Enhanced thermal stability and fracture toughness of TiAlN coatings by Cr, Nb and V-alloying

Y.H. Chen[1,*], J.J. Roa[2,3], C.H. Yu[1], M.P. Johansson-Jöesaar[1,4], J. M. Andersson[4], M.J. Anglada[2,3], M. Odén[1], and L. Rogström[1]

[1] Nanostructured Materials, Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden

[2] Department of Materials Science and Metallurgical Engineering, Universitat Politècnica de Catalunya, Campus Diagonal Besòs-EEBE, 08019 Barcelona, Spain

[3] Centre for Research in Multiscale Engineering of Barcelona, Universitat Politècnica de Catalunya, Campus Diagonal Besòs-EEBE, 08019 Barcelona, Spain

[4] R&D Material and Technology Development, SECO Tools AB, SE-737 82 Fagersta, Sweden

* Corresponding author: yuhch@ifm.liu.se

Abstract

The effect of metal alloying on mechanical properties including hardness and fracture toughness were investigated in three alloys, $Ti_{\sim0.33}Al_{0.50}(Me)_{\sim0.17}N$ (Me = Cr, Nb and V), and compared to $Ti_{0.50}Al_{0.50}N$, in the as-deposited state and after annealing. All studied alloys display similar as-deposited hardness while the hardness evolution during annealing is found to be connected to phase transformations, related to the alloy's thermal stability. The most pronounced hardening was observed in $Ti_{0.50}Al_{0.50}N$, while all the coatings with additional metal elements sustain their hardness better and they are harder than $Ti_{0.50}Al_{0.50}N$ after annealing at 1100 °C. Fracture toughness properties were extracted from scratch tests. In all tested conditions, as-deposited and annealed at 900 and 1100 °C, $Ti_{0.33}Al_{0.51}Nb_{0.17}N$ show the least surface and sub-surface damage when scratched despite the differences in decomposition behavior and h-AlN formation. Theoretically estimated ductility of phases

existing in the coatings correlates well with their crack resistance. In summary, $Ti_{0.33}Al_{0.51}Nb_{0.17}N$ is the toughest alloy in both as-deposited and post-annealed states.

Keywords: Thermal stability; Quaternary transition metal nitrides; Scratch test; Fracture toughness; Arc evaporation

1. Introduction

Superior mechanical properties in terms of wear-resistance are essential for coatings used for high-speed cutting tools, where the operating temperatures can be above 900 ℃ [1]. As a result, thermal stability of coatings with enhanced mechanical properties is desired. Cubic (c-) $Ti_{1-x}Al_xN$ coatings have been extensively studied and used due to its enhanced hardness (H) that is related to a spinodal decomposition at high temperature [2]. While the formation of coherently strained c-TiN and c-AlN rich domains gives rise to age hardening during high temperature heat treatment, further annealing induces hexagonal h-AlN phase transformation, which degrades the coating's mechanical properties [3, 4].

It has been shown that the thermal stability and hardness can be improved by alloying $Ti_{1-x}Al_xN$ with an additional transition metal (Me) [5-9]. For example, $Ti_{1-x-y}Al_x(Cr)_yN$ has shown enhanced hardness after annealing above 1000 ℃ [7, 10]. Still, brittleness remains as a drawback of ceramic coatings [11, 12]. Theoretical studies predict that quaternary $Ti_{1-x-y}Al_x(Me)_yN$ alloys may have higher toughness and ductility than TiAlN [13-15]. Experimentally, the fracture toughness of $Ti_{1-x-y}Al_x(Nb)_yN$ has been found to enhance with the addition of Nb [16]. With theoretical predictions based on the valence electron concentrations (VEC), the toughness of $Ti_{1-x-y}Al_x(V)_yN$ also increases by V alloying [13, 17].

In addition, V in $Ti_{1-x-y}Al_x(V)_yN$ has also been observed to improve lubrication and wear-resistance properties [18].

