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Decomposition routes and strain evolution in arc deposited TiZrAlN coatings

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Abstract

Phase, microstructure, and strain evolution during annealing of arc deposited TiZrAlN coatings are studied using *in situ* x-ray scattering and *ex situ* transmission electron microscopy. We find that the decomposition route changes from nucleation and growth of wurtzite AlN to spinodal decomposition when the Zr-content is decreased and the Al-content increases. Decomposition of $\text{Ti}_{0.31}\text{Zr}_{0.24}\text{Al}_{0.45}\text{N}$ results in homogeneously distributed wurtzite AlN grains in a cubic, dislocation-dense matrix of TiZrN consisting of domains of different chemical composition. The combination of high dislocation density, variation of chemical composition within the cubic grains, and evenly distributed wurtzite AlN grains results in high compressive strains, -1.1 %, which are retained after 3 h at 1100 °C. In coatings with higher Zr-content, the strains relax during annealing above 900 °C due to grain growth and defect annihilation.

Keywords: Ti-Zr-Al-N; Hard coatings; Thermal stability; Strain evolution

1. Introduction

The complexity of wear resistant coatings used to sustain the harsh conditions of high-speed machining is steadily increasing. Such complexity enhancement is for example seen when TiAlN is used as a starting point and more alloying elements are added [1] and when nanostructured materials such as multilayers include TiAlN [2]. TiAlN exhibits age hardening related to the formation of a microstructure caused by spinodal decomposition consisting of isostructural, coherent, and nm-sized Al-rich and Ti-rich domains [3, 4]. Adding a fourth element to TiAlN drastically increases the complexity of the decomposition process and offers a way to tune the decomposition, the associated microstructure evolution and in extent, control the evolution of mechanical properties.

Several studies on for example phase stability, oxidation resistance, and mechanical properties reveal improved properties when alloying TiAlN with Cr, Zr or Nb of both as-deposited and heat treated samples [5-11]. In Cr-alloyed TiAlN coatings, the complexity of the quaternary alloys is illustrated by two competing mechanisms of decomposition, spinodal decomposition and nucleation and growth of w-AlN, controlled by the chemical composition of the material [12]. The varying microstructure that evolves during heat treatment due to different decomposition routes also affect the thermal stability of the formed CrAlN domains [13]. ZrAlN is a compound with a larger miscibility gap compared to TiAlN [14, 15] that frequently causes phase separation already during growth [16-20]. Quaternary TiZrAlN alloys can be synthesized with varying structures depending on the chemical composition [21] and the Zr alloying changes the high temperature properties compared to TiAlN [6, 22]. The complexity of quaternary systems requires input from theoretical studies in order to predict their behavior. Such data is becoming more available and detailed as the computing power is improved. Theoretical studies can for example predict phase stability and decomposition routes [1, 15], elastic properties [23, 24] and interface structures [25]. To predict the material behavior at elevated temperature, the knowledge on for example phase stability and elasticity needs to be linked to the evolution of strains and stresses in the coating, which are important aspects influencing how the mechanical properties evolve. In TiAlN coatings, the strain evolution during decomposition is mainly affected by the formation of w-AlN [26] since the larger molar volume of w-AlN compared to the cubic phases results in large compressive strains in the cubic phase. For quaternary Ti(X)AlN-alloys (X is a transition metal), the situation is more complex where, in addition to w-AlN, several cubic phases also might form during decomposition [5] and the evolving microstructure is highly dependent on chemical composition [13].

Here, we use the TiZrAlN system to study the effects of phase stability and decomposition route on the strain evolution. We have previously observed that the decomposition route for c-TiZrAlN coatings is highly dependent on the Zr-content [27]. Three c-TiZrAlN coatings with different chemical

