Morphological changes of the PVD coatings after isothermal annealing

P Babincová, M Sahul, P Drobný and Ľ Čaplovič
Slovak University of Technology in Bratislava, Faculty of Materials Science and Technology in Trnava, Ulica Jána Bottu č. 2781/25, 917 24 Trnava, Slovak Republic

Abstract. The main of this work is to investigate the impact of the isothermal annealing on the structure and morphological changes on the PVD hard coatings. Three different coatings based on the AlTiN system were deposited onto cemented carbide substrates containing 6 wt% of Co. Two coatings AlTiN/TiAlN and AlTiN/TiN with an initial thickness of 3 µm has a coarse-grained columnar structure with a chemically graded nanomultilayering consisting of alternating Ti-rich and Al-rich layers. In the case of the AlTiN/TiAlN coating, a total of 20 layers were applied. Ten layers had a thickness of 200 nm (AlTiN) and 10 layers with the thickness of 100 nm (TiAlN). The same number of nanolayers was also retained for the AlTiN/TiN multilayer coating. The TiN layers were 100 nm thick. The third coating was a nanocomposite sandwich coating formed by a TiSiN adhesive layer (50nm), a functional nanocomposite AlTiSiN layer (2 µm) and a top functional TiSiN layer with a thickness of 1 µm. The coatings were prepared by cathodic arc evaporation using the LARC® technology.

After deposition, the samples were annealed at high temperatures (700 °C, 800 °C, 900 °C, 1000 °C) for one hour in air. With X-ray diffraction and scanning electron microscopy, the morphology, structure and phase composition of coatings and oxide layers after annealing were evaluated.

After the heat-treatment at 800 °C, cross-sectional and surface morphology images revealed, that an oxide layer has grown on top of the all coatings. EDS analysis showed that the oxide layers on the multilayers coatings had a layered structure, which was found to be the consequence of the high diffusion rate of Al. The interface with the coatings was very rough. It was depleted of Al, which diffused to the upper surface of the oxide. The oxidation process of nanocomposite AlTiSiN/TiSiN coating started by forming an oxide layer of ternary Ti–Si–O at the interface. This system segregated into two phases of TiO₂ and SiO₂. The nanocomposite coating remained stable even after annealing at 1000 °C. The surface of the multilayers was accompanied by a network of cracks at this temperature. An interesting phenomenon was also observed on the substrates itself during the annealing. As a result of oxidation, unprotected sides of the substrates expanded. Globular oxides based on tungsten and cobalt were also formed on the surface of the samples at the places where the coating was peeled off. The reasons for the differences are discussed.

1. Introduction
The AlTiN system has found a lot of industrial applications as hard and wear resistant coatings for cutting tools to enhance their life-time. These coatings with cubic NaCl (c) structure, where Al substitutes for Ti in the TiN based structure, are one of the most preferred wear resistant materials for
advanced machining processes. Coatings combine very good mechanical and chemical properties, such as high oxidation resistance and high thermal and chemical stability. Thermal stability is a general term used to describe the changes occurring in the material as a function of temperature. These include oxidation, microstructure, composition or mechanical properties. This is a very important issue for industrial applications, as during the high-performance metal cutting operations, degradation of the coating occurs by wear related to oxidation or diffusion. Aluminum, present in the AlTiN system is an efficient additive improving oxidation and wear resistance and enhancing the thermal stability. Coatings can be applied up to temperatures of 800 °C. On the coating surface is grown a stable protective Al$_2$O$_3$ film in oxidizing environment. It is a highly insulating oxide, with low ion mobility and creates an effective oxygen diffusion barrier. Similar oxidation resistance was obtained by the addition of Si to TiN system where the protective barrier from oxygen diffusion is formed by amorphous oxides of silicon (SiO$_2$). TiSiN and AlTiSiN are nanocomposite coatings due to formation of amorphous phase of Si$_3$N$_4$ which is form around the AlTiN (TiN) crystals and also create barrier for oxygen diffusion [1-11].

