

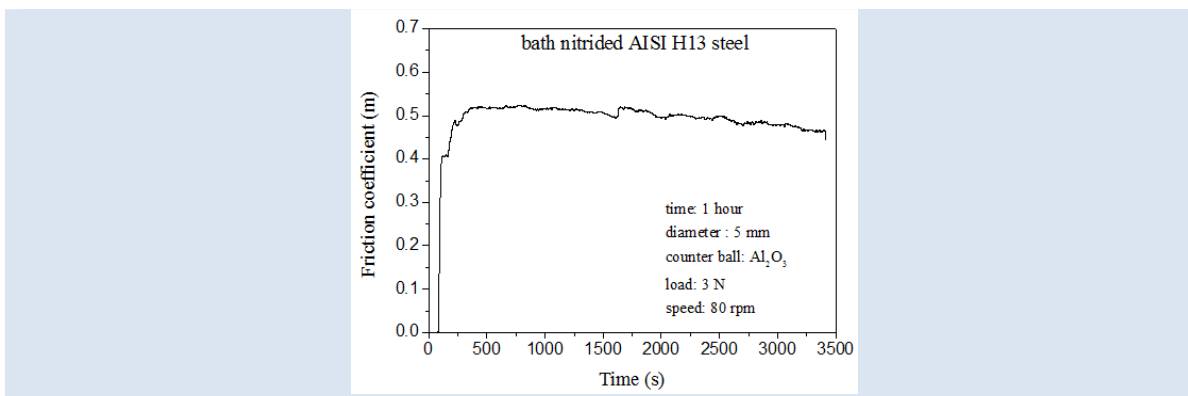
DEPOSITION AND CHARACTERIZATION OF DUPLEX TREATED COATING SYSTEM APPLIED ON HOT WORK STEEL AISI H13

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ABSTRACT

AISI H13 steel is widely used for extrusion moulds and other hot work tools fabrication, due to its high toughness, strength and hardness around 56 HRC (Rockwell C). However, this steel possesses a relatively low wear resistance, which reduces its life time under high loading conditions. The aim of this work was to enhance the wear resistance of the steel H13 using the following surface treatments: austenitizing + quenching + tempering (further called “tempering”), tempering and bath nitriding, tempering and coated with chromium nitride (CrN), tempering + bath nitriding + coated with CrN (further called “Duplex coating”). The properties of the treated samples were compared with each other in dependence of the made surface treatment. The coatings were deposited using the r.f. balanced magnetron sputtering deposition technique. The total thickness of the coatings was maintained at 5 μm , while the thickness of the nitrided zone was approximately 140 μm . The microstructure and the crystalline phase composition were investigated by Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD) technique, respectively. The hardness and the adhesion of the coatings were determined by micro indentation measurements and the Rockwell indentation test, respectively. The wear resistance of the coatings was evaluated using ball on disc tests. The duplex treated samples presented a hardness three order of magnitude higher and showed a wear rate six times smaller than those samples only tempered.

Keywords: Magnetron sputtering, Chromium nitrides, Duplex treatment, Wear resistance

DEPOSICIÓN Y CARACTERIZACIÓN DE UN SISTEMA DE RECUBRIMIENTO DUPLEX APLICADO SOBRE ACERO PARA TRABAJO EN CALIENTE AISI H13

