

# Evaluation of duplex (Zr,Al)CN coatings with improved tribological performance

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Duplex coatings consisting of nitrided HSS steel substrates and (Zr,Al)CN layers were produced. Plasma nitriding of the steel was carried out for 3 h in an atmosphere of N<sub>2</sub> (30%) and H<sub>2</sub> (70%) gases, at 480°C. The (Zr,Al)CN coatings were deposited by cathodic arc technique on the nitrided steel surfaces. For the nitrided layer, a thickness and surface microhardness of about 60 µm and 1580HV<sub>0.02</sub>, respectively, were measured. The (Zr,Al)CN coatings, with a highly over stoichiometric composition ((C+N)/(Zr+Al) ~ 2) and single solid solution nanostructure, had hardness of ~ 36 GPa and a thickness of ~ 4.8 µm. The duplex coatings produced were found to exhibit superior friction and wear performance when compared to plasma nitrided substrates.

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## 1. Introduction

Hard coatings are widely applied on the surface of cutting and forming tools to increase their wear and corrosion resistance. Duplex treatment is one of the most applied methods to improve adhesion between different steel substrates and the hard coatings in order to increase service life of the coated parts and tools used in industrial applications. It consists of two independent steps: plasma nitriding followed by the deposition of thin films.

Titanium and zirconium nitride coatings, prepared by PVD or CVD techniques, are two of the most widely accepted coatings in industrial applications [1-3]. Despite their good wear resistance, TiN and ZrN coatings do not provide sufficient corrosion and oxidation resistance. For further improving the performance of TiN or ZrN coatings, Al was introduced in order to enhance their oxidation resistance and hardness. However, the incorporation of Al led to a higher friction coefficient and a lower toughness in the coating system [4,5]. Therefore, adding C to the TiAlN or ZrAlN coating is considered to be a promising approach for those applications where an improved wear resistance is necessary [6,7]. Despite all the data gathered with regard to the properties of TiAlCN [6-8], little is known about the ZrAlCN coatings. The tribological properties of duplex-coated steels have been investigated extensively in the literature. However, wear mechanism and its dependence on nitriding conditions and the choice of the best hard duplex coating system are still unsolved problems so far.

The aim of this work is to investigate the characteristics of (Zr,Al)CN hard coatings deposited by

duplex technology on high-speed steel (HSS) substrates. Both the nitriding treatment and the film deposition were performed in a cathodic arc deposition unit. The nitrided layers were characterized for microhardness depth profiles, while the deposited films were analyzed in terms of elemental and phase composition, chemical binding state, texture, and hardness. To appreciate the benefits of the duplex technology as compared to simple plasma nitriding or untreated samples, friction and wear resistance of the untreated, nitrided substrates and of the films deposited on nitrided HSS samples were comparatively investigated.

## 2. Experimental details

The duplex process was conducted in a cathodic arc unit equipped with two cathodes made of Zr and Al [9]. AISI M2 high speed steel (HSS) plates (30x30x10 mm) were used as substrates. The HSS steel in the as-received condition has a hot deformed structure with a hardness of 9.3 GPa. Its chemical composition given is in Table 1. The samples were polished to a surface roughness of 14 nm (R<sub>a</sub>) and chemically cleaned for 10 minutes in an ultrasonic bath with isopropyl alcohol. The base pressure in the deposition chamber was typically about 6x10<sup>-4</sup> Pa. Prior to the nitriding, the specimens were sputter cleaned for 15 min in a gaseous mixture of N<sub>2</sub> and H<sub>2</sub> (10 Pa, 960 V, 250 °C) on a rotating substrate support.

Table 1. Chemical compositions (wt.%) of AISI M2 high speed steel (HSS).

C	W	Mo	Cr	V	Cu	Mn	Ni	Si	P	S	Fe
0.85	6.40	5.00	4.10	1.90	0.12	0.25	0.30	0.30	0.03	0.03	balance

The parameters of the nitriding process were as follows: reactive atmosphere – a mixture of N<sub>2</sub> (30%) and H<sub>2</sub> (70%) gases, total gas pressure – 7x10<sup>2</sup> Pa, voltage applied on the samples – 360 V, nitriding temperature – 480<sup>0</sup> C, nitriding duration – 3 h.