2. Experimental details

2.1. Coating deposition

In this work the structure and morphological changes of the PVD coatings after isothermal annealing were investigated. The coatings were deposited on WC-Co (6 wt. % Co) cemented carbides discs with a 12 mm in diameter and a mirror-polished surface. The substrate samples were then ultrasonically cleaned for 15 minutes in acetone.

Three different coatings based on the AlTiN system were prepared by cathodic arc evaporation using the LARC® technology PLATIT π$_80^+$DLC. Three combination of cylindrical rotating cathodes (Al, Ti, TiSi) are shown in Figure 1. Two coatings were multilayers with coarse-grained columnar structure with a chemically graded nanomultilayering. Both multilayers have an initial thickness of 3 µm. AlTiN/TiAlN consisting 20 layers – 10 layers of Al-rich AlTiN with 200 nm thick and 10 layers of Ti-rich TiAlN with 100 nm thick. For AlTiN/TiN multilayer was applied 10 AlTiN layers with the same thickness of 200 nm and 10 layers of TiN with the 100 nm thick. The third coating was a nanocomposite sandwich coating formed by a TiSiN adhesive layer (50 nm), a functional nanocomposite AlTiSiN layer (2 µm) and a top functional TiSiN layer with a thickness of 1 µm. The current values and the chemical composition of the coating are shown in Table 1. The reactive gas was N and the chamber pressure was 1.9 Pa. The temperature during the deposition was 470 °C and the negative bias voltage on the substrates was −60 V.

Figure 1. PLATIT π80+DLC chamber, cathode arrangement for individual deposition.
Table 1. Deposition DC current and chemical composition.

| Coating          | DC current [A] | Chemical composition [at. %] |
|------------------|----------------|-----------------------------|
|                  | Al  | Ti  | TiSi | N   | Al  | Ti  | Si  |
| AlTiN/TiAlN      | 162 | 95  | -    | 55  | 27.5| 17.5| -   |
| TiAlN            | 95  | 95  | -    | 55  | 12.6| 32.4| -   |
| AlTiN/TiN        | 162 | 95  | -    | 55  | 27.5| 17.5| -   |
| TiN              | -   | 150 | -    | 53  | -   | 47  | -   |
| TiXCo<sup>3</sup>|     |     |      | 54.5| 25.4| 16.3| 3.8 |
| TiSiN            | -   | -   | 150  | 57.2| -   | 33.2| 8.6 |

2.2. Isothermal annealing

The oxidation resistance of the coatings was determined by an annealing process at temperatures of 700, 800, 900 and 1000 °C without a protective atmosphere in a laboratory annealing furnace for 1 hour, followed by continuous cooling in air. At 1000 °C, the holding time was only 20 minutes to avoid deformation of the substrate.

2.3. Chemical and structural characterization

The morphology and structure of the fracture areas of the individual coatings before and after their heating were observed by a JEOL JSM 7600F scanning electron microscope. Imaging was done using a secondary electron detector (LEI) or a backscattered electron detector (RBEI). Parameters during observation were: \( U = 20 \text{ keV}, \ I = 2 \text{ nA} \) and \( WD = 15 \text{ mm} \). Quantitative point and area analysis using a Si (Li) EDX detector X-Max 50 mm<sup>2</sup> from Oxford Instruments was used to identify the chemical composition of the coatings as well as oxidation products on the surface of the coatings. Using the same detector, changes in element content after the annealing processes from the surface of the coatings to the base material were also monitored by qualitative linescan EDX analysis.

Identification of phases present in the investigated coatings was performed by X-ray diffraction analysis using an Empyrean diffractometer from PANalytical with an anode CoK\( \alpha \) (\( \lambda = 0.178897 \text{ nm} \)), with Bragg-Brentan geometry \( \Theta - \Theta \), X-ray mirror to achieve primary parallel beam and positionally sensitive PIXcel3 detector. Analysis of individual samples was performed using GIXRD (Grazing Incidence X-ray Diffraction) geometry at a constant angle of incidence of a parallel X-ray beam to the sample surface \( \omega = 0.5^\circ \). In this way, controlled penetration of X-ray radiation into the surface layers of the materials is only achieved, and thus this method is suitable for identifying the phase composition of the coatings. The parameters for the Co anode used during the measurement were as follows: \( U = 40 \text{ kV}, \ I = 40 \text{ mA} \), angular interval \( 2\Theta (35 \div 100^\circ) \).