RESUMEN

El acero AISI H13 es ampliamente utilizado en la fabricación de moldes de extrusión y de otras herramientas para el conformado en caliente debido a su tenacidad, elevada resistencia mecánica, y dureza de aproximadamente 56 HRC (Rockwell C). Sin embargo, este acero posee una relativa baja resistencia al desgaste, que reduce su vida útil cuando es sometido a esfuerzos elevados. El propósito de este trabajo consistió en mejorar la resistencia al desgaste del acero H13 mediante los siguientes tratamientos superficiales: austenización + temple + revenido (denominado en adelante “revenido”), revenido y nitruración líquida, revenido y recubrimiento de nitruro de cromo (CrN), revenido + nitruración líquida + recubrimiento de CrN (denominado en adelante “recubrimiento Duplex”). Las propiedades de las muestras tratadas fueron comparadas en función del tipo de tratamiento superficial realizado. Todos los recubrimientos se depositaron por la pulverización catódica reactiva r.f. y asistida por un campo magnético balanceado. El espesor promedio de los recubrimientos fue de 5 micras, mientras que el espesor de la zona nitrurada del acero fue alrededor de 140 micras. La microestructura y las fases cristalinas presentes en las muestras fueron investigadas mediante microscopía electrónica de barrido (SEM) y difracción de rayos X (XRD), respectivamente. La dureza y la adherencia fueron determinadas por mediciones de microindentación y el método de indentación Rockwell C, respectivamente. La resistencia al desgaste de las muestras fue evaluada mediante ensayos de bola sobre disco. Las muestras tratadas con los recubrimientos dúplex presentaron una dureza tres órdenes de magnitud mayor y una tasa de desgaste seis veces menor que las muestras de acero templadas solamente.

Palabras Claves: Pulverización catódica, Nitruro de cromo, Recubrimientos dúplex, Resistencia al desgaste

1. INTRODUCTION

AISI H13 steel is one of the most frequently used material for hot work tools for different industrial application fields, because of its physical and mechanical properties including high hardenability with minimum amount of dimensional change, high strength and ductility, good tempering resistance and moderate costs, among others. During the production of aluminum- and copper alloys, for example, hot billets are pressed through a die at high pressures and elevated temperatures about 450 - 650°C. Under these work conditions the die must have high hardness and strength, as well as high wear resistance at elevated temperatures in order to minimize the dimensional change of the extruded products and to optimize the production times [1, 2].

Several surface treatments are used for this purpose, among others, bath, gas and plasma nitriding, as well as the PAPVD (plasma assisted physical vapor deposition) and PACVD (plasma assisted chemical vapor deposition) coatings technology. Nitriding is by far the most common surface treatment applied for hot work tool steel. Nitriding of steel involves the diffusion of nitrogen into the surface at temperatures ranging from 450 to 580°C in a liquid, gaseous or vacuum process. After nitriding, a compound layer of carbonitrides and iron nitrides is normally formed at the substrate surface. Below the compound layer, there is a diffusion layer, where the steel matrix is supersaturated with nitrogen atoms. Both physical phenomena conduce to an increase of hardness and wear resistance of steel surface [1, 3].

Nevertheless, higher hardness values and wear resistance are obtained using PAPVD and PACVD hard coatings like TiN, CrN, TiAlN, ZrN, CrAlN. However, these coatings normally flake off from substrate after a relatively short time, if the tools work under very high pressure or tensile load, or at changing load conditions, because of their relatively low adhesion to the substrate. The main points are the large difference in hardness and/or in the thermal expansions coefficient between coating and substrate which results in coating failure due to a plastic deformation of substrate and the consequent delamination of the coating [4, 5].

A strategy for the improvement of the adhesion of hard coating is the use of so-called duplex coatings. In this case the surface of the substrate is first nitrided and coated then with a hard material to

obtain a smooth and coherent transition of the mechanical properties between substrate and the top coating [6, 7]. The aim of this research was to increase the wear resistance of AISI H13 hot work steel by using the four different surface treatments: tempering; tempering and nitriding; tempering and coating with CrN; tempering and duplex treated (bath nitriding + CrN coating). The mechanical and tribological properties of the treated samples were characterized and compared with each other.