composition were grown by cathodic arc evaporation, selected to have different phase stability according to theoretical predictions. The phase stability and strain evolution during annealing were studied by *in situ* wide-angle scattering experiments using high energy x-rays. Two decomposition mechanisms are observed, nucleation and growth of w-AlN mainly at column boundaries and spinodal decomposition of the c-TiZrAlN phase. For coatings with a high driving force for spinodal decomposition, this mechanism dominates resulting in formation of cubic domains enriched in either Zr or Ti and/or Al. In the coating with highest Al-content studied here ($\text{Ti}_{0.31}\text{Zr}_{0.24}\text{Al}_{0.45}\text{N}$), a dislocation-dense structure forms subsequent to spinodal decomposition, resulting in a highly strained, cubic phase after annealing at 1100 °C. For coatings with lower Al-content ($\text{Ti}_{0.21}\text{Zr}_{0.48}\text{Al}_{0.31}\text{N}$ and $\text{Ti}_{0.13}\text{Zr}_{0.69}\text{Al}_{0.18}\text{N}$), annealing above 900 °C results in strain relaxation related to grain growth. In summary, the results reveal that the decomposition route determines both the evolving microstructure and the strain state of the coatings, thus in extension also the mechanical properties. The theoretical predictions of the phase stability and the decomposition routes match the experimental results well and are essential to identify coatings with the right chemical composition for an optimized high temperature behavior.

2. Experimental details

TiZrAlN coatings were grown on polished WC-Co substrates (12 wt.% Co, ISO SNUN120408) using an Oerlikon Balzers Innova cathodic arc deposition system with a base pressure of less than 5×10^{-2} Pa. One $\text{Ti}_{33}\text{Al}_{67}$ and one Zr cathode were placed next to each other in the chamber to obtain different coating compositions along the dashed line in Figure 1a. Substrates were placed at three different positions S1-S3 as shown in Fig. 1b and the substrates were kept stationary during deposition (no rotation). The deposition was performed in a 3.5 Pa pure N_2 atmosphere, at an evaporation current of 160 A, a substrate temperature of 400 °C, and a negative substrate bias of 30 V. The deposition rate was approximately 170 nm/min.

Coating morphology and thickness were evaluated by scanning electron microscopy (SEM) of fractured cross-sectional samples using a LEO 1550 FEG-SEM. The chemical composition was determined by an Oxford X-Max electron dispersive x-ray spectroscopy (EDS) detector in the SEM, operated at an acceleration voltage of 20 kV. The detailed microstructure of as-deposited and annealed samples was studied by analytical (scanning) transmission electron microscopy (TEM/STEM) using either a FEI Technai G2 instrument operated at 200 kV or a FEI Titan3 G2 60-300 dual aberration-corrected TEM/STEM instrument. Cross-sectional samples for TEM were prepared either by mechanical polishing followed by Ar ion etching to electron transparency using a Gatan precision ion polishing instrument

or by focused ion beam milling using a 1540 EsB cross beam instrument. X-ray diffractometry (XRD) using a Panalytical Cubix diffractometer in θ -2 θ configuration and Cu-K α radiation was employed to establish the coating's phase content.

The hardness was evaluated by nanoindentation experiments on polished, tapered cross-sections using a UMIS 2000 system equipped with a Berkovich diamond tip and a load of 50 mN, resulting in indentation depths of 200-250 nm. The data was analyzed using the method of Oliver and Pharr [28] and the reported hardness is an average over 20 indents for each sample.

Figure 1: (a) Mixing free energy and tendency for spinodal decomposition for TiZrAlN showing samples S1, S2 and S3 [27], (b) Schematic illustration of the sample and cathode positions during deposition, and (c) illustration of the experimental setup during *in situ* WAXS annealing experiments. The surface normal (SN), the in-plane direction (IP) and the tilt angle (ψ) are indicated in (b).

In situ wide-angle x-ray scattering (WAXS) experiments during annealing were performed at the high-energy materials science beamline P07 at Petra III, DESY, Hamburg. Data was recorded in transmission geometry as schematically shown in Figure 1c and for this purpose samples, about 1 mm thick, were prepared. The samples were placed in a Ta-holder inside a boron-nitride coated graphite tube heater positioned inside a vacuum chamber. The pressure was kept below 0.67 mPa during the annealing experiment. The annealing sequence consisted of an initial step of constant heating rate to the maximum temperature, T_{max} , followed by a 3 h holding time at T_{max} and further cooling to room temperature using the same rate as for heating. A Eurotherm controller was used to control the temperature, and heating and cooling rates to 20 K/min. All three samples were heated to $T_{max} = 1100$ °C and for sample S1 an additional experiment was performed with $T_{max} = 900$ °C. The scattered x-rays were detected by a two-dimensional 400x400 mm² PerkinElmer detector with a pixel size of 0.2x0.2 mm². The wavelength was 0.168 Å or 0.231 Å since the measurements were performed at two different occasions. In each case, the detector was positioned to collect the complete cubic 111 and 200 diffraction rings and the exact sample-to-detector distance was determined by a LaB₆ NIST standard powder.

