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The Effect of the Metal Phase on the Compressive and Tensile Stresses Reduction in the Superhard Nitride Coatings

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Abstract: The influence of the compressive and tensile stresses forming in the nanostructured Ti–Al–N coatings during deposition on their physical-mechanical properties was studied. The modifying influence of metal components (Ni and Cu) introduction into Ti–Al–N coatings, which do not interact with nitrogen and have limited solubility with the nitride phase, was also under research. Coatings were deposited on WC–(6 wt.%)Co carbide cutting inserts with an arc-PVD method using a cathodic vacuum arc evaporation apparatus. The introduction of Ni and Cu to the composition leads to the reduction of nitride phases grain size in both investigated coatings from 120 to 10–12 nm for Ti–Al–Cu–N and to 15–18 nm for Ti–Al–Ni–N. Thus, the hardness increases from 29 to 43 and 51 GPa for the mentioned above coatings, respectively. Meanwhile, Ti–Al–Cu–N and Ti–Al–Ni–N coatings are characterized by tensile stresses about 0.12–0.32 MPa against the much higher value of compressive stresses in Ti–Al–N coatings (4.29–5.31 GPa). The modification of Ti–Al–N coatings also leads to the changing of their destruction mechanism during the scratch-test. The critical loads characterizing the emergence of the first cracks in the coatings and complete abrasion of the coating (L_{c1} and L_{c3}) were determined. They had the value of 20; 22 N (L_{c1}) and 64; 57 N (L_{c3}) for Ti–Al–Ni–N; Ti–Al–Cu–N coatings, respectively. The L_{c1} parameter for Ti–Al–N coatings was much lower and was equal to 11 N. Along with those, Ti–Al–N coatings destructed according to the adhesion mechanism when the critical load was 35 N. In addition, the decreasing level of compressive stresses in Ti–Al–Cu–N and Ti–Al–Ni–N coatings as compared to that in the Ti–Al–N coating, their crack resistance during multi-cycle shock-dynamic impact test was significantly higher. The results can indicate that high hardness and crack resistance of the coatings is to a greater extent determined by coatings nanostructuring, not the stresses value. In addition, it confirms the possibility to obtain coatings with low stresses value while maintaining their superhardness.

Keywords: coating; compressive and tensile stresses; hardness; adhesion strength; crack resistance

1. Introduction

Many experts believe that the high values of hardness of PVD coatings as well as their crack resistance are largely associated with the intensive compressive stresses occurring in these coatings [1–5]. Meanwhile, it has been emphasized in a number of studies that hardness also depends on other characteristics of coatings, in particular on grain size [6,7]. However, high intrinsic stresses can result in decreased adhesive strength of the coatings, crack formation, and subsequent peeling off the substrate under high tensile stresses or coating swelling and detachment from the substrate under high compressive stresses [8].

It was found that the magnitude of the stresses in coatings can be controlled by reducing the energy of bombarding ions [9] and the deposition temperature (T_s) with respect to T_m , the melting point of the coating [10].

Some authors have reported that individual components added to the coating composition (e.g., Si added to the Zr–N [11] and Ta–N [12] coatings, Al added to the Ta–C coating [13], Cu added to the Al–N coating [14], and Cu and Ni added to the Ti–N coating [15]) have a significant effect on reduction of intrinsic stresses while maintaining the hardness. The possibility of obtaining low-stress metal-ceramic nanostructured Ti–Al–Cu–N and Ti–Al–Ni–N coatings characterized by high hardness and enhanced crack resistance was investigated in this study. Cu and Ni were added to the coatings due to the absence of their noticeable solubility in transition metal nitrides and low tendency for nitride formation. This fact predetermines refinement of the grain structure of the coating ceramic phase [16–18]. Maintaining of copper and nickel in the metallic state within the coatings may result in relaxation of thermal components of stresses, occurring due to the difference in linear thermal expansion coefficients of coatings and substrates, and of structure-phase components of stresses, caused by structural and phase heterogeneities appearing in the coatings during the process of their growth. Its mechanism is related to the relaxation of the strain field around the crack tip through the ductile phase, and the yielding and bridging of cracks by ligaments of the ductile phase [19,20].

As opposed to other studies determination of stresses was conducted by means of a complex technique involving bending and $\sin^2\Psi$ methods. These experiments were performed using substrates of different compositions allowing one to identify the effect of relaxation in the ductile metal phase of the coating both on the structural-phase and the thermal components of stresses. Thus, the stress state of Ti–Al–Cu–N and Ti–Al–Ni–N coatings was first complexly analyzed.

The modifying effect of introduced metallic components (Cu and Ni) on the possibility to form low-stressed coatings based on Ti–Al–N was researched. The results are of interest in obtaining wear-resistant and adaptive coatings providing further probable use of scientific results for practical purposes in the future.