2. EXPERIMENTAL PART

AISI H13 steel samples were cut in to cylindrical shape with a height of 4 mm and a diameter of 19 mm. All samples were heat treated by austenitizing at 1,050°C for 2 hours, oil quenching and double tempering at 540°C and 560°C for 1 hour, respectively. The average hardness of the tempered samples was 52 ± 2 HRC and 580 ± 15 HK_{0.015} as determined using the Rockwell and the Knoop hardness test, respectively. A load of 150 mN was applied for the Knoop test. The substrates were mechanically polished to a surface finish of Ra=0.8 µm, which was determined using an optical profilometer with a resolution of 0.01 µm. One set of these samples were nitrided using the so called "Tenifer bath nitriding" at 560°C for 3 hours, which conducted to a 140 ± 5 µm thick nitrided zone with an average surface hardness of $1,280 \pm 12$ HV_{0.025} (Vickers Hardness). The nitrided samples were polished down with diamond paste to a roughness of Ra=0.05 µm to eliminate the white layer, which normally affects the adhesion of the coatings, if it is present [8]. The average Vickers hardness of the nitrided steel samples after elimination of the white layer was $1,100 \pm 25$ HV_{0.025}. Some tempered and nitrided samples were coated with a 5 µm thick CrN coating (duplex coating) and another set of the tempered samples were directly coated with the same CrN coating without nitriding. The coating's thickness of prepared cross section of selected coated samples was determined using a JEOL scanning electron microscope. All coatings were deposited using the reactive balanced r.f. magnetron sputtering technique (13.56 Mhz) in an Ar/N₂ atmosphere, pressure of 2.1×10^{-2} mbar and a substrate rotation speed of 20 rpm. The deposition parameters are consigned in table 1. Additional descriptions of the vacuum chamber can be found in an earlier publication [9].

Table 1. Parameter for plasma cleaning and deposition of the CrN monolayer

CrN monolayer	
Substrate temperature (°C)	250
Plasma cleaning of target and substrates	
r.f. Target power Cr (W)	100
Cleaning time (min.)	20
Argon flow (sccm)	50
Substrate voltage (V)	-300
Deposition parameters of CrN	
r.f. Target power Cr (W)	350
Deposition time (h)	3
Argon flow (sccm)	50 (93.0%)
Nitrogen flow (sccm)	3.7 (7.0%)
Bias voltage (V)	-100

Thereafter, the cross section of selected nitrided steel samples was analyzed by optical microscopy to evaluate their microstructure. The phase constitution of the nitrided samples and of some coated silicon samples was investigated by X-ray diffraction using an accelerating voltage of 40 kV, beam current of 30 mA, an incident angle of 2° and Cu K α ($\lambda=0.154$ nm) radiation. The cross section hardness of the nitrided samples were measured using the Vickers test method and a load of 250 mN, while the surface hardness of all treated samples and duplex coated one were determined by the Knoop test method using a load of 150 mN. The adhesion of the coatings was qualitative determined using the Rockwell indentation test (VDI 3198) [10]. According to the Rockwell indentation test six different adhesion conditions are classified, which are characterized from HF1 to HF6. The condition HF1 to HF4 corresponds to an acceptable adhesion. The remaining conditions HF4 to HF6 do not show good adhesion. Wear resistance tests with the ball-on-disc method were carried out at the room temperature. An Al₂O₃ - corundum ball with 6 mm in diameter was used as counter specimen. During the pin-on-disc test the stationary ball was pressed with a load of 3 N onto the disc rotating in a horizontal plane for 1 hour. The rotational speed of the disc with the specimen was 80 rpm and a wear track of 5 mm diameter. The friction coefficient between the ball and disc was measured during the test. For the analysis of the wear behavior of the

investigated samples, prior and afterwards to each test, the samples and counterparts were cleaned in ultrasound bath with ethanol and weighed to determine the mass loss. The coatings wear rate was calculated using the equation (1):

$$K = \frac{M}{Fs} \quad (1)$$

Where F is the applied load (N), s is the total test sliding distance (m) and M is the mass loss (kg). The mechanical and tribological properties of the samples were then compared with each other in dependence of the made surface treatment.

3. RESULTS AND DISCUSSION

3.1 Microstructure of the nitrided samples

After the initial heat treatment, all samples exhibited a tempered martensitic microstructure with an average hardness of 52 $\pm$ 2 HRC. After the metallographic evaluation the nitrided samples were divided into three zones: a light gray one, which corresponds to the metallic matrix of tempered martensite in which fine carbides are uniformly distributed, a dark gray nitrided surface layer with an approximately thickness of 140 μ m, and a thin white layer with a thickness of about 20 μ m, as it can be seen in figure 1.