After nitriding, the samples were sputtered by Ar<sup>+</sup> ion bombardment (1 keV) for 30 min, in order to eliminate the possible surface contamination with absorbed gases after plasma nitriding, since this process takes place at a much higher pressure (7x10<sup>2</sup> Pa) as compared to the one used for the film deposition (~6x10<sup>-2</sup> Pa). Subsequently, the (Zr,Al)CN films were deposited by activating the two cathodes.

Preliminary experiments were conducted to select the optimum conditions to deposit films with the highest hardness. These conditions were as follows. Reactive atmosphere: mixture of N<sub>2</sub> and CH<sub>4</sub> gases; N<sub>2</sub> and CH<sub>4</sub> flow rates = 70 and 30 sccm, respectively; currents at Zr and Al cathodes = 60 and 90 A, respectively; substrate bias voltage = -100 V; deposition duration = 60 min. Under these conditions, (Zr,Al)CN coatings of 4.8 μm were produced.

X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray analysis (EDS) were used to investigate the elemental compositions of the films. XPS investigation was performed on a VG ESCA 3 MKII spectrometer, using AlK<sub>α</sub> radiation. The sample preparation and the spectra processing were similar to those described in Ref. [10]. EDS analysis were carried out on a scanning electron microscope (XL-30 – ESEM TMP), equipped with energy dispersive X-ray spectroscopy. Phase composition, texture and crystallite size of deposited films were determined by X-ray diffraction analysis (Rigaku MiniFlex II, with Cu K<sub>α</sub> radiation). To estimate the crystallite size *d* and the microstrain  $\epsilon$  of the coatings, the Williamson–Hall method has been employed [11, 12], in which the broadening ( $\beta$ ) of a Lorentzian shaped XRD peak can be expressed as the direct sum of the instrumental broadening ( $\beta_i$ ), crystallite size related broadening ( $\beta_{CS}$ ), and microstrain  $\epsilon$  related broadening ( $\beta_\epsilon$ ):

$$\beta = \beta_i + \beta_{CS} + \beta_\epsilon$$

where:

$$\beta_{CS} = \frac{0.9\lambda}{d \cdot \cos\theta}$$

and

$$\beta_\epsilon = 4\epsilon \cdot \tan\theta$$

where  $\lambda$  is the wavelength of the used X-rays (0.15405 nm), *d* is the crystallite size, and  $\theta$  is the Bragg's angle. From a plot of  $(\beta - \beta_i)\cos\theta/\lambda$  vs.  $\sin\theta/\lambda$ , one can evaluate the contribution of microstrain and crystallite size to the XRD line broadening. The intercept of the plot with the ordinate (with values expressed in radians) represents the

reciprocal of the average crystallite size, and, from the slope of the line,  $\epsilon$  is obtained, which is related to the microstrains present in the film.

The thickness of nitrided layers was determined by microscope examination of the cross section through the nitrided layer. The roughness of the studied samples and the thickness of the coatings were evaluated with a Dektak 150 surface profiler. The hardness of the coatings and the hardness profile of the nitrided region were measured with a FM-700 Digital Microhardness Tester (0.05 N load for the coatings, and 0.2 N load for the nitrided layers). Scratch tests were carried out to estimate the adhesion strength of the coatings. The testing conditions were: indenter – 0.2 mm radius diamond tip, load – continuous increase from 0 to 100 N, scratching speed – 10 mm/min, scratching distance – 10 mm. The critical load L<sub>c</sub>, defined as the load where film flaking starts, was determined by optical microscope examination of the scratch tracks.

For the tribological evaluation of the untreated HSS, nitrided HSS (denoted as HSS-1) and duplex coatings, a pin-on-disc Tribometer (CSM Instruments) with a sapphire ball counterpart of 6 mm diameter was used. The experiments were carried out without lubrication for 35 min, corresponding to a sliding distance of 400 m, using a normal load of 3 N and a linear speed of 0.2 m/s. The tribological experiments were performed under laboratory conditions of 22°C and 40% relative humidity. The wear tracks of the coatings were quantified using a stylus profilometer (Dektak 150).

### 3. Results and discussion

#### 3.1 Characterization of nitrided layers

Fig 1 shows the structure of the cross section of the nitrided layer. After nital-etching (2%), the nitrided part of the substrate appears as a dark zone in the optical micrograph. From the micrograph, a nitriding depth of approximately 58 μm was estimated. The uniformity of the thickness of nitrided layer was confirmed. It can also be seen that martensitic structure, with secondary precipitates of metallic nitrides and carbides, are formed in the nitride layer.