2. Materials and Methods

Coatings were deposited under a nitrogen atmosphere on carbide cutting inserts and silicon substrates with an arc-PVD method using a cathodic vacuum arc evaporation apparatus. Three disposed of flat arc evaporators with a filtration of vapor-ion flow were used, which were then used for the deposition of the coating to significantly reduce the formation of droplets during coating. The surface temperature of the substrate during the formation of the coatings was about 500 °C. The substrates were cleaned through the Ar ion etching process. The Ar–N₂ gas mixture was fed to the chamber at a pressure of 2.7 Pa with a N₂ partial pressure of 1.3 Pa. Two titanium cathodes and a cathode made of Ti–Ni alloy containing 50 at.% of Ti and 50 at.% of Ni were used to deposit the Ti–Al–Ni–N coatings. In addition, two titanium cathodes and a copper cathode were used to obtain the Ti–Al–Cu–N coatings. The evaporating arc current (I) remained constant ~120 A at the titanium cathodes and the Ti–Ni alloy cathode during all processes. The substrate bias voltage was –120 V, the deposition time was 90 min, and coating thickness fluctuated between 3.9 and 4.1 µm. The Ti–Al–N coatings obtained under similar conditions were used as samples for comparison. The parameters of coatings under research and the corresponding reference samples made it possible to achieve a nickel content of approximately 7–8 at.% and Cu content of 2–3 at.%, which, according to [14], ensured their best physical-mechanical and operational properties.

For microstructural studies of samples of carbide substrates with coatings, a scanning electron microscope (SEM) JSM-6700 (JEOL, Tokyo, Japan) with energy-dispersive X-ray spectroscopy (EDS, JEOL, Tokyo, Japan) was used. The accelerating voltage was 20 kV. The structure of the coatings was observed by a JEM 2100 high-resolution transmission electron microscope (TEM, JEOL, Tokyo, Japan). The accelerating voltage was 200 kV. The samples were thinned by argon ion etching on a PIPS ion polisher (Pleasanton, CA, USA).

The X-ray diffraction (XRD, JEOL, Tokyo, Japan) analysis was performed on an Ultima 4 diffractometer (Rigaku, Tokyo, Japan) using $\text{CoK}\alpha$ radiation and a diffracted beam graphite monochromator in asymmetrical geometry (the angle between the incident beam and the sample was 5°). The quantitative phase composition was analyzed following the Rietveld method [21].

The chemical composition and the bond energy of the phase elements of the coating were determined on a PHI 5500 ESCA X-ray photoelectron spectrometer, XPS (Perkin-Elmer, Waltham, MA, USA). In order to excite the photoemission monochromatic Al $\text{K}\alpha$ irradiation with power, 25 W was used ($h\nu = 1486.6 \text{ eV}$). High-resolution spectra were recorded at the transmission energy of the analyzer (11.75 eV) with a scanning density of 0.1 eV/step.

To determine the stresses in the coatings, the $\sin^2\Psi$ estimation method [22–24] was used. It allows to measure stresses at a constant depth of penetration of the X-rays into the sample. In this case, positions of all reflections are measured when exposed in an asymmetric geometry. Each reflection has its own angle of leaving the symmetric position $\psi = 2\theta - \alpha$ (θ is a diffraction angle, α is an angle between the incident ray and the sample). Each lattice constant is calculated by the shift of each diffraction line: $a_\psi(\text{HKL}) = a_0\sigma f(\psi) + a_0$ (a_0 is the lattice parameter for the condition of equilibrium, a_ψ is stress). Then, the dependence of this value on the function is built: $f(\psi) = \frac{1}{2}s_2 \sin^2 \psi + 2s_1$, where $s_1 = -\frac{\vartheta}{E}$, $\frac{1}{2}s_2 = \frac{(1+\vartheta)}{E}$. The values of Young modulus (E) and Poisson ratio (ϑ) are taken specifically for each crystallographic plane (HKL). The stresses (σ) are calculated by the straight-line slope $a_\psi = kf(\psi) + b$ and the lattice constant.

The Stoney equation [25,26] is typically used to calculate the stresses in a coating (t_f) with thickness much lower than that of a substrate (t_s), based on the radius of curvature of the coating–substrate system bent due to the stresses related to both difference in specific phase volume and difference in thermal expansion coefficients of the coating and the substrate:

$$\sigma = \frac{1}{6} \left(\frac{1}{R} - \frac{1}{R_0} \right) \frac{E_s t_s^2}{(1 - \vartheta_s) t_f} \quad (1)$$

where E_s is the Young modulus; ϑ_s is the Poisson ratio of the substrate; R and R_0 are the radii of curvature of the composite before and after the coating had been deposited, respectively. These parameters are calculated on the basis of the profilograms:

$$R = \frac{L^2}{8b} \quad (2)$$

where L is the sample length from edge to edge upon bending; b is the deflection parameter. The profilograms were obtained using a WYKO NT1100 optical profilometer (Veeco, Plainview, NY, USA).

