



# Article Structural, Mechanical, and Thermal Properties of the TiAlTaN/TiAlBN Multilayer

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Abstract: A multilayer structure and incorporation of the fourth element are promising strategies to improve the properties of TiAlN coatings. In this study, the structural, mechanical, and thermal properties of the Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N/Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N multilayer, as well as the Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N and Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N monolithic coatings, were carefully researched. Coherent growth of the multilayer structure induces a single-phase cubic structure of the Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N/Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N coatings have a single-phase cubic structure and a mixed cubic and wurtzite structure, respectively. The Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N/Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N multilayer reveals a higher hardness of 38.2 ± 0.9 GPa due to interfacial strengthening, corresponding to 32.4 ± 0.6 GPa of Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N and 32.7 ± 0.9 GPa of Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N. During annealing, our three kinds of coating demonstrate an age-hardening effect. The Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N/Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N multilayer presents a hardness peak of 40.0 ± 0.9 GPa at 1000 °C, whereas the Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N and Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N coatings show the hardness peaks of 37.1 ± 0.7 and 35.0 ± 0.6 GPa at 900 °C, respectively. Furthermore, the improved oxidation resistance is obtained by the Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N/Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N multilayer.

Keywords: TiAlTaN/TiAlBN; multilayer; hardness; thermal stability; oxidation resistance

# 1. Introduction

Metastable TiAlN coatings have been used extensively in the machining industry to improve the cutting performance of cutting tools for their superb mechanical and thermal properties [1–3]. The thermal decomposition process of TiAlN coatings attracts researchers' attention. On the hand, the spinodal decomposition of supersaturated cubic TiAlN into nanosized Al-rich and Ti-rich domains leads to an excellent age-hardening effect [4,5]. On the other hand, with further increase in thermal load, the metastable cubic (c) Al-rich domain would gradually transform into stable wurtzite (w) AlN phase [6], which worsens its mechanical properties [7]. Furthermore, the oxidation resistance is another critical factor for surface-covered coatings in several significant industrial properties [8]. The oxidation resistance of TiAlN coatings is inadequate to meet the current growing demand, as the oxidation temperature is lower than 850  $^{\circ}$ C [9].

Numerous modification methods have been developed to improve the performance of TiAlN coatings. Alloying various elements into TiAlN coatings have been one of the main strategies [10], such as Ta [11–14], B [15–18], V [19], Zr [20], Si [15,21], etc. For instance, many reports show that TiAlN alloying with Ta can increase its hardness and fracture toughness [22,23]. Ta-incorporation also improves thermal stability by delaying the w-AlN formation and perfects the oxidation resistance via inhibiting the formation of a-TiO<sub>2</sub> [13,14,24]. B-addition can modify the properties of TiAlN coatings based on theoretical calculations and experiments. From our previous studies, the addition of B positively affects oxidation resistance by promoting the generating of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [16,25]. Nevertheless, alloying with B reduces the solid solubility of Al in c-TiN and thus promotes the formation of wurtzite AlN phases, which weakens its hardness [16].



Citation: Li, Z.; Chen, L.; Zhang, J.; Sun, X. Structural, Mechanical, and Thermal Properties of the TiAlTaN/TiAlBN Multilayer. *Coatings* 2022, *12*, 1951. https://doi.org/ 10.3390/coatings12121951

Academic Editor: Alexander D. Modestov

Received: 12 November 2022 Accepted: 9 December 2022 Published: 12 December 2022

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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Multilayered architecture is another promising strategy to enhance its properties, which can effectively improve its hardness, wear resistance, and thermal stability, etc. [26,27]. Some studies have reported that TiAlTaN/TiAlN [11], TiAlN/TaAlN [14], and TiAlBN/TiAlN [28] multilayers demonstrate superior mechanical and thermal properties than their corresponding monolithic coatings. Multilayers can combine the advantages of corresponding monolithic coatings [23,28]. Moreover, coherent interfaces promote spinodal decomposition due to the interface-directed effect, which refines the thermal stability of the coating [29,30].

Based on these effective methods, we committed to building a TiAlTaN/TiAlBN multilayer that can combine the advantages of both TiAlTaN and TiAlBN coatings. Correspondingly, for TiAlTaN/TiAlBN multilayer and TiAlTaN, TiAlBN monolithic coatings, we scientifically studied their structure, mechanical, and thermal properties.

