Investigations of nanocrystalline and gradient coatings produced by cathodic arc evaporation technology

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ABSTRACT

Purpose: The main aim of this research was the investigation of the microstructure, corrosion resistance and the mechanical properties of the nanocrystalline TiAlSiN, CrAlSiN, AlTiCrN and the gradient TiAlN, TiCN, AlSiCrN coatings deposited by cathodic arc evaporation technology onto the X40CrMoV5-1 hot work tool steel substrate.

Design/methodology/approach: The surfaces’ topography and the microstructure of the investigated coatings were observed on the scanning electron microscopy. Diffraction and thin film structure were tested with the use of the transmission electron microscopy. The microhardness tests were made on the dynamic ultra-microhardness tester. Tests of the coatings’ adhesion to the substrate material were made using the scratch test.

Findings: It was found that the microstructure of the nanocrystalline coatings consisted of fine crystallites, while their average size fitted within the range of 11-25 nm, depending on the coating type. The critical load \( L_{C1} \) lies within the range of 46-54 N. In case of the gradient coatings it was found that the microstructure consisted of crystallites while their average size fitted within the range of 25-50 nm, depending on the coating type. The coatings demonstrated columnar structure as well as good adhesion to the substrate. The critical load \( L_{C2} \) lies within the range 46-59 N. The coatings demonstrate a high hardness (40 GPa) and corrosion resistance.

Practical implications: In order to evaluate with more detail the possibility of applying these surface layers in tools, further investigations should be concentrated on the determination of the thermal fatigue resistance of the coatings. The very good mechanical properties of the nanocrystalline and gradient coatings make them suitable in industrial applications.

Originality/value: The investigation results will provide useful information to applying the nanocrystalline and gradient coatings for the improvement of mechanical properties of the hot work tool steels.

Keywords: Thin and thick coatings; Nanocrystalline coatings; Gradient coatings; Microstructure; Mechanical properties

Reference to this paper should be given in the following way:
1. Introduction

For several decades, tool material designers have been trying to develop and produce an ideal tool material of high ductility and maximum possible wear resistance characteristics in working conditions. Such combination is practically impossible to obtain. Therefore, various attempts were made to find at least a partial solution to the issue, by creation of layer structures, the methods included without limitation of thermal-chemical treatment, composite material production and monolayer or multilayer coating deposition by the CVD and PVD methods as well as overlaying welding or hard layer spraying by the spray metallization method [1-5].

The research issues concerning the production of coatings is one of the more important directions of surface engineering development, ensuring the obtaining of coatings of high usable properties in the scope of mechanical characteristics and wear resistance. The progress in the field of producing coatings in the physical vapour deposition process enables the obtainment of coatings of nanocrystal structure presenting high mechanical and usable properties. The coatings of such structure are able to maintain a low friction coefficient in numerous working environments, maintaining high hardness and increased resistance [6, 7]. The main concept in the achievement of high hardness of nanostructure coatings and good mechanical properties and high strength related to it, particularly in case of nanocomposite coatings is the restriction of the rise and the movement of dislocations [8-11]. Nanostructure coatings comprise at least two phases, a nanocrystalline phase and a matrix phase, where the matrix can be either nanocrystalline or amorphous phase [12, 13].

Functional gradient coatings create a new class of coatings with properties and structure changing gradually. Gradient coatings deposited on the tool material substrate and providing appropriately high resistance to abrasive wear in tool operating conditions, core ductility and stress relaxation between the particular coating layers and between the gradient coating and tool material coating are seen as a solution to the issue due to the inappropriate adhesion of the layer produced or the excessive stresses between the surface layer and the substrate [14, 15]. Frequently a rapid difference between the coating and substrate properties occurs causing a stress concentration in this area, both during the manufacturing and operation of the tools. This causes fast degradation demonstrated by cracks and delamination of the coatings. The application of functional gradient coatings offers a possible solution to the issue. Gradient coatings can be applied in manufacturing modern machining tools, due to their resistance to high-temperature oxidation and erosion as well as abrasive wear [16,17].

The purpose of this paper is to examine the microstructure, mechanical properties and corrosion resistance of nanocrystalline and gradient coatings deposited by PVD technique on the X40CrMoV5-1 hot work tool steel substrate.

2. Investigation methodology

The tests were made on samples of the X40CrMoV5-1 hot work tool steel deposited by PVD process with TiAlSiN, CrAlSiN, ALTiCrN nanocrystalline coatings and TiAlN, TiCN, AlSiCrN gradient coatings. The coating deposition process was made in a device based on the cathodic arc evaporation method in an Ar, C2H2 and N2 atmosphere. Cathodes containing pure metals (Cr, Ti) and the AlSi (88:12 wt.%) alloy were used for deposition of the coatings. The base pressure was $5 \times 10^{-6}$ mbar. The deposition conditions are summarized in Tables 1 and 2.

Specimens were subjected to heat treatment consisting in quenching and tempering; austenizing was carried out in the vacuum furnace at 1020°C with a soaking time of 0.5 h. Two isothermal holds were used during heating up to the austenizing temperature, the first at the temperature of 640°C and the second at 840°C. The specimens were tempered twice after quenching, each time for 2 hours at the temperature of 560°C and next at 510°C. To ensure a proper quality, the surfaces of the steel specimens have been subjected to mechanical grinding and polishing ($R_s=0.03$ µm).

Observations of surface and structures of the deposited coatings were carried out on cross sections in the SUPRA 35 scanning electron microscope. Detection of secondary electron was used for generation of fracture images with 15 kV bias voltage.

Diffraction and thin film structure were tested with the use of the JEOL JEM 3010UHR transmission electron microscope, at 300 kV bias voltage. Thin foils were made by mechanical grinding and further ion polished using the Gatan apparatus.

Phase identification of the investigated coatings was performed by glancing angle X-ray diffraction (GAXRD). The cross-sectional atomic composition of the samples was obtained by using a glow discharge optical spectrometer, GDOS-750 QDP from Leco Instruments. The following operation conditions of the spectrometer Grimm lamp were fixed during the tests:

- lamp inner diameter-4 mm;
- lamp supply voltage-700 V;
- lamp current-20 mA;
- working pressure-100 Pa.

Tests of the coatings’ adhesion to the substrate material were made using the scratch test on the CSM REVETEST device. The tests were made using the following parameters:

- load range: 0-100 N;
- load increase rate (dL/dt): 100 N/min,1
- indenter’s sliding speed (dx/dt): 10 mm/min,1
- acoustic emission detector’s sensitivity AE: 1.

The critical load Lc, causing the loss of the coating adhesion to the material, was determined on the basis of the values of the acoustic emission, AE, and friction force, $F_r$, and observation of the damage developed in the track using a LEICA MEF4A optical microscope.

X-ray line broadening technique was used to determine crystalite size of the coatings using Scherrer formula with silicon as internal standard:

$$D = \frac{(0.9 \lambda)}{(B \cos \theta_0)}$$

where:
- D - crystallite size,
- $B$ - full width at half-maximum XRD peak in radians,
- $\lambda$ - wavelength of the X-ray radiation,
- $\theta_0$ - the Bragg angle in radians.
1. Introduction

For several decades, tool material designers have been trying to improve the properties of cutting tools, primarily to enhance their wear resistance and their service life. One of the most promising methods of achieving these goals is the deposition of coatings onto a metal substrate. 

2. Investigation methodology and gradient coatings deposited by PVD technique on the mechanical properties and corrosion resistance of nanocrystalline fast degradation demonstrated by cracks and delamination of the frequently a rapid difference between the coating and substrate conditions, core ductility and stress relaxation between the appropriately high resistance to abrasive wear in tool operating with properties and structure changing gradually. Gradient dislocations [8-11]. Nanocomposite coatings comprise at least two strength related to it, particularly in case of nanocomposite [6, 7]. The main concept in the achievement of high hardness of environments, maintaining high hardness and increased resistance maintain a low friction coefficient in numerous working coatings of nanocrystal structure presenting high mechanical and physical vapour deposition process enables the obtainment of development, ensuring the obtainment of coatings of high usable one of the more important directions of surface engineering overlaying welding or hard layer spraying by the spray coating deposition by the CVD and PVD methods as well as composite material production and monolayer or multilayer solution to the issue, by creation of layer structures, the methods.

3. Discussion of results

The nanocrystalline coatings present a compact structure, without any visible delaminations or defects. The investigated coatings test show a columnar structure that may be considered compatible with the Thornton model (zone I), except the fact that in TiCN the cross-section morphology is dense (Figs. 3, 4).

Transmission electron microscopy (TEM) examination of the nanocrystalline coatings showed that they consisted of fine crystallites, of average size ca. 11-25 nm, depending on the kind of coating (Fig. 5). Single large grains were only observed in case of the TiAlSiN coating, which may suggest the occurrence of the epitaxial phenomenon as the consequence of large crystallite occurrence in the coating. The gradient TiAIN and TiCN coating observations in the TEM (Fig. 6) indicate that such coatings consists of fine crystallites, of average size ca. 25-50 nm, depending on the kind of coating. Generally, there are no foundations to confirm the epitaxial growth of the investigated coatings. Several large grains were observed in the AISiCrN coating and the possibility of epitaxy due to the presence of large crystallites may be deduced upon examination of the SAED pattern.

![Fig. 1. Fracture of the nanocrystalline TiAlSiN coating deposited onto the X40CrMoV5-1 steel substrate](image-url)
Fig. 2. Fracture of the nanocrystalline CrAlSiN coating deposited onto the X40CrMoV5-1 steel substrate

Fig. 3. Fracture of the gradient TiAlN coating deposited onto the X40CrMoV5-1 steel substrate

Fig. 4. Fracture of the gradient TiCN coating deposited onto the X40CrMoV5-1 steel substrate

Fig. 5. a) Structure of the thin foil from the nanocrystalline CrAlSiN coating deposited onto the hot work tool steel X40CrMoV5-1, b) diffraction pattern from the area as in figure a and solution of the diffraction pattern

Basing on the glancing angle X-ray diffraction (GAXRD) of the samples examined (Fig. 7), the occurrence of fcc phases was only observed in the coatings. The hexagonal AlN of wurtzite type was not discovered in the coatings examined, which could have been caused by a low amount of aluminium in the coatings. In case of the TiAlSiN coating a lattice parameter of 0.426 nm was derived, which is greater than that of bulk TiN (0.424 nm). The highest lattice parameter corresponds to a system where a partial Si segregation occurred, which might be enough to nucleate and develop a Si$_3$N$_4$ amorphous phase. Also, decrease
intensities of the reflections, showing an increase in the amorphous content in the coatings. Basing on the results obtained, using Scherer method, the size of crystallites in the coatings examined was determined. The results were presented in Table 3.

The hardness of the X40CrMoV5-1 steel substrate without coating is 2.1 GPa, as settled upon hardness tests. The deposition of the PVD coatings onto the specimens causes the growth of hardness of the surface layer ranging from 30 to 32 GPa in case of gradient coatings and from 36 to 40 GPa in case of nanocrystalline coatings (Table 3).

The critical load values $L_{C1}$ and $L_{C2}$ were determined by the scratch test method (Figs. 8, 9). The load at which the first coating defects appear is known in the references as the first critical load $L_{C1}$. The first critical load $L_{C1}$ corresponds to the point at which first damage is observed; the first appearance of microcraking, surface flaking outside or inside the track without any exposure of the substrate material - the first cohesion-related failure event. $L_{C1}$ corresponds to the first small jump on the acoustic emission signal, as well as on the friction force curve. The second critical load $L_{C2}$ is the point at which complete delamination of the coatings starts; the first appearance of cracking, chipping, spallation and delamination outside or inside the track with the exposure of the substrate material - the first adhesion-related failure event. After this point the acoustic emission graph and friction forces have a disturbed run (become noisier). The cumulative specification of the test results are presented in Table 3. In order to establish the nature of damage responsible for the occurring increase of the acoustic emission intensity, the cracks produced during the test were examined by the light microscope coupled with the measuring device, determining the critical load $L_{C1}$ and $L_{C2}$ in virtue of metallographic observations.

In case of the nanocrystalline coatings examined, it was found that coating AlTiCrN had the highest critical load value $L_{C1}$=24 N and $L_{C2}$=54 N. In case of the gradient coatings examined, it was found that the TiCN coating had the highest critical load of $L_{C1}$ = 33 and $L_{C2}$ = 59 N, whereas AlSiCrN and the TiAlN coatings had the lowest $L_{C1}$ = 19 and $L_{C2}$ = 46 N. The TiCN coatings show the best adhesion to the substrate of all the gradient coatings tested, which is not only due to the adhesion itself, but also due to mixing of the elements in the transition zone between the coating and the substrate as a result of diffusion, because the TiCN coatings’ deposition process temperature was 500°C.

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Changes of coating component concentration and substrate material made in GDS were presented in Figs. 10, 11. The tests carried out with the use of GDS indicate the occurrence of a transition zone between the substrate material and the coating, which results in the improved adhesion between the coatings and the substrate. In the transition zone between the coatings and the substrate the concentration of the elements of the substrate increases with simultaneous rapid decrease of concentration of elements contained in the coatings.
### Table 3.
The characteristics of the tested coatings

<table>
<thead>
<tr>
<th>Coating</th>
<th>Thickness, µm</th>
<th>Microhardness, GPa</th>
<th>Crystallite size, nm</th>
<th>Critical load L_{C1}, N</th>
<th>Critical load L_{C2}, N</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlTiCrN</td>
<td>2.4</td>
<td>38</td>
<td>17</td>
<td>24</td>
<td>54</td>
</tr>
<tr>
<td>CrAlSiN</td>
<td>2.9</td>
<td>40</td>
<td>25</td>
<td>18</td>
<td>49</td>
</tr>
<tr>
<td>TiAlSiN</td>
<td>2.1</td>
<td>36</td>
<td>11</td>
<td>16</td>
<td>46</td>
</tr>
<tr>
<td>TiAlN</td>
<td>2.8</td>
<td>32</td>
<td>25</td>
<td>19</td>
<td>46</td>
</tr>
<tr>
<td>AlSiCrN</td>
<td>2.1</td>
<td>32</td>
<td>34</td>
<td>25</td>
<td>46</td>
</tr>
<tr>
<td>TiCN</td>
<td>4.2</td>
<td>30</td>
<td>50</td>
<td>28</td>
<td>59</td>
</tr>
</tbody>
</table>

**Nanocrystalline coatings**

**Gradient coatings**

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Fig. 8. Diagram of the dependence of the acoustic emission (AE) and friction force F_t on the load for the X40CrMoV5-1 steel with the:

a) AlTiCrN, b) TiAlSiN coating

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Fig. 9. Scratch failure pictures of the AlTiCrN coating on X40CrMoV5-1 steel substrate at: (a) L_{C1}, (b) L_{C2}
The existence of the transition zone should be connected with the increase of desorption of the substrate surface and the occurrence of defects in the substrate and the relocation of the elements within the connection zone as a result of a high energy ion reaction. Such results, however, cannot be interpreted explicitly, due to the non-homogeneous evaporation of the material from the sample surface.

Fig. 10. Changes of constituent concentration of the nanocrystalline AlTiCrN coating and the substrate materials

Fig. 11. Changes of constituent concentration of the gradient TiCN coating and the substrate materials

As a result of tests on the electrochemical corrosion, it was observed that the coatings deposited by PVD process on the substrate made of the X40CrMoV5-1 steel constitute effective protection of the substrate material against the corrosive effect of the aggressive factor. The potentiodynamic polarisation curve analysis (Figs. 12, 13) and that of the corrosion rate confirm the better corrosion resistance of the samples with coatings layers in comparison to the uncovered sample. During the anode scanning the current density is always lower for the sample with a coating deposited on its surface in comparison to the uncovered sample. The fact that the corrosive potential of the uncoated substrate significantly grows after a 60-minute experiment is also worth noting.

Fig. 12. Potentiodynamic polarization curves of the gradient materials in 1 M HCl solution

Fig. 13. Potentiodynamic polarization curves of the nanocrystalline coatings in 1 M HCl solution

4. Summary

In case of nanocrystalline coatings the compact structure of the coatings without any visible delaminations was observed as a result of tests in the scanning electron microscope. The fracture morphology of the coatings tested is characterised with a dense structure. Basing on the thin film test in the transmission electron
microscope, it was observed that the coatings are built of fine crystallites. Their size is 11-25 nm. The coating adhesion scratch tests disclose the cohesion and adhesion properties of the coatings tested. In virtue of the tests carried out, it was found that the critical load \( L_{c2} \) fitted within the range 46-54 N for the coatings deposited on a substrate made of hot work tool steel. The tests made with the use of GDOS indicate the occurrence of a transition zone between the substrate material and the coating, which affects the improved adhesion between the coatings and the substrate. As a result of the potentiodynamic polarisation curve analysis, the corrosion current density - corrosion rate was determined. It confirms the better corrosion resistance of samples coated with the use of the PVD technique to the uncoated samples made of the austenitic steel (11.65 \( \mu \text{Acm}^{-2} \)). The corrosion current density for the coatings tested fits within the range 0.15-0.77 \( \mu \text{Acm}^{-2} \), which proves their good anti-corrosion properties.

In case of gradient coatings the compact structure of the coatings without any visible delamination was observed in the scanning electron microscope. The investigated TiAlN and CrAlSiN coatings show columnar structure, which may be considered compatible with the Thornton model (zone I). Upon examination of the thin films obtained from TiAlN and TiCN coatings, it was found that the coatings were composed of fine crystallites. The scratch tests on coating adhesion the reveal the cohesive and adhesive properties of the coatings deposited on the substrate of the X40CrMoV5-1 hot work tool steel. On the basis of the above examinations, it was found that the critical load of \( L_{c2} \) is between 46-59 N. The biggest value of the critical load was obtained for the TiCN coating. The GDOS investigations indicate the existence of the transition zone between the substrate material and the coating resulting in the improved adhesion of the coatings deposited to the substrate.

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