The micro-hardness tester (CSM Instruments, Needham, MA, USA) equipped with a Berkovich diamond tip was used to study the mechanical characteristics of the coatings. The progressive load mode CMC [27] was carried out with the minimum applied load of 10 mN and maximum of -50 mN . For each sample, 20 measurements were carried out, the two lowest and two highest values were ignored, and then the average value was determined. The hardness and elastic modulus were determined according to the method by Oliver and Pharr.

The adhesion/cohesion strength in the coating-substrate system was evaluated by the scratch-test, which results in the destruction of the samples at a growing load. These tests were performed using a Revetest device (CSM Instruments, Needham, MA, USA). The studied surface was scratched with a Rockwell diamond indenter that had a tip radius of $200 \mu\text{m}$ at a continuously increasing load. The critical loads were determined: L_{c1} defines the instant that the first crack appears, and L_{c3} corresponds to the complete abrasion of the coating to expose the substrate [28]. The acoustic emission (AE), indenter friction force (FF), and friction coefficient (μ) were measured during the test, the coating destruction along the scratch was observed with the help of a microscope.

The crack resistance of the Ti–Al–N, Ti–Al–Cu–N, and Ti–Al–Ni–N coatings deposited onto a carbide insert to the multi-cyclic dynamic impacts test was studied on a CemeCon apparatus (AG, Würselen, Germany). The piston of the impact tester, with a holder for a counter body mounted onto it, provided a cyclic load of 250 N (10^4 and 5×10^5 cycles with a frequency of 50 Hz). During the test, the deformation zone of the sample was cooled by compressed air. A ball, 5 mm in diameter, made of WC–Co alloy was used as a counter body.

3. Results and Discussion

The (Ti,Al)N (2–3 at.% Cu) and (Ti,Al)N (7–8 at.% Ni) coatings were selected to be investigated. The aluminium content of the coatings was ~2 at.%. The stoichiometry of the complex nitride was ~0.87. In all series, the surface morphology of the coatings was characterized by a lamellar structure (Figures 1a, 2a and 3a) which is typical for arc-PVD coatings deposited onto carbide inserts [15].

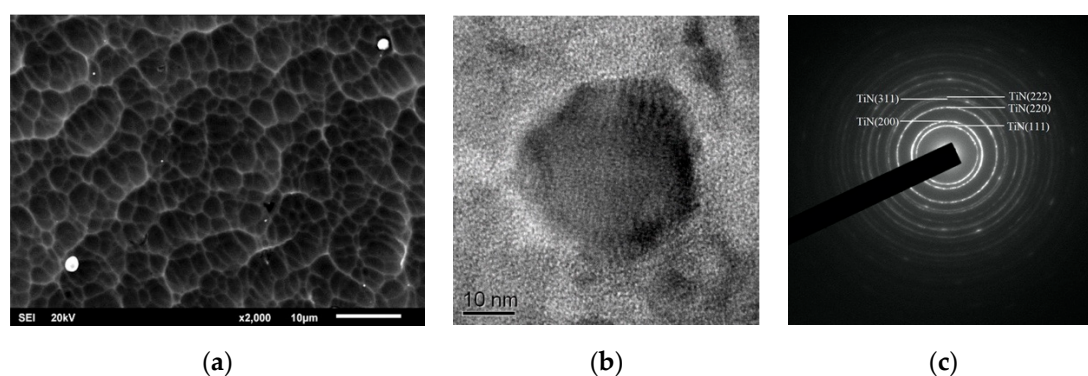


Figure 1. SEM images of surface, (a) high-resolution electron microscopic images of the coating structure, (b) and TEM patterns (c) of the Ti–Al–Cu–N coatings.

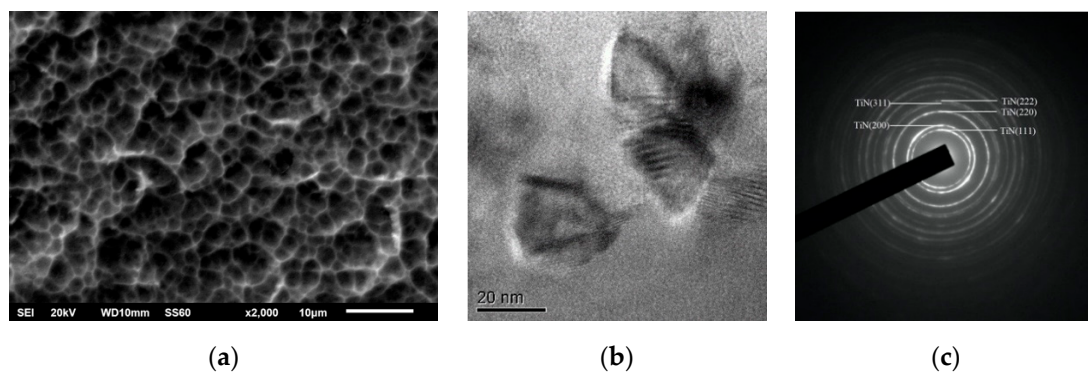


Figure 2. SEM images of surface, (a) high-resolution electron microscopic images of the coating structure, (b) and TEM patterns (c) of the Ti–Al–Ni–N coatings.

