Effect of the Post-Deposition Thermal Treatment on the Mechanical Properties of a Compositionally Modulated CrAlSiN-AlSiN Coating

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Abstract: A CrAlSiN-AlSiN coating with periodically modulated composition was investigated regarding dependence of the mechanical properties and toughness, morphology, composition, and structure on thermal treatment in the interval of 600–900 °C in argon ambience. The coating exhibited superhardness and high toughness up to 800 °C. A very slight decrease in the nanohardness, resistance to elastic strain to failure, and plastic deformation were observed. The coating had enhanced elastic recovery stable up to 700 °C. It was found that the coating morphology was not substantially influenced by the thermal treatment. X-ray diffraction (XRD) analysis revealed that the modulated coating had a nanocomposite structure, which did not change after annealing, even at 900 °C. The grains were composed mainly of fcc-CrN and h-AlN phases embedded into an amorphous Si3N4 matrix. A small amount of an h-Cr2N phase appeared after heating at temperatures above 700 °C. The coating composition was examined by energy-dispersive X-ray spectroscopy (EDS). The coating had stoichiometric up to 800 °C. It became sub-stoichiometric with respect to nitrogen after annealing at 800 °C and 900 °C. It is thus concluded that the CrAlSiN-AlSiN coating with a periodically modulated structure keeps the combination of superhardness (45.3 GPa) and improved toughness (H2/E2 = 0.362 GPa, elastic recovery 57%) at temperatures up to 800 °C, and is suitable for high thermal applications.

Keywords: nanocomposites; mechanical properties; structural properties; cathodic arc deposition

1. Introduction

The needs of present-day industry are posing demanding requirements for the mechanical and tribological properties of the tools, details, and pieces used in machining and forming technologies, high-speed machining, hard turning, micro-manufacturing, dry machining, and so on. The same requirements apply to the coatings used in surface engineering to enhance the hardness, thermal stability, wear, and corrosion resistance of modern materials used in industrial areas. Modern coatings are required to combine incompatible properties, such as superhardness with high toughness, thermal stability, and wear resistance. This goal is unachievable in conventional monolayer coatings based on nitrides and carbides of transition metals, despite the useful properties they possess [1–4]. Graded and multilayer structures offer an appropriate approach to overcome the limited potential of monolayer coatings. These configurations allow changes in the structure and composition of the coating period so that several properties are strengthened simultaneously [5–7].