3. Results

3.1. Morphology and structure of the fracture areas

Figure 2 shows the morphology of all investigated coatings after deposition. Macroparticles of various sizes have been observed on the coatings, the formation of which is related to the deposition process. Also imperfections in the form of peeled parts of coatings can be seen. At a detailed magnification (5000x), an interesting network structure can be seen, which is present in all observed coatings, and its formation is probably due to the presence of plasma in the coating process.

The fracture areas of the coatings (Figure 3) show the samples structure perpendicular to the coatings. The individual layers of the coatings can be recognized by the material contrast of the RBEI detector. In the case of multilayers, the thinner TiAlN and TiN layers appear lighter due to the higher titanium content, the atomic number of which is higher than that of aluminum. On the contrary, thicker layers of AlTiN with higher aluminum content appear darker. The coatings are characterized by a columnar structure.
3.2. Isothermal annealing

3.2.1. AlTiN/TiAlN multilayer. The AlTiN/TiAlN coating was exposed to the air atmosphere at an elevated temperature of 700 °C for 1h. The coating morphology did not appear to have changed after heating. The occurrence of macroparticles as well as the network structure was maintained after annealing to the appropriate temperature. EDX qualitative point analysis was performed on the coating. The results show the presence of oxygen at 20 at.%, which indicates the formation of local oxides at a higher temperature but did not form a continuous oxide layer and the coating may be considered stable.

In Figure 4a, there is a macroscopic view of a sample that was annealed without a protective atmosphere at 800 °C. The coating changed color, indicating oxidation of the surface. It is also evident that after annealing, the substrate itself oxidized at the no-coated edges of the sample.
An oxide layer with a thickness of more than 1 mm was formed which lined the edges of the sample. By its expansion, the substrate damaged the coating on the edges, as can be seen in the detail of Figure 4b.

The morphology of the multilayer surface (Figure 5a) did not show signs of oxidation even after annealing to 800 °C. It can be stated that despite the expansion of the substrate at the edges of the sample, the layer retains integrity and protects the base material. At a larger magnification (Figure 5b) was not observe the classical fine network structure but the presence of oxides was noted. Their formation is the result of the early oxidation of the coating. The presence of oxygen in the coating has increased significantly by approximately 25 at. % compared to the results giving the chemical composition values after annealing at 700 °C.

![Figure 5. Morphology of the AlTiN/TiAlN multilayer after annealing at 800 °C a) 1000x, b) 10 000x.](image)

Substrate oxidation was also confirmed by quantitative point EDX analysis. The measured values of the elements are given in Table 2, the points showing the area of analysis are documented in Figure 6. Spectrum 1 confirmed the presence of a damage coating at the edge of the substrate and spectrum 2 and 3 showed oxidation of the base material. Based on the literature and analyzed oxygen content (Table 2), it can be assumed that the oxidation products of the sintered carbide are probably oxides of WO$_3$ or MWO$_4$ (M = Co).

The top layer of the coating about 0.35 µm thickness has changed. It creates a different color contrast, which can confirm the theory that an oxide layer is beginning to form on the surface. However, the structure of the multilayer is still stable, free from cracks and with good adhesion to the base material. A linescan EDX analysis of the fracture area was also performed for analysis.