Microhardness was measured along with depth on the cross-section of nitrided layer, in Fig. 2 being presented the microhardness profiles. The nitriding treatment determined an increase of the microhardness from 932 HV<sub>0.2</sub> for the untreated HSS substrate to 1580 HV<sub>0.2</sub> on surface of the nitrided layer. This significant increase in hardness is probably due to formation of precipitates of metallic nitrides, including the specific  $\gamma'$ -Fe<sub>4</sub>N (hard) and  $\epsilon$ -Fe<sub>2,3</sub>N (wear resistant) phases, as also reported by Pessin [13], and multicomponent (W,Mo,V)-N. In order to support this hypothesis, the EDS line profiles of Fe, W,

Mo, and V in the nitrated layer are presented in Figure 3. In the dark gray spots, one can observe a substantial increase in atomic concentrations of W, Mo and V, indicating the formation of their nitrides. In the light gray spots, Fe concentration is dominant. A SEM micrograph of the sample cross section is also shown.

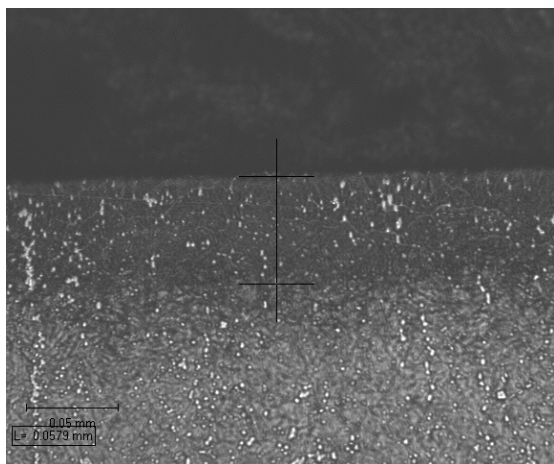


Fig. 1. Optical micrograph of a nitrated layer; the cross-section was polished and subsequently etched in nital (2%)

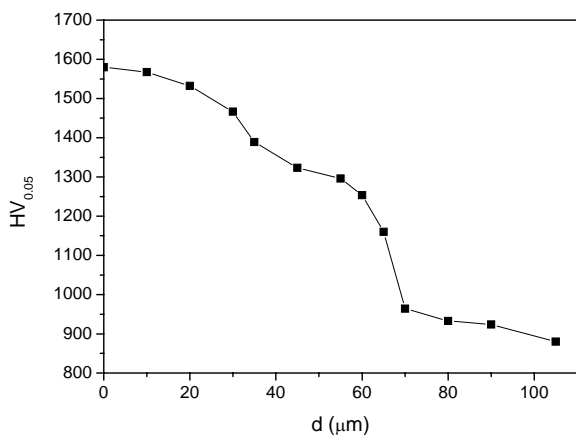


Fig. 2. Microhardness profiles of nitrated sample

### 3.2 Characterization of duplex (Zr,Al)CN coatings Elemental composition and chemical bonding

Using XPS, the elemental composition and the chemical binding state on the film surface, sputtered with 5 keV Ar ions for 10 min., were determined. The XPS spectra of the metals in the (Zr,Al)CN films are shown in Fig. 4. The peak assignments, according to the data in the literature [14], were as follows. The Zr  $2p_{3/2}$  peaks at 180.3 and 181.5 eV were attributed to Zr-C-N and Zr-C-N-O bonding, respectively; the Al  $2p_{3/2}$  peaks at 73.7 and 76.7 eV to Al-C-N and Al-O, respectively. These results indicate the formation of an oxide rich region at the topmost layer, as a result of the surface oxidation in free atmosphere. The presence of oxygen on film surface is a typical effect in deposition of nitrides or carbonitrides of

transition metals [15, 16], since these metals have a high affinity to oxygen.