Among the coatings widely used in industry, Cr-based coatings demonstrate better wear resistance under severe tribological conditions, such as high pressure and high temperature, due to their lower friction coefficient, high chemical stability, and high melting...
point. They also exhibit better corrosion and oxidation resistance because of the formation of protective oxides, which suppress oxygen diffusion [8,9]. Cr(Al, Si)N coatings with the best fracture wear and plasticity index were successfully developed as alternative to hexavalent chromium for milling applications [10]. Recently, many studies have shown that the properties of Cr-based monolayer coatings can be enhanced by the formation of a structure with a modulated composition. Thus, the presence of a metallic interlayer in the functionally graded Cr/CrN multilayer increases the coating adhesion to the substrate from 7 N (CrN) to 10 N (Cr/CrN) for the first critical load and from 37 N (CrN) to 40 N (Cr/CrN) at total delamination [11]. This coating also exhibits improved hardness after thermal treatment at 500 °C and excellent corrosion resistance in salt fog [12]. The coating hardness was increased from 1356 HV at 300 °C to 1684 HV after heating in air for 1 h due to the decreased amount of the ductile Cr and nanocrystalline structure formation. Chemical analysis revealed no corrosion products on the coating surface after 120 h treatment in salt fog. P.M. Samim et al. reported that a ZrN/CrN coating has excellent electrochemical behavior due to the many interfaces in the nanomultilayer structure which prevent the penetration of the agent into the substrate. This structure and the chemical inertness of the ZrN and CrN compounds cause the high corrosion resistance of the coating [13]. A comparative study of CrAlSiN monolayer and CrN/AlSiN superlattice multilayer coatings showed that the multilayer structure is not destroyed during high thermal treatment at 650 °C in a 100% steam atmosphere. Besides, the large number of interfaces hinders ionic mobility, which makes this structure highly applicable for such severe operating conditions [14]. Deposition of a thick Cr layer in a multilayer coating Cr/CrAlSiN improves the oxidation behavior in 1200 °C steam due to the formation of high-quality oxides grown over the thick Cr-rich layer [15]. As is well-known, Al incorporation in the CrN lattice has a positive effect on the mechanical properties, thermal stability, and oxidation resistance. CrAlN coatings exhibit improved mechanical characteristics expressed in higher hardness (30 GPa) and reduced elastic modulus (303 GPa) [16]. Moreover, they have good electrochemical behavior and high temperature oxidation resistance [16,17]. The use of CrAlN in multilayer structures imparts to systems better performance in terms of adhesion, oxidation, and mechanical characteristics as compared to monolayer structures [18–21]. Nanocomposite CrAlN/BN coating exhibited hardness as high as 46 GPa, which remained stable up to 800 °C in air [19]. Depending on the composition of the second sublayer and the bilayer period, the maximum hardness differs significantly, from 32.8 GPa (CrAlN/AION [18]) to 47.2 GPa (CrAlN/ZrO2 [21]). The bilayer composition also causes the adhesion strength, which can reach a value of 98 N (TiAlN/CrAlN [20]). These multilayer coatings showed better thermal properties than monolayer CrAlN ones, and their oxidation occurred at temperatures above 900 °C. Self-lubricating CrAlN/VN multilayer coatings with a very low wear rate of 1.1 × 10^{-7} mm/N.m, suitable for dry machining applications, have been reported as well [22]. Even multilayer structures composed of Cr-based compounds only, such as CrN/CrAlN or Cr/CrN/CrAlN, causes increased hardness up to 46 GPa [23] and better tribological and electrochemical properties [24]. Further improvement was achieved in the architectures containing a CrAlSiN layer. Varying the Al content through the technological parameters, coatings that possess high hardness, higher resistance to cracking, and high adhesive strength can be achieved [25]. As J.F. Tang et al. have shown, the presence of Si in the CrN/CrAlSiN multilayer refines the columnar structure and improves the coating hardness from 16.4 GPa to 20.1 GPa at the period thickness of 3.2 nm. Decreasing the bilayer period to 3.2 nm increases the coating/substrate adhesion strength up to 77 N [26]. Addition of V in the CrAlSiN coating composition assisted formation of V2O5 during heating up to 800 °C, which resulted in a significant decrease of the friction coefficient to 0.21 [27]. Significant improvement of the electrochemical and oxidation corrosion resistance was reported for Al2O3/CrAlSiN multilayer coating obtained by magnetron sputtering and atomic layer deposition [28]. Enhancement of the tribological properties was reported for nanocomposite CrAlSiN/gradient-CrAlSiCN coatings due to the addition of the carbon content, which causes a decrease in the coefficient of friction [29]. Studies are mostly
focused on the oxidation and corrosion resistance of CrAlSiN-based multilayer structures. To the best of our knowledge, the effect of high temperature treatment on the mechanical and tribological properties of CrAlSiN-based coatings with a modulated composition is insufficiently investigated.

Our previous study on the mechanical and structural properties of a CrAlSiN-AlSiN coating with periodically modulated composition exhibited both enhanced superhardness (54 GPa) and improved toughness (H/E* = 0.11, H3/E*2 = 0.72, Wc = 70%) [30]. This study aims to investigate the stability of the coating superhardness and enhanced toughness under high thermal treatment in the interval of 600–900 °C, for high-temperature industrial applications.

2. Materials and Methods

2.1. Coating Preparation

The coating studied was obtained on two types of substrates. One group was 10 mm in diameter and 5 mm thick high-speed stainless steel (HSS) coupons, which were used for investigation of mechanical properties. The second group was 10 mm × 10 mm square stainless steel DIN 1.4541 plates used for studying the morphology, composition, and structure. The modulated CrAlSiN-AlSiN structure was deposited in a Platit π80+ LARC® system from two lateral rotating cathodes of Cr (99.99 wt. %) and AlSi alloy (82 at.% Al, 18 at.% Si). A detailed description of the pre-deposition substrate treatment and deposition process is presented elsewhere [30]. The coating structure consisted of a contact layer and a periodical structure. The contact layer started with a Cr adhesion film, which gradually continued in a CrN transition layer, followed by a CrAlSiN gradient layer. The periodical structure was formed by seven alternate periods with modulated composition. With variations in cathode current, the period composition was gradually modulated from a Cr-rich to an Al-rich region. The Cr-rich region was obtained at a current of the Cr and Al+Si cathodes of 125 A and 140 A, respectively. At this step, the bias voltage was maintained at –45 V. The gradual transition to the Al-rich region was achieved by decreasing the Cr cathode current (I_{Cr}) to 135 A and by increasing the Al+Si cathode (I_{Al+Si}) current to 160 A. As these values were reached, the Al-reach zone was formed at a bias voltage of –90 V. The transition between periods was made by variation of I_{Cr} and I_{Al+Si} from 135 A to 125 A, and from 160 A to 140 A, respectively, while the bias voltage was changed to 45 V. The coating structure was completed with a CrAlSiN top layer.