Experimental studies of the fracture toughness of hard coatings are sparse, mainly due to the lack of established test methods for thin films. Tribological tests such as scratch or wear tests effectively evaluate the coating's mechanical strength and adhesion properties by analyzing the failure events [19-23]. However, the focus of these studies is limited to the damage events occurring on the surface. A more detailed understanding can be achieved by studying the fracture behavior of the coating. Here we use a focused ion beam (FIB) to make cross sectional investigations of the damage events that enable observation of differences in crack resistance between coatings. We also report the fracture behavior of post-annealed samples and correlate the results to mechanical properties such as hardness and ductility. The alloying elements affect the microstructure and phase evolution during annealing that impact the coating's ductility, e.g. the formation of h-AlN is important for the fracture behavior.

2. Experimental details

The quaternary coatings were grown by cathodic arc deposition in a Sulzer Metaplas MZR323 system on polished cemented carbide (WC-Co) substrates in 4.5 Pa N_2 atmosphere, at a substrate temperature of about 550 °C, and a substrate bias of -60 V. Four depositions were made to grow $Ti_{1-x-y}Al_x(Me)_yN$ (Me = Cr, Nb or V) and a reference $Ti_{1-x}Al_xN$ coating. The set-up and used cathodes for the different alloying elements are schematically shown in Figure 1. Three 100 mm metallic compound cathodes with different composition were used to achieve plasma mixing and to grow a set of coatings with different compositions. For this specific study, samples with similar Ti:Al:Me ratio were chosen. The composition of the deposited coatings was measured by energy-dispersive x-ray spectroscopy (EDS) in a Leo

1550 Gemini scanning electron microscope (SEM) operated at 20 kV and based on these results four samples were selected: $Ti_{0.49}Al_{0.51}N$; $Ti_{0.33}Al_{0.51}Cr_{0.17}N$; $Ti_{0.33}Al_{0.51}Nb_{0.17}N$; $Ti_{0.37}Al_{0.45}V_{0.18}N$. These are labelled as TiAlN, TiAl(Cr)N, TiAl(Nb)N, and TiAl(V)N in the text below.

Thermal annealing of the samples was done in a 1.6 mPa vacuum environment at constant annealing temperatures with a holding time of 20 min, and heating/cooling rates of 20 °C/min. The temperature was monitored by a thermocouple located near the sample and the thermocouple reading was calibrated by a two-color CellaTemp pyrometer. Grazing incidence x-ray diffraction (GIXRD) using a Bruker D8 Advance x-ray diffractometer was applied to identify the phases in the coatings in both as-deposited and annealed states. Cu Kα radiation was used with a fixed incident angle of 2°. The residual stress of the as-deposited samples was extracted by the $\sin^2\psi$ method using the c-220 diffraction peak, with the elastic constants of $v = 0.22$, $E = 432$ GPa (TiAlN); $v = 0.39$, $E = 420$ GPa (TiAl(Nb)N); $v = 0.38$, $E = 429$ GPa (TiAl(V)N) [15], and $v = 0.22$ (assumption, the value for TiAlN), $E = 454$ GPa (TiAl(Cr)N) [24]. The strain-free d-spacing was determined at the invariant tilt angle ψ^*, and was 1.477 Å for TiAlN, 1.473 Å for TiAl(Cr)N, 1.487 Å for TiAl(Nb)N, and 1.476 Å for TiAl(V)N.

The mechanical properties were studied for both as-deposited and post-annealed samples. The H of the coatings was measured using a UMIS nanoindenter equipped with a Berkovich diamond tip. 20-30 indents with a maximum load of 50 mN were made on polished tapered cross-sections of each sample. The maximum penetration depth into the surface is between 0.20 to 0.24 μm, which fulfills the 10 % empirical rule for avoiding substrate influence [25]. The loading-displacement curve was treated by means of the Oliver and Pharr method [26] to extract H for the coating system and the results presented are averaged from all indents.

Scratch tests were carried out by an Anton Paar Revetest instrument with a 200 μm radius Rockwell C diamond indenter. The scratch length was 5 mm with linearly increasing load from 1-150 N with loading rate of 100 N/min. Three scratches were done for each sample. Surface and sub-surface damage of the scratch tracks and cross-sections of specific spallation events were examined by SEM and focused ion beam (FIB) in a dual beam Workstation (Zeiss Neon 40). The specimens were coarse milled using a 30 kV/2 nA Ga^+ ion beam followed by 500 pA final polish.