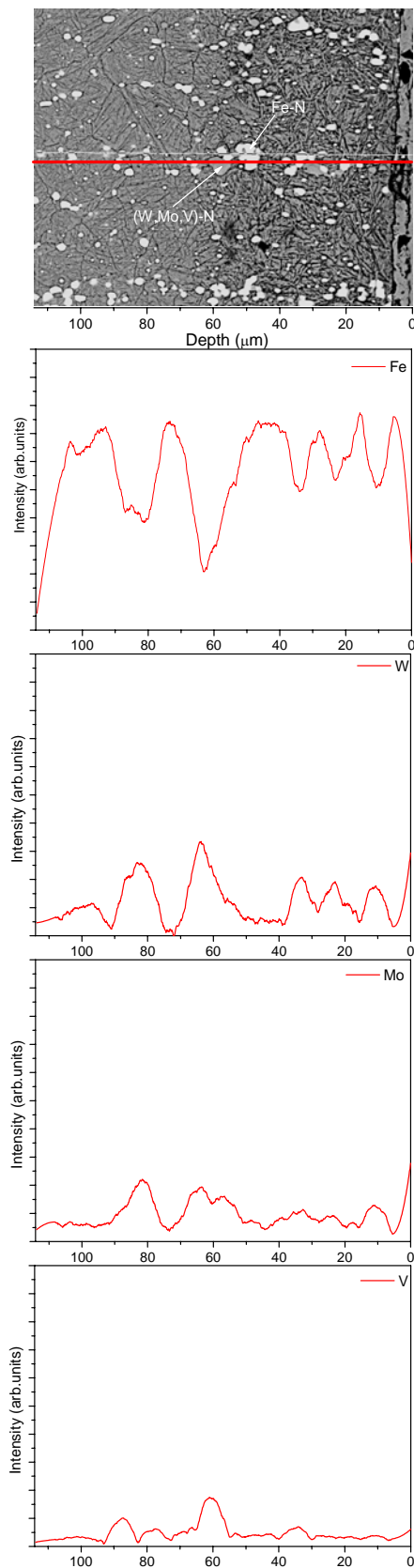


Fig. 3. EDS line profiles of Fe, W, Mo and V in the nitrated layer.

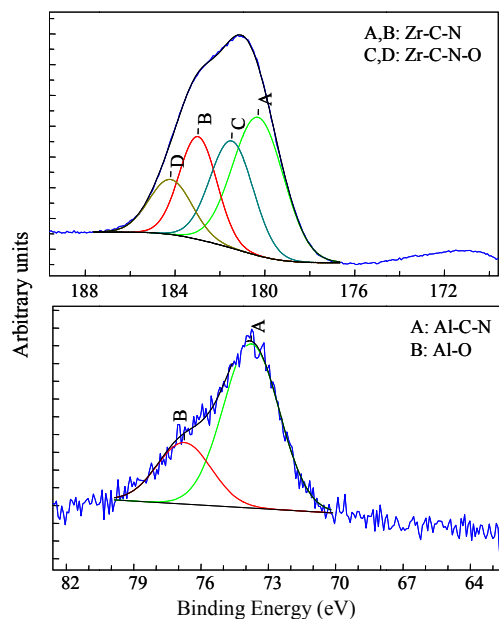


Fig. 4. XPS Zr 2p and Al 2p spectra of the (Zr,Al)CN coatings.

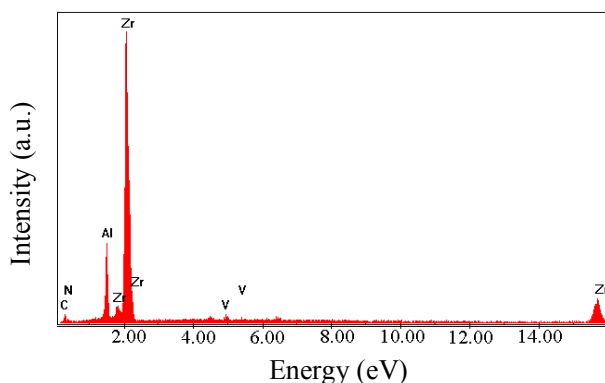


Fig. 5. EDS spectrum of the (Zr,Al)CN duplex coating.

Fig. 5 shows the EDS spectrum of the (Zr,Al)CN coatings. The elemental compositions of the coatings, as derived from quantitative EDS analysis, are: Zr – 21.1 at.%, Al – 11.6 at.%, C – 36.9 at.% and N – 30.4 at.%. It should be noted that the (Zr,Al)CN coating is highly overstoichiometric: (C+N)/(Zr+Al) ratio ~ 2.