The coating deposition was performed at a constant temperature of 500 °C, followed by post-deposition annealing at 525 °C in the same chamber in nitrogen ambience for two hours. These samples were named “as-deposited”. Thermal treatment was carried out in a resistance furnace, in Ar atmosphere, at 600 °C, 700 °C, 800 °C, and 900 °C for 2 h at each temperature. Afterwards, the specimens were cooled down in an Ar atmosphere and characterized.

2.2. Characterization Methods

The total coating thickness and the period thickness were measured by a compact Calotester CAT² (Anton Paar, Graz, Austria) using a ball-erosion method. The spherical crater through the coating and in the substrate was formed by a rotating steel ball with a diameter of 20 mm and abrasive diamond suspension with a grain size of 0.5 μm. The sublayers of the multilayer coating appeared as concentric circumferences whose diameters were determined by a 100–500× magnification optical microscope (Anton Paar Tritec SA, Corcelles, Switzerland). On the basis of the measured diameters, the sublayer thickness and the total coating thickness were calculated by the specialized Video Software Version 9.0.12 of the equipment.

Nanoindentation within the loading interval of 5-500 mN was performed to evaluate the mechanical properties using the Oliver–Pharr method [31]. The measurements were done by a Compact Platform CPX (MHT/NHT) system (CSM Instruments, Anton Paar, Graz, Austria) equipped with a certificated diamond Berkovich indenter. Nanoindentation
was performed at advanced mode with linear constant loading and a pause at maximum load of 5 s.

To study the coating composition, a cross-section of the samples was made after thermal treatment at each temperature. The cross-section was prepared in an ion milling machine IM 4000 Plus (Hitachi, Japan). The cross-section was obtained by 100 µm etching of the sample edge. The etching was performed using an ion gun in argon ambience at an accelerating voltage $U_{\text{acc}} = 6$ kV and a discharge voltage of 1.5 kV. During etching, a constant argon flow of 0.1 sccm was maintained, the swing of the holder was $\pm 30^\circ$, and a speed of 30 reciprocations/min was maintained. The observation of the coating surface/cross-section and composition measurements were made on Hitachi SU 5000 Schottky field emission scanning electron microscope (Hitachi, Tokyo, Japan) equipped with an energy dispersive X-ray microanalysis system (Thermo Scientific, Madison, WI, USA). Both secondary electron (SE) and backscattered electron (BSE) images were taken to characterize samples by topology and element composition, respectively. Energy-dispersive X-ray spectroscopy (EDS) was used for element analyses in a point mode.

Powder X-ray diffraction patterns were collected within the range from 5.3 to 80$^\circ$2θ with a constant increment of 0.02$^\circ$2θ on a Bruker D8 Advance diffractometer (Bruker AXS Advanced X-ray Solutions GmbH, Karlsruhe, Germany) with Cu Kα radiation and a LynxEye detector. Phase identification was performed with the Diffracplus EVA using the ICDD-PDF2 database. Unit cell parameters as well as mean crystallite size were determined with the Topas-4.2 software package using the fundamental parameters peak shape description, including appropriate corrections for instrumental broadening and diffractometer geometry.

3. Results and Discussion

3.1. Mechanical Properties

The dependence of the nanohardness on the penetration depth as determined from the load-displacement curves of the as-deposited sample and after treatment, and the substrate in the temperature interval investigated is presented in Figure 1a.

The dependences exhibit the typical tendency of nanohardness decrease with indentation depth. The curves did not show a noticeable distinction after heating at 700 °C. They displayed a similar gradual decrease in the coating depth due to the increasing substrate influence. This result suggests that heating up to 800 °C did not lead to considerable changes in the coating composition and structure. Heating at 800 °C caused a slight decrease in the nanohardness in the depth interval of 466 nm, where the substrate effect could be considered negligible. With the increase in the indentation depth, the nanohardness decreased more steeply due to the initial distortion of the substrate hardening at this temperature. Pronounced reduction of the hardness up to 450 nm was observed after heating at 900 °C. A further decrease in the hardness in the coating depth followed the same tendency as after heating at 800 °C. The dependence of the substrate hardness is presented in Figure 1a as well. The substrate possessed as-deposited hardness of 11.5 GPa, which is typical for a hardened HSS material. The hardness decreased gradually to 3.5 GPa with temperature increase up to 900 °C. The similar tendency exhibits the coating hardness after 500 nm indentation depth, which is under the limit of 10% of the total coating thickness, and the influence of the substrate is noticeable.

