Multilayer coatings based on CrN/Cr for molds of plastics

F. Cova Caiazzo, V. Sisti, S. Trasatti

Many problems related to the efficiency of tribological steel substrates have been improved by the introduction of ceramic coatings based on nitrides of transition metals, as applied by physical vapor deposition (PVD) [1]. Multilayer PVD coatings are currently being developed so as to achieve a further increase in performance from both tribological and corrosion resistance. The principle of the method is to create a coating characterized by a high number of layers stacked in such a way as to block the growth of the columnar structure with high porosity. In this work a series of mono-and multilayer coatings were taken into account. These consist of CrN and Cr multilayers coatings made in a deposition chamber using cathodic arc PVD at the company CRT. As steel substrate AISI H11was chosen in the following surface state conditions: mirror finish, electroeroded, ground and sandblasted

Keywords: Steel - Corrosion - Coatings - Materials characterization - Electron Scanning Microscopy

INTRODUCTION

Cathodic arc physical vapor deposition allows to get coatings having a very good adhesion and with very high deposition rate. The metal ions deposed are generated by an arc discharge triggered between and anode and cathode on witch there is the metal target to be deposited. The discharge current is between 50 and 100 A/h and is concentrated on a very small area (1-10 µm) on the target surface. This supports currents of 10^6 – 10^8 A/cm^2 which raise the local temperature up to 7000K causing a fast target ionization. Cations obtained migrate towards the substrates located on rotating stand kept at a negative tension. If the target is the production of metallic layer, Ar is required. In case of nitride-based coatings, the nitrogen introduction grants the formation of metal nitrides. The coatings applied are made of nitrides of transition metals such as TiN, ZrN and CrN witch confer protection against wear and corrosion by making a chemically and thermically stable film. The coatings obtained through the cathodic arc PVD technique are characterized by defects due to the columnar growth of the nitrides layers witch cause micropores and pinholes. Another defect is the inclusion in the growing coating of small droplets of liquid metal originated from the cathodic spot [2]. The presence of these defects is responsible for both mechanical breakings and the exposure of the substrate to the environment, thus decreasing the mechanical resistance and the corrosion of the coated tool [3]. To improve the qualities of these coatings the most efficient strategy has been the production of a multilayer architecture coatings in which nitride layers are alternated with nitride metal layers [4]. The target of this method is to create a series of homogeneous interfaces but distinct between two different layer of the multilayers system to avoid the formation of pinholes and cutting off the pores [5,6]. For multilayer Cr/CrN based coatings usually Cr layer is kept as top-layer because it can make a thick Cr_2O_3 layer working as passivating layer [5].

Fabio Cova Caiazzo, Stefano Trasatti

Università degli Studi di Milano, Dipartimento di Chimica, Via C.Golgi 19, 20133 Milano

Valentina Sisti

C.R.T., T.T.N. group S.p.A. Nerviano, Via Primo Maggio 30 , Nerviano (Mi)

MATERIALS

The bare samples are AISI H11 steel 30x30x80mm parallelepipeds (C 0.40%, Cr 5.00%, Mo 1.30%, V 0.40%). The four surfaces of each sample have undergone four different surface treatments to simulate the main required finish in molding industries: mirror, ground, electroeroded and sandblasted. In the deposition chamber we also put simples of AISI D2 (C 1.55%, Cr 11.5%, Mo 0.70%, V 1.00%, Mn 0.30%, Si 0.30) mirror finish disk-shaped Ø30x4mm to be employed for adhesion, thickness and composition characterization because the parallelepiped-shaped samples were too big for the equipment holder.