### 3.3 X-ray structural analysis

Fig. 6 shows the XRD diffraction pattern of the duplex (Zr,Al)CN coating. The (Zr,Al)CN peaks revealed the formation of a carbonitride single fcc solid solution, with a (111) preferred orientation. This texture, commonly reported for the films deposited by this method with intense energetic ion bombardment [17], was predicted under the deposition conditions for which strain energy was dominant as compared to the surface energy [18].

As a rough approximation, the values of the average crystallite size  $d$  and micro-strain  $\epsilon$  were calculated using the Williamson-Hall method. The  $d$  value obtained for the

(Zr,Al)CN coating was of about 43.9 nm. The strain value in the films was of about 0.01556.

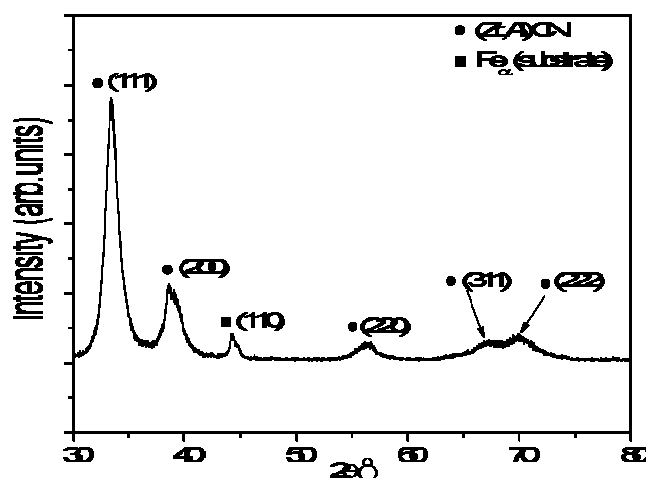


Fig. 6. X-ray diffraction pattern of the (Zr,Al)CN film deposited on the 480°C nitrided substrate.

### 3.4 Mechanical and tribological characteristics

Hardness ( $H$ ), roughness ( $R_a$ ), scratch-test adhesion critical load ( $L_c$ ), friction coefficient ( $\mu$ ) and wear rate ( $K$ ) of the duplex (Zr,Al)CN coating are listed in Table 2. For comparison purposes, values of mechanical and tribological properties of untreated and nitrided steel are also presented.

The high hardness of the (Zr,Al)CN coating (~36 GPa) as compared to commonly used TiN or ZrN coatings (21 – 26 GPa), also reported for other complex carbonitride coating systems (e.g. TiAlZrCN [19] or TiMoCN [20]), may be due to the combining effect of several factors such as defect hardening mechanism [21], lattice deformation [22, 23], solid solution strengthening mechanism [3, 24] and enhancement of the ion bombardment of the substrate [25], due to an increased plasma density generated by the additional Al cathode. The role played by each factor is difficult to be evaluated without a complex study of the microstructure and morphology of the films.

As a result of the surface treatment, surface roughness  $R_a$  increased from 14 nm (HSS) to 70 nm (HSS-1) and then increased to 450 nm ( (Zr,Al)CN on HSS-1). Fig. 7 shows the 3D images obtained by using the surface profiler. Comparison of surface morphology before (Fig. 7(a)) and after nitriding (Fig. 7(b)) illustrates the increase in surface roughness after nitriding.

A good adhesion of the duplex (Zr,Al)CN coatings was found, the critical load values being of about 56 N.

The results of the dry sliding tests on the duplex (Zr,Al)CN coatings were summarized in terms of the wear rate  $K$  and friction coefficient  $\mu$  at the end of the tribometer test (Table 2) and also as the variation of the friction coefficient vs. sliding distance. For comparison, data for HSS and HSS-1 samples are also given.

Table 2. Hardness ( $H$ ), roughness ( $R_a$ ), scratch-test adhesion critical load ( $L_c$ ), friction coefficient ( $\mu$ ) and wear rate ( $K$ ) of the samples.