![Figure 6. Substrate oxides after sample annealing at 800 °C.](image)
Table 2. Results of point EDX analysis of substrate edge after annealing at 800 °C in at. %.

|       | C   | O     | Al  | Ti   | Co  | W   |
|-------|-----|-------|-----|------|-----|-----|
| Spektrum 1 | 5.16 | 70.37 | 5.77 | 11.88 | 1.66 | 5.16 |
| Spektrum 2 |     |       |     |      | 8.23 | 17.99 |
| Spektrum 3 | 21.62 | 53.02 |     | 11.79 |     | 13.57 |

In Figure 7 the course of the chemical composition from the surface of the coating to the substrate is shown. The overall graph shows that there is an increased concentration of oxygen on the surface of the coating, whose content decreases towards the coating. The thickness corresponds to the thickness of the top layer. The nitrogen concentration in this layer decreases. Also, an increased concentration of aluminum is recorded on the surface of the coating, suggesting that oxygen preferentially binds to aluminum resulting in the formation of aluminum oxides (probably Al$_2$O$_3$). The presence of this type of oxides on the surface of the coatings is considered to be a beneficial consequence of the oxidation process as they result in an increase in their wear resistance.

![Figure 7](image)

**Figure 7.** EDX linescan of fracture area of multilayer AlTiN/TiAlN after annealing at 800 °C.

After annealing the sample at 900 °C, it can be seen that the substrate, by its oxidation damage the multilayer at the edges of the sample as a previously case. The globular substrate oxides were also re-formed and became trapped at the edge of the coating (Figure 8a). At a small magnification, the multilayer morphology does not show significant signs of oxidation.

![Figure 8](image)

**Figure 8.** a) Edge of the coating with substrate oxides, b) AlTiN/TiAlN coating morphology after annealing at 900 °C.
On the surface there are sporadically visible substrate oxides, which are formed at delaminated areas of the coating where oxygen diffused into the exposed base material. At a larger magnification (Figure 8b), it is possible to see oxides on the surface of the multilayer.

EDX linescan analysis (Figure 9) confirmed the increased oxygen concentration at the surface of the coating and confirmed consisting of two layers. Aluminium oxides (Al$_2$O$_3$) are likely to be formed on the surface, and an oxide sublayer is formed beneath this layer, which appears to be a combination of titanium oxides (TiO$_2$) and aluminum oxides (Al$_2$O$_3$). The presence of nitrogen was observed again under the oxide layer, and its content was of heterogeneous character.

Figure 9. EDX linescan of fracture area of multilayer AlTiN/TiAlN after annealing at 900 °C.

After annealing at 1000 °C, a continuous oxide layer was formed on the AlTiN/TiAlN multilayer (Figure 10b). Cracks are visible on the entire surface of the coating (Figure 10a). The fracture area of the coating shows that the AlTiN/TiAlN coating is degraded to a considerable depth (Figure 11). The initial coating thickness of 3.2 µm was reduced to approximately 2.7 µm. A third, already from the reduced layer thickness, represents a continuous oxide layer.

The course of the EDX linescan analysis has not changed significantly from the previous case. Only the oxide layer/coating interface has advanced to a higher depth. Their course is shown in Figure 11. The oxide layer is predominantly composed of two types of oxides - Al$_2$O$_3$ and TiO$_2$.

Figure 10. AlTiN/TiAlN coating morphology after annealing at 1000°C a) 500x, b) 5 000x.
3.2.2. AlTiN/TiN multilayer

The development of the AlTiN/TiN coating after annealing at individual temperatures was very similar as in case of the previous multilayer. The morphology of the coating after heating to 700 °C is not different from the morphology before annealing. It contains the macroparticles that were formed during the deposition process and also a typical network structure. Substrate oxidation occurs at 800 °C. According to Figure 12b, it is evident that it is the same mechanism as the AlTiN/TiAlN coating. The globular substrate oxides increased by scrolling and captured on the coating edges, which were damaged by the expansion of the cemented carbide due to the elevated temperature.

By means of EDX analysis, a qualitative linescan analysis was also performed on the fracture area. The analysis results are shown in Figure 13. The highest amount of oxygen is recorded at the top of the coating and decreases towards the substrate. The depth of its highest concentration corresponds to the thickness of the top layer. It can also be seen from the change in concentration that the top layer is depleted of titanium and nitrogen as a result of diffusion. Apart from oxygen, is predominantly aluminum on the top, and thus is believed to formation of an Al₂O₃ passivation layer. The interface of the coating-substrate system is intact, the layer is stable and the adhesion has not deteriorated.