#### 2. Materials and Methods

The TiAlTaN/TiAlBN multilayer and TiAlTaN and TiAlBN monolithic coatings were synthesized by commercial cathodic arc evaporation equipment (Oerlikon Balzers IN-NOVA, Balzers, Liechtenstein) with the deposition parameters of an N<sub>2</sub> pressure of ~3.2 Pa, a temperature of 550 °C, a substrate bias of -40 V, and a target current of 180 A. A variety of substrates were used to meet different experimental requirements, including cemented carbide (WC-6 wt.% Co), low alloy steel foils, polycrystalline corundum plates, and tungsten (W) sheets. Before deposition, all these substrates were cleaned by the ultrasonic wave in alcohol and acetone and then etched in an atmosphere of argon. TiAlTaN and TiAlBN monolithic coatings were deposited by Ti<sub>0.30</sub>Al<sub>0.60</sub>Ta<sub>0.10</sub> and Ti<sub>0.35</sub>Al<sub>0.60</sub>B<sub>0.05</sub> powder metallurgical targets (99.99% purity), respectively. Meanwhile, TiAlTaN/TiAlBN multilayers were prepared from two Ti<sub>0.30</sub>Al<sub>0.60</sub>Ta<sub>0.10</sub> and two Ti<sub>0.35</sub>Al<sub>0.60</sub>B<sub>0.05</sub> targets by spinning substrates with a rotary speed of 2.2 r/min. More information about the preparation of the multilayer is outlined in reference [31]. Figure 1 displays the deposition schematic diagram of TiAlTaN/TiAlBN multilayers in the arc evaporation equipment.



**Figure 1.** A schematic diagram of the deposition system containing the sample fixture and positions of targets for TiAlTaN/TiAlBN multilayers.

Coating powder samples were prepared to eliminate the impact of the substrate on the annealing and oxidation experiments. To eliminate the intervention of the substrate, coatings deposited on low-alloyed steel sheets were etched by 10 mol% nitric acids to separate the coating from the substrate. After filtration, cleaning, drying, and grinding, pure powder samples were obtained. Coating powder samples were executed by a differential scanning calorimeter (DSC, Netzsch QMS 403 Aëolos, Netzsch, Selb, Germany) in pure Ar gas (99.99% purity, 20 sccm flow rate) to the specified temperatures ( $T_a = 800, 900, 1000, 1100, 1200, 1300, and 1450 \,^\circ$ C) at a programming rate of 10 K/min and then immediately cooling down to room temperature at a rate of 50 K/min. Coated W pieces were annealed in a vacuum furnace (COD533R, pressure  $\leq 10^{-3}$  Pa) for 30 min at given temperatures with a heating rate of 10 K/min and then cooled in the furnace.

Powder samples were oxidized at the target temperature (Set a  $T_a$  every 100 °C from 800 to 1200 °C)to evaluate the oxidation resistance of our coatings. The process was conducted with a heating rate of 10 K/min and then a cooling rate of 50 K/min in a synthetic air (79 vol% N<sub>2</sub>, 21 vol% O<sub>2</sub>, 20 sccm flowing rate) atmosphere by DSC equipment. Coated corundum sheets were isothermally oxidized in the DSC device with synthetic air at 950 °C for 10 h. Moreover, reference [19] provides more information on the annealing and oxidation treatments.

The fracture cross-section of the deposited and oxide coatings was conducted by scanning electron microscopy (SEM, Zeiss Supre 55, Zeiss, Jena, Germany). Energy dispersive X-ray spectroscopy (EDX), equipped with SEM, was utilized to investigate the chemical composition and line scan profiles. Moreover, light element B was recharacterized using inductively coupled plasma mass spectrometry (ICP-mass, ELAN DRC-e, ELAN, Hsinchu, China) to compensate for the insufficiency of EDX measurement. XRD measurements with Cu (K $\alpha$ ) radiation using a Bruker D8 in Bragg-Brentano arrangement operated at 40 mA and 40 kV were employed to investigate the structural evolution of powder specimens in different experiments during annealing and oxidation. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM, FEI Titan G2 60–300, FEI, Hillsborough, NC, USA) with a field emission gun operating at 300 kV were applied to determine the microstructure of the TiAlTaN/TiAlBN multilayer in detail. Before TEM and STEM characterization, the dual-beam focused ion beam (FIB) system (FEI Helios Nanolab 600I, FEI, Hillsborough, NC, USA) was used to strip the atoms on the sample's surface, and the thickness of the piece was thinned to less than 50 nm. The nanoindenter with a Berkovich diamond indenter tip was used to measure the hardness and elastic modulus. Measurements were under an applied load of 15nN following the Oliver and Pharr method [32]. The average and error values were conducted and calculated from more than twenty indents on each sample.