The obtained Ti–Al–Cu–N and Ti–Al–Ni–N coatings had a homogeneous structure characterized by a uniform distribution of nanosized equiaxial nitride phase grains 15–20 nm in size, with 1–2 nm thick interlayers of metallic copper and nickel phases (Figures 1b and 2b, respectively). Structural studies of the Ti–Al–N reference samples indicated the presence of columnar crystals based on titanium nitride (Figure 3b,c). Copper and nickel are X-ray amorphous and cannot be identified neither by XRD patterns nor by electron diffraction patterns (Figures 1c, 2c and 4). XPS data and the analysis of high-resolution Cu 2p and Ni 2p photoelectron spectra for coatings demonstrated that the maxima of the Cu 2p_{3/2} and Ni 2p_{3/2} peaks localized at bond energies of 933.0 (Figure 5a) and 852.8 eV (Figure 5b), respectively (corresponding to the energies of the bond between metal copper and nickel) [29,30].

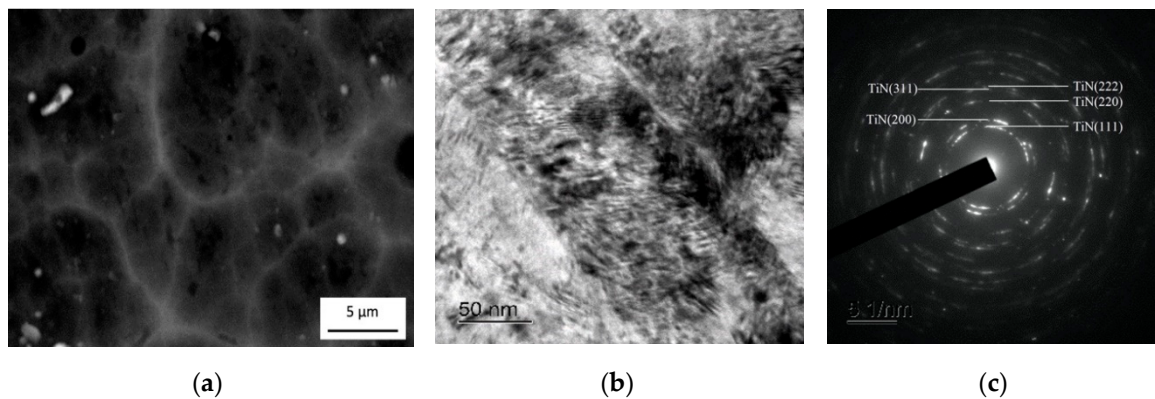


Figure 3. SEM images of surface, (a) high-resolution electron microscopic images of the coating structure, (b) and TEM patterns (c) of the Ti–Al–N coatings.

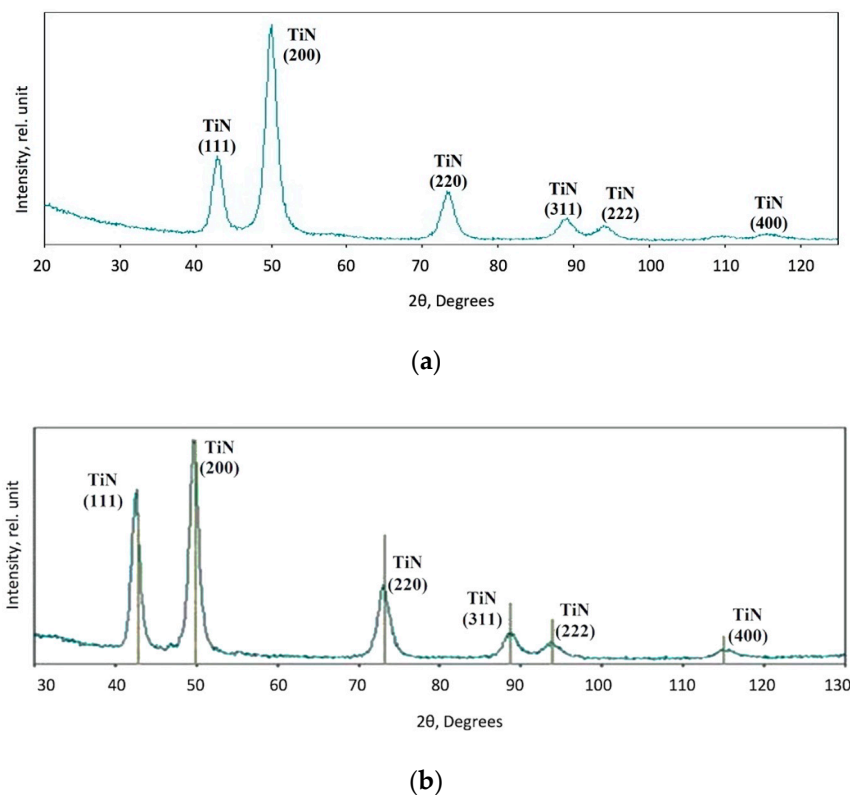


Figure 4. The XRD patterns of the Ti–Al–Cu–N (a) and Ti–Al–Ni–N (b) coatings.