The edges of the sample after heating to 900 °C have the same oxidation behavior as in the previous multilayer (Figure 14). By oxidizing the substrate tears the layers and damages the edges of the coating. The coating morphology is characterized by the presence of small crystals of oxides. The initial coating thickness - 3.1 µm was reduced by 0.4 µm. The missing portion of the coating was degraded by oxidation. The top of the coating (approximately 0.2 µm) is oxidized. However, the remainder of the coating up to the substrate is stable as in the previous cases. Oxygen did not diffuse to a depth of more than 0.8 µm.
Figure 13. EDX linescan of fracture area of multilayer AlTiN/TiN after annealing at 800 °C.

Figure 14. a) Morphology of the AlTiN/TiN multilayer after annealing at 900 °C, b) Edge of the coating with substrate oxides.

After annealing the coating at 1000 °C, the oxide layer of the cemented carbide reached a thickness of more than 1.5 mm. The multilayer analyzed after oxidation had the same behavior as the AlTiN/TiAlN multilayer. A large amount of oxides and cracks was present on the surface coating (Figure 15a).

Figure 15. AlTiN/TiN coating morphology after annealing at 1000 °C a) 50x, b) 2000x.
From the fracture area of the multilayer, is obvious that its thickness has dropped by almost 0.8 µm and the oxidized layer of the remaining coating is also 0.8 µm but has no homogeneous thickness over the entire coating (Figure 16).

![Figure 16. EDX linescan of fracture area of multilayer AlTiN/TiN after annealing at 1000 °C.](image)

3.2.3. TiXCo$^3$. The TiXCo$^3$ nanocomposite coating retained its morphology as it had before heating to 700 °C. Using quantitative point EDX analysis, the surface showed the presence of oxygen (approximately 40 at.%). However, there is no continuous oxide layer on the coating; it is the formation of local oxides. Once the sample has been heated to 800 °C, the substrate is also oxidized. The oxide layer of cemented carbide has the same character as in the previous two cases of multilayers. The mechanism of formation of globular oxides of sintered carbide also has two methods of formation in this coating. The first is the scrolling of the oxides towards the coating and subsequent capture at its edge. The second mechanism is the formation of oxides at places where the coating had a damaged structure (peeled off parts of coatings due to the residual stresses) and oxygen could diffuse directly into the substrate. Figure 17 b documents the substrate oxide formed at the peeled part of the coating. Coating residues are visible on the oxide. The morphology of the coating after heating to 800 °C already shows signs of oxidation. In Figure 17a, small crystalline formations are seen, which are apparently titanium oxides (TiO$_2$). The fracture area showed that the sandwich nanocomposite coating increased its thickness by 0.4 µm after annealing. This is obviously an oxide layer containing titanium oxides, preferably TiO$_2$, but the formation of silicon oxides (SiO$_2$) is possible. Interestingly, unlike multilayers, the oxide layer has grown on the coating and has not oxidized the top coating layer.

![Figure 17. a) TiXCo$^3$ coating morphology after annealing at 800 °C, b) Substrate oxide on the coating surface.](image)
A TiXCo$_3$ coated sample after annealing at 900 °C is shown in Figure 18a. The substrate underwent oxidation and formed an oxide layer up to 2.5 mm thick. The oxide layer was formed in layers. The coating morphology was oxidized as in the previous case. A larger magnification indicates that the coating is coated with a continuous layer of oxides having a different morphology than that of multilayers (Figure 18b). On the fracture area of the sandwich nanocomposite coating, it is possible to observe a continuous oxide layer formed on its surface. While after annealing at 800 °C, it appeared that the oxide layer was formed on the coating and did not affect TiXCo$_3$ alone, in Figure 19 it can be seen that the thickness of the top layer decreased in this case and oxidation also occurred in the coating itself. The total layer thickness after heating at 900 °C is 3.59 µm and the oxide layer has reached 0.74 µm.