Figure 1b presents the change of the maximum measured nanohardness and the corresponding elastic modulus of the coating and substrate with an increase in the treatment temperature. The maximum hardness was determined at a coating depth of about 180 nm ± 20 nm. This depth is within the limit of 10% of the total coating thickness where the surface influence is considered negligible. Therefore, the values obtained can be attributed to the coating itself [32]. A value of 52.2 GPa was measured for the as-deposited coating. It was shown that two mechanisms, solid solution hardening and nanocomposite structure formation, are responsible for the obtained superhardness [30]. The achieved hardness is considerably higher than one recently reported for CrAlSiN monolayers and
CrAlSiN-based multilayers [27,29]. Similar nanohardness of 50.1 GPa and 49 GPa was determined after heating at 600 °C and 700 °C, respectively. A very slight decrease to 45.3 GPa was detected for the sample treated at 800 °C, assuming that the structure and composition of the modulated CrAlSiN-AlSiN coating are stable up to temperatures as high as 800 °C. The obtained high-heat hardness stability demonstrated the advantages of modulated structures over hard CrAlSiN monolayers, the hardness of which decreased by 30% during RT treatment up to 700 °C [33].

Figure 1. Mechanical properties of modulated CrAlSiN-AlSiN coating and substrate in the temperature interval 600–900 °C: (a) dependence of nanohardness on indentation depth; (b) dependence of nanohardness and elastic modulus on temperature.
After post-deposition annealing at 900 °C, the hardness was reduced almost by 30% to 37.1 GPa. Several mechanisms could be responsible for the observed change. Most probably, it was related to transformations in the coating composition and structure. On the other hand, very small changes were observed for the elastic modulus in the investigated temperature interval. It decreased from 504 GPa for the as-deposited and annealed at 600 °C and 700 °C specimens, to 454 GPa after heat treatment at 900 °C, suggesting insignificant changes in the structure and composition. Moreover, the decrease in the coating hardness could be also attributed to the change in the grain size rather than to changes in the composition and structure [34]. Formation of oxides on the coating surface whose growth may penetrate the near-surface area is not excluded. It should be noted that despite the observed decrease, the nanohardness remained sufficiently high even after the high-temperature treatment, while the multilayer coatings with similar composition to CrAlSiN/CrAlN exhibited a much lower hardness of 33.1 GPa after deposition without thermal treatment [35].

A more pronounced decrease from 302 GPa to 228 GPa of the elastic module was observed for the substrate. The decrease is noticeable after heating at 800 °C, suggesting structural and composition changes. The coating toughness after thermal treatment in the interval 600–900 °C was evaluated by the H/E* and H^3/E^2 ratios (Figure 2a) proposed by A. Leynad and A. Matthews as parameters correlated with the toughness of the coatings [36]. For calculation of the effective elastic modulus, the Poisson’s ratio of the coating and substrate were assumed to be 0.25 and 0.3, respectively. The as-deposited coating and those annealed at 600 °C and 700 °C exhibited high H/E* ratios of 0.11, 0.10, and 0.10, respectively. Heating at temperatures up to 900 °C caused a very small decrease in the elastic strain to failure to 0.08, which is higher than the monolayer homogenous CrAlSiN coating with similar Si [37] and Al [38] contents. This result implies excellent resistance of the compositionally modulated CrAlSiN-AlSiN coating against mechanical degradation under external stress, even after heating at temperatures as high as 900 °C. The coating studied also demonstrated high resistance to plastic deformation: H^3/E^2 = 0.452 GPa up to thermal treatment at 700 °C. The low plastic deformation indicates that the stress due to external influence is evenly distributed and the coating can absorb more energy before fracture. Further increase in the annealing temperature caused a decrease in the resistance to plastic deformation, which was 0.362 GPa after annealing at 800 °C. A more pronounced decrease was observed for the sample treated at 900 °C, when the H^3/E^2 ratio was reduced to 0.218 GPa. A similar tendency was reported for superhard CrAlSiN superlattice coatings [39]. This phenomenon is related to the more noticeable reduction of hardness with increased temperature over 800 °C. It should be noted that even after high thermal treatment, the H^3/E^2 ratio remained high (0.238 GPa) compared to other CrAlSiN-based multilayers (Al₂O₃/CrAlSiN—0.06 GPa, CrAlSiN/TiVN—0.13 GPa), which were not heated [28,40]. This result implies the role of the coating architecture for the toughness enhancement and its stability at high temperatures.