DEPOSITION PROCESS

Before the deposition, the samples have been degreased via ultrasounds cleaning. Sandblasted, electroeroded and

ground faces have been also cleaned through a glass microspheres sandblast. The coatings have been deposited by an industrial cathodic arc system Sulzer Metaplas MZ333/028 equipped with 8 cathodes. The 99.99% pure Cr targets are on the cathodes which works at 60 A/h each. Ones inserted in the deposition chamber, on planetary stand, the samples have undergone a further cleaning by ionic etching carried out with AEGD system (arc-enhanced glow discharge). Before the deposition samples were pre-warmed up to 500 °C in high vacuum. The deposition takes place at a pressure between $5x10^{-3}$ an $3x10^{-2}$ mbar. Nitrogen is the reactive gas used for the formation of CrN, the temperature of deposition is kept at 500 °C. To get the multilayer structure the flow of nitrogen is stopped at regular intervals to obtain deposition of Cr layers. The variation in the thickness has been controlled by varying the amount of A/h provided at the cathode. After the deposition the samples have been brushed to eliminate less adherent droplets. The coatings produced are:

- Monolayer, a single layer of CrN
- Multilayer 4, four double* layer of CrN-Cr with Cr toplayer
- Multilayer 8, eight double* layer of CrN-Cr with Cr toplayer

**Double layer is meant as coupling of a nitride layer and a metallic one.*

CHARACTERIZATION METHODS

Metallographic analysis

Microstructure of the steel have been verified by metallographic analysis. The samples have been obtained from the section of the different faces at different finish. To prepare the samples the section have been polished by abrasive paper and diamond paste up to 0.25 micron. The metallographic etching is Nital 2%.

Adhesion tests

Adhesion has been assessed through Rockwell indentation test/Mercedes test. The test procedure is based comparing the edges of an indentation Rockwell charging 150Kg, to the reference document proposed by Mercedes in which adhesion is estimated in 6 degrees.

Thickness measurement

The thickness is obtained through a Calo Test/ Ball Crate Test. Digging a spherical print in the coating, one or more (in case of multilayer coatings) circular sectors are visible. Their diameters allow us to calculate the thickness with an error less than 0.1 μm. The following equation can be used:

$$Thickness = \sqrt{\left[(10000)^2 - \left(\frac{\emptyset <}{2}\right)^2\right]} - \sqrt{(10000)^2 - \left(\frac{\emptyset >}{2}\right)^2}$$

Roughness analysis

The roughness assessment has been carried out through a surface optical measurement station Sensortech model Microfocus.

Spectrometric analysis GDOES (Gloss Discharge Optical Emission Spectroscopy)

The assessment of the structure and stoichiometry of the coating layers has been carried out by a GDOES spectrometric analysis employing a quantometer LECO SDP-750.

Electron Scanning Microscopy examination (SEM)

The morphology of the corrosive attack has been investigated through Electron Scanning Microscopy. The instrument employed is a scanning Microscope model LEO ZEISS 1430.

Potentiodynamic polarizations in NaCl 0.001M

The concentration has been chosen on the result of a previous experimentation. To record the polarization curves we have employed a potentiostat EG&G Model 73 working according to the following operating parameters: sample area 1.00 cm^2, scan rate 0.166 mV/s, Initial potential $1x10^{-3}$ v vs. OCP, Initial delay 600 s, SCE as reference electrode, Pt wire as Counter.

RESULTS AND DISCUSSIONS

Metallographic analysis

The metallographic analysis confirms the martensitic structure of AISI H11 steel. In picture 1 we can notice how the mirror and ground finish shows sections which are particularly clean and without defects. As far the electroeroded finish we can notice the white layer. The development of this layer is caused by the re-solidification of the material melted during the application of the electroerosion discharge, this consists mainly in iron carbides in acicular or globular shape distributed in an austenitic matrix. The increase of the carbon content in the layer of re-solidification is due to the solubilization in the austenitic cell of the carbon from the pyrolysis of the dielectric fluid [7]. Because of the superficial stresses induced by the electroerosion process, the white layer shows a series of cracks, micropores and a lack of homogeneity. The white layer does not look uniform and evenly thick and in some cases is totally absent. Finally the sandblasted finish shows a section particularly rich in defects and cracks and sharp crests which make the superficial area very irregular and easily vulnerable to attack.