![Figure 18. a) Oxidation of the WC-Co sample coated with TiXCo$_3$ after annealing at 900 °C b) TiXCo$_3$ coating morphology after annealing at 900 °C.](image)

![Figure 19. EDX linescan of fracture area of TiXCo$_3$ after annealing at 900 °C.](image)

After annealing at 1000°C there is a continuous oxide layer on the TiXCo$_3$ coating (Figure 20a). This is confirmed by a quantitative EDX analysis which recorded an amount of oxygen of about 70 at.% on the surface. Occasionally substrate oxides are also present on the oxide layer. In Figure 20b, the substrate oxide formed in damaged areas of the coating is shown. The globular oxide gradually disrupted the coating during its growth, causing an interesting morphology around the oxide.

The fracture area of the coating (Figure 21) has an interesting structure. The total coating thickness, due to the oxide layer, increased by 1.38 µm. The nanocomposite functional layer did not change its thickness, but the top layer thinned by 0.5 µm. The oxide layer consists of two different layers. The first one is 0.63 µm thick and the second one is 0.74 µm thick. By EDX linescan analysis it is not possible to determine exactly what type of oxides it is. Both layers have approximately the same chemical composition, but the lighter layer has a higher proportion of O and less Ti and Si.
However, the coating protected the sintered carbide even when heated to the highest temperature of 1000 °C. It should also be pointed out that the functional and adhesive layer resisted by oxidation and remained intact. At 1000 °C, the TiXCo$^3$ nanocomposite coating is able to protect its substrate from oxidation.

3.3. Phase composition analysis

Qualitative X-ray diffraction analysis confirmed the presence of one phase in all three deposited layers. It is the cubic phase of TiN, whose preferred orientation was in the crystallographic plane (002). In addition to this plane, the TiN phase also diffracted significantly on planes (111) and (022), also for all three coatings. For both multilayers, a shift to the right of the diffraction maxima for planes (002) and (022) was noted, which represents a reduction in the lattice parameter due to the substitution of aluminum atoms into the lattice of the cubic solid TiN solution. In addition to the phase present in the coatings, two phases belonging to the base material were identified. It is the hexagonal phase of WC diffracting on planes (010), (011) and (001) and hexagonal phase Co.

X-ray diffraction analysis was also used to identify oxidation products, by analyzing selected samples at various heating (AlTiN/TiAlN multilayer after heating to 800 °C, multilayer AlTiN/TiN after heating to 900 °C, multilayer AlTiN/TiAlN after heating to 1000 °C and nanocomposite TiXCo$^3$ sandwich coating after heating to 1000 °C). Given the thickness of the coatings and especially the thickness of the oxide layers, this analysis was also carried out in GIXRD geometry. From the diffraction pattern shown in Figure 22a was observed that the oxidation of the surface layers was already at 800 °C.
The hexagonal Al$_2$O$_3$ phase and the tetragonal TiO$_2$ phase were identified as oxidation products and the cubic Al$_2$O phase was detected in the case of the AlTiN/TiAlN multilayer annealed at 1000 °C. However, in the case of oxides, diffraction occurs over a wide-angle range, with the individual angles being very similar, and therefore it is not excluded that other types of Al and Ti-based oxides may have formed on the surface of the coatings. In addition to the layer oxides, the oxides of the base material in the form of oxides WO$_3$ and CoWO$_4$ from the edges of the samples were also detected (Figures 22, 23).

4. Discussion and conclusion

As a result of isothermal annealing, continuous oxide layers were formed already at 800 °C. For both multilayers, progressive oxidation evolution was the same by increasing temperatures. The formation of an oxide layer was predominantly made up of Al$_2$O$_3$ and TiO$_2$ oxides. Wu and Lee, who investigated the oxidation resistance of AlTiN-based coatings, confirmed the presence of these oxides.