#### 3. Results and Discussion

#### 3.1. Microstructure and Mechanical Properties

To simplify notations, the atomic ratios of (Ti + Al + Ta)/N and (Ti + Al + B)/N are approximately normalized to 1:1. According to EDX and ICP-mass, the nominal components of TiAlTaN and TiAlBN monolithic coatings are  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  and  $Ti_{0.42}Al_{0.54}B_{0.04}N$ , respectively. The ionization rates of various elements during arc evaporation, gas scattering, and the resputtering procedure are the main reasons for the minor composition variation between the coating and the corresponding target [33]. The XRD patterns of  $Ti_{0.42}Al_{0.54}B_{0.04}N$ ,  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  monolithic, and  $Ti_{0.34}Al_{0.48}Ta_{0.18}N/Ti_{0.42}Al_{0.54}B_{0.04}N$  multilayered coatings are shown in Figure 2, and the inserted image in Figure 2 is a partially enlarged view of the XRD pattern of  $Ti_{0.42}Al_{0.54}B_{0.04}N$  coating at this position.

The Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N coating emerges as a cubic and wurtzite dual-phase structure. However, the Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N coating exhibits a single cubic structure. It agrees with the previous research; the Ta and B additions have a reverse effect on the solid solubility of Al in c-TiN (ICDD 00-038-1420) [16,34,35]. The single cubic structure of the Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N/Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N multilayer suggests the epitaxial growth between the Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N and Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N sublayers. The substitution solution of Ta with a larger atomic radius (1.46 Å) induces a larger lattice constant of 4.192  $\pm$  0.001 Å, compared to 4.150  $\pm$  0.001 Å for Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N. The diffraction peaks of our multilayer are situated between these two monolithic coatings, corresponding to the lattice constant of 4.163  $\pm$  0.001 Å. The growth morphology of the Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N, Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N coatings are demonstrated in the SEM fracture cross-section of Figure 3.



Figure 2. The (a) XRD patterns and (b) lattice constants of  $Ti_{0.42}Al_{0.54}B_{0.04}N$ ,  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  and  $Ti_{0.34}Al_{0.48}Ta_{0.18}N/Ti_{0.42}Al_{0.54}B_{0.04}N$  coatings.



Figure 3. SEM fracture cross-sections of the (a)  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$ , (b)  $Ti_{0.42}Al_{0.54}B_{0.04}N$ , and (c)  $Ti_{0.34}Al_{0.48}Ta_{0.18}N/Ti_{0.42}Al_{0.54}B_{0.04}N$  coatings.

The  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  coating (~3.66  $\mu m$ ) shows a distinct columnar growth morphology. As shown in Figure 3b, a distinct difference in the growth morphology of the  $Ti_{0.42}Al_{0.54}B_{0.04}N$  coating (~3.04  $\mu m$ ) can be observed. The competitive growth of cubic and wurtzite phases interrupts the columnar growth and thus leads to a featureless morphology. However, the  $Ti_{0.34}Al_{0.48}Ta_{0.18}N/Ti_{0.42}Al_{0.54}B_{0.04}N$  coating (~2.77  $\mu m$ ) reveals a columnar growth morphology again. It is related to the signal cubic structure arising from the coherent growth between the  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  and  $Ti_{0.42}Al_{0.54}B_{0.04}N$  sublayers.

Crossing TEM analyses were conducted to further investigate the interfacial structure of  $Ti_{0.34}Al_{0.48}Ta_{0.18}N/Ti_{0.42}Al_{0.54}B_{0.04}N$  multilayer interfacial structure. The TEM brightfield (BF) image demonstrates a clear columnar growth with well-defined alternating bright  $Ti_{0.42}Al_{0.54}B_{0.04}N$  and dark  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  layers, depicted in Figure 4a. The selected area electron diffraction (SAED) image specifically indicates a single-phase cubic structure, consistent with the above XRD results. According to the high-resolution transmission electron microscope (HRTEM) image in Figure 4b, the coherent growth between the  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  and  $Ti_{0.42}Al_{0.54}B_{0.04}N$  sublayers can be affirmed by the continuing lattice fringes across several adjacent bilayer periods. It is illustrated more clearly in the filtered inverse fast Fourier transformation (IFFT) image. The Z-contrast STEM high angle annular dark-field (HAADF) image in Figure 4c explicates that the bilayer period is ~6.5 nm, consisting of bright  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  (~3.6 nm) and dark  $Ti_{0.42}Al_{0.54}B_{0.04}N$  (~2.9 nm) sublayers.