The two-dimensional data was integrated in 10°-wide bins centered at $\psi = 0^\circ$ (along the surface normal, SN) and in a bin centered at $\psi = 55^\circ$, to study the evolution of the cubic 200 and 111 peaks, respectively. The strain and stress was calculated using the $\sin^2\psi$ method. The plane spacing (d) of 200 was determined from data integrated in 5°-wide bins. Due to the texture of the coatings, the 200 signal could only be collected for $\psi = [0^\circ: \pm 35^\circ]$ and $\psi = [\pm 65^\circ: \pm 90^\circ]$. The d vs $\sin^2\psi$ dependence was assumed to be linear for the full $\psi = [0^\circ: \pm 90^\circ]$ range. The strain-free plane spacing was calculated at the invariant tilt angle ψ^* . Poisson's ratios and elastic moduli were taken from *ab initio* calculations [24] and are presented in Table 2.

Samples for microstructural investigations and hardness measurements were annealed using the same annealing chamber and annealing conditions as used during *in situ* experiments. Samples were annealed at 850 °C (ramping to 850 °C followed by immediate cooling to room temperature) and for 2 h at 1100 °C.

3. Results and Discussion

All three coatings exhibit a dense columnar structure with columnar widths of approximately 200-500 nm as observed from the fractured cross sectional SEM micrographs in Figure 2a. The thickness is between 8 and 13 μm (see Table 1). The chemical compositions of the samples as determined by EDS are S1: $\text{Ti}_{0.31}\text{Zr}_{0.24}\text{Al}_{0.45}\text{N}$, S2: $\text{Ti}_{0.21}\text{Zr}_{0.48}\text{Al}_{0.31}\text{N}$ and S3: $\text{Ti}_{0.13}\text{Zr}_{0.69}\text{Al}_{0.18}\text{N}$, also shown in Table 1. The variation in nitrogen-to-metal ratio between the samples as determined by EDS is small and is not further considered here.

Figure 2: (a) Fractured cross sections and (b) θ - 2θ diffractograms from the as-deposited coatings. (c) shows a two-dimensional diffraction pattern from the as-deposited S1 ($\text{Ti}_{0.31}\text{Zr}_{0.24}\text{Al}_{0.45}\text{N}$) sample. Diffraction signal from the substrate is labelled S. The in-plane (IP) and surface normal (SN) are marked in (b).

Table 1: Chemical composition determined by EDS and thickness of the as-deposited samples.

Sample	Composition	Ti at.%	Zr at.%	Al at.%	N at.%	Thickness (μm)
S1	$\text{Ti}_{0.31}\text{Zr}_{0.24}\text{Al}_{0.45}\text{N}$	15.0	11.8	22.5	50.8	9.6
S2	$\text{Ti}_{0.21}\text{Zr}_{0.48}\text{Al}_{0.31}\text{N}$	10.3	23.0	15.1	51.7	12.6
S3	$\text{Ti}_{0.13}\text{Zr}_{0.69}\text{Al}_{0.18}\text{N}$	6.0	32.8	8.8	52.4	8.3

Figure 2b shows θ -2 θ diffractograms from the as-deposited S1, S2 and S3 coatings. All three coatings reveal a 200 textured cubic structure. The weak diffraction peak centered at 43.5° is assigned to small amounts of a TiAlN phase. Figure 2c shows a two-dimensional WAXS diffraction pattern from the S1 coating confirming the 200-textured cubic structure. Similar diffraction patterns were also collected for the other two samples. The weaker signal at the bottom half of the image is due to absorption of diffracted x-rays by the WC-Co substrate. The strain-free lattice parameter extracted from the 2D data is presented in Table 2. It agrees well with the calculated lattice parameter for a solid solution c-TiZrAlN phase [24]. Table 2 also shows the strain and stress of the as-deposited samples as deduced by the $\sin^2\psi$ method. The stress is similar for S1 and S2 and slightly larger for S3. This is understood as an effect of S3 facing the Zr-cathode during growth which results in a larger amount of Zr-ions with a large mass and a high average charge state [29] and thus high ion energy arriving to the substrate, causing an increased amount of point defects. A similar trend was observed for TiAlN coatings [26] where the strain increased with increased Ti-content.