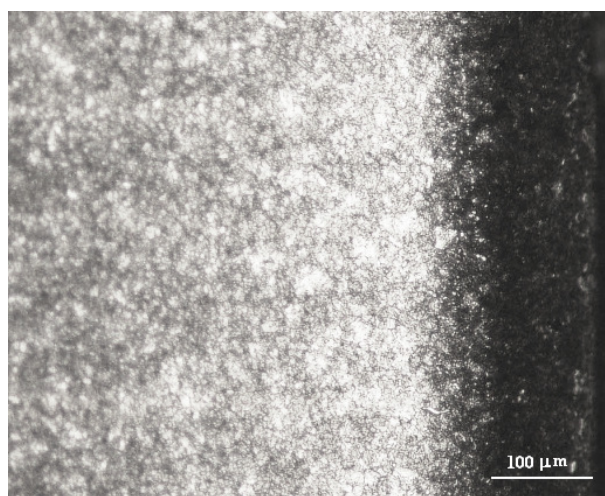


Figure 1. Microstructure of a selected nitrided AISI H13 hot work steel sample (etched using 5% aqueous HNO₃)

3.2 Crystal structure of the nitrided samples

The phase constitution of the nitrided samples determined using the X-ray diffraction technique is shown in figure 2. The nitrided layer contained a

first diffusion zone of $\text{Fe}\alpha(\text{N})$, in which the nitrogen atoms did not react with iron, but they are completely dissolved as interstitial atoms in the $\alpha\text{-Fe}$ lattice. After reaching the dissolution limit, the nitrogen atoms react with iron and segregated as needle-shaped iron nitrides $\epsilon\text{-Fe}_{2-3}\text{N}$ and $\gamma'\text{-Fe}_4\text{N}$ on the grain boundaries and within the grains to form a hard compound zone. The above observed white layer is normally composed of a mixture of $\epsilon\text{-Fe}_{2-3}\text{N}$ and $\gamma'\text{-Fe}_4\text{N}$ [1]. There are peaks of iron oxide in the spectrogram caused by contamination of the vacuum chamber with oxygen.

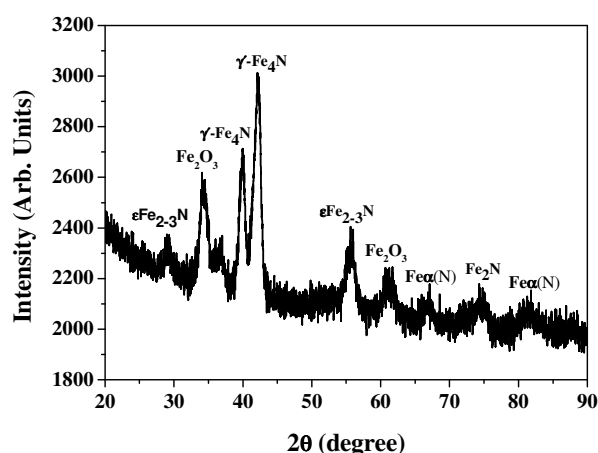


Figure 2. XRD patterns of the nitrided steel AISI H13

3.3 Hardness of the nitrided samples

In figure 3 the Vickers micro hardness ($\text{HV}_{0.025}$) of the nitrided layer in dependence on its thickness is registered. The maximum measured hardness near to the surface was $1,280 \pm 10$ HV, while the value decreased to a minimum of 580 ± 5 HV (approx. 52 HRC) in a depth of about 150 μm , which corresponds to the hardness of the metallic steel matrix. The hardness behavior of the nitrided samples suits the observed microstructure in figure 1 and the determined phase composition by XRD, because of the presence of hard iron nitrides $\epsilon\text{-Fe}_{2-3}\text{N}$ and $\gamma'\text{-Fe}_4\text{N}$.