Compositions and physical and mechanical properties of the Ti–Al–Cu–N and Ti–Al–Ni–N coatings and the reference coating sample are summarized in Table 1. The coefficients $\sigma(1)$ and $\sigma(2)$ indicate stresses determined by $\sin^2\Psi$ and by bending methods, respectively. In addition, the stresses in the “coating-silicon substrate” and “coating-carbide inserts” systems were indicated through “/” in Table 1.

Investigation of the stress state of Ti–Al–Cu–N (a) and Ti–Al–Ni–N (b) coatings compared to the Ti–Al–N coating by means of $\sin^2\Psi$ and bending methods (Figure 6 and Table 1) demonstrates the decrease in their absolute values from -4.29 – -5.31 to 0.12 – 0.32 GPa. Figure 6 shows the characteristic dependences of the lattice parameter of (Ti,Al)N nitride on function $f(\Psi)$, which are used to calculate stresses by means of the above mentioned method. Despite the formation of small-magnitude tensile stresses, the Ti–Al–Cu–N and Ti–Al–Ni–N coatings are characterized by high hardness: 43 and 51 GPa

vs. 29 GPa in the Ti–Al–N coating, respectively. The obtained results allow one to assert that the nano-grain structure of the coating is the key factor for their high level of hardness.

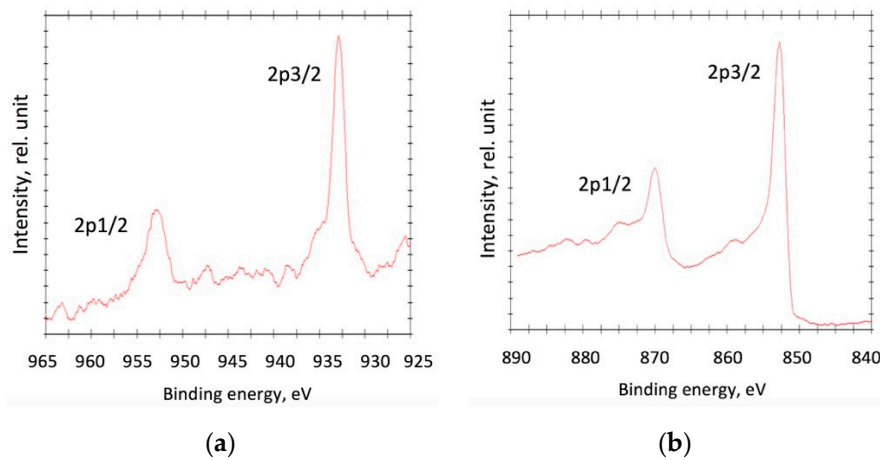


Figure 5. Cu2p (a) and Ni2p (b) X-ray photoelectron spectra of the Ti–Al–Cu–N and Ti–Al–Ni–N coatings.

Table 1. Composition and properties of the Ti–Al–Cu–N, Ti–Al–Ni–N, and Ti–Al–N coatings.

Sample	Composition, at. %				<i>H</i> (GPa)	<i>E</i> (GPa)	H^3/E^2 (GPa)	<i>H/E</i>	$\sigma(1)$ (GPa)	$\sigma(2)$ (GPa)
	Ti	Al	Cu/Ni	N						
Ti–Al–Cu–N	51	2	3	44	43 ± 3	649 ± 31	0.189	0.066	+0.13/+0.19	+0.27/+0.32
Ti–Al–Ni–N	48	2	8	42	51 ± 5	680 ± 25	0.287	0.075	+0.12/+0.17	+0.21/+0.25
Ti–Al–N	53	2	–	45	29 ± 1	561 ± 16	0.077	0.052	−4.80/−4.29	−5.31/−4.73