The CrAlSiN-AlSiN coating demonstrated high ability for recovery after deformation (Figure 2b). Enhanced elastic recovery of 68% was determined for the as-deposited coating. This value does not change even after annealing at 700 °C. A visible change to 57% was observed between 700 °C and 800 °C, with no further decrease afterwards. Most probably, the essential changes of the coating structure and composition that affect the mechanical properties occurred in that temperature interval. However, despite this decrease, the elastic recovery is high enough to suggest improved toughness of the coating even after high thermal treatment in comparison to the CrAlSiN monolayers [25]. Comparison between the behavior of the coating and substrate presented in Figure 2 shows the improvement of the surface toughness due to the coating deposition.
Figure 2. Temperature dependence of elastic strain to failure (a), resistance to plastic deformation (b), and elastic recovery (c) of modulated CrAlSiN-AlSiN coating and substrate.

3.2. Surface Morphology and Composition

Surface morphology is an essential feature for coating applications in cutting and forming tools. The surface quality depends strongly on the process parameters, such as deposition method, substrate temperature, bias voltage, and nitrogen flow during deposition [25,41–45]. Zhang et al. showed that increase of the nitrogen flow causes decrease of the grain size in the CrAlSiN coatings [45]. Surface SEM images of the as-deposited and thermal-treated coatings are presented in Figure 3. The surface of all samples is uneven but without cracks or cavities. Two features inherent to the cathodic arc deposition technology, macroparticles and shallow craters, are distinguishable on it [46]. The spherical shape of the macroparticles indicates that they originate from droplets emitted from the target material by the arc spot movement [47]. At the bias voltages used during coating deposition, the atoms and ions agglomerate and solidify, before reaching the surface and adhering to it as solids. The pressure at which the deposition was performed also supports the agglomeration of the atoms and ions before they reach the surface. As is seen in Figure 3, the macroparticle dimensions differ in a wide range. Thus, the biggest particles on the surface of the as-deposited sample, with a diameter of about 1.54 µm and higher, are very few. The droplets with dimensions from 400 nm to 800 nm are rare, while those with a diameter of about 300 nm are less predominant.
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Figure 3. SEM images of CrAlSiN-AlSiN surface: (a) as-deposited; and after thermal treatment (b) 600 °C, (c) 700 °C, (d) 800 °C, and (e) 900 °C.

The parameters of two processes, deposition temperature and bias voltage, determine the surface morphology with opposite effects. The high deposition temperature benefits the nanocomposite structure formation, which relates to high hardness and wear resistance [48]. At the same time, the high deposition temperature assists atom mobility on the surface.
and atomic diffusion, intensifying the grain growth and increasing the grain size and surface roughness [49]. The latter effect could be limited by applying bias voltage with a certain value at which the re-sputtering becomes significant in the process dynamics, leading to a decrease in the surface roughness. Thus, a balance between deposition temperature and bias voltage supports the decrease in the macroparticle density and surface roughness, respectively. The bias voltages used during deposition support the relatively low macroparticle density and the presence of Si in the coating composition contributes to the finer grain size as well. A very small quantity of shallow craters was observed on the coating surface. Their presence is due to the droplets peeling off the surface of the deposited coating.

The increase in the annealing temperature did not cause a considerable change in the macroparticle dimensions. A decrease in their density was observed at 900 °C, which could result from the re-melting of the solid metal droplets [39].

The element composition of the surface was investigated in three characteristic points: matrix, macroparticle, and crater. The concentration of the element composition is summarized in Table 1. Five measurements were made in the same point at the same conditions, and an average value was presented. The maximum deviation was determined to be 3.1% for N, 2.5% for Si, 1.5% for Al, and 3% for Cr. The EDS measurements reveal that the surface matrix of the as-deposited coating and those annealed at temperatures up to 800 °C could be considered stoichiometric with regard to the $\frac{N}{Cr+Al+Si}$ ratio. This ratio decreased to 0.93 and 0.81 after thermal treatment at temperatures of 800 °C and 900 °C, respectively, implying non-stoichiometric composition of the surface matrix. Most probably, the latter is due to the volatilization of the nitrogen at higher temperatures, leading to a change of the chemical composition. The composition of macroparticles deviates significantly from the stoichiometry in the as-deposited and thermally treated samples. A nitrogen amount of less than 50% in the macroparticle composition indicates that the droplets could not react with nitrogen completely before reaching the surface. The composition of the craters differs significantly from that of the matrix and macroparticles. Here, the Cr/Al ratio is 0.82 in the as-deposited sample and varies between 0.27–0.80 with a change of the annealing temperature. The higher Al amount in the crater composition implies that they were formed during the Al-rich area growth. The higher bias voltage applied during this technological step stimulate the droplet removal [42]. The formed craters were partially covered by the Cr-rich area deposited subsequently.