3.4 Crystal structure of the CrN coating

The diffraction patterns in figure 4 of a silicon sample coated with CrN reveal a mono-phase fcc structure only and were indexed as emanating from single phase B1-NaCl structure reflections. No second hexagonal phase of Cr_2N type was observed. The θ - 2θ scan from the 5 μm thick CrN layer deposited on silicon substrate consists of the (200),

(220), (211) and (222) peaks centered at $2\theta = 43.25^\circ, 63.43^\circ, 74.12^\circ$ and 80.41° , respectively. The observed peak of Cr_2O_3 is attributed of the chamber contamination with oxygen. The intensity of the mean (200) peak indicates the high crystalline structure of the deposited CrN coating. The calculated lattice parameter $a_{\perp}^{200} = 0.4178$ nm using the Bragg Equation was found to be higher than published data for unstrained bulk CrN ($a_{\perp}^{200} = 0.4140$ nm) [11] and to the data given in the JCPDS database (No. 35-803) for powder CrN, indicating the in-plane compression in films due to the ion bombardment of CrN coatings during its growth. Similar results were obtained by Mayrhofer et al. [12].

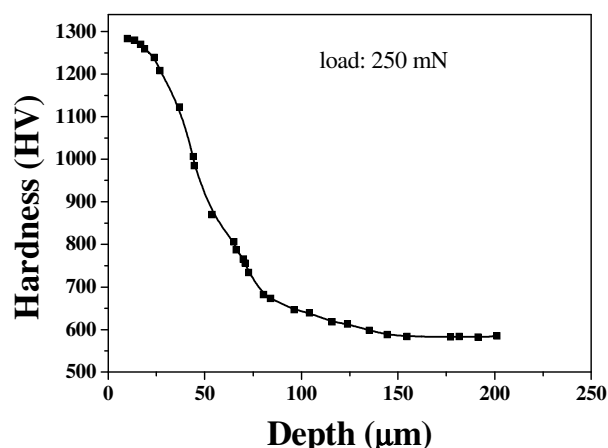


Figure 3. Vickers microhardness profile of a nitrided AISI H13 steel sample

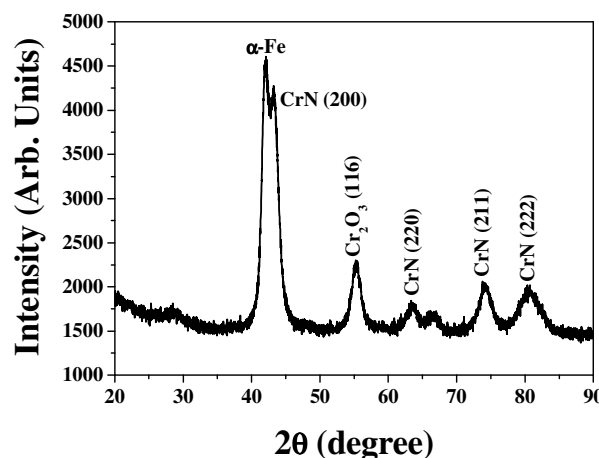


Figure 4. XRD patterns of a silicon sample coated with a CrN monolayer

Figure 5 shows a SEM cross section image of the CrN coating deposited on a steel sample used to

determine the average thickness of the coating.

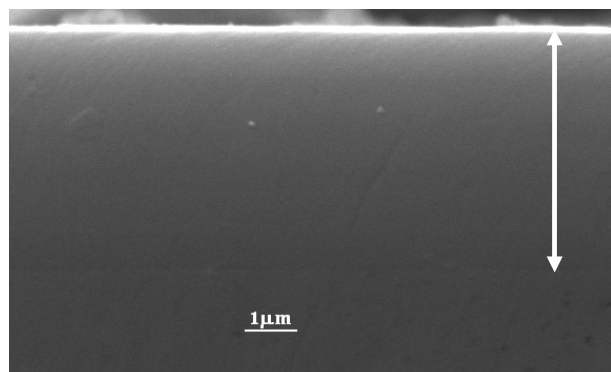


Figure 5. SEM cross section (double arrow) micrograph of the deposited CrN coating

3.5 Mechanical and tribological properties of the treated samples

The Knoop micro hardness values of the four types of surface treatment of the AISI H13 steel samples are shown in the figure 6. It is to point out that the hardness measured with a load of 150 mN does not represent the real hardness of the CrN coating, since this incorporates the influence of the softer substrate in agreement with the standard ISO 4516-1980, that suggests a value of the load, with which an indenter penetration greater than tenth of the coating's thickness is not exceeded. The nitrided zone improves the mechanical support for the single-layered CrN coating so that an increased hardness up to $2,467 \pm 15$ HK_{0.015} of the duplex-treated coating/substrate system was measured. This hardness value is characteristic of the CrN coating deposited onto plasma nitrided steel [13], which represents a hardness increment of about 303% compared to the tempered and uncoated steel sample.