Figure 3 shows lineouts from 10° -wide bins centered at the 200 ($\psi = 0^\circ$) and 111 ($\psi = 55^\circ$) diffraction signal of S1 and S2 for different annealing times and temperatures. During heating to 1100°C , the c-TiZrAlN 200 peak shifts to larger d-values due to thermal expansion and a change in chemical composition as discussed further below. In the temperature range of 900 - 1050°C , both samples reveal additional broad peaks close to the 200 and 111 c-TiZrAlN diffraction peaks. For S1 (Fig. 3a), additional peaks appear both at smaller and higher d-values close to the c-TiZrAlN 200 (along the surface normal, $\psi=0^\circ$), 111 ($\psi=55^\circ$) and 220 ($\psi=45^\circ$, not shown) diffraction peaks. These peaks can be assigned to two additional cubic phases that form during the annealing stage, one with a smaller lattice parameter and one with a larger lattice parameter compared to the original c-TiZrAlN phase. For S2 (Fig. 3b), only the diffraction peaks attributed to a cubic phase with larger lattice parameter compared to the original c-TiZrAlN is observed in the lineouts. The additional cubic phases grow with approximately the same amount of mosaicity as the original cubic c-TiZrAlN phase in both samples, as determined by the width of the peak in the ψ -direction.

Table 2: Lattice parameter (a), strain and stress of the as-deposited samples. Shown is also the calculated values [24] for the lattice parameter (a), the elastic constants (E and ν) and the Zener anisotropy ratio (A).

Sample	a (meas) (Å)	Strain (%)	Stress (GPa)	a (calc) (Å)	E(100) (calc) (GPa)	ν (calc)	A (calc)
S1	4.29	-0.71	-2.6	4.285	370	0.216	1.3
S2	4.40	-0.73	-2.7	4.400	369	0.238	1.0
S3	4.47	-0.83	-3.5	4.480	420	0.243	0.80

Figure 3: Lineouts integrated in a bin centered at $\psi=0^\circ$ (left) and in a bin centered at $\psi=55^\circ$ (right) for (a) S1 ($\text{Ti}_{0.31}\text{Zr}_{0.24}\text{Al}_{0.45}\text{N}$) and (b) S2 ($\text{Ti}_{0.21}\text{Zr}_{0.48}\text{Al}_{0.31}\text{N}$).

The 200 diffraction peak of the cubic phase with a larger lattice parameter is centered at approximately 2.3-2.4 Å, where the smaller value is found for the low Zr-content coating (S1). This is close to the expected position of c-ZrN ($d_{\text{ZrN}200}=2.31$ Å at 1100 °C [30, 31]) and thus we attribute this peak to a Zr-rich c-(Ti)ZrN phase. The parenthesis indicates that small amounts of Ti might be present in this phase. The additional broad diffraction signal appearing at smaller d-values compared to the original c-TiZrAlN phase in S1 is likely a phase that is rich in Al or Ti. In addition, a peak from c-TiAlN is present in the as-deposited sample and observed at temperatures below 1050 °C. The amount of this phase is larger in S1 compared to S2. However, due to the small amount of c-TiAlN in the as-deposited sample, it is unlikely that this phase is the sole contribution to the shoulder and instead the shoulder contains additional contributions from Al- or Ti-rich phases that form during decomposition of c-TiZrAlN.

Figure 4 shows the change of the strain-free lattice parameter (a^*) with annealing temperature and time of the main c-TiZrAlN phase (giving the highest diffracted intensity) relative to the value of the as-deposited coatings. The lattice parameter was determined from the 200 diffraction line. For all three coatings, the linear increase of a^* between room temperature and approximately 600 °C is assigned to thermal expansion. For S3, the increase of the lattice parameter is linear up to 1100 °C, thus no other contributions than thermal expansion appear to be affecting the lattice parameter in this case. Table 3 presents the lattice parameters after 3 h at 1100 °C for the three samples. The small change in lattice parameter for S3 during annealing at 1100 °C indicates either a minor change in chemical composition of this phase or that annihilation of point defects (e.g. vacancies) affects the lattice parameter [32]. An earlier study revealed formation of AlN-rich precipitates during annealing at 1100 °C [27] for a coating with the same composition as S3. Thus, formation of small amounts of w-AlN in the coating is likely contributing to the change of lattice parameter. If all the Al is relocated from the cubic phase to w-AlN the lattice parameter of c-TiZrN would be 4.55 Å based on theoretical work [24]. Since the lattice parameter of S3 is smaller than this (see Table 3), the cubic phase still contains some Al.