Table 1. Element composition of the main surface features of modulated CrAlSiN-AlSiN coating.

| Treatment Temperature | Feature     | Element Concentration, at.% |
|-----------------------|-------------|----------------------------|
|                       |             | N  | Al  | Si  | Cr  |
| As-deposited          | matrix      | 49.5 | 17.7 | 6.4 | 26.4 |
|                       | macroparticle | 45.9 | 17.6 | 6.9 | 29.6 |
|                       | crater      | 32.7 | 33.4 | 6.4 | 27.5 |
| 600 °C                | matrix      | 49.9 | 18.3 | 4.8 | 27.0 |
|                       | macroparticle | 41.3 | 21.8 | 5.5 | 31.4 |
|                       | crater      | 38.5 | 41.7 | 8.7 | 11.1 |
| 700 °C                | matrix      | 49.9 | 18.9 | 5.0 | 26.9 |
|                       | macroparticle | 37.7 | 23.8 | 5.7 | 32.8 |
|                       | crater      | 34.6 | 34.0 | 7.3 | 24.1 |
| 800 °C                | matrix      | 48.2 | 19.6 | 4.8 | 27.4 |
|                       | macroparticle | 40.3 | 16.4 | 9.2 | 34.1 |
|                       | crater      | 36.5 | 33.7 | 6.8 | 23.0 |
| 900 °C                | matrix      | 44.6 | 18.0 | 6.8 | 30.6 |
|                       | macroparticle | 40.2 | 19.2 | 7.7 | 32.9 |
|                       | crater      | 33.6 | 32.7 | 7.4 | 26.3 |
3.3. Coating Composition and Structure

The protocol of coating and period thickness as measured by calotest is presented in Table 2. Figure 4 compares coating thicknesses as measured by the calotest and the SEM image of the cross section. The adhesion Cr film and the transition CrN-gradient CrAlSiN layers, as well as the periodically modulated structure, are very well distinguishable in the calotest crater. According to the results, the total coating thickness and the average period thickness are 4.01 μm and 516 nm, respectively.

Table 2. Protocol of the period and total coating thickness measurement by calotest.

| Diameter [µm] | D1 Inner | D2 | D3 | D4 | D5 | D6 | D7 | D8 | D9 Outer |
|--------------|---------|----|----|----|----|----|----|----|--------|
| Test #1      | 461.81  | 493.22 | 536.81 | 574.19 | 601.20 | 634.75 | 664.50 | 694.09 | 730.61 |
| Layer th. [µm] | Total | LT 1–2 | LT 2–3 | LT 3–4 | LT 4–5 | LT 5–6 | LT 6–7 | LT 7–8 | LT 8–9 |
| Test #1      | 4.008  | 0.375 | 0.561 | 0.519 | 0.397 | 0.519 | 0.483 | 0.503 | 0.651 |

Figure 4. Coating and period thickness as measured by: (a) calotester and (b) SEM cross-section image of the as-deposited CrAlSiN-AlSiN coating.

It can be seen that the total thickness of the coating and periods measured by the calotest method and on the SEM cross-section image are very close. A total coating thickness of 4.30 µm was determined from the cross-section image of the as-deposited sample. Accordingly, the period thickness was 574 nm. The high resolution scanning of the Electron microscopy allowed us to measure the thickness of the Cr-rich and Al-rich areas, which were 280 nm and 293 nm, respectively.

The cross-sections of the as-deposited and annealed at 900 °C samples are presented in Figure 5. Both SEM (SE) images display a dense coating structure without defects and cavities. The Cr-rich and Al-rich areas are well expressed, as no interdiffusion and change of their thickness was observed. This result suggests that the coating architecture is stable during thermal treatment up to 900 °C.