3. Results

3.1 Phase evolution during thermal annealing

Figure 2 shows the x-ray diffractograms of TiAlN and TiAl(Me)N in the as-deposited and annealed states. All as-deposited alloys exhibit c-TiAlN or c-TiAl(Me)N solid solutions. The weak peak located at $2\theta \approx 41°$, easiest observed for TiAl(Nb)N but existing in all samples, is a c-200 peak originating from diffraction of W $L\alpha_1$ radiation. The W radiation is a result of contamination of the Cu anode of the x-ray tube by evaporated W from the cathode filament. In TiAl(Nb)N, a low intensity diffraction signal corresponding to Nb is shown, which indicates the existence of metallic impurities in the coating (e.g. macroparticles). SEM studies of the surface confirm that TiAl(Nb)N exhibits the highest macroparticle concentration. A potential reason for this phenomenon is related to the higher melting point of Nb (2750 K) compared to Ti, Cr and V (ranging from 1941-2183 K). This results in that the Ti or Al grains in the Ti (or Al)-Nb cathode melts before Nb-grains and the inhomogeneous distribution of liquid cathode material generates formation of macroparticles [27]. Fractured cross sections were used to measure the coating thickness by SEM to be

between 2.2 and 3.3 μm as noted in Table 1. Table 1 also shows the residual stress for the as-deposited samples.

Table 1 The coating thickness and residual stress of as-deposited samples.

	Coating thickness (μm)	Residual stress (GPa)
TiAlN	2.8	- 3.0 ± 0.2
TiAl(Cr)N	2.2	- 3.2 ± 0.2
TiAl(Nb)N	3.3	- 1.8 ± 0.1
TiAl(V)N	2.6	- 3.2 ± 0.1

After annealing, additional cubic phases are observed at temperatures above 900 °C. For the TiAlN alloy, the formed phases are c-TiN and c-AlN. For TiAl(Cr)N, they are c-Ti(Cr)N and c-Al(Cr)N as suggested by the decomposition route predicted by theoretical calculations [28]. For Me = Nb and V, the path of decomposition is unknown but according to the lattice spacing obtained from Figure 2, the decomposition process should result in c-Ti(Me)N and c-Al(Ti,Me)N. The peak positions of c-Ti$_x$(Me)$_{1-x}$N and c-Al$_{0.5}$(Me)$_{0.5}$N, estimated from the lattice parameters obtained theoretically [15, 28] are labeled in Figure 2. The peak positions are given as a guide for the reader while the chemical composition of the Al-rich domains is unknown.

At 1000 °C, h-AlN has formed for all alloys except for TiAl(Nb)N, for which it forms only when annealed at 1100 °C. At 1100 °C, c-TiN has formed in TiAlN, while c-Ti$_{\sim0.7}$(Me)$_{\sim0.3}$N has formed for the TiAl(Me)N alloys. The Al-rich phases (AlN, (Ti)AlN and Al(Ti,Me)N) vanish due to h-AlN formation. The composition of c-Ti(Me)N phases is estimated from the plane spacing from c-111 and c-200 diffraction peaks by Vegard's law.

To further investigate the onset of spinodal decomposition during thermal annealing, the full-width at half maximum (FWHM) of the c-200 diffraction peak of as-deposited and annealed states is shown in Figure 3 (a). The increase of the FWHM between as-deposited and 900 °C is related to arising compositional fluctuations. There are some differences in FWHM values between the as-deposited samples (plotted at the deposition temperature, i.e. 550 °C), because these values are affected by grain sizes and microstrain [29]. Since SEM cross-sectional studies reveal similar columnar structures with similar grain size for all samples, we conclude that the microstrain is higher in TiAl(Cr)N and TiAl(V)N samples. This is related to differences in the defect density as a result of varying ion flux and ion bombardment during growth of the different alloys [30, 31]. Such differences may also contribute to the fact that the same coatings also exhibit the largest macrostress (Table 1). The macrostress of the coating is additionally affected by the difference in coefficient of thermal expansion between coating and substrate.