The Adhesion of the CrN coatings deposited on the H13 steel samples was also investigated using the Rockwell indentation test (according to the standard VDI 3198), which indicates a HF-1 condition for the duplex CrN- hard coatings with no chipping of the coating around the indented trace (see figure 7b) and therefore also represents a better adhesion as the CrN monolayer deposited on the steel sample without nitriding as can be observed in figure 7a). This behavior is on the one hand attributed to the smooth and coherent transition of the mechanical properties between the substrate and the top CrN coating and on the other hand to the mechanical

support for the CrN coating by the nitrided surface of the steel samples [14, 15].

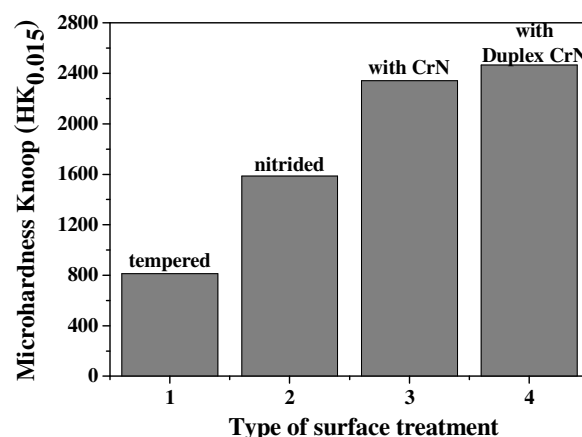


Figure 6. Micro hardness of the AISI H13 steel samples as a function of their surface treatment

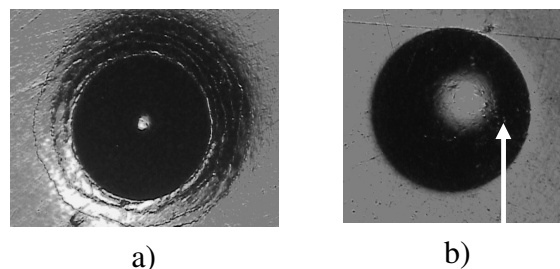


Figure 7. Qualitative adhesion test results of selected steel samples a) coated with CrN monolayer: and b) coated with duplex CrN coating system as determined by the Rockwell indentation test.

The investigated coatings were subjected to the ball-on-disc test carried out at room temperature (20°C) to determine their wear resistance. Figure 8 shows the friction coefficient values in the steady regime as a function of the different surface treatments. Despite of an increase of the surface roughness of the steel samples after nitriding, the friction coefficient decreased from 0.45 for the nitrided samples to 0.38 for those coated with the duplex system (figure 8). This fact additional contributed to the lower wear rate of the duplex treated steel samples as discussed later.

Figure 9 shows the wear rate of the steel samples in relation of their surface treatment. The lowest wear rate was obtained by the sample coated with the duplex system, but there is no big difference to the wear rate of the sample coated with the CrN

monolayer, because the test time was not long enough to reach the nitrided steel surface. The duplex treated samples showed a wear rate six times smaller than those samples only heat treated due to their higher hardness and lower friction coefficient compared to the uncoated samples.