Figure 5. SEM cross-section images of as-deposited (a) and annealed at 900 °C (b) CrAlSiN-AlSiN coating.
The coating chemical composition was studied by an EDS analysis of the cross-section after annealing at temperatures in the interval of 600–900 °C. The dependence of the element concentration on the annealing temperature is presented in Figure 6 for Cr-rich (Figure 6a) and Al-rich (Figure 6b) areas. As can be seen, thermal treatment up to 700 °C did not cause any change of the atomic concentration of the elements composing the coating. This result relates to the almost constant coating nanohardness measured after annealing at these temperatures. Further increase of the annealing temperature to 900 °C initiated variation of the element content in the coating. The main special feature is the decrease in the nitrogen content, which is explained by its volatilization during the heating. In both areas, this reduction is more pronounced after heating at 800 °C, suggesting that the essential change of the chemical compounds was performed at this temperature. The same tendency was observed in the CrAlSiN superlattice coating after post-deposition heating in vacuum [39]. Simultaneously, an increase in the Cr content was observed in both areas after treatment at the same temperature. This increase is associated with the decrease in nitrogen in the coating composition. Thus, the nitrogen amount decreases 1.14 times to each 1.15 times increase of chromium, which suggests that transformation in the compound with a Cr-N bond occurred. No essential changes of the aluminum or silicon contents were observed with an increase in the heating temperature in the Cr-rich area. A very slight increase in the Al and Si amounts was detected in the Al-rich area with the temperature increase.

The XRD patterns of the as-deposited and annealed CrAlSiN-AlSiN coatings are presented in Figure 7. In the as-deposited coating, three phases, fcc-CrN, h-AlN, and h-Cr$_2$N, were detected. Diffraction peaks of the fcc-CrN phase were indexed as (111), (200), (220), and (311). The preferred growth orientation is (200), presented with a peak centered at 43.57°. Compared to the standard PDF 01-077-0047 card, the position of this peak is shifted toward the lower 2θ angles, suggesting an increased lattice parameter, which might be due to the substitution of Cr atoms by larger Al atoms in the CrN lattice. The latter presumes formation of a metastable fcc-(CrAl)N phase and generates internal lattice strain. The presence of (CrAl)N solid solution in the composition significantly improves the hardness and corrosion resistance of the coating [50]. However, these properties are sensitive to the Al quantity. The excess of Al content (over 64 at.%) causes a change of the cubic-centered crystal structure to wurtzite structure, which results in a decrease in the coating hardness, and the decrease of the oxidation resistance [51]. The position of the diffraction peaks does not change during the thermal treatment up to 800 °C, implying a stable structure and composition. After annealing at 800 °C, all peaks shifted to higher 2θ. Further heating to 900 °C does not affect the position of the peak. This result indicates that changes in the coating structure and composition occur during heating at 800 °C. A second h-AlN phase is presented in powder diffraction patterns of coatings with two diffraction peaks, (100) and (110). The position of the (100) peak is shifted to higher angles, suggesting tensile stress [52]. This result is in agreement with the size of the lattice parameters. Both cell parameters are larger than the standard PDF 00-025-1133 card. The observed crick of the lattice parameters is supposedly due to the tendency for AlN lattice to match the CrN lattice. The third phase, h-Cr$_2$N (PDF 00-035-0803), is detected at a peak position of 42.67°. This phase was not observed in the as-deposited and annealed at 600 °C coatings, and it appeared as a very small peak after treatment at 700 °C. Its intensity increased after heating at 800 °C and 900 °C. This increase is accompanied by intensity decrease of the (200) peak of the CrN phase, which could be related to the transformation of fcc-CrN phase to h-Cr$_2$N and nitrogen volatilization. Moreover, the lattice parameter is lower, which might be due to the presence of vacancies in the lattice. This result agrees well with the EDS measurements, which revealed that after annealing at 800 °C and 900 °C, a decrease in nitrogen content was observed. The measured values for both temperatures are within the error limit [53], and it could be accepted that they do not differ. A similar result was reported regarding the thermal treatment of CrAlSiN in vacuum [38] and during heating in air [50]. The nitrogen loss and formation of hexagonal Cr$_2$N after annealing at 900 °C
were detected for similar (CrAlSiN/CrAlN) multilayers, as it was shown that the presence of silicon in the coating composition defers the thermal decomposition and N-loss [29]. These results allow consideration of the temperature of 900 °C as critical for changes in the composition of the CrAlSiN-based coatings.