Figure 4: Relative change in un-strained lattice parameter as a function of annealing temperature and time. Filled symbols represents isothermal annealing at 1100 °C and the open symbols the isothermal annealing of $\text{Ti}_{0.31}\text{Zr}_{0.24}\text{Al}_{0.45}\text{N}$ at 900 °C.

For S1 and S2, there is a change in expansion rate at 600 °C, indicating that the lattice parameter is affected by the decomposition or by annihilation of defects (e.g. vacancies) as well as the thermal expansion. Between 900 and 1100 °C, there is an additional change in expansion rate that is understood as depletion of Al from the cubic phase due to formation of w-AlN. For S1, this results in a drastic increase of the lattice parameter. The lattice parameter continues to increase slightly during isothermal annealing at 1100 °C suggesting that the chemical composition of the c-TiZrAlN phase continues to change throughout the 3 h long annealing. After the 3 h isothermal anneal, S1 shows the largest change of lattice parameter Δa , see Table 3. Some Al is still likely present in the c-TiZrAlN phase after annealing for 3 h considering that the lattice parameter is still increasing. For the same coating annealed at 900 °C, there is no drastic increase of the lattice parameter, thus temperatures above 900 °C are required to cause nucleation of w-AlN and a corresponding large change in chemical composition of the cubic phase. For S2, the lattice parameter is approximately constant during isothermal annealing, thus no or only small changes in chemical composition of the c-TiZrAlN phase occurs once 1100 °C has been reached. The main c-TiZrAlN phase may still contain some Al after annealing, similar to the case of the S3 sample.

Table 3: Lattice parameter (a) and strain of samples annealed for 3 h at 1100 °C samples. The strain is measured during annealing and the lattice parameter is the room temperature value after annealing. The change in lattice parameter (Δa) is the difference in value for the annealed and the as-deposited sample.

Sample	a (Å)	Δa (%)	Strain (%)
S1	4.40	2.4	-1.1
S2	4.45	1.1	-0.24
S3	4.50	0.6	-0.17

Figure 5 shows the strain of the main c-TiZrAlN phase (i.e. the phase giving the strongest diffraction signal) as a function of annealing temperature and time. An increase of the strain between room temperature and 600 °C of approximately 0.3 %, similar to the increase observed for the three samples, is estimated based on the difference in TEC of the substrate ($\sim 5 \times 10^{-6} \text{ K}^{-1}$ [33]) and the coating ($9.48 \times 10^{-6} \text{ K}^{-1}$ for $\text{Ti}_{0.75}\text{Al}_{0.25}\text{N}$ and $1.01 \times 10^{-5} \text{ K}^{-1}$ for $\text{Ti}_{0.50}\text{Al}_{0.50}\text{N}$ [34]). At temperatures above 800 °C the strain decreases for S3 as is commonly observed for arc deposited coatings due to defect annihilation and grain growth [26, 35]. In contrast, the strain increases at a faster rate between 600 °C and approximately 900 °C for both S2 and S1.

Figure 5: In-plane strain of the c-TiZrAlN phase as a function of annealing temperature and time. Filled symbols represents isothermal annealing at 1100 °C and the open symbols the isothermal annealing of S1 at 900 °C.

Figure 6 shows elemental contrast STEM (Figure 6a and c) and high-resolution HR-TEM (Figure 6b and d) cross-sectional micrographs along the [011] zone axis of S1 (Figure 6a and b) and S2 (Figure 6c and d) annealed at 850 °C. Both coatings consist of large, columnar grains predominantly oriented with the