----- c-TiN; ----- w-AIN



**Figure 4.** (a) Cross-sectional TEM bright-field with an inset of SAED pattern, (b) the HRTEM image with the IFFT image, and (c) the STEM HAADF picture of the  $Ti_{0.34}Al_{0.48}Ta_{0.18}N/Ti_{0.42}Al_{0.54}B_{0.04}N$  multilayer.

As shown in Figure 5, the deposition hardness, elastic modulus, and  $H^3/E^2$  ratio of our  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$ ,  $Ti_{0.42}Al_{0.54}B_{0.04}N$ , and  $Ti_{0.34}Al_{0.48}Ta_{0.18}N/Ti_{0.42}Al_{0.54}B_{0.04}N$  coatings are exhibited. The  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  and  $Ti_{0.42}Al_{0.54}B_{0.04}N$  monolithic coatings exhibit a similar hardness, with values of  $32.4 \pm 0.9$  and  $32.7 \pm 0.9$  GPa, respectively. The interfacial strengthening and grain refinement causes a higher hardness of  $38.2 \pm 0.9$  GPa for the  $Ti_{0.34}Al_{0.48}Ta_{0.18}N/Ti_{0.42}Al_{0.54}B_{0.04}N$  multilayer [23,36,37]. Furthermore, this hardening can be attributed to its overall cubic structure, corresponding to the mixed c/w- $Ti_{0.42}Al_{0.54}B_{0.04}N$  coating. The w-AlN formation of the  $Ti_{0.42}Al_{0.54}B_{0.04}N$  coating induces the lowest indentation modulus of  $418.8 \pm 8.9$  GPa, whereas the indentation modulus of the  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  and  $Ti_{0.34}Al_{0.48}Ta_{0.18}N/Ti_{0.42}Al_{0.54}B_{0.04}N$  coatings are  $457.6 \pm 10.4$  and  $486.4 \pm 14.0$  GPa, respectively. Consequently, the  $Ti_{0.34}Al_{0.48}Ta_{0.18}N/Ti_{0.42}Al_{0.54}B_{0.04}N$  multilayer reveals a maximum  $H^3/E^2$  ratio of 0.24, which means it has the best resistance of materials to plastic deformation [38].



**Figure 5.** The hardnesses (H), elastic moduli (E), and  $H^3/E^2$  ratios of  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$ ,  $Ti_{0.42}Al_{0.54}B_{0.04}N$  monolithic, and  $Ti_{0.34}Al_{0.48}Ta_{0.18}N/Ti_{0.42}Al_{0.54}B_{0.04}N$  multilayered coatings.

#### 3.2. Thermal Stability

Figure 6 displays the XRD patterns of the powdered samples after annealing. As shown in Figure 6a, the original diffraction peaks of  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  slightly move to higher 2 $\theta$  angles after annealing at  $T_a = 800$  and 900 °C, suggesting the recovery and relaxation processes. When  $T_a$  reaches 1000 and 1100 °C, the shoulder peaks of (111) and (200) matrix diffraction peaks mean the spinodal decomposition towards metastable c-Ti(Ta)N-rich and c-AlN-rich domains. The c-AlN-rich domain conversion into stable w-AlN occurs at  $T_a = 1200$  °C, where a tiny diffraction signal at ~33.2 and ~36.1° can be observed. At  $T_a = 1300$  and 1450 °C, the  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  decomposes entirely into the stable phases c-Ti(Ta)N and w-AlN. Annealing of  $Ti_{0.42}Al_{0.54}B_{0.04}N$  between 900 and 1000 °C leads to a broader diffraction peak of the cubic structured matrix phase, (see Figure 6b,) indicative of the spinodal decomposition. Simultaneously, a slight move to a higher 2 $\theta$  position and an increased intensity in the diffraction peaks of wurtzite structured matrix phases means the decomposition towards stable phases c-TiN and w-AlN. With further annealing at  $T_a \geq 1200$  °C, the  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  almost decomposes into its stable

phases c-Ti(B)N and w-AlN. The Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N/Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N multilayer behaves in a similar thermal decomposition process with Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N, (see Figure 6c,) where the spinodal decomposition and w-AlN formations temperatures are 1000 and 1200 °C, respectively, followed by an entire decomposition at T<sub>a</sub> = 1300 and 1450 °C.