During annealing, the evolution of the FWHM is different between the alloys. For TiAl(Nb)N, its c-200 width increases clearly at 700 °C, which shows that compositional variations within the cubic phase have already formed, while the FWHM is approximately constant for the other alloys. When the annealing temperature increases to 800 °C, the width of the c-TiAlN 200 peak starts to increase; the peak widths increase for TiAl(Cr)N and TiAl(V)N when annealed at 900 °C. These results show that spinodal decomposition occurs at different annealing temperatures for the four samples. Table 2 summarizes the temperatures when spinodal decomposition and h-AlN formation (from Figure 2) are observed for all samples.

At the end of the annealing process at 1100 °C, the FWHM of the 200 diffraction peak of the formed c-TiN and c-Ti(Me)N is also shown in Figure 3 (a). At this stage of decomposition, grain size should be the main contribution to the peak width since the

decomposition is complete, thus a smaller FWHM corresponds to a larger grain size by the Scherrer equation. Therefore, c-TiN shows the largest grain size while the remaining c-Ti(Me)N in the other samples shows similar values and c-Ti(V)N has the smallest grain size. Figure 3 (b) shows the FWHM of the h-100 peak of the formed h-AlN in 1100 °C-annealed alloys. Similar values for TiAlN and TiAl(Cr)N alloys are found, while TiAl(Nb)N shows the smallest h-AlN grain size.

Table 2 The annealing temperature required for spinodal decomposition and h-AlN formation for the four alloys.

	Spinodal decomposition observed at	h-AlN formation observed at
TiAlN	800 °C	1000 °C
TiAl(Cr)N	900 °C	1000 °C
TiAl(Nb)N	700 °C	1100 °C
TiAl(V)N	900 °C	1000 °C

3.2 Mechanical properties and scratch tests

The hardness of as-deposited and annealed alloys is shown in Figure 4. In the as-deposited state, the four alloys exhibit similar hardness, H, ranging between 32 and 34 GPa. After annealing, however, the trend of H is different for the different alloys. For TiAlN and TiAl(Nb)N, the maximum hardness (H_{max}) is found after annealing at 800 °C, 38.0 ± 1.2 GPa for TiAlN and 36.0 ± 1.4 GPa for TiAl(Nb)N. When the annealing temperature reaches 900 °C, H_{max} for TiAl(Cr)N (36.7 ± 1.5 GPa) and TiAl(V)N (35.1 ± 0.4 GPa) is observed. At this temperature the hardness of TiAlN and TiAl(Nb)N starts decreasing. At annealing temperatures exceeding 900 °C, H drops for all alloys. At 1100 °C, H drops to ~30 GPa for TiAl(Me)N alloys while H of TiAlN decreases to 27.7 ± 0.8 GPa.

The scratch tracks of the four as-deposited alloys were examined by SEM and similar critical load, L_c, (~110 N) for recovery spallation was found for all alloys. Table 3 shows L_c for the observed recovery spallation averaged over three scratches. Figure 5 shows the SEM images near the maximum scratch load (150 N). The areas with bright contrast are confirmed by EDS to be exposed substrate. Both recovery and buckle spallation [19] are clearly observed on the surface for all samples. Recovery spallation was selected for detailed studies since the mechanism behind such failure is strongly related to the elastic properties of the coatings. TiAl(V)N shows the highest degree of recovery spallation among all samples (Figure 5 (d)). The rest of the alloys show similar degree of spallation on the surfaces; however, their response below the surface varies.