As mentioned in the experimental section, coatings were deposited under identical conditions onto carbide inserts and silicon substrates, which are characterized by significantly different linear thermal expansion coefficients. The coefficients were equal to $4.46 \times 10^{-6} \text{ K}^{-1}$ for the first substrate and $3.39 \times 10^{-6} \text{ K}^{-1}$ for the second one. This predetermines a different contribution of the thermal component of stresses to the total stress. The results demonstrated that no significant differences were observed between the stresses of the coatings formed on different substrates, being indicative that the metal phase and the formed structure have a relaxation effect both on the structural-phase and the thermal component of stresses. Whilst discussing the mechanism of stress relaxation in the metal-ceramic coatings under study it should be noted that the mechanism proposed in [19,20] and related to the relaxation of the strain field around the crack tip in the ductile phase and disintegration of ligaments of the ductile phase in the bridge structure behind the crack tip seems not to be working in our case. This depends on the low scale of the ductile metal phase, making the dislocation deformation mechanism impossible. Lattice and grain boundary dislocations as a lattice defect in the copper and nickel layer with thickness of several nanometers or several fractions of nanometers are not possible. Intrinsic stresses relaxation is possible here due to absorption of elastic energy by branched interphase (TiAlN/Ni; TiAlN/Cu) and intercrystallite (Ni/Ni; Cu/Cu) boundaries which are formed during the coating deposition and are characterized by a large surface area. As mentioned above, a number of researchers believe that the stresses value has a significant effect on fatigue strength of the coatings. It increases with rising compressive stresses and decreases with tensile stresses.

The results of the multi-cycle dynamic impact test of the coatings under study are shown in Figures 7 and 8. The Ti–Al–N, Ti–Al–Cu–N, and Ti–Al–Ni–N coatings performed almost identically after 10^4 cycles of impact loading (Figure 7a–c). No coating degradation was observed. Fragments of the wear products of the carbide counter body were detected on their surface. Judging by the size of the wear spot, the degree of wear in the counter body was greater in the case of Ti–Al–Ni–N and

Ti–Al–Cu–N coatings, manifesting itself as the increased contact area of the counter body with the samples under study.