Adhesion tests

From assessing the adhesion of coatings on AISI D2 samples we can notice an increase in the number of cracks at the indentation edges shifting from the monolayer coating to the multilayer 4 and then multilayer 8. Anyway all the adhesion levels can be compared to the degree 1 of the Mercedes reference document. The increase in the number of cracks is a symptom of the ordinary rise in the coating

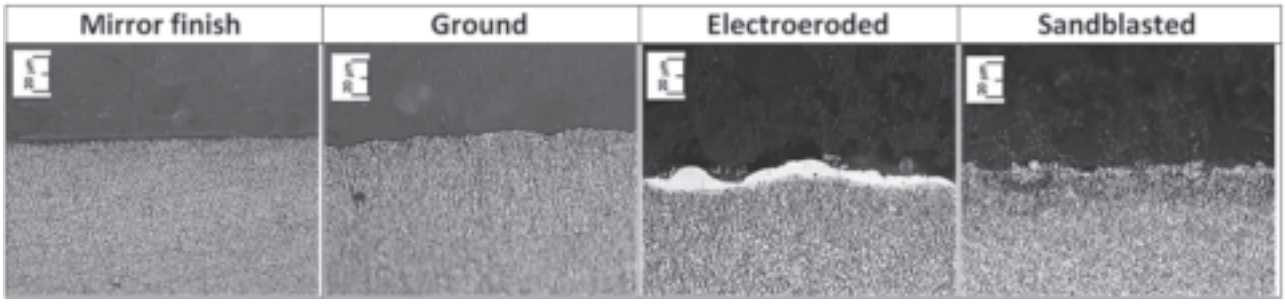


Fig. 1 - Metallographic sections cut from the different surfaces

Fig. 1 - Sezioni metallografiche ottenute in corrispondenza delle diverse superfici.

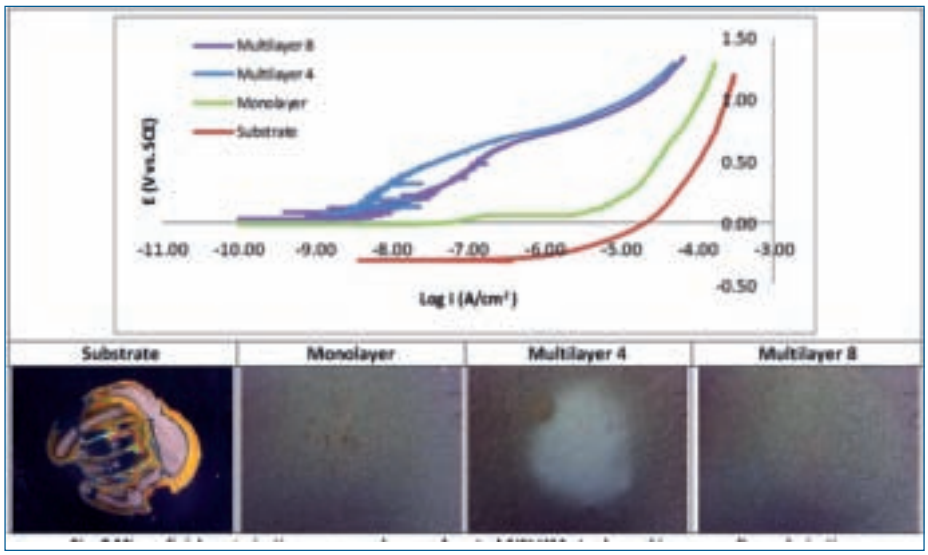


Fig. 2 - Mirror finish: polarization curves on bare and coated AISI H11 steel, working areas after polarization.

Fig. 2 - Finitura a specchio: curve di polarizzazione su AISI H11 tal quale e rivestito, aree di lavoro dopo polarizzazione.

	Substrate	Monolayer	Multilayer 4	Multilayer 8
Mirror finish	0.033 µm	0.062 µm	0.065 µm	0.125 µm
Ground	1.189 µm	0.672 µm	0.829 µm	0.566 µm
Electroeroded	2.499 µm	2.507 µm	2.383 µm	2.389 µm
Sandblasted	0.802 µm	0.809 µm	0.966 µm	1.344 µm

Table 1 - Average roughness values (Ra)

Table 1 - Valori di rugosità media (Ra).

tension when the total thickness of the film goes up.