Figure 6. XRD patterns of (a)  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$ , (b)  $Ti_{0.42}Al_{0.54}B_{0.04}N$ , and (c)  $Ti_{0.34}Al_{0.48}Ta_{0.18}N/Ti_{0.42}Al_{0.54}B_{0.04}N$  after annealing at setting temperatures.

The structural evolutions proceeding during the annealing of investigated coatings lead to the change in hardness. All coatings reveal an age-hardening effect, (see Figure 7) which arises from the coherent strain between the products of spinodal decomposition (c-TiN-rich and c-AlN-rich domains) and remaining matrix [39]. The Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N and Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N coatings reach the hardness peaks of  $35.0 \pm 0.6$  GPa and  $37.1 \pm 0.7$  GPa at T<sub>a</sub> = 900 °C, respectively, while the peak hardness of  $40.0 \pm 0.9$  GPa for the Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N/Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N multilayer appears at T<sub>a</sub> = 1000 °C. Further annealing with raised temperature leads to a drop in hardness due to the coarsening of c-TiN-rich and c-AlN-rich domains along with the transition towards w-AlN. By contrast, the hardness of Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N coating presents a mild downtrend. Ultimately, as T<sub>a</sub> = 1200 °C, the hardness of Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N, Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N, and Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N/Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N, and Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N/Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N



**Figure 7.** The hardness of  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$ ,  $Ti_{0.42}Al_{0.54}B_{0.04}N$  monolithic, and  $Ti_{0.34}Al_{0.48}Ta_{0.18}N/Ti_{0.42}Al_{0.54}B_{0.04}N$  multilayered coatings as a function of annealing temperatures.

## 3.3. Oxidation Resistance

As shown in Figure 7, XRD determinations of powdered coatings after oxidation at specific temperatures in the synthetic air are performed to investigate the oxidation resistance. No oxidic product can be observed after the oxidation of  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  at 800 °C, see Figure 8a. Further oxidation at 900 and 1000 °C brings about the formation of rutile (r-) TiO<sub>2</sub> (ICDD 00-021-1276) as well as the concomitant spinodal decomposition. Except for the enhanced intensity of r-TiO<sub>2</sub> diffraction peaks, the diffraction peaks of corundum ( $\alpha$ -) Al<sub>2</sub>O<sub>3</sub> (ICDD 00-046-1212) appear with oxidation temperature increased to 1100 °C. Here, the diffraction peaks of the remaining coatings can be still observed. Eventually, the  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  has been fully oxidized, leaving the oxidation products of r-TiO<sub>2</sub>,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, and h-Ta<sub>2</sub>O<sub>5</sub> (ICDD 00-018-1304) at 1200 °C. After oxidation of Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N at 800 °C, (see Figure 7b,) the appearance of metastable anatase (a-) TiO<sub>2</sub> (ICDD 00-021-1272) hints the worse oxidation resistance than Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N. The transformation of metastable anatase a-TiO<sub>2</sub> into its stable r-TiO<sub>2</sub> occurs at 900 °C. Further oxidation at 1000 °C leads to the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> formation. With the oxidation temperature increasing to 1100 °C, the Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N has been completely oxidized, where the TiO<sub>2</sub> transformation finishes. Additionally, the orthorhombic (0-)Al<sub>5</sub>(BO<sub>3</sub>)O<sub>6</sub> (ICD 00-034-1039) of B-containing oxide can be observed. The Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N/Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N multilayer presents a similar oxidation process with  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  except for the anatase-to-rutile  $TiO_2$  transformation instead of the direct formation  $r-TiO_2$  (see Figure 7c). This difference can be ascribed to the lower Ta content [13,14,24]. The onset temperatures of r-TiO<sub>2</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are 900 and 1100  $^{\circ}$ C, respectively, where the end temperatures of anatase-to-rutile TiO<sub>2</sub> transformation and complete oxidation are 1100 and 1200 °C.



**Figure 8.** XRD patterns of (a)  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$ , (b)  $Ti_{0.42}Al_{0.54}B_{0.04}N$ , and (c)  $Ti_{0.34}Al_{0.48}Ta_{0.18}N/Ti_{0.42}Al_{0.54}B_{0.04}N$  after oxidation in synthetic air at setting temperatures.