cubic [100] direction along the surface normal (SN). During annealing at 850 °C, phase separation occurs in both samples. For S1, Figure 6a shows Al-rich domains (dark contrast) elongated in the elastically compliant <100> directions [24], throughout the coating thickness. Since the image is obtained along the [011] zone axis, the Al-rich domains are predominantly observed in the in-plane (IP) direction. Figure 6b shows a HR-TEM micrograph of the same sample with the corresponding FFT, revealing a cubic structure, also across the Al-rich precipitates (indicated with arrows). Sample S2, Figure 6c, shows large, bright contrast columnar grains together with dark contrast precipitates at column boundaries. The dark contrast precipitates observed in the column boundaries have a size of approximately 10 nm and are enriched in Al as confirmed by EDS. HR-TEM and FFT confirm that the largest of the precipitates are w-AlN (not shown). The diffraction signal from w-AlN cannot be observed in the 2D WAXS data and consequently the evolution of this phase cannot be determined from WAXS. One reason is that the signal from w-AlN overlaps with the broad diffraction signal from c-(Ti)ZrN. The broad peaks centered at ~ 2.65 Å and ~ 2.35 Å may contain diffraction signal from both c-(Ti)ZrN and w-AlN ($d_{\text{AlN}002}=2.51$ Å and $d_{\text{AlN}101}=2.38$ Å at 1100 °C [36, 37]). The broad diffraction peak centered at ~ 2.35 Å shifts to smaller values during heat treatment between 950 °C and 1080 °C which may indicate an increasing amount of w-AlN in the coatings. Its peak position remains approximately constant during further annealing at 1100 °C.

Figure 6: Elemental contrast STEM (a,c) and HR-TEM (b,d) cross-sectional micrographs from the S1 ($\text{Ti}_{0.31}\text{Zr}_{0.24}\text{Al}_{0.45}\text{N}$) (a,b) and S2 ($\text{Ti}_{0.21}\text{Zr}_{0.48}\text{Al}_{0.31}\text{N}$) (c,d) coatings annealed at 850 °C with no holding time. The arrows in (b) point at Al-rich precipitates and the surface normal (SN) is marked in (c).

Within the columnar grains of S2 (Figure 6c), fine compositional modulations are observed. The HR-TEM micrograph (Figure 6d) reveals a structure with small crystalline domains, 1-2 nm, separated by regions that have a different structure or orientation. The crystalline domains have a cubic structure as revealed by the HR-TEM micrograph and the corresponding FFT. The size of the domains is on the same length scale as the compositional modulations observed in Figure 6c. Thus, separation into Al-rich and Al-depleted domains has occurred during annealing in both samples. In S1, this results in a coherent, cubic structure while in S2, domains of different chemical composition form within the columnar grains and, in addition, w-AlN grains nucleate at column boundaries. The difference in elastic anisotropy between the samples [24], see Table 2, results in different shapes of the domains with cubic structure, where the domains are approximately equiaxed in the isotropic S2 sample.

The maximum strain was found to occur after annealing at 850 °C. For TiAlN, a combination of experiments and phase field simulations revealed that only very small changes in strain of the c-TiAlN phase is expected upon spinodal decomposition [26], as long as the formed domains of different chemical composition are coherent. The formation of w-AlN, however, can increase the compressive strains in the c-TiAlN phase [38, 39]. Thus, formation of small w-AlN grains is likely the reason for the increased strain in S2 below 900 °C. Also, formation of domains with a different structure or orientation within the columns can contribute to the compressive strain in S2. For S1 annealed at 900 °C, most of the Al is retained within the cubic structure as revealed by the small change in lattice parameter (Figure 4). The high strain in this sample (Figure 5) confirms that it is the structure of the cubic phase that is causing the high compressive strain. Thus, the more complex phase evolution in the quaternary TiZrAlN alloy compared to TiAlN, where also formation of Ti- and Zr-rich phases takes place, results in compressive strain.

Figure 7 shows elemental contrast STEM (Figure 7a and d), high-resolution HR-TEM (Figure 7b and e) and elemental contrast, high-resolution HR-STEM micrographs (Figure 7c and f) of S1 (Figure 7a-c) and S2 (Figure 7d-f) annealed for 2 h at 1100 °C. For S1, dark contrast, almost equiaxed Al-rich grains (indicated with arrows) have formed. One embedded Al-rich grain is imaged in Figure 7b. A FFT of this grain displays a hexagonal structure, indicating that such Al-rich grains are w-AlN. The inserted FFT is obtained from the full image and reveal the existence of both cubic and wurtzite phases. The w-AlN grains form with their $\langle 0001 \rangle$ directions parallel to the cubic $\langle 001 \rangle$ directions. Yalamanchili et al. [25] calculated the interfacial energy for different interface structures for c-TiN, c-ZrN and w-AlN and found that $c\text{-}(110)[001] \parallel w\text{-}(10\text{-}10)[0001]$ is one of the favored interface structures for c-ZrN and w-AlN.