Figure 6. Dependence of element composition of CrAlSiN-AlSiN modulated coating on treatment temperature: (a) Cr-rich region; (b) Al-rich region.
The XRD patterns of the as-deposited and annealed CrAlSiN-AlSiN coatings are presented in Figure 7. In the as-deposited coating, three phases, fcc-CrN, h-AlN, and h-Cr$_2$N, were detected. Diffraction peaks of the fcc-CrN phase were indexed as (111), (200), (220), and (311). The preferred growth orientation is (200), presented with a peak centered at 43.57°$^\circ _{2\theta}$. Compared to the standard PDF 01-077-0047 card, the position of this peak is shifted toward the lower 2$^\circ _{2\theta}$ angles, suggesting an increased lattice parameter, which might be due to the substitution of Cr atoms by larger Al atoms in the CrN lattice. The latter presumes formation of a metastable fcc-(CrAl)N phase and generates internal lattice strain. The presence of (CrAl)N solid solution in the composition significantly improves the hardness and corrosion resistance of the coating [50]. However, these properties are sensitive to the Al quantity. The excess of Al content (over 64 at.%) causes a change of the cubic-centered crystal structure to wurtzite structure, which results in a decrease in the coating hardness, and the decrease of the oxidation resistance [51]. The position of the diffraction peaks does not change during the thermal treatment up to 800 °C, implying a stable structure and composition. After annealing at 800 °C, all peaks shifted to higher 2$^\circ _{2\theta}$. Further heating to 900 °C does not affect the position of the peak. This result indicates that changes in the coating structure and composition occur during heating at 800 °C. A second h-AlN phase is presented in powder diffraction patterns of coatings with two diffraction peaks, (100) and (110). The position of the (100) peak is shifted to higher angles, suggesting tensile stress [52]. This result is in agreement with the lattice parameters. Both cell parameters are larger than the standard PDF 00-025-1133 card. The observed crick of the lattice parameters is supposedly due to the tendency for AlN lattice to match the CrN lattice. The third phase, h-Cr$_2$N (PDF 00-035-0803), is detected at a peak position of 42.67°$^\circ _{2\theta}$. This phase was not observed in the as-deposited and annealed at 600 °C coatings, and it appeared as a very small peak after treatment at 700 °C. Its intensity increased after heating at 800 °C and 900 °C. This increase is accompanied by intensity decrease of the (200) peak of the CrN phase, which could be related to the transformation of fcc-CrN phase to h-Cr$_2$N and nitrogen volatilization. Moreover, the lattice parameter is lower, which might be due to the presence of vacancies in the lattice. This result agrees well with the EDS measurements, which revealed that after annealing at 800 °C and 900 °C, a decrease in nitrogen content was observed. The measured values for both temperatures are within the error limit [53], and it could be accepted that they do not differ. A similar result was reported regarding the thermal treatment of CrAlSiN in vacuum [38] and during heating in air [50]. The nitrogen loss and formation of hexagonal Cr$_2$N after annealing at 900 °C were detected for similar (CrAlSiN/CrAlN) multilayers, as it was shown that the presence of silicon in the coating composition defers the thermal decomposition and N-loss [29]. These results allow consideration of the temperature of 900 °C as critical for changes in the composition of the CrAlSiN-based coatings.

The XRD diffraction patterns did not show a crystal phase containing silicon and it could be supposed that Si$_x$N$_y$ exists as an amorphous matrix. The incorporation of Si into an AlN lattice is less possible because the c/a lattice ratio is higher (c/a = 1.63) than that on the standard PDF 00-025-1133 card. The presences of an amorphous Si$_x$N$_y$ phase in the coating composition caused a change of the preferable crystal growth from (111) to (200) [54].
The thermal stability of a CrAlSi-AlSiN coating with periodically modulated composition was investigated. The as-deposited coating exhibited stable superhardness of 52.2 GPa, which did not change significantly during thermal treatment up to 800 °C in nitrogen. Although the high-heat hardness decreased to 37.1 GPa after heating at 900 °C, it was still high. Besides the high-heat hardness, the coating demonstrated high elasticity (0.09), and high resistance to plastic deformation (0.362 GPa) even at a high temperature of 800 °C. Enhanced elastic recovery of 68% of the as-deposited coating remained high enough (57%) after annealing at 900 °C. The surface morphology is the typical one of coatings deposited by cathodic arc evaporation and was not affected significantly by the thermal treatment. The EDS and XRD analyses revealed that coating composition and structure depended on the treatment temperature. Thus, both areas, Cr-rich and Al-rich, of the as-deposited coating are stoichiometric with respect to nitrogen, Cr$_{0.27}$Al$_{0.19}$Si$_{0.04}$N$_{0.50}$, and Al$_{0.41}$Cr$_{0.02}$Si$_{0.07}$N$_{0.50}$, respectively. The as-deposited CrAlSiN-AlSiN coating has a nanocomposite structure of grains embedded in a Si$_3$N$_4$ matrix 

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Figure 7. XRD pattern of as-deposited and treated at different temperatures. CrAlSiN-AlSiN coating.
sources, R.K.; supervision, L.K.; validation, L.K., R.K. and D.K.; visualization, L.K.; writing—Original draft, L.K. and D.K.; writing—Review and editing, L.K., R.K. and D.K. All authors have read and agreed to the published version of the manuscript.

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