Thickness measurement

From the measurement of the internal and external diameters of the prints, obtained by Ball Crater, on the coatings applied to AISI D2 samples, the following thickness values are resulted: 1.74 µm monolayer, 3.10 µm multilayer 4, 7.20 µm multilayer 8.

Roughness analysis

As is possible to notice in table 1, as a consequence of a coating growth not perfectly even, the mirror finish shows a large increase of roughness related to the rise of the coating thickness as to the substrate. The sandblasted finish has the same behavior as the mirror finish. The rectified finish, differently , shows a decrease of Ra when the coating thickness grows. This is due to the leveling effect of the coating against the rectifying tracks. The electroeroded finish does not shows a significant roughness change.

Spectrometric analysis GDOES

The GDOES analysis carried out on AISI D2 samples has allowed to identify and quantify, for each coating, the number of layers under the change of the composition based on the depth of the nitrogen and chromium atomic percentage.

Potentiodynamic polarizations in NaCl 0.001 M

From the polarization curves as in figure 2 recorded on the mirror finish surface we can notice an active dissolution of the substrate. The same active behavior is kept after the introduction of the monolayer coating, even if the applied potential being equal, the curve is moved towards lower currents. The corrosion behavior improves greatly when using multilayer 4 and 8 coatings. In this cases a barrier effect is created against the external environment, which slows down the kinetics of the corrosive process putting it under diffusion control. The images of the working areas show the uniform attack of the substrate, the lo-

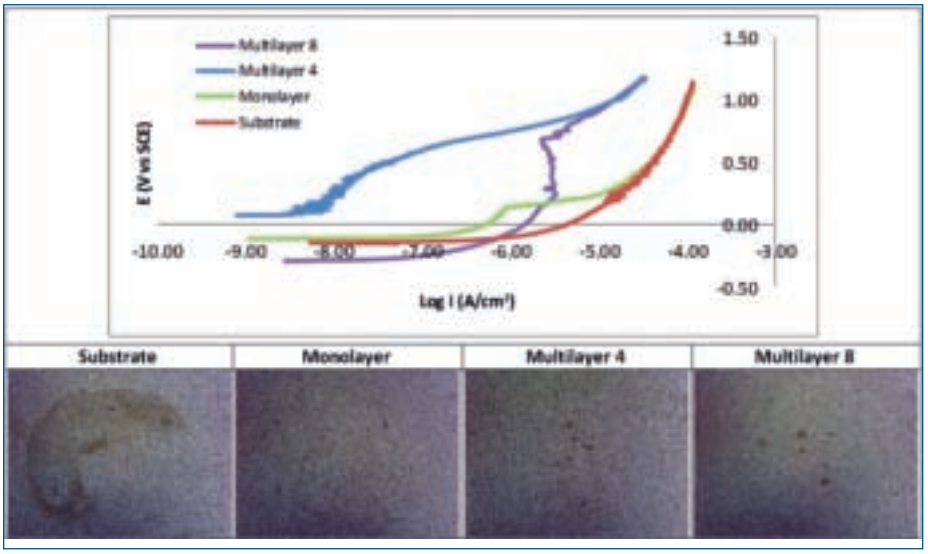


Fig. 3 - Electroeroded finish: polarization curves on bare and coated AISI H11 steel, working areas after polarization.

Fig. 3 - Finitura elettroerosa: curve di polarizzazione su AISI H11 tal quale e rivestito, aree di lavoro dopo polarizzazione.

calized attack of the monolayer coating and the slight loss of brightness of the multilayer 4 and 8 coatings. On the ground finish surface only the multilayer 8 coating manages to protect from corrosion. The monolayer and multilayer 4 coatings, because of the low thickness, have not been able to fit the basic finish and therefore they have not succeeded in providing any protection.

About the electroeroded finish, in figure 3, