CHARACTERIZATION AND PERFORMANCE OF DUPLEX-COATINGS ON Cr-V COLD WORK TOOL STEEL

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Resume

Specimens made of Vanadis 6 steel were heat treated, plasma nitrided and coated with Cr_2N. The microstructure, phase constitution and mechanical properties of plasma nitrided areas and duplex-coatings have been investigated using the light microscopy, scanning electron microscopy, X-ray diffraction and microhardness measurements. The adhesion of the coatings and the wear performance were studied using the scratch test and ring-on-plate tribological testing. Worn surfaces were examined by scanning electron microscopy. Nitrided areas formed at lower temperature were free of compound “white” layer while hose developed at higher temperatures contained as the white layer so the nitrided network. Significant increase in substrate hardness was detected due to the nitriding. Beneficial effect of the nitriding on the adhesion of Cr_2N coatings was clearly determined whereas the extent in improvement of the adhesion depends on the presence/no presence of “white” layer on the surface. The extent of beneficial effect of plasma nitriding on the wear performance follows the impact of the constitution of nitrided areas on the adhesion. The amelioration of wear performance of Cr_2N coatings can be attributed to the supporting effect of hard nitrided intermediate region, which provides excellent resistance of the substrate against plastic deformation, under heavy loading in particular. Practical testing demonstrated many times prolonged service-time of duplex-treated tools for sheet metal working.

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1. Introduction

Thin Cr_xN_y coatings have been developed over the past three decades. They have early gained an interest and popularity in a variety of industrial applications due to good wear performance, high corrosion resistance and good cutting properties in copper machining, aluminium die casting and forming but also in wood processing.

Cr_xN_y coatings can be synthetized in wide range of chemistry, phase constitution and properties. The microhardness of coatings ranges commonly between 1500 and 3000 HV [1 - 3] and is a function of the grain size [3] and phase constitution whereas it is higher when they contain Cr_2N-phase [4, 5] than those formed of CrN.

The Young modulus of Cr_xN_y coatings can be modified in a wide range. Mercs et al. [1] have reported that the Young modulus ranged between 240 and 320 GPa and that it was directly proportioned to the hardness of coating.

The Young modulus of the chromium nitride films depends on the stoichiometry of the film whereas it is higher for the Cr_2N [5]. The most important information is, however, that some of investigations indicated that the Cr_xN_y films can be deposited with the Young modulus not much different from the steel substrate.

Growth of Cr_xN_y films is connected with high compressive residual stresses. They can reach up to 5 GPa in some cases [6] and have detrimental effect on the adhesion of the coatings. From this reason, Odén et al. [2] and Broszeit et al. [7] have suggested the heat treatment (annealing) to modify the stress situation in CrN coatings. This post-deposition annealing led to reduction of stresses by 70 % and improvement in adhesion of coatings [2, 7].

The adhesion of coatings is influenced by many factors – production method itself, substrate nature and structure, phase constitution and chemistry of coating and also the stress state. Generally, a good adhesion can be achieved when ledeburitic steels or cemented carbides are used as substrates [2, 6, 8], due to their high hardness. Adhesion also increases as the portion of the phase CrN decreases and Cr_2N and/or (Cr) solid solution increases [1, 7].

A commonly known complication in the use of ceramic coatings is their often insufficient adhesion on steel substrates when heavily loaded. At these circumstances, the steel substrate undergoes extensive plastic deformation whereas the depth of deformed zone exceeds the coating thickness. The coating, however, has very limited plasticity and cannot deform together with the substrate. As a result, the coating fails due to its brittleness. Hence, the attempts how to modify the mechanical properties of the substrate (hardness, Young modulus), in order to enhance its load carrying capacity, are logical.

The problem with the modification of mechanical properties of the steel substrates can be effectively solved by plasma nitriding prior to coating deposition. The beneficial effect of nitriding is based on the fact that the heat treatment affects the Young modulus (E) of the steels in a very limited range. On the other hand, the hardness (H) can be increased very significantly with an appropriate heat treatment. Further hardness improvement (and also the hardness/Young modulus ratio) can be achieved by nitriding. As reported previously [9], for the Vanadis 6 steel after plasma nitriding the hardness of 1100 HV can be achieved. Therefore, one can say that the plasma nitriding will improve such important characteristics of the substrate like the H/E (elastic strain to failure resistance) and H^3/E^2 ratios (the resistance against plastic deformation). These characteristics are associated with the fraction toughness and are in a close relationship with wear resistance [10, 11]. In other words, the higher the hardness (at constant E) the better is the fraction toughness and the wear resistance.

The first comprehensive study on the duplex-coating (TiN + plasma nitrided inter-layer) deposited on AISI D2 steel was published by Fox-Rabinovich [12]. He arrived to several times prolonged tool service life and to intensified metalworking productivity. Van Stappen et al. [13] have reported better adhesion behaviour of duplex-coating (TiN + plasma nitriding) in some industrial applications. Further, laboratory investigations focused to the optimization of sub-processes (plasma nitriding, deposition of coatings) led to the finding that the Cr_xN_y coating showed better adhesion on pre-nitrided steels than single Cr_xN_y coatings [14 - 16] and better wear resistance, also [15, 17].

Leskovšek et al. [18] have carried out the industrial testing of TiCN deposited on pre-nitrided H11 hot work tool steel. The obtained results indicate that the combination of nitriding and TiCN coating is a promising technique for the surface modification of forging-die inserts.

Pellizzari [19] has tested various thin films with/without the presence of pre-nitrided region. The testing was carried out in the application of an extrusion of aluminium alloy. It was found that the delamination of the coating was restricted in duplex-PVD coatings to the outermost region of the coating-compound layer. However, it was also established that the presence of compound nitrided layer decreases the adhesion of the PVD coatings, thus, it did not allow to fully appreciating the benefits of the hard PVD coating supported by the hard nitrided layer.

Yang, S. et al. [20] have stated for the CrAlN coatings combined with nitrided inter-layer that the hard CrAlN coating protected the steel surfaces from sliding wear under heavy testing conditions and, for the pre-nitrided materials, that the plastic deformation of the coating and substrate surface were also minimised indicating the advantages of the outer surface coating, e.g. wear resistance, can be exploited to reduce fatigue and plastic deformation induced failures of the coating-substrate system.

The main challenge to carry out the current experiments was the fact that no reports on duplex-coating of PM cold work ledeburitic steels are available yet. In this paper, it is reported on the results of the investigation of the microstructure, mechnical propertiees and wear mechanism of the Cr_xN_y + plasma nitriding duplex-layers deposited on the Vanadis 6 substrate. Moreover, some practical industrial results are presented.

2. Experimental

2.1 Substrate material and processing

Plate specimens 70 x 18 x 8 mm made of the steel Vanadis 6 (2.1 % C, 7 % Cr, 6 % V, Fe bal.) were used as a substrate. They were mechanically ground and subjected to heat treatment bringing a hardness of 60 HRC. Then, the specimens were polished to a mirror finish.

Plasma nitriding was performed on the RUBIG Micropuls – Plasmatechnik® device, at temperatures of 500 and of 530 °C and processing times of 60 and of 120 min., respectively. Standard low-pressure atmosphere contained nitrogen and hydrogen in a ratio of $N_2 : H_2 = 1 : 3$. Prior to the nitriding, the samples were sputter cleaned for 30 min. After the plasma nitriding, the surface roughness increased to $R_a = 0.09 – 0.1$ μm.

The Cr_xN_y coatings were deposited by chromium evaporation in a Balzers BAI 730M thermionic arc ion device. Chromium was evaporated with Ar (working gas) at a constant partial pressure of 1.5×10^{-3} mbar. The nitrogen partial pressure was kept constant for the deposition procedure, also, and it was 1.5×10^{-3} mbar in order to obtain preferably the Cr_2N compound. Also, other arc parameters were kept constant for the deposition, e.g. substrate bias of – 125 V, substrate temperature of 450 °C.

2.2 Investigation methods

The microstructure was characterized using the light microscopy and the scanning electron microscopy (SEM). Samples were standardly prepared, e.g. ground and polished with the 1 μm diamond slurry and etched with Nital-reagent. The surfaces after the ring-on-plate tribological testing were characterized by the SEM, also. The SEM observations have been conducted using a JEOL JSM 7600F field emission scanning electron microscope equipped with an Oxford Instruments detector, in a secondary electron (SE) detection regime.

Hardness measurements in nitrided areas were performed using a Zwick ZHV10 hardness tester, by the Vickers´s method applying a load of 10 kg (HV 10) for surface hardness and 50 g (HV 0.05) for hardness depth profiles determination. The depth profiles were measured on carefully prepared specimen cross-sections. For details regarding the specimen preparation see Ref. [21]. The distance between the adjacent indents was 20 μm, in order to avoid the influence of the plastically deformed zone surrounding the nearest two indents. Hardness testing of the system coating/substrate (determination of load carrying capacity) was completed using the same experimental device, however, different loads, namely 10 g (HV 0.01), 25 g (HV 0.025), 50 g (HV 0.05), 100 g (HV 0.1) and 2 kg (HV 2) were applied.

Adhesion of layers was examined by use of CSM Revetest apparatus. The load was increased linearly from 0 to 150 N, at the load rate of 50 $N.min^{-1}$. Rockwell diamond indenter with a tip radius of 0.2 mm was used. The critical load L_c was determined as the first adhesion failure, by identification of acoustic emission echo as well as by viewing of micrographs of scratches. Here, the first indications of coating spallation inside the scratches were taken as a criterion for the L_c.

Glow discharge optical emission spectroscopy (GDEOS) was used to determine the elements depth profiles in the surface layers and their vicinity.

The phase constitution of Cr_xN_y layers was identified with X-ray diffraction. X-ray diffraction patterns have been recorded using a Panalytical Empyrean diffractometer with Bragg-Brentano geometry and iron filtered CuK_α characteristic radiation (λ = 0.15418 nm). Incident beam was equipped with parallel beam optics. Diffracted radiation has been collected with scintillation detector with 0.27° parallel plate collimator. Samples were measured at a room temperature and without sample spinning. The spectra were recorded over a two-theta angle range 25 – 75°.

Wear testing was carried out without lubrication, using the ring-on-plate configuration of the specimen and the counterpart, Fig. 1, at loads of 50 and 150 N, respectively. Hollow cylinders made of 100Cr6 ball bearing steel (heat treated to 60 HRC) were used as counterparts. The total testing distance (sliding in a combination with slow rotation) was 10 km but the wear weight loss was determined also after distances of 1, 2.5 a 5 km, respectively. The testing was carried out at an ambient temperature and at a standard air humidity of 40 – 50 %. The determination of the wear loss has been done using a laboratory weighing machine LIBRA HZK210 with an accuracy of 0.001 g.

For the practical testing, the punches for sheet metal working, with a diameter of 16 mm were made of experimental material, heat treated and surface processed with plasma nitriding or duplex-coating (Cr_2N with a thickness of 2 μm). They were installed into standard production line of automotive components (body of door locks for Škoda, VW, Opel etc.).

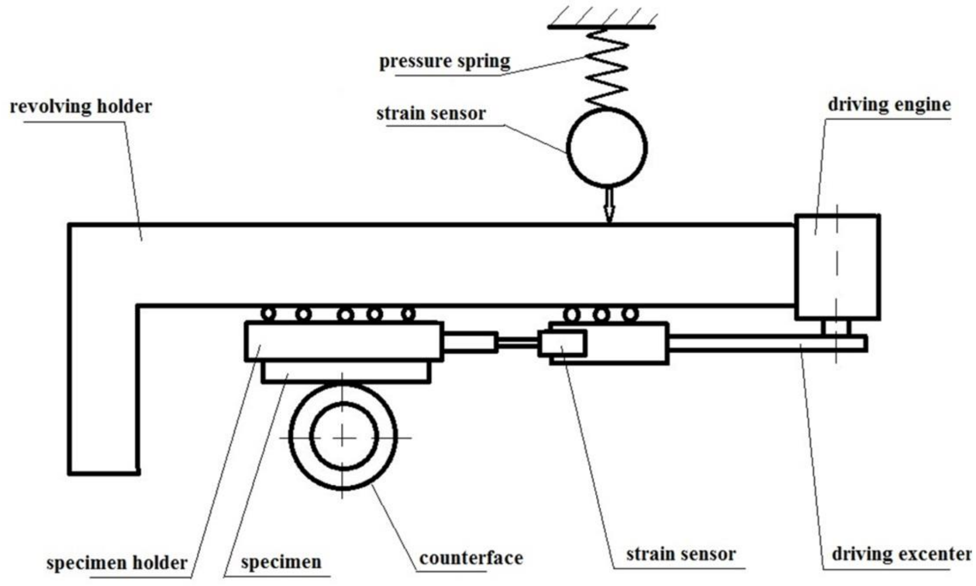


Fig. 1. Experimental setup for the wear testing.

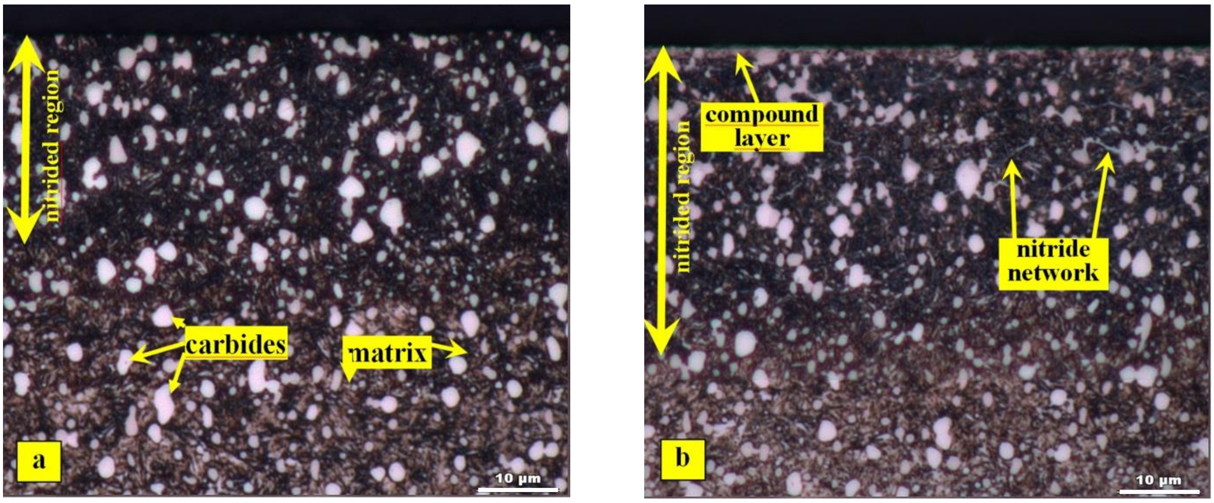
The locks are manufactured from the DIN 1.4301 (0.07 % C, 17.5 % Cr, 8 % Ni) austenitic stainless steel sheets with a thickness of 4 mm. The service–time of punches was evaluated as a number of pieces made.

3. Results

3.1 Characterization of nitride inter-layers

Light micrographs, Figs 2 a b, show nitrided regions formed at 500 °C for 60 min and 530 °C for 120 min, respectively. Nitrided regions differ from the no-nitrided material mainly in the dark appearance, which can be referred to the presence of fine precipitates within the matrix. In the specimen processed at lower temperature and shorter processing time, Fig. 2a, neither the surface compound layer nor the nitride network is visible. On the other hand, these structural constituents are clearly visible in the material nitrided at 530 °C for 120 min., Fig. 2b.

The surface hardness of the samples nitrided at temperatures of 500 °C for 60 min and 530 °C for 120 min was 971 and 1122 HV 10, respectively, Fig. 3. Microhardness measurements revealed very high near-surface hardness (exceeding 1500 HV 0.05) for both realized processes.



a) *b)*

Fig. 2. Light micrographs showing the microstructure of plasma nitrided areas developed at a) 500 °C for 60 min, b) 530 °C for 120 min.
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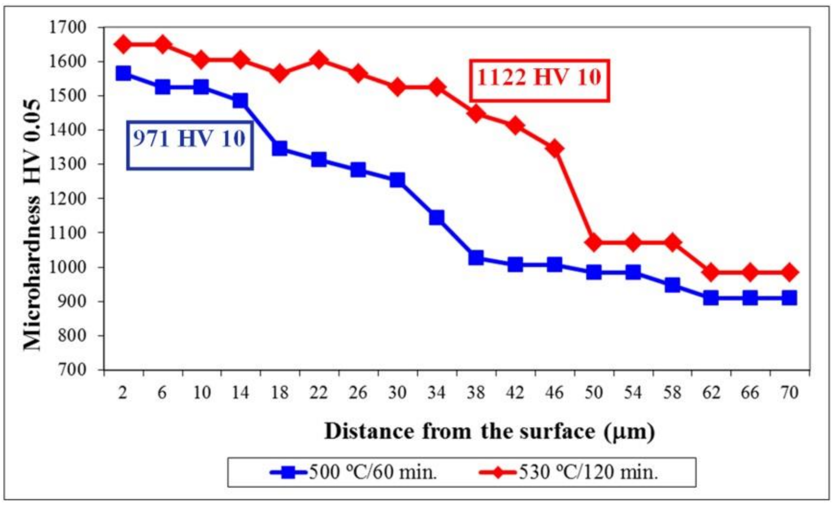

Fig. 3. Surface hardness HV 10 and microhardness depth profiles in nitrided areas.
(full colour version available online)

However, the microhardness values fall down distinctly in a depth of around 35 μm in the case of the samples nitrided at 500 °C while the similar rapid decrease in microhardness was observed only in a depth of around 48 μm in the case of the material nitrided at 530 °C.

3.2 Characterization of coatings

Fig. 4 brings representative XRD profile of the Cr_xN_y coating. There are two diffraction peaks identified. The first ones are the peaks belonging to the coating, indicating that the film is really Cr_2N. The second one, being positioned at 44.24° of the two-theta belongs to the substrate material (tempered martensite). There were some important diffraction peaks of Cr_2N found, namely (110), (111), (112) and (300), being positioned at the two-theta angles of 37.35, 42.61, 56.01 and 67.35°, respectively. It is worth noticing at this place that the peak (002), normally positioned at 40.19° of the two-theta angle, was not detected or is superimposed with the (111). The (111) diffraction peak is very strong, indicating that the coating grown with this preferred orientation.

Fig. 5 shows typical example of the duplex coating (Cr_2N + plasma nitriding). On the surface, Cr_2N coating with a thickness of 2 μm is visible.

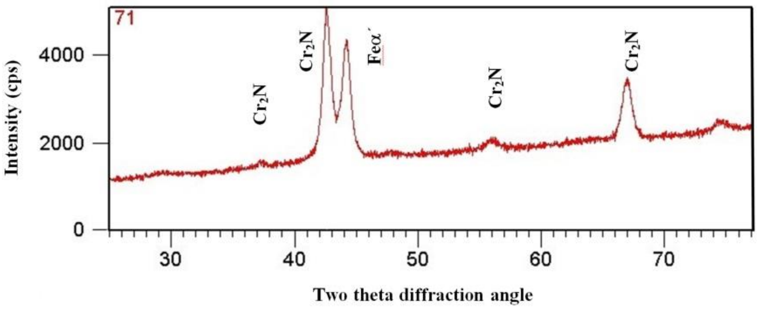

Fig. 4. XRD patterns of as-deposited surface coating.
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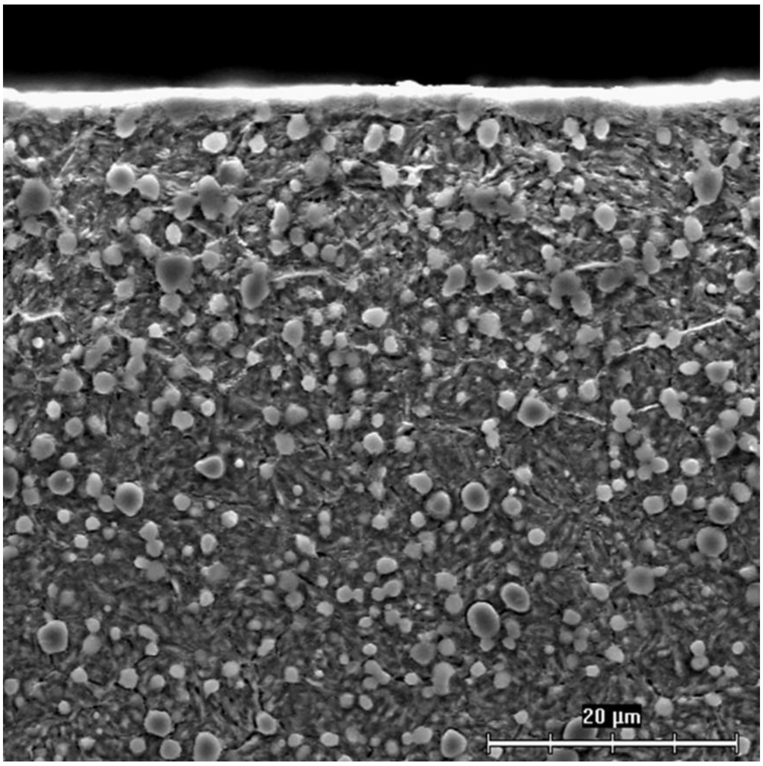

Fig. 5. Duplex-layer (Cr_2N + plasma nitriding) developed on the surface of Vanadis 6 tool steel.

The nitrided inter-layer made at 500 °C for 60 min. has a thickness of 25 μm. It differs from no-nitrided steel substrate mainly in the topography caused by etching. There are only negligible indications on the presence of continuous nitrides alongside the original grains of the Vanadis 6 steel visible. This indicates that the nitriding was performed properly and would not influence both the toughness of the material and the coating adhesion negatively. No inhomogeneities like cracks, pores are shown at the Cr_2N/nitrided region interface.

Fig. 6 depicts an example of concentration depth profile of main elements in Cr_2N coating and its vicinity. It is shown that the Cr_2N coating contains more than 93 wt. % of chromium and less than 7 wt. % of nitrogen, which can be referred to the actual stoichiometry of the coating. This is in excellent agreement with the results of XRD analysis as well as with our expectations that the chosen deposition parameters will lead to the formation of Cr_2N on the surface. The total thickness of Cr_2N compound is of around 2 μm. Below the Cr_2N, there is a nitrided inter-layer, characterized with enhanced but slightly depth-decreasing nitrogen content – the nitrogen content was measured to be 3.7 wt. % at the Cr_2N/substrate interface but it decreased to approx. 1 wt. % in a depth of 14 μm.

Fig. 7 depicts the critical load L_c (being represented the adhesion of the film) as a function of the surface processing. The critical loads of the Cr_2N with a thickness of 2 μm and 5 μm were 18 N and 26 N, respectively. The beneficial effect of the pre-nitriding is clearly visible here. Corresponding critical loads for the specimens pre-nitrided at a temperature of 500 °C for 60 min were 78 and 103 N and those for the specimens pre-nitrided at a temperature of 530 °C for 120 min were 44 and 90 N, respectively.

The results of tribological testing at a load of 50 N, Fig. 8, show that plasma nitriding prior to PVD did not bring any significant amelioration to the wear behaviour. When comparing the columns belonging the samples it is shown that the best wear behaviour was identified when the plasma nitriding was carried out at a temperature of 500 °C for 60 min. However, the improvement makes only 0.002 g and 0.004 g for the coatings with a thickness of 2 μm and 5 μm, respectively.

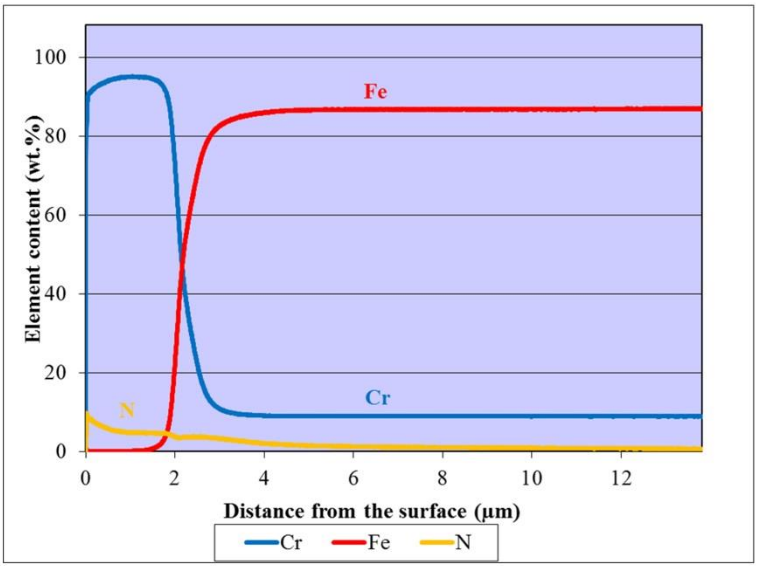

Fig. 6. Concentration depth profiles of Cr, Fe and N in Cr_2N coating and below.
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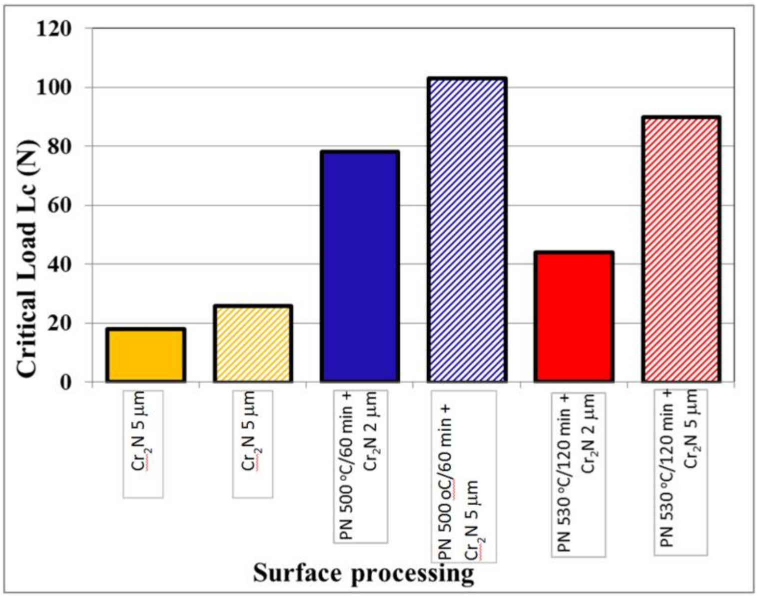

Fig. 7. Critical load Lc for the specimens surface processed via various schedules.
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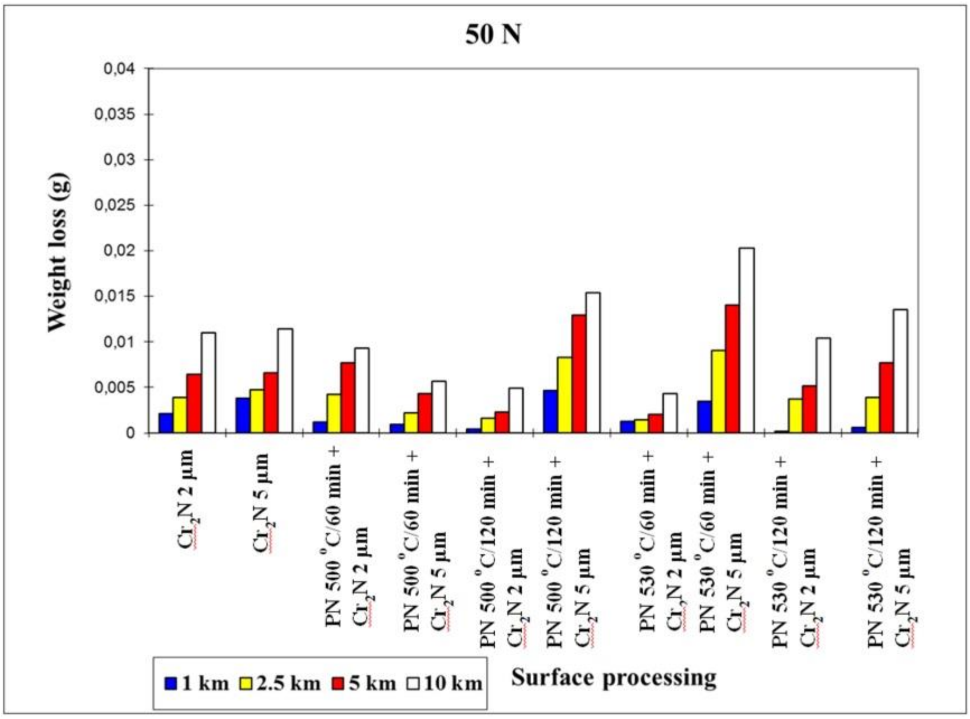

Fig. 8. Weight loss of specimens processed by different schedules due to ring-on-plate tribological testing at a load of 50 N.
(full colour version available online)

Other combinations of the parameters of plasma nitriding did not bring any improvement (530 ºC/120 min.) or the improvement was detected for one thickness of the Cr_2N coating while the testing of the sample with other thickness of Cr_2N caused gave worsening of the results.

The testing at a load 150 N led to the coating failure in the case of simple Cr_2N with a thickness of 2 μm, Fig. 9. On the other hand, the coating with a thickness of 5 μm showed much better wear behaviour. The application of plasma nitriding prior to the PVD improved the wear behaviour of corresponding Cr_2N layers.

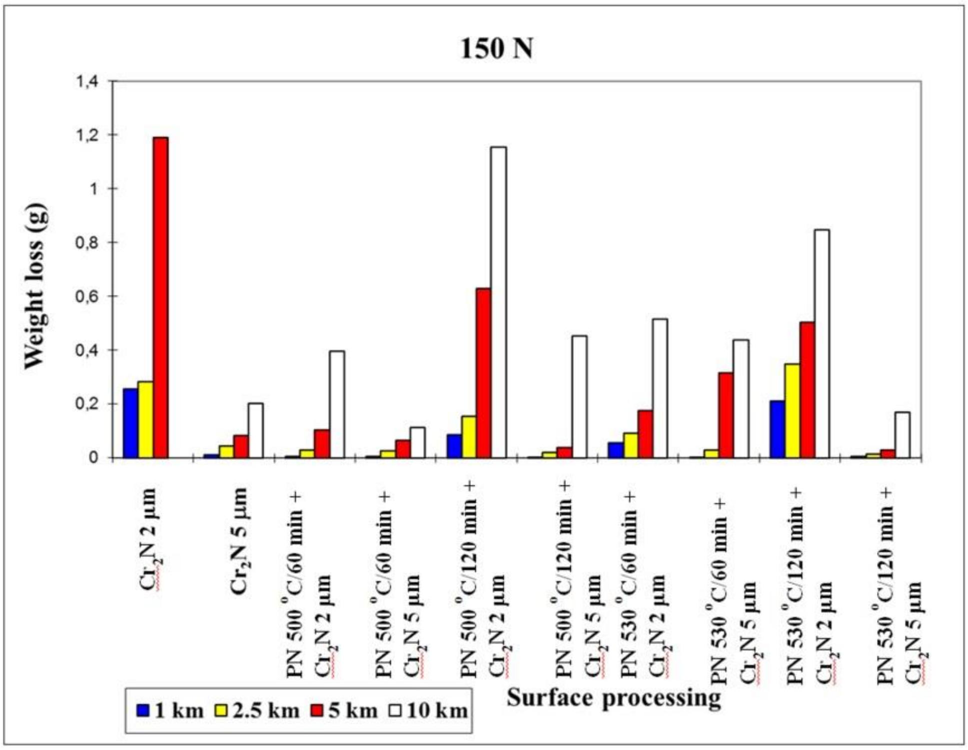

Fig. 9. Weight loss of specimens processed by different schedules due to ring-on-plate tribological testing at a load of 150 N.
(full colour version available online)

For instance, in the case of the Cr_2N with a thickness of 2 µm, the application of plasma nitriding carried out at the parameters 500 °C/60 min., 500 °C/120 min., 530 °C/6 min. and 530 °C/120 min led to reduction of the weight loss (after a sliding distance of 5 km) by 11 times, 2 times, 7 times and 2.4 times, respectively. In the case of the coatings with a thickness of 5 µm, the improvement was detected only for the plasma nitriding realized at a temperature of 500 °C for 60 min. The application of other parameters of plasma nitriding did not improve the wear resistance (530 °C/120 min.) or led to its slight worsening.

3.3 Fractography of worn surfaces

Fig. 10 shows the surface of specimen with an excellent coating adhesion. The surface shows two areas of different micromorphology. The first one (A) is characterised with parallel tracks typical formed during the sliding of the counterpart on the coated surface.

The second area (B), the coating underwent certain deformation with semi-circle cracking butt with no indications of flaking and/or spallation. The coating was kept on the substrate throughout the wear track. Hence, a good adhesion of the coating has been confirmed.

In the case of poor coating adhesion of the coating (Cr_2N without a supporting nitrided region) the situation is significantly different, see Fig. 11. The wear of the coating commenced probably by the same mechanism as what is depicted in Fig. 10, e.g. with the development of semi-circular cracks in the coating (A). However, the coating fails very early, after short testing time, which is clearly demonstrated in area designated (B). Here, a cracking of the coating is clearly visible whereas the coating becomes gradually removed from the substrate while flaking and fragmenting (area C). Removed fragments of Cr_2N coating then accelerated the wear, which is demonstrated by rapid increase in the weight loss on the specimen.

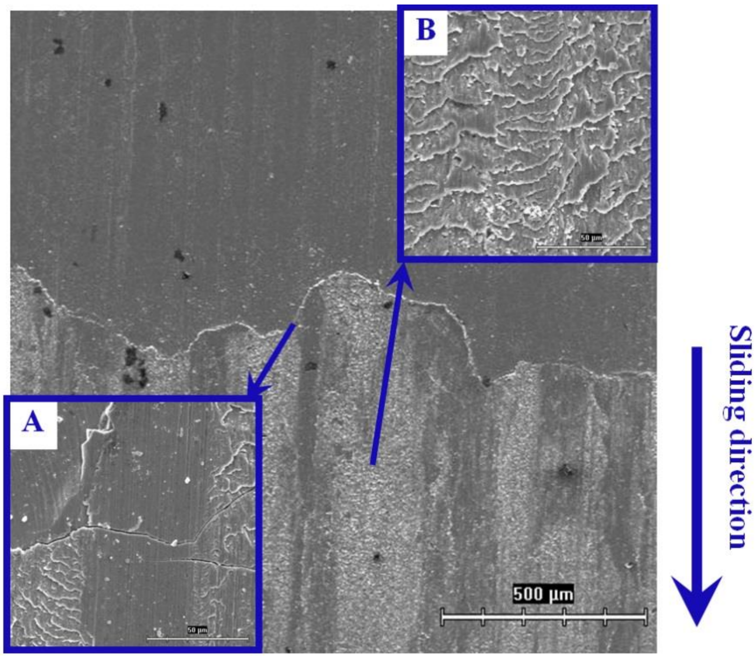

Fig. 10. SEM micrograph of worn surface of the specimen with a good adhesion of Cr_2N coating.
(full colour version available online)

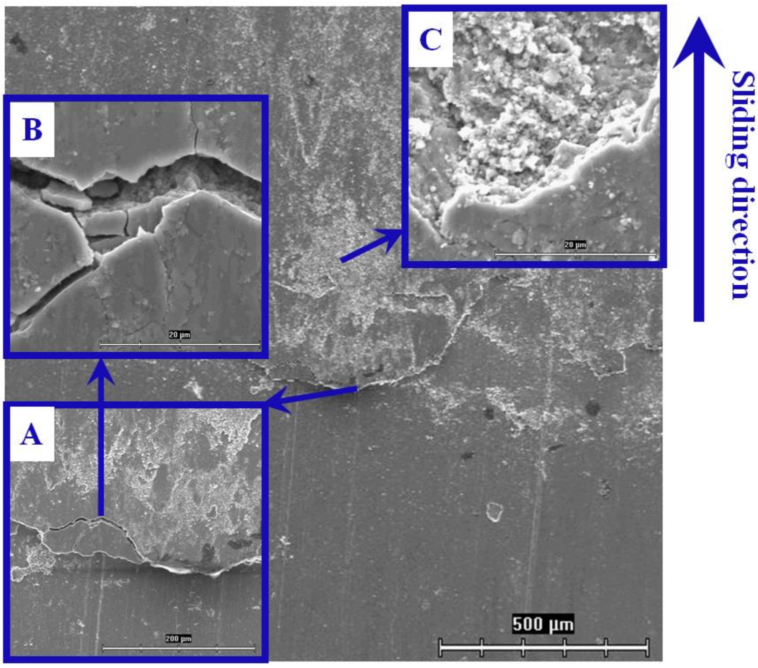

Fig. 11. SEM micrograph of worn surface with a poor adhesion of the Cr_2N coating.
(full colour version available online)

3.4 Practical tests

Practical testing in real industrial conditions have shown that the tool service-time was limited by "low – cycle fatigue" when no-surface processed. The average service-time of punches was 3100 pieces made. The plasma nitriding increased the tool service-time to 46 000 pieces made. The service-time has been interrupted by the fracture of the tools, however, the time of the fracture initiation was delayed due to presence of compressive stresses in nitrided region and, the initiation site of the crack was shifted from the surface to the nitrided region. The service-time of tools is increased again when duplex-treatment is used for surfacing. The service-time was prolonged to 65 000 pieces (note that the tools are still in operation). One can suggest that the Cr_2N-coating protects the tool against wear while the nitrided inter-layer makes a mechanical support for the Cr_2N-layer and increases the resistance of the tool against fatigue.

4. Discussion

The hardness increase due to the plasma nitriding is logical. Plasma nitriding induces the formation of disperse Fe_4N and CrN nitrides [9] that increase the hardness of nitrided material significantly. In addition, the formation of nitrides is associated with the development of compressive strain fields around the nitrides, due to the misfit of the lattice of the nitrides and the matrix. These stresses were documented to exceed 1000 MPa [9], thus, they can contribute to the hardness increase also. It is worth noticing at this place that the hardness itself is not only the key criterion for successful application of nitrided tools or components. The second key criterion for the tool service-time is the toughness of nitrided material. As reported elsewhere [21], plasma nitriding decreases the toughness of the material whereas the lowering in toughness is marginal when no surface compound layer is formed (or nitride network along the grain boundaries) but it is considerable when these two constituents are present. Hence, the effort leads not only to the achievement of the highest possible hardness but the hardness should be high at an acceptable toughness. In other words, the mechanical properties of nitrided materials are always a compromise between the strength and the hardness on the one side and the toughness on the other side.

The deposition parameters were adjusted to form the Cr_2N compound on the substrate rather than CrN. This choice was based on the findings reported recently [22], stated that the Cr_2N has better adhesion on the hard ledeburitic steel substrates than the CrN and is thus more suitable as a candidate coating for heavy industrial applications. It should be noted here that it is generally believed that this is the CrN that has slightly better adhesion compared to the Cr_2N [23 - 25]. However, an opposite tendency in the adhesion behavior is possible at specific deposition conditions and, in particular, with respect to the properties of the substrate. The quality of the substrate material (hardness, toughness, phase constitution) is similar in the case of the present paper and that reported previously [22], thus, the choice of the Cr_2N can be considered as correct.

The wear performance of the Cr_2N coating is influenced only marginally when tested under a load of 50 N, Fig. 8. This could be expected because various authors [12, 13, 26] have recommended the duplex-coating mainly for applications where heavy loading takes place.

The use of higher load (150 N) led to increased differences in the wear behaviour between the specimens processed by various combinations of plasma nitriding and Cr_2N- layering (Fig. 9). However, the general tendency that the plasma nitrided inter-layer increases the wear performance of the coating was kept.