Figure 6 shows FIB cross-sections taken on the edge of the scratch track in the regions marked with dashed squares in Figure 5. Regions with parts of the coating left on the surface were chosen for cross-sectional investigations to be able to study the coating behavior. However, the information obtained from the cross-sections can be affected by the chosen position on the surface. As indicated in Figure 6 (a), all cross-sections shown in this paper are imaged from the end of the scratch track, thus containing information from inside the scratch track to the left and information from the edge of the track to the right. The coatings are imaged with darker contrast compared to the substrate. The thinner coating at the left hand side in the cross-sections is related to buckle spallation taking place inside the scratch track [32]. TiAlN and TiAl(V)N coatings show similar fracture behavior at this load, where the cracks propagate extensively at the coating-substrate interfaces and also inside the coating. The cracks will eventually emerge at the surface and result in spallation; therefore, the recovery spallation areas in TiAlN and TiAl(V)N are relatively large compared to the other samples shown in Figure 5. For TiAl(Cr)N, in the region selected for the cross sectional view, the substrate is partly exposed and the remaining coating is thin. Where the substrate is

exposed, long and dense cracks extend into substrate connected with the thin remaining coating. For TiAl(Nb)N, only few cracks are found to propagate through the coating and the cracks do not follow the coating-substrate interface. In short, less extensive cracks and less spallation in the scratch track (Figure 5) are found for TiAl(Nb)N compared to the other alloys.

Two different annealing conditions were chosen for scratch tests, 900 °C and 1100 °C, since spinodal decomposition and h-AlN formation has taken place at these temperatures for all alloys, respectively. Figure 7 (a) shows a SEM overview of the scratch tracks on the 900 °C annealed samples. Unlike the as-deposited samples, clear differences in L_c for recovery spallation were observed between the alloys. The recovery spallation is extensive in TiAlN and the first damage event appears at a load of ~80 N, which is the lowest among all samples. The TiAl(Cr)N and TiAl(V)N samples have similar L_c of ~100 N, whereas TiAl(Nb)N exhibited the highest L_c of ~120 N among the samples. The degree of damage is also relatively minor for this sample.

FIB cross-sections, shown in Figure 7 (b-e), were done at a scratch load of ~100 N within the regions marked with white squares in Figure 7 (a). In TiAlN, shown in Figure 7 (b), spallation of the coating from the substrate is clearly observed with cracks extending along the coating-substrate interface as well as through the full thickness of the coating. This contributes to the large regions of recovery spallation on the surface for TiAlN. At the crack opening, re-deposition of substrate material has occurred during ion milling, resulting in bright contrast. This is also observed for large cracks in the other samples.

For TiAl(Me)N shown in Figure 7 (c-e), the coatings remain more intact compared with TiAlN. Although cracks can be observed along the interfaces and through the coating surface, the crack openings are smaller than for TiAlN. The crack openings in TiAl(Cr)N are

larger compared to the other TiAl(Me)N samples, especially inside the coating. A lower resistance for crack formation may also be responsible for the larger amount of spallation seen for TiAl(Cr)N compared to other TiAl(Me)N samples. For TiAl(Nb)N and TiAl(V)N, cracks propagating both within the coatings and at the interfaces are observed, but the damage degree is lower than for TiAl(Cr)N. The cracks are slightly thinner in the case of TiAl(Nb)N.

Figure 8 (a) shows the scratch tracks of the four samples annealed at 1100 °C. The highest degree of recovery spallation is again observed in TiAlN. The areas with white contrast at 30-60 N are surface contaminations of substrate materials debris caused by the moving tip, as confirmed by SEM investigations. Similar L_c of ~80 N is found for TiAlN and TiAl(Cr)N, while TiAl(Nb)N and TiAl(V)N has higher L_c of ~100 N. The degree of recovery spallation for TiAl(Me)N samples is the highest in TiAl(V)N.

Cross-sections of the edge of the scratch track at a load of ~100 N show that all alloys except for TiAl(Nb)N behave similarly, see Figure 8 (b-e). A minimum of two cross-sections were prepared for each sample here to prevent misinterpretation of the local information from the cross-sections. In Figure 8 (b, c, e), cracks are observed to propagate along the interfaces and continue through the coating to the surface. On the other hand, in TiAl(Nb)N shown in Figure 8 (d), the interface seems intact without any visible cracks. Some cracks are observed inside the coating and some small degree of spallation, which are both located near the surface. The opening of cracks in the TiAl(Nb)N coating is also smaller than observed in the other alloys.