Further oxidation of coated polycrystalline corundum plates was conducted at 950 °C for 10 h in synthetic air to better explore their oxidation resistance. Figure 9 exhibits the cross-sectional SEM line scan images of  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  and  $Ti_{0.34}Al_{0.48}Ta_{0.18}N/Ti_{0.42}Al_{0.54}B_{0.04}N$  coatings, where the  $Ti_{0.42}Al_{0.54}B_{0.04}N$  coating has been completely oxidized (not shown).  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  and  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  and  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  and  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  coating state a bilayer oxide scale with an Al-rich top-layer and Ti-rich interlayer. The oxide scales of  $Ti_{0.34}Al_{0.48}Ta_{0.18}N/Ti_{0.42}Al_{0.54}B_{0.04}N$  coatings are ~2.07 and ~1.25 µm, respectively, which indicates that the  $Ti_{0.34}Al_{0.48}Ta_{0.18}N/Ti_{0.42}Al_{0.54}B_{0.04}N$  multilayer possesses the best oxidation



resistance. This drop in the oxide scale is mainly attributed to the Ti-rich interlayer, which suggests the combined effect of Ta and B retards the growth of the Ti-rich interlayer.

**Figure 9.** The SEM fracture cross-sections and EDX line scan profiles of (**a**)  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  monolithic and (**b**)  $Ti_{0.34}Al_{0.48}Ta_{0.18}N/Ti_{0.42}Al_{0.54}B_{0.04}N$  multilayered coatings after isothermal oxidation in synthetic air at 950 °C for 10 h.

## 4. Conclusions

In this work, the structural, mechanical, and thermal properties of Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N,  $Ti_{0.34}Al_{0.48}Ta_{0.18}N/Ti_{0.42}Al_{0.54}B_{0.04}N$  $Ti_{0.42}Al_{0.54}B_{0.04}N$ , and coatings are studied. The Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N coating shows a single cubic structure, while the Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N coating demonstrates a cubic and wurtzite dual-phase structure. The templating effect of the cubic  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  sublayer brings a single-phase cubic structure to the  $Ti_{0.34}Al_{0.48}Ta_{0.18}N/$ Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N multilayer. The interfacial strengthening of the multilayer leads to a significantly increased hardness to  $38.2 \pm 0.9$  GPa for the Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N/Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N multilayer, where the hardness of the Ti\_{0.34}Al\_{0.48}Ta\_{0.18}N and Ti\_{0.42}Al\_{0.54}B\_{0.04}N coatings are 32.4  $\pm$  0.9 and  $32.7 \pm 0.9$  GPa, respectively. All coatings during annealing present age-hardening abilities due to spinodal decomposition. The hardness peak of the Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N/Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N multilayer with the value of  $40.0 \pm 0.9$  GPa appears at 1000 °C, whereas the Ti<sub>0.34</sub>Al<sub>0.48</sub>Ta<sub>0.18</sub>N and  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  coatings at 900 °C show hardness peaks of 37.1  $\pm$  0.7 and 35.0  $\pm$  0.6 GPa, respectively. This indicates a better thermal stability of the multilayer. Furthermore, the  $Ti_{0.34}Al_{0.48}Ta_{0.18}N/Ti_{0.42}Al_{0.54}B_{0.04}N$  multilayer behaves with the best oxidation resistance. After oxidation at 950 °C for 10 h, the Ti<sub>0.42</sub>Al<sub>0.54</sub>B<sub>0.04</sub>N has been completely oxidized, whereas the oxide scales of  $Ti_{0.34}Al_{0.48}Ta_{0.18}N$  and  $Ti_{0.34}Al_{0.48}Ta_{0.18}N/Ti_{0.42}Al_{0.54}B_{0.04}N$  coatings are ~2.07 and ~1.25 µm, respectively.

**Author Contributions:** Visualization, writing—original draft, Z.L.; conceptualization, methodology, funding acquisition, L.C.; investigation, J.Z. and X.S. All authors have read and agreed to the published version of the manuscript.

**Funding:** This study was financially supported by the National Natural Science Foundation of China: 51775560.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

**Acknowledgments:** Li Chen is grateful for the support of the State Key Laboratory of Powder Metallurgy of Central South University.

Conflicts of Interest: The authors declare no conflict of interest.

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