Improved wear performance of duplex coatings with a reference to the Cr_2N coatings without a presence of nitrided region can be attributed to several factors. The first one is demonstrated in Fig. 12. For instance, the microhardness HV 0.01 of the system coating-substrate was 1850, 2585, 2490 and 2416 for the single Cr_2N with a thickness of 2 μm, single Cr_2N thick 5 μm, duplex coating with thinner Cr_2N and duplex coating with thicker Cr_2N, respectively. Hence, only in the case of the Cr_2N with a thickness of 2 μm, the microhardness at such a low load is influenced by the substrate in more substantial extent. Corresponding microhardness HV 0.1 was 989, 1840, 1765 and 1984 for the single Cr_2N with a thickness of 2 μm, single Cr_2N thick 5 μm, duplex coating with thinner Cr_2N and duplex coating with thicker Cr_2N, respectively. Here, the effect of relatively softer substrate is already more evident, in the case of single Cr_2N coating with a thickness of 2 μm in particular. And finally, the hardness HV 2 was 780, 886, 1130 and 1180 for the single Cr_2N with a thickness 2 μm, single Cr_2N with a thickness of 5 μm, duplex coating with thinner Cr_2N and duplex coating with the Cr_2N layer having a thickness of 5 μm, respectively. It is thus clearly evident the influence of substrate on the hardness of the system substrate/coating. The lowest value, e.g. 780 HV 2 in the case of thinner Cr_2N is close to the nominal substrate hardness after heat treatment (705 HV). Correspondingly, elevated hardness detected for the system with thicker Cr_2N coating can be referred to the thickness of the coating itself only. On the other hand, the systems with duplex coatings have much higher hardness HV 2, which is attributed to the increased hardness of nitrided intermediate region formed at a temperature of 500 °C and for 60 min (971 HV 10). Summarizing these facts it is obvious that the first factor influencing better wear behaviour of duplex coated samples is higher load carrying capacity of nitrided substrate compared to what was achieved by quenching and tempering only.

The second factor, which influences the adhesion (and the wear resistance as a consequence) positively, is the lowering in the stress discontinuity at the coating/substrate interface. As above mentioned [2, 6, 7, 23], the growth of Cr_xN_y coatings is connected with a formation of high internal compressive stresses. The substrate, on the other hand, is in a relatively weak stress situation after high temperature tempering (2×530 °C for 2 h). The results on the effect of plasma nitriding on the characteristics of the Vanadis 6 steel show that plasma nitriding introduces compressive stresses into the near surface region and, that these stresses exceed 1000 MPa [9]. Hence, one can claim that the plasma nitriding reduces the stress discontinuity at the coating/substrate interface and thereby influences the adhesion (and the wear performance) of the Cr_2N coatings favourable. At this place it should be mentioned that this finding is "indirectly" in line with the observation by Odén et al. [2]. They have also established that the reduction of the stress discontinuity at the coating/substrate interface, albeit obtained by the post-deposition annealing of the coating and not by plasma nitriding of the substrate, tends to amelioration of the wear behaviour.

Thirdly, it should be noted that the plasma nitriding can be carried out in two different ways:

i) with a goal to form the surface compound („white“) layer,

ii) in order to avoid the formation of compound layer.

The opinions on the role of surface compound "white" layer with respect to the adhesion of ceramic coatings are very adverse. Some authors have reported that the effect of this layer cannot be detrimental [26] while others referred unambiguously negative impact of nitrided compound layers on the adhesion [27]. In our experiments, the plasma nitriding processes carried out at a temperature of 530 °C led to the formation of compound layer (see also Fig. 2b). Also, a processing carried out for 120 min. at a temperature of 500 °C forms probably a compound layer although not visible by light microscopy – very thin nitride network has been observed along original grain boundaries. Correspondingly, the adhesion of the Cr_2N formed on the samples with a presence of nitride compound layer was lowered, Fig. 7 and the wear performance of duplex coatings was worsened, at higher loading in particular, Fig. 9.

And finally, the plasma nitriding leads to elevated surface hardness of the substrate, at a constant elastic modulus E (223 GPa) while the Cr_2N had an elastic modulus of 325 ± 27 GPa. Therefore, both the elastic strain to failure resistance (*H/E*) and the resistance against plastic deformation H^3/E^2 of the substrate was improved and thereby the discontinuity in these characteristics were minimised at the substrate/coating interface. As well known [10], these characteristics are in a close relationship with the wear resistance, thus, the improvement in wear performance due to the plasma nitriding can be considered as logical.

5. Conclusions

1) Nitrided areas differ from no-nitrided material in dark appearance, due to the presence of fine nitrides. Specimens processed at lower temperature and shorter time do not contain surface "white" layer while those processed at higher temperature manifest indications of its presence.

2) Nitrided material has elevated hardness compared to no-nitrided steel. The increase in hardness can make over 400 HV 10, e.g. the resulting hardness may easily exceed 1100 HV 10. It is thus expected that the nitrided material has good resistance against plastic deformation and can effectively support the coating.

3) It was found that the deposition parameters were properly chosen to obtain pure Cr_2N coating. The coating has grown in a preferred (111) orientation. No inhomogeneities like pores or crack were identified at the coating/substrate interface.

4) The application of plasma nitriding improves the adhesion of the Cr_2N coatings. In the plasma nitriding, the presence of compound "white" layer seems to be a key factor influencing the adhesion – the adhesion is better when no compound layer is formed during the nitriding.

5) Wear performance of the Cr_2N coating is improved only slightly when tested under a load of 50 N. This is in line with general expectations where the duplex-coating is recommended mainly for heavy loaded systems.

6) The use of a load of 150 N highlighted the difference in the wear behaviour of the specimens surfaced via different schedules. Generally, the application of pre-nitriding improves the wear resistance of the material. The best wear behaviour was detected in the case of the material with no presence of compound "white" layer. In other words, the wear performance was the best for the materials with the best adhesion of Cr_2N layers.

7) Industrial testing has shown considerably prolonged service-time of cold work tools when duplex treated.

8) A common practical recommendation can be derived from obtained results, e.g. the plasma nitriding should be done very carefully, to avoid the presence of compound "with" layer, when the largest extent of amelioration of wear performance should be achieved.

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