Figure 7: Elemental contrast STEM (a,d), HR-TEM (b,e) and elemental contrast HR-STEM (c,f) cross-sectional micrographs from the S1 ($\text{Ti}_{0.31}\text{Zr}_{0.24}\text{Al}_{0.45}\text{N}$) (a-c) and S2 ($\text{Ti}_{0.21}\text{Zr}_{0.48}\text{Al}_{0.31}\text{N}$) (d-f) coatings annealed for 2 h at 1100 °C. The arrows in (a,b) point at Al-rich precipitates and the surface normal (SN) is marked in (d).

This relation has also been observed experimentally [20]. Thus, the w-AlN grains grow such that the interfacial energy is minimized. The structure surrounding the w-AlN grains is cubic as revealed by the HR-TEM micrographs in Figure 7b-c. The elemental contrast HR micrograph in Figure 7c reveals varying contrast within the cubic structure corresponding to differences in Ti- and Zr-content. The cubic structure has a high density of dislocations and stacking faults where the dislocations are mainly located on (111) planes with their Burgers vector in the [111] direction as determined by Burgers circuits around the observed dislocations. These are interpreted as Frank partial dislocations outlining stacking faults in the structure. Thus, depletion of Al from the cubic phase and the nucleation of w-AlN grains are associated with a change in orientation of the interfaces between cubic domains, from (100)

interfaces to (111) interfaces. It has been observed that during spinodal decomposition of Cu-Ni-Fe alloys, a change in orientation, from (100) coherent interfaces to (110) oriented interfaces [40, 41], caused by concentration of dislocations to the interfaces between phases, lowers the interfacial energy since the Burgers vector of the dislocations is located in this plane. Similarly, in the TiZrAlN coatings, the change of interface orientation to contain the Burgers vector of the dislocations can lower the interfacial energy and thus be favorable. There are additional compositional modulations within the cubic domains aligned along $\langle 111 \rangle$ directions as observed in Figure 7c. The large variation in composition within the cubic phase and the local strain resulting from dislocations result in broad diffraction peaks that appear during annealing (Figure 3).

In S2, the Al-rich precipitates have grown during annealing at 1100 °C and they are still mainly located at column boundaries as observed in Figure 7d. There are still fine-scale compositional modulations within the cubic, columnar grains as revealed by the higher magnification STEM insert in Figure 7d. The elemental contrast HR-STEM micrograph recorded along the [001] zone axis in Figure 7f show cubic structure domains that are 3-4 nm in size with varying contrast, corresponding to variations in composition between the domains. The HR-TEM micrograph in Figure 7e, recorded along the [011] zone axis, reveal that some domains have either a different orientation or a different structure than the major part of the column interior. In the inserted FFT (Figure 7e), there are weak spots (marked with *) along the cubic [100] direction that can be assigned to either cubic (111) or wurtzite (0002) planes. In contrast to S1, larger w-AlN grains are only found at the column boundaries and not within the columns for this sample.

Above 900 °C the growth of w-AlN grains at column boundaries result in strain relaxation of the c-TiZr(Al)N phase (Figure 5), similar to the case of TiAlN where the strains relaxes when the w-AlN grains increase in size [26]. In contrast, relaxation does not take place in S1 above 900 °C. Instead, the stable and dense dislocation structure and nucleation of w-AlN within the cubic structure cause the coating to remain in a compressive stress state. The stable dislocation structure is caused by the sessile partial dislocations with a [111] oriented Burgers vector. Such dislocations require other mechanisms to move then glide, such as climb, which likely contribute to the slow strain relaxation throughout the 3 h long annealing. Comparing the strain evolution of S1 and S2 during growth of w-AlN between 900 C and 1100 °C it is obvious that the nucleation site for w-AlN is important for the strain evolution. Nucleation and growth of w-AlN in the column boundaries in S2 results in strain relaxation of the cubic phase, while nucleation of w-AlN within the cubic grains results in retained compressive strains. This is understood by column boundaries having lower density then the interior of the columns. This allows growth of the larger molar volume w-AlN phase without compressing the cubic, columnar grains. In contrast, the formation of w-AlN within the cubic, columnar grains likely results in an internal

compressive stress. The compressive stress of S2 and S3 after 3 h at 1100 °C is mainly due to the difference in thermal expansion between substrate and coating. The strain determined at room temperature after 3 h at 1100 °C is -0.05 % for S3, corresponding to an approximate compressive stress of 0.2 GPa (using the same elastic constants as for the as-deposited coating).