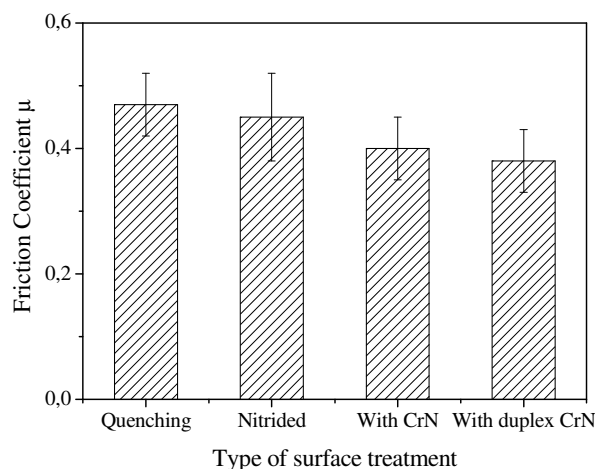


Figure 8. Average stationary friction coefficient of the steel samples as a function of the surface treatment.

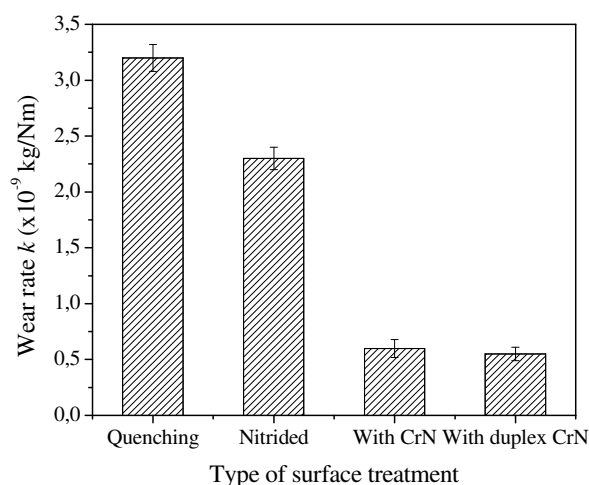


Figure 9. Average sliding wear rate of the steel samples in dependence on the surface treatment.

Figure 10 shows the aspect of the alumina ball and the coating after the dry sliding friction and wear test. In figure 10a debris of a brown colour can be seen. These suggest the presence of products of tribochemical reactions. After cleaning with ethanol, adhered small stains remained on the surface of the ball (fig. 10b). These stains possibly correspond to adhered reaction products; the alumina balls did not show any wear (fig. 10b). The debris found on the

coating was brown colour as well as the worn surface (figures 10c y 10d), possibly this colour is due to the formation of oxides of iron or other alloying elements; part of these debris were not adhered, and were removed during cleaning with ethanol (figure. 10d).

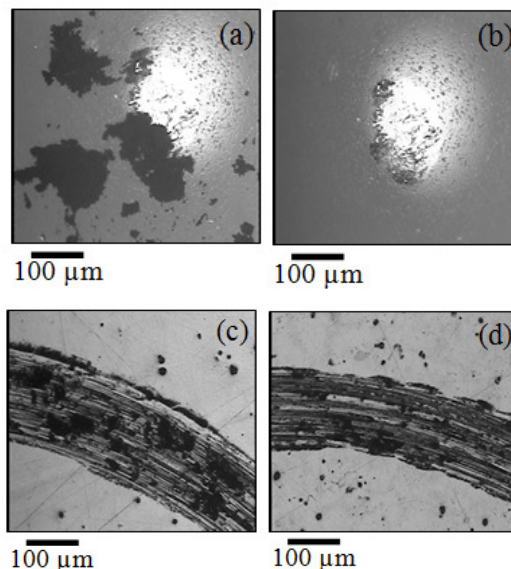


Figure 10. Images of the tribological contact surfaces obtained after of the test with the nitrided steel surface; a) ball aspect before of remove the debris, b) ball aspect after of remove the debris, c) wear track before of remove the debris and d) wear track after of remove the debris.

Figure 11 shows two micrographs of the wear track obtained in the dry sliding wear test of the duplex coating; the micrographs has been obtained after a test time of 1 hour. In the Figure 11a can be observed the presence of debris which was eliminated with ethanol. Figure 11b reveals that the coating has been worn in a very continuous and smooth mode corresponding to adhesive wear.

