M. O'Sullivan, A. Reiter, W. Rechberger, W. Grogger, and C. Mitterer, Surf. Coat. Tech. **201**, 2553 (2006).
- ⁴¹J. Neidhardt, Z. Czigány, B. Sartory, R. Tessadri, and C. Mitterer, Int. J. Refract. Met. H. **28**, 23 (2010).
- ⁴²CoTa₂, "Powder Diffraction File: 01-071-7590," JCPDS International Centre for Diffraction Data (2010).
- ⁴³M. El Khakani, M. Chaker, A. Jean, S. Boily, and J. Kieffer, J. Mater. Res. **9**, 96 (1994).
- ⁴⁴H. Holleck, J. Vac. Sci. Technol. A **4**, 2661 (1986).
- ⁴⁵H. Kuwahara, N. Mazaki, M. Takahashi, T. Watanabe, X. Yang, and T. Aizawa, Mater. Sci. Eng. A-Struct. **319-321**, 687 (2001).