Table 3 The critical load (L_c) for recovery spallation during scratching for the four alloys under various states.

	Critical load (N)		
	as-deposited	900 °C	1100 °C
TiAlN	114 ± 11	75 ± 4	81 ± 5
TiAl(Cr)N	110 ± 4	102 ± 2	75 ± 7
TiAl(Nb)N	120 ± 5	118 ± 3	101 ± 10
TiAl(V)N	108 ± 5	96 ± 2	102 ± 3

4. Discussion

4.1 Thermal stability of TiAlN and TiAl(Me)N alloys

The observed difference in thermal stability agrees well with theoretical results of the predicted phase stability. The mixing free energies obtained from theoretical calculations of cubic TiAlN, TiAl(Cr)N, TiAl(Nb)N and TiAl(V)N [15, 28], with the compositions discussed in this study, are summarized in Table 4. A higher mixing energy for TiAl(Nb)N and a lower mixing energy for TiAl(Cr)N and TiAl(V)N compared with TiAlN are found. Higher mixing free energy corresponds to higher instability of the coating, which suggests that spinodal decomposition may start at lower temperature [33]. These results are in accord with the different temperatures observed for spinodal decomposition to start (Table 2), i.e. decomposition occurs at a lower temperature for the alloy with higher mixing free energy. The decomposition process can also be affected by different kinetics between the alloys, due to e.g. different diffusion coefficients between the alloys and different diffusion paths as a result of varying microstructure between samples. The exact reason for the observed difference in thermal stability between samples is beyond the scope of this paper, while we explore how the difference does influence the mechanical properties of the annealed samples.

Table 4 Mixing free energy at 0 K for cubic solid solution of TiAlN and TiAl(Me)N

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	Mixing free energy (eV/atom) [15, 28]
TiAlN	0.1205
TiAl(Cr)N	0.1079
TiAl(Nb)N	0.1330
TiAl(V)N	0.0885

h-AlN formation is not directly linked to the mixing energy of the cubic solution. The stability of the cubic Al-rich domains depends on the microstructure and grain size [7, 34-36]. The purity of the Al-rich domains does also likely influence their stability, which is different for different alloying elements [15, 28]. The highest annealing temperature needed for h-AlN formation is found for TiAl(Nb)N. This suggests that the c-Al(Ti,Nb)N phase formed in TiAl(Nb)N has higher stability than c-AlN and c-Al(Ti,Me)N formed in the other samples, which can be related both to the presence of Ti and/or Nb in the Al-rich domains and to the microstructure of the decomposed sample. Norrby et al. [32] showed that the microstructure strongly affects the phase transformation to h-AlN in TiAlN.

4.2 Evolution of hardness during annealing

Changes in hardness behavior during the annealing process (cf. Fig. 4) are related to the phase transformation in the alloys. The enhancement in hardness is caused by formation of nanometer (nm)-size domains [2, 37-39] for all alloys, resulting in domains with varying elastic properties as well as strains between domains with different lattice parameters. Thus, the maximum hardness is expected to be found at different temperatures for the different alloys. Above this temperature the hardness decreases due to coarsening of the domains causing loss of coherency [33, 40]. When h-AlN formation takes place, the decrease of H is related to the soft properties of h-AlN or the incoherent interfaces formed [2, 41]. It is also

worth noting that in TiAl(Nb)N the spinodal decomposition starts at the lowest annealing temperature, but h-AlN forms at the highest temperature among the studied samples. The spinodal decomposition and the h-AlN formation are diffusion-controlled processes. Nb has the largest atomic radius and it is therefore expected to diffuse slower than the other elements. Consequently, the domains formed during spinodal decomposition of TiAl(Nb)N grow slower during annealing such that the coherency between domains is retained to higher temperatures. For TiAl(Nb)N this results in an early peak of hardness while the subsequent softening is slow in comparison to for example TiAlN for which the hardness decreases rapidly above 900 °C.