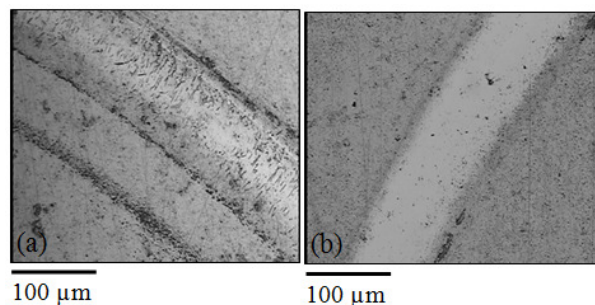


Figure 11. Wear track obtained in the ball-on-disc test. The surface treatment is duplex a) before of the cleaning with ethanol and b) after of the cleaning with ethanol.

4. CONCLUSIONS

Homogeneous and adherent duplex coatings with high hardness and high wear resistance were successfully deposited onto AISI H13 steel samples. The adhesion tests of the treated samples reveal the better cohesive and adhesive properties of the CrN coatings deposited onto the nitrided hot work steel. The high hardness and low friction coefficient of the duplex treated samples come along with the good results of the ball-on-disc test for this coating system. As compared with CrN monolayer, duplex coatings are a more promising and efficient surface treatment for hot work tools applications. The use of these duplex coatings could lead to an increase of the life time of hot work steel and to a reduction of maintenance and production costs of different industrial processes, as aluminum extrusion or milling of nonferrous materials.

Future Highlights

- Aluminum will be incorporated into the cubic matrix of CrN and its influence on the chemical composition and mechanical properties of the duplex coatings will be investigated.
- The influence of duplex CrN and AlCrN coatings on the life time of selected extrusion dies will be determined under production conditions.

5. ACKNOWLEDGMENTS

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6. REFERENCES

- [1]. Kugler G, Turk R, Vecko- Pirtovsek T, Tercelj M. *Metallurgy*. 2006; 45 (1): 21-29.
- [2]. Björk T, Westergård R, Hogmark S. *Wear*. 2001; 249: 316-23.
- [3]. Schacherl R.E. Growth kinetics and microstructure of gaseous nitrided iron chromium alloys, Dissertation Ph.D. Stuttgart (Alemania): Stuttgart University, 2004.
- [4]. Polok-Rubiniack M, Dobrzański L.A, Adamiak M. "Comparison of PVD coatings". *Archives of Materials Science and Engineering*. 2009; 38 (2): 118-125.
- [5]. Yang S, Cooke K.E, Li X, McIntosh F, Teer D.G. *J. Phys. D: Appl. Phys.* 2009; 42: 1-8.
- [6]. Zlatanovic M. "Combined plasma surface treatments for wear and corrosion protection". En *Proceedings de la 8th International Tribology Conference*. Belgrade (Serbia): 2003, p. 25-30.
- [7]. Dybowski K, Kaczmarek L, Pietrasik R, Smolik J, Kołodziejczyk L, Batory D, Gzik M, Stegliński M. *Journal of Achievements in Materials and Manufacturing Engineering*. 2009; 37 (2): 422-27.
- [8]. Ma S, Li Y, Xu K. *Surf. Coat. Technol.* 2001; 137: 116-121.
- [9]. Bejarano G, Caicedo J.C, Saldaña J.M. *Revista Facultad de Ingeniería*. 2008; (44): 36-42.
- [10]. Verein Deutscher Ingenieure Normen, VDI 3198, VDI- Verlag, Düsseldorf 1991.
- [11]. Daniel R, Martinschitz K.J, Keckes J, Mitterer C. *J. Phys. D: Appl. Phys.* 2009; 42: 1-13.
- [12]. Mayrhofer P.H, Tischler G, Mitterer C. *Surf. Coat. Technol.* 2001; 142-144: 78-84.
- [13]. Polok-Rubiniack M, Dobrzański L.A, Adamiak M. *Jornal of Achievements in Materials and Manufacturing Engineering*. 2008; 30 (2): 165-171.
- [14]. Shengli Ma, Yanhuai Li, Kewei Xu. *Surf. Coat. Technol.* 2001; 137: 116-121.
- [15]. Hoy R, Kamminga J.-D, Janssen G.C.A. *Surf. Coat. Technol.* 2006; 200: 3856-3860.