Figure 8: Decomposition routes of the three coatings showing phase transformation by spinodal decomposition (SD) and nucleation and growth (N&G) mechanisms. Parenthesis indicates elements that exist in minor amounts and phases in bold text are the main phases.

Figure 8 summarizes the decomposition routes of the three studied samples. S3 (Ti_{0.13}Zr_{0.69}Al_{0.18}N) decomposes by nucleation and growth (N&G) into an Al-depleted c-TiZr(Al)N phase and w-AlN in agreement with theoretical predictions [27]. In S2 (Ti_{0.21}Zr_{0.48}Al_{0.31}N), theoretical work found a small driving force for spinodal decomposition (SD). Here, we find two co-occurring mechanisms for decomposition. Spinodal decomposition of the c-TiZrAlN phase results in domains enriched in Ti or Zr, while there is simultaneous growth of w-AlN mainly in the column boundaries of the coating. This is similar to what previously has been observed for TiCrAlN [12]. After 3 h at 1100 °C the final phases are w-AlN, a Zr-rich c-TiZrN phase, and the main c-TiZr(Al)N phase. The driving force for spinodal decomposition is the highest for S1 (Ti_{0.31}Zr_{0.24}Al_{0.45}N) [27] and below 900 °C only spinodal decomposition is observed, resulting in cubic domains enriched in Al and Zr. Nucleation and growth of w-AlN occurs subsequent to the spinodal decomposition at temperatures above 900 °C. The w-AlN phase forms from c-AlN-rich domains within the cubic grains, resulting in well-dispersed w-AlN grains throughout the coating. The continuous change in lattice parameter of the main c-TiZrAlN phase during isothermal annealing suggests that its chemical composition is still changing at 1100 °C. During

isothermal annealing at 900 °C, the changes in lattice parameter are relatively small, thus most of the Al is still contained within the cubic phase, even after 3 h of annealing.

Figure 9 shows the hardness evolution during annealing. The hardness decreases during annealing for S3 due to strain relaxation and nucleation and growth of w-AlN. In contrast, the hardness is constant for S2 to annealing temperatures of 1100 C° (hold time of 25 min) despite the strain relaxation that takes place above 900 °C. This is assigned to the formation of nm-sized domains within the cubic structure, resulting in age hardening similar to the case of TiAlN [42]. For S1, the hardness increases slightly during annealing at 850 °C (no hold) due to the formation of elongated, coherent AlN-rich cubic domains. During annealing at 1100 °C the hardness decreases slightly but remains high (31 GPa) even after 2 h at 1100 °C as a result of the dislocation-dense structure formed and the high compressive strain.

Figure 9: Hardness of the samples as a function of annealing temperature and time.

4. Conclusions

The decomposition route of c-TiZrAlN changes from nucleation and growth of w-AlN to spinodal decomposition when the Zr-content in the coating decreases and the Al-content increases. Spinodal decomposition during annealing results in cubic domains enriched in Zr or Ti/Al and the formed microstructure depends on coating composition. In $\text{Ti}_{0.31}\text{Zr}_{0.24}\text{Al}_{0.45}\text{N}$, spinodal decomposition below 900 °C results in cubic domains elongated in $\langle 100 \rangle$ directions. During further annealing, there is a change in orientation of the interfaces between the domains, resulting in (111) oriented semi-coherent interfaces. The dislocation-dense structure formed and additional nucleation of w-AlN within the columnar grains result in high compressive strain of the cubic phase during isothermal annealing at 1100 °C. In $\text{Ti}_{0.21}\text{Zr}_{0.48}\text{Al}_{0.31}\text{N}$, loss of coherency occurs at lower temperatures and above 900 °C recrystallization and grain growth result in a decreased strain.

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