4.3 Scratch damage and toughness properties

Various mechanical properties of the coating including hardness [42], ductility [21], and residual stress [43] affect the damage behavior during scratch tests. An additional factor that may affect the scratch response is the coating thickness [44]. However, Holmberg et al. [45] showed that thickness plays a less important role compared to the elastic properties of the coating. The coating thickness variations in this study are small (2.8 ± 0.6 μm) while Wang et al. [15] have shown that the elastic properties of these alloys varies considerably. Thus, the effect of coating thickness is not further considered in this study.

It has been demonstrated that the damage that occur under sliding conditions can be improved by higher ductility of the coatings [21] since a brittle behavior contributes to spallation. The ratio of shear to bulk moduli (G/B) and the Cauchy pressure ($C_{12} - C_{44}$) can reveal the ductility according to the Pugh and Pettifor criteria [46, 47], where materials with G/B lower than 0.5 and positive Cauchy pressure are considered as ductile. Figure 9 shows the G/B vs Cauchy pressure map of the relevant alloys using values from ref. [15], while no literature data related to the elastic constants of TiAl(Cr)N is available. The as-deposited

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alloys (black filled squares) show only minor differences between the alloys. TiAl(Nb)N is located nearest to the ductile region and TiAlN is furthest away. This agrees with the surface and cross-sectional investigations showing superior crack resistance of TiAl(Nb)N, and demonstrating a higher ductility of this coating.

It has been found that an increased compressive residual stress leads to easier spallation of coatings during scratch tests [42]. This is primarily due to poorer adhesion properties when the coating's elastic energy is increased. Among the studied alloys the lowest stress is found in TiAl(Nb)N (Table 1), which, in combination with its high ductility, is responsible for the observed high crack resistance. TiAl(V)N exhibits the highest compressive stress among the samples, while it does not present more sub-surface damage than TiAlN, due to its higher ductility.

For the samples annealed at 900 °C, there is a difference in hardness between the alloys; TiAlN and TiAl(Cr)N alloys exhibit higher H, while TiAl(Nb)N has the lowest H. This may contribute to lower degree of damage for TiAl(Nb)N and higher density of damage events (i.e. spallation and fracture) of TiAlN and TiAl(Cr)N. It has been shown that higher H corresponds to lower L_c in scratch tests [42], which is in accord with the commonly observed trend of increased brittleness with increased H [48]. Since the chemical composition of the existing phases are not known after annealing at 900 °C, precise differences in ductility between the samples cannot be predicted. Nevertheless, decomposition into binary or ternary phases has occurred in all samples annealed at 900 °C (Figure 2 and 3). The ductility of the coating at 900 °C can be estimated as a combination of the values for the cubic phase of the as-deposited sample, the cubic phase of the sample post-annealed at 1100 °C, and the values for the cubic Al-rich phase. The composition of the formed cubic phases at 900 °C should be similar to the cubic phases that exist at 1100 °C while also cubic phases with the same composition as in the as-deposited samples exist. The G/B ratio and the Cauchy pressure of

the Ti-rich phases formed at 1100 °C are shown in Figure 9 (blue half-filled squares). It indicates that the Ti-rich domains formed in TiAlN at 900 °C exhibit lower ductility than the rest of the alloys. Shown in Figure 9 are also the Al-rich domains that may exist at 900 °C: c-AlN (in TiAlN), c-$Al_{0.5}V_{0.5}N$ (in TiAl(V)N), c-$Al_{0.5}Nb_{0.5}N$ (in TiAl(Nb)N) and c-$Ti_{0.5}Al_{0.5}N$ (labeled TiAlN, in TiAl(Nb or V)N). The extremely low ductility of c-AlN ($C_{12} - C_{44}$ = -143 and G/B = 0.88) compared to the Al-rich phases that may exist in all other samples again emphasizes the relatively lower ductility of the TiAlN coating at 900 °C. The differences in ductility corresponds well with the highest crack density and largest spallation in TiAlN; a better fracture resistance for the other alloys, as demonstrated by the cross-sections in Figure 7 (b-e). AlCrN has been experimentally shown to have higher toughness than TiN [48]. A phase with a composition close to $Al_{0.6}Cr_{0.4}N$ is formed in the TiAl(Cr)N alloy studied here, which may also contribute to improve the damage resistance seen after annealing at 900 °C when comparing to TiAlN.