[12-13] After performing X-ray diffraction analysis showed the presence of hexagonal phase Al$_2$O$_3$ and tetragonal phase TiO$_2$, but the presence of other types of oxides based on Ti and Al was not excluded. Titanium Dioxide - Rutile is a nanostructured phase with the space group P 42/m n m and crystallographic parameters $a = b \neq c$, $\alpha = \beta = \gamma$ (90°, 90°, 90°). Aluminium Oxide (Al$_2$O$_3$) is
a hexagonal phase with the space group R - 3 c and crystallographic parameters \(a = b \neq c, \alpha = \beta \neq \gamma\) (90°, 90°, 120°). \(\text{Al}_2\text{O}_3\) passivation layer was formed on the surface. This phenomenon occurs in many literature publications that focus on AlTiN-based coatings analyzes. This formation was also confirmed in this case. Due to its slow ion mobility, the layer acts as an effective barrier to oxygen diffusion. In addition to acting as a protective coating, it also improves mechanical properties due to its hardness. However, based on analyzes, it can be concluded that the layer is only stable up to a certain temperature. After annealing at 900 °C, the multilayers gradually degraded. Their thickness decreased and the thickness of the oxide layer increased. Nevertheless, the coating showed stability.

When the coating was heated to 1000 °C, the degradation of the multilayers was complete. In addition to the fact that the coatings have lost a considerable part of their thickness as a result of oxidation, the surface has cracked and thus completely degraded.

The sandwich nanocomposite coating had a different course of oxide layer formation. At 700 °C the oxygen content of the coating was increased and at higher temperatures small crystals of oxides were already formed. However, these oxides were not formed at the expense of the coating but as an additional layer on the coating. At higher temperatures, the continuous oxide layer has already penetrated into the coating. The different course of oxidation is probably due to the presence of Si. In his study, Choi examined the effect of silicon on the formation of an oxide layer and found that the higher the silicon content of the coating, the higher the oxidation resistance. According to studies by Choi and Zhang, the presence of \(\text{TiO}_2\) or \(\text{SiO}_2\) oxides was suggested [14-15]. X-ray diffraction analysis confirmed only the presence of titanium oxides, since \(\text{SiO}_2\) is characterized by an amorphous structure and its formation on the coating is therefore not excluded. Unlike multilayers, the nanocomposite coating has maintained its stability even at 1000 °C. No degradation due to cracking. The coating thickness did not decrease significantly. An interesting feature was the formation of a two-layered oxidic film that was formed at this temperature. Segregation of titanium and silicon oxides is believed to have occurred. Silicon oxides act as a high temperature barrier to the diffusion of oxygen.

In addition to the oxidation of the coatings themselves, the WC-Co base material was also oxidized. The edges of the samples were not protected by coatings and therefore oxygen was directly exposed to the substrate, causing its oxidation. As a result, the edges of the samples began to expand and the coating on the edges was damaged. Globular oxides have also been observed which have been attached to the edges of the coatings by scrolling. Their occurrence has also been documented on surface of coatings. Their formation is associated with coating defects. Due to the high stress in the coatings, small parts of the coating are peeled off during the deposition process. In some cases, the delamination will completely uncover the base material. Such sites are then exposed to an air atmosphere at elevated temperatures and the substrate is oxidized. Substrate oxides increased at these sites and were observed in the form of globular formations. X-ray diffraction analysis showed that they are oxides of \(\text{WO}_3\) and \(\text{CoWO}_4\), which they also reported in their studies by Ghadami and Geng. [16-17] Although the coating protects the substrate at elevated temperatures, the presence of these local oxides in the weakened areas is not desirable as they may tear off and damage the layer in the machining process.