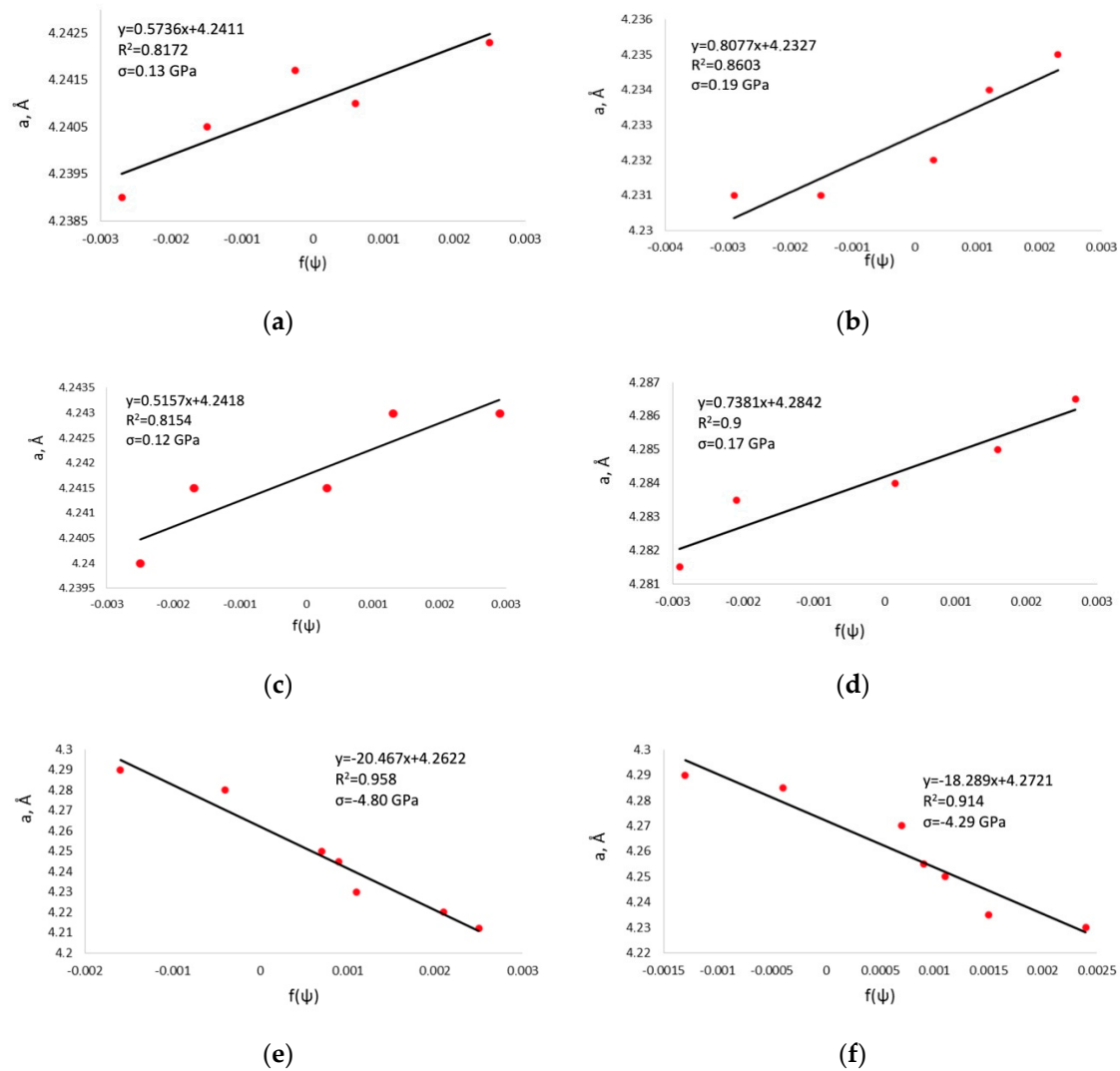


Figure 6. Lattice parameter $a\Psi$ (Ti,Al)N as a function of $f(\psi) = \frac{1}{2}s_2 \sin^2 \psi + 2s_1$ for the coatings: Ti–Al–Cu–N (a,b); Ti–Al–Ni–N (c,d); and Ti–Al–N (e,f) deposited onto silicon (a,c,e) and carbide inserts (b,d,f).

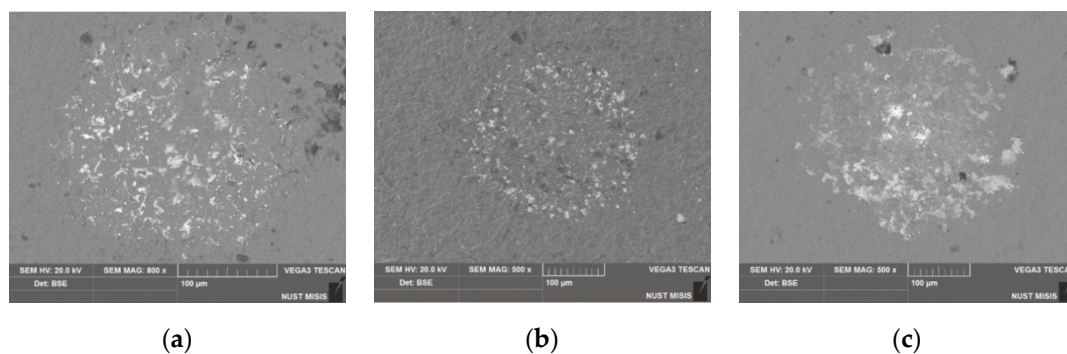
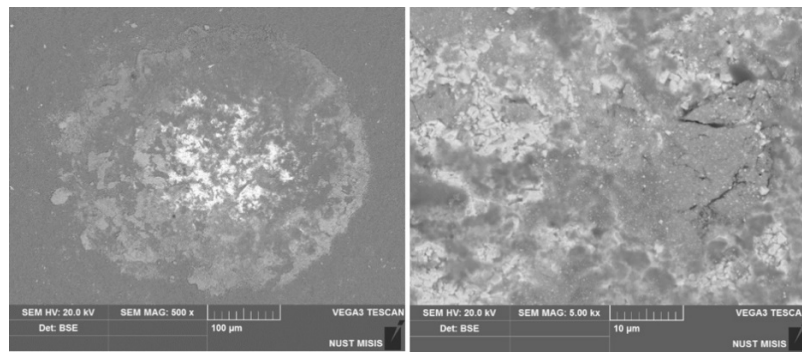
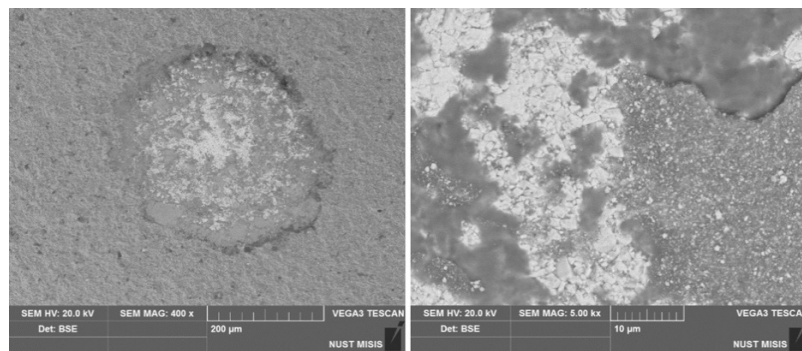


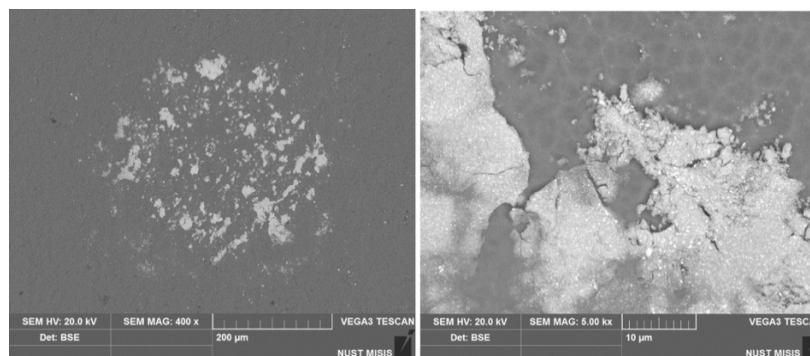
Figure 7. SEM micrographs of impact cavities after testing in air at an applied load of 250 N for 1×10^4 cycles: (a) Ti–Al–N; (b) Ti–Al–Cu–N; and (c) Ti–Al–Ni–N coatings.