Larger differences in the ductility between the alloys after annealing at 900 °C than in their as-deposited states is expected based on the formation of more ductile phases in the TiAl(Me)N (Figure 9). From Figure 6 and 7 (b-e), we also observe that the crack opening at the coating/substrate interface in TiAlN grows larger after annealing. For TiAl(Me)N, the crack density becomes lower and the cracks do not result in spallation or deformation of the coatings as in the as-deposited state.

At 1100 °C, the phases formed during decomposition have reached the chemical composition of TiN, Ti(Me)N, and h-AlN phases as indicated in Figure 9. Among the formed phases, TiNbN is the closest to the ductile region (with $C_{12} - C_{44}$ = 0 and G/B = 0.58) and TiVN is slightly more brittle but still close to the ductile region. For the TiN phase, relatively brittle properties are found ($C_{12} - C_{44}$ = - 40 and G/B = 0.68). These differences in ductility

result in significantly higher critical loads L_c for TiAl(Nb)N and TiAl(V)N annealed 1100 °C compared to the other two alloys.

Another essential factor to consider is the formed h-AlN at 1100 °C. h-AlN is more brittle ($C_{12} - C_{66}$ = - 130 [49] and G/B = 0.84) than the Ti-rich phases. h-AlN has formed in all alloys at this temperature, and in accord with our experimental findings TiAl(Nb)N is expected to contain less h-AlN than the other alloys. In addition, the formed h-AlN in TiAl(Nb)N has a smaller grain size compared to the other alloys. During the initial stage of h-AlN formation, the h-AlN can form coherent interfaces with cubic domains that improve the toughness or wear resistance [39, 50-53]. Thus, this is more likely for TiAl(Nb)N compared to the other coatings. On the contrary, large grains of h-AlN are found to deteriorate the mechanical properties due to the loss of coherency between phases [2, 51]. This can be the reason for the extreme variation in fracture behavior between TiAl(Nb)N and TiAl(V)N samples, which both have Ti-rich phases with similar ductility (Figure 8 (d, e)).

H again plays a minor effect among 1100 °C annealed samples as the TiAlN is the softest coating while it displays the most severe scratch damage. However, the decrease in H compared with 900 °C annealed samples results in less damage during the scratch tests for all alloys. The hardness decrease is the greatest for TiAlN and it clearly becomes less damaged after annealed at 1100 °C compared to 900 °C. Despite the similar H values between TiAl(Me)N, superior fracture resistance is observed for TiAl(Nb)N, which is assigned to the delayed h-AlN formation.

5. Conclusion

The mechanical properties and fracture behavior during scratch tests of TiAlN and TiAl(Me)N coatings has been studied and correlated to their phase evolution during annealing. Hardness is mainly affected by spinodal decomposition and h-AlN formation. The annealing temperature resulting in the phase evolution is found to connect with the thermal stability of alloys, which is different among samples.

Detailed studies of the fracture behavior reveal better fracture resistance of TiAl(Nb)N compared with TiAlN and the other TiAl(Me)N samples. The improved crack resistance of the as-deposited coating is related to the higher ductility of the c-TiAlNbN phase. After annealing at 900 °C, while spinodal decomposition has occurred in all samples, the difference in fracture behavior between the samples is understood as a difference in ductility between phases that form during decomposition. In this state, the best fracture tolerance of TiAl(Nb)N can also be related to its lower hardness compared to the other samples. After annealing at 1100 °C, the formation of the brittle h-AlN phase is crucial for the fracture behavior. The smaller size of h-AlN grains in the TiAl(Nb)N coating results in an improved fracture resistance compared to the other alloys.

The results suggest that, despite that the largest age hardening is observed for TiAlN, alloying with a fourth element can sustain the hardness even after annealing at 1100 °C. Further, changing the elastic properties as well as the thermal stability with Nb alloying, results in coatings that have a superior fracture behavior at high temperatures.

Acknowledgment

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