Coating type	H (GPa)	$L_c$ (N)	$R_a$ (nm)	$\mu$	K ( $\times 10^{-6} \text{mm}^3/\text{Nm}$ )
HSS	9.3	-	14	0.93	7.4
HSS-1	15.8	-	70	0.82	6.8
(Zr,Al)CN/HSS-1	35.9	56	450	0.55	0.53

After a sliding distance of 75 m, the friction coefficient values of the tested samples reached already a plateau corresponding to a value of  $\sim 0.5$  for the duplex treated sample (Zr,Al)CN/HSS-1, while the other samples exhibited significantly higher friction coefficients ( $\mu = 0.82$  for HSS-1 and  $\mu = 0.93$  for HSS), as presented in Fig. 8.

Fig. 8 shows 3-D images and the profiles of wear tracks at the end of friction tests. Unlike untreated HSS, for the nitrided and duplex coated samples some transferred material is visible at both sides of the wear tracks. From the wear track profile, the wear rate  $K$  was calculated. It was found (Table 2) that the wear rate of the (Zr,Al)CN/HSS-1 sample was lower than those of HSS or HSS-1 specimens. Due to high hardness of the duplex coating, its plastic deformation is lower than those of the reference samples under the same loading level. Consequently, the contact area between the ball and the sample is lower in the case of the duplex coating, resulting in a reduced wear rate. The fact that the most wear-resistant sample was the duplex (Zr,Al)CN coating, also exhibiting the highest microhardness, implies that the wear follows the abrasive wear mechanism [26], [27].

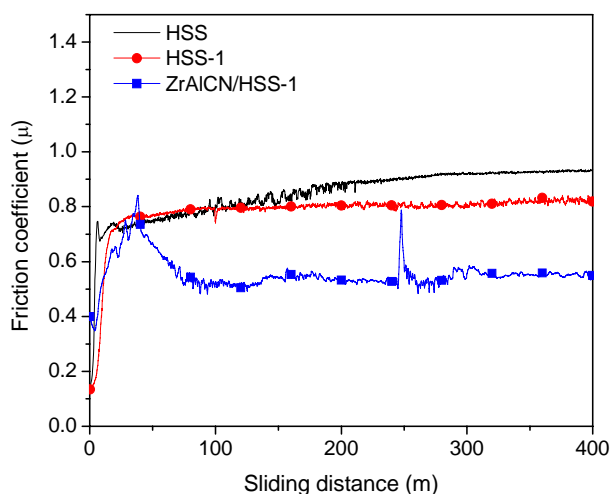


Fig. 8. Friction coefficient  $\mu$  for HSS, HSS-1 and (Zr,Al)CN/HSS-1 as a function of sliding distance.

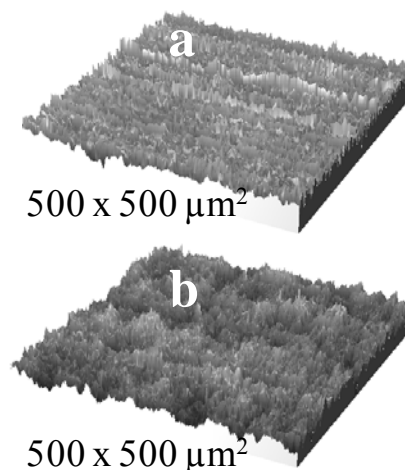


Fig. 7. 3D surface profilometry of (a): untreated steel (HSS); (b) nitrided steel (HSS-1) samples.

#### 4. Conclusions

A novel type of duplex coatings, namely (Zr,Al)CN, were produced by the cathodic arc method on plasma nitrided HSS substrates. The nitrided specimens were prepared in a mixture of  $\text{N}_2$  (70%) and  $\text{H}_2$  (30%) gases for 3 h at  $480^\circ\text{C}$  nitriding temperature.

The EDS and XPS analyses showed that the coatings were highly over-stoichiometric,  $(\text{C}+\text{N})/(\text{Zr}+\text{Al})$  ratio was calculated to be of 2. X-ray diffraction patterns revealed the formation a crystalline nanostructure consisting of a carbonitride fcc solid solution ((111) texture).

For the (Zr,Al)CN film deposited on nitrided HSS steel substrate, a high hardness of about  $\sim 36$  GPa was measured. Tribological tests, carried out under dry conditions, revealed that both friction coefficient and wear resistance of the duplex coatings were superior to those of the untreated or nitrided specimens.

The experimental results demonstrated that the (Zr,Al)CN duplex coatings, investigated in this work, could be promising candidates for protective coatings to be used in various tribological applications.