(a)



(b)



(c)

Figure 8. SEM micrographs of impact cavities after testing in air at an applied load of 250 N for 5×10^5 cycles: (a) Ti–Al–N; (b) Ti–Al–Cu–N; and (c) Ti–Al–Ni–N coatings.

This is apparently due to their higher level of hardness as compared to that of the Ti–Al–N coating. Examination of the wear spots after 5×10^5 loading cycles demonstrates a significant difference in the coatings performance. The mechanisms of their degradation are different. Cracks and signs of brittle degradation of coating resulting in substrate exposure were observed on the surface of the Ti–Al–N coating (Figure 8a). The Ti–Al–Ni–N sample under these experimental conditions did not show any signs of degradation with substrate exposure and maintained its integrity (Figure 8c). Similar to the case of 10^4 loading cycles only wear products of the counter body were observed on its surface. The Ti–Al–Cu–N coating sample demonstrated signs of its detachment from the substrate. Detachment followed the contour of the wear spot. This fact may be indicative of the adhesion mechanism of coating degradation (Figure 8b).

Thus, despite the decreasing level of compressive stresses in the Ti–Al–Cu–N and Ti–Al–Ni–N coatings as compared to that in Ti–Al–N, their crack resistance under fatigue degradation was much

higher. We can therefore conclude that in this case the determining influence is made by transition to the nano-grain isomorphous structure (due to reduction of the grain size from 100–120 nm for Ti–Al–N to ~15–20 nm for Ti–Al–Cu–N and Ti–Al–Ni–N) rather than the level of compressive stresses inhibiting crack propagation. The results attesting to a greater resistance to multi-cycle dynamic impact loading of Ti–Al–Ni–N coating compared to that of the Ti–Al–Cu–N coating are related to the higher H^3/E^2 and H/E parameters (Table 1) that characterize the resistance of the coating material to plastic and elastic deformation and can be attributed to the difference in adhesive strength of these coatings with the carbide inserts [30]. The scratch-test for these coatings demonstrated a cohesive mechanism of their degradation. The first crack load (L_{c1}) was ~20–22 N for both compositions. This stage of coating degradation was accompanied by a noticeable increase in acoustic emission intensity. The Ti–Al–Ni–N and Ti–Al–Cu–N coatings were uniformly worn out as the load was increased and a lot of cracks were formed at the scratch bottom. Exposure of the substrate material at the crack bottom (local wearing of the coating) was observed only after the load L_{c3} of 64 and 57 N for the former and latter coatings, respectively, had been attained. The L_{c1} parameter for Ti–Al–N coating was equal to 11 N, along with the fact that this coating destructed according to the adhesion mechanism when the load L_{c2} was 35 N.

4. Conclusions

Investigation of the effect of copper and nickel on the stress state of the Ti–Al–Cu–N and Ti–Al–Ni–N coatings with the equiaxial nano-grain structure (15–20 nm) demonstrated that the absolute stresses value decreased from –4.29––5.31 GPa, being typical of the Ti–Al–N coatings with the columnar structure and grain size of ~120 nm to 0.12–0.32 GPa. The intrinsic stresses relaxation in metal-ceramic coatings was apparently related to the absorption of elastic energy by branched interface (TiAlN/Ni; TiAlN/Cu) and intercrystallite boundaries (Ni/Ni; Cu/Cu) which are formed during the coating deposition and are characterized by a large surface area.

Despite the decreasing level of compressive stresses in Ti–Al–Cu–N and Ti–Al–Ni–N coatings as compared to that in the Ti–Al–N coating, their crack resistance under conditions of fatigue degradation during the multi-cycle dynamic impact test was significantly higher. These coatings were also characterized by high hardness values of 43 and 51 GPa, respectively, vs. 29 GPa for the Ti–Al–N coatings. Transition to the nano-size isomorphous structure, rather than the level of compressive stresses, played the key role in this case.

A better crack resistance of Ti–Al–Ni–N coatings under multi-cycle dynamic impact loading as compared to that of Ti–Al–Cu–N coatings was related to higher H^3/E^2 and H/E parameters and attributed to the difference in adhesion of these coatings to the carbide inserts.

The obtained results can indicate the prevailing role of the nanostructure of the coatings as compared to the stresses in achieving their high hardness values and resistance to the crack formation.

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