Acknowledgments
This publication was supported by the Project of VEGA Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic and Slovak Academy of Sciences, No. 1/0540/19: “Research of possibilities of increasing the thermal and oxidation stability of Al-Ti-N based hard coatings” and also by the Slovak Research and Development Agency with grant number APVV-15-0168: “Research of modification of phase interfaces in the coating/substrate system to increase the adhesion of hard coatings” and the Operational Program Research and Innovation for the project: "Independent research and development of new superhard coatings and their characterization by advanced experimental techniques" (ITMS code: NFP313010T598), co-financed by the European Regional Development Fund.
References

[1] Parlinska-Wojtan M 2016 Oxygen diffusion in columnar TiAlSiN coatings investigated by electron microscopy Thin Solid Films 616 437-443
[2] Chang Y Y and Yang S M 2010 High temperature oxidation behavior of multicomponent TiAlSiN coatings Thin Solid Films 518 (21) S34-S37
[3] Chen L, Xu Y X, Du Y and Liu Y 2015 Effect of bilayer period on structure, mechanical and thermal properties of TiAIN/AlTiN multilayer coatings Thin Solid Films 592 Part A 207-214
[4] PalDey S and Deevi S C 2003 Single layer and multilayer wear resistant coatings of (Ti,Al)N Mater. Sci. Eng. A 342 58-79
[5] McIntyre D, Greene J E, Hakansson G, Sundgren J -E and Münz W –D 1990 Oxidation of metastable single-phase polycrystalline Ti0.5Al0.5N films: kinetics and mechanisms J. Appl. Phys. 67 1542–1553
[6] Hörling A, Hultman L, Odén M, Sjölen J and Karlsson L 2005 Mechanical properties and machining performance of Ti1−xAlxN-coated cutting tools Surf. Coat. Tech. 191 (2-3) 384-392
[7] Mayrhofer P H, Hörling A, Karlsson L, Sjölen J, Larsson T, Mitterer C and Hultman L 2003 Self-organized nanostructures in the Ti–Al–N system Appl. Phys. 83 2049-2051
[8] Parlinska-Wojtan M, Karimi A, Coddet O, Cselle T and Morstein M 2004 Characterization of thermally treated TiAlSiN coatings by TEM and nanoindentation Surf. Coat. Tech. 188–189 344
[9] Hofmann S 1990 Formation and diffusion properties of oxide films on metals and on nitride coatings studied with Auger electron spectroscopy and X-ray photoelectron spectroscopy Thin Solid Films 193/194 648
[10] Jarms C, Stock H –R and Mayr P 1998 Mechanical properties, structure and oxidation behaviour of Ti1−xAl,N-hard coatings deposited by pulsed dc plasma-assisted chemical vapour deposition (PACVD) Surf. Coat. Tech. 108–109 206-210
[11] Knotek O, Munz W D and Leyendecker T 1987 Industrial deposition of binary, ternary, and quaternary nitrides of titanium, zirconium, and aluminum J. Vac. Sci. Technol. A 5 2173–2179
[12] Wu Z T, Sun P, Qi Z B, Wei B B and Wang Z C 2017 High temperature oxidation behavior and wear resistance of Ti0.53Al0.47N coatings by cathodic arc evaporation Vacuum 135 34-43
[13] Lee K S and Seo S M 2005 Oxidation behaviors of TiAl(La)N coatings deposited by ion plating Scripta Materialia 52 445-448
[14] Choi J B, Kurn CH, Lee M H and Kim K H 2004 Effect of Si content and free Si on oxidation behavior of Ti-Si-N coatings layers Thin Solid Films 447 365-370
[15] Zhang C H, Lu X C , Wang H, Luo J B, Shen Y G and Li K Y 2006 Microstructure, mechanical properties, and oxidation resistance of nanocomposite Ti-Si-N coatings App. Surf. Sci. 252 6141-6153
[16] Ghadami F, Ghadami S and Abdollah-pour H 2013 Structural and oxidation behavior of atmospheric heat treated plasma sprayed WC-Co coatings Vacuum 94 64-68
[17] Geng Z, Hou A, Shi G, Duan S and Li A 2016 Tribological behavior at various temperatures of WC-Co coatings prepared using different thermal spraying techniques Tribolog Int. 104 36-44