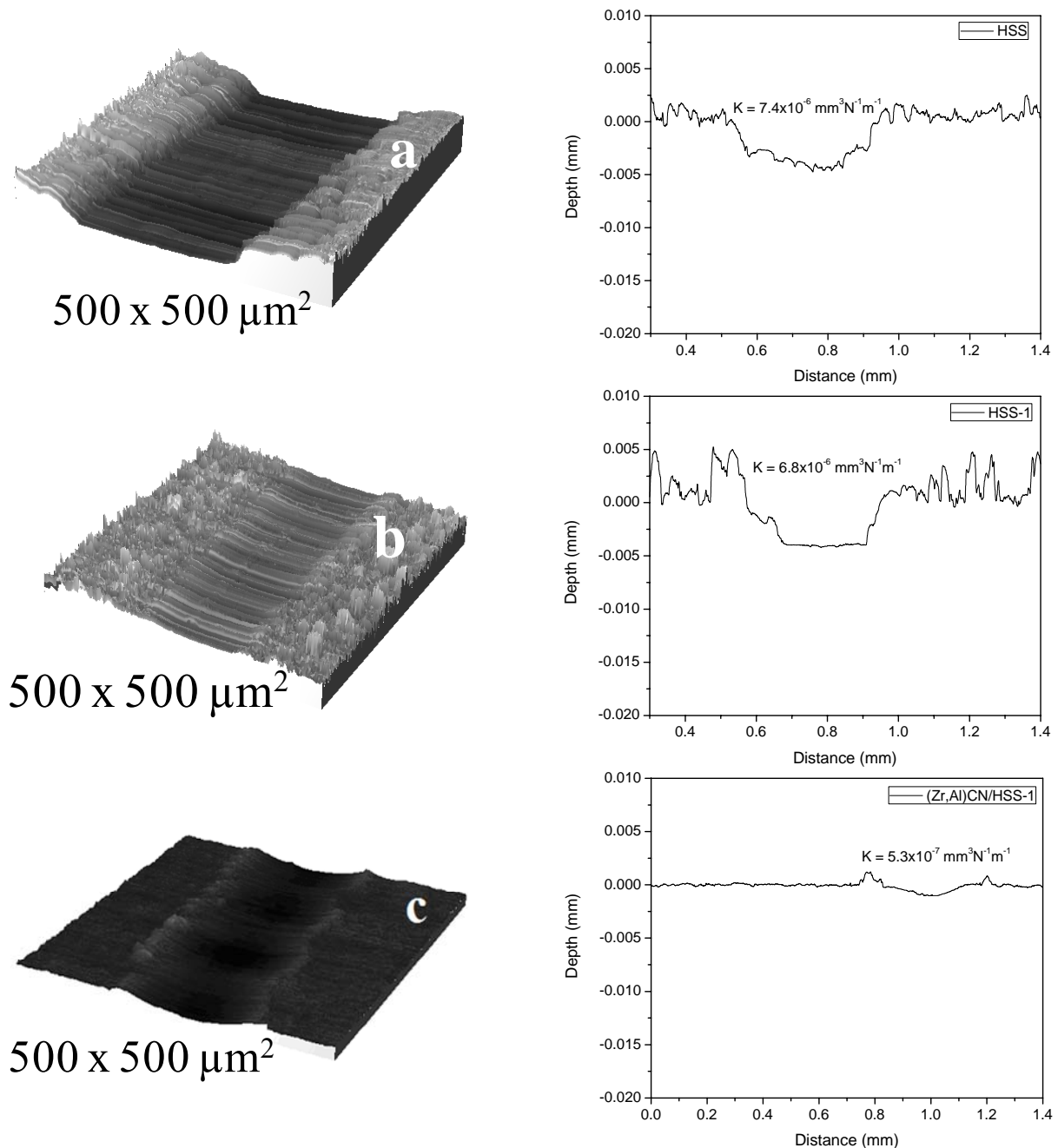


Fig.8. Three 3-D images of the wear tracks, obtained with a Dektak 150 surface profiler, for: (a) untreated HSS steel; (b) nitrided steel (HSS-1); (c) (Zr,Al)CN coating deposited on nitrided steel (HSS-1), after the sliding test of 400 m.

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### References

- [1] J. E. Sundgren, B. O. Johansson, S. E. Karlsson, *Thin Solid Films* **105**, 353 (1983).
- [2] W.D. Sproul, M.E. Graham, M.S. Wong, P.J. Rudnik, *Surf. Coat. Technol.* **61**, 139 (1993).
- [3] H. Holleck, *Surf. Eng.* **7**, 137 (1991).
- [4] S. PalDey and S.C. Deevi, *Mater. Sci. Eng. A* **342**, 58 (2003).
- [5] J.J. Araiza, O. Sánchez, J.M. Albella, *Vacuum* **83**, 1236 (2009).
- [6] J. M. Lackner, W. Waldhauser, R. Ebner, R. J. Bakker, T. Schöberl, B. Major, *Thin Solid Films* **468**, 125 (2004).
- [7] Cheng-Hsun Hsu, Chun-Ying Lee, Chien-Chih Lee, *Thin Solid Films* **517**, 5212 (2009).

- [8] M.Stueber, P.B.Barna, M.C.Simmonds, U.Albers, H. Leiste, C. Ziebert, H. Holleck, A. Kovács, P. Hovsepián, I.Gee, *Thin Solid Films* **493**, 104 (2005).
- [9] A. Vladescu, A. Kiss, A. Popescu, M. Braic, M. Balaceanu, V. Braic, I. Tudor, C. Logofatu, C.C. Negrila, R. Ripeanu, *J. Nanosci. Nanotechnol.* **8**, 717 (2008).
- [10] C.C. Negrila, C. Logofatu, R.V. Ghita, C. Cotirlan, F. Ungureanu, A.S. Manea, M.F.Lazarescu, *J. Cryst. Growth* **310**, 1576 (2008).
- [11] G.K.Williamson, W.H.Hall, *Acta Metall.* **1**, 22 (1953).
- [12] B.D.Cullity, S.R.Stock, *Elements of X-ray Diffraction*, 3 ed. Prentice Hall, New Jersey (2001).
- [13] M.A. Pessin, M.D. Tier, T.R. Strohaecker, A. Bloyce, Y. Sun, T. Bell, *Tribol. Lett.* **8**, 223 (2000).
- [14] *Handbooks of Monochromatic XPS Spectra*, vol.5 (ed. XPS International), Mountain View (2004).
- [15] V. Braic, M.Balaceanu, M.Braic, A.Vladescu, S. Panseri, A. Russo, *J. Mech. Behav. Biomed.* **10**, 197 (2012).
- [16] J. Musil, P.Baroch, P.Zeman, *Hard nanocomposite coatings. Present status and trends*, in R.Weil (Ed.), *Plasma Surface Engineering Research and its Practical Applications*, Research Signpost Publisher, USA (2008).
- [17] *Handbook of Vacuum Arc Science and Technology*, Ed. R.L.Boxman, D.M.Sanders, P.J.Martin, Noyes Publications, Park Ridge, N.J., U.S.A (1995).
- [18] U.C.Oh, Jung Ho Je, *J.Appl.Phys.* **74**, 1692 (1993).
- [19] M. Balaceanu, V. Braic, A. Kiss, C.N. Zoita, A. Vladescu, M. Braic, I. Tudor, A. Popescu, R. Ripeanu, C. Logofatu, C.C. Negrila, *Surf.Coat. Technol.* **202**, 3981 (2008).
- [20] A. Chavanes, E. Pauty, M. Woydt, *Wear* **256**, 647 (2004).
- [21] Chul Sik Jang, Jun-Ha Jeon, Pung Keun Song, Myung Chang Kang and Kwang Ho Kim, *Surf.Coat.Technol.* **200**, 1501 (2005).
- [22] S.Veprek, *J.Vac.Sci.Technol. A* **17**, 2401 (1999).
- [23] J.Musil, *Surf.Coat.Technol.* **125**, 322 (2000).
- [24] S. Zhang,H.L.Wang, S.-E. Ong, D. Sun, X. L. Bui, *Plasma Process. Polym.* **4**, 219 (2007).
- [25] E. Kelesoglu, C. Mitterer, M. K. Kazmanli, M. Ürgen, *Surf.Coat.Technol.* **116-119**, 133 (1999).
- [26] A. M. Peters, M. Nastasi, *Vacuum* **67**, 169 (2002).
- [27] A. Matthews, A. Leyland, K. Holmberg, H. Ronkainen, *Surf. Coat. Technol.* **100-101**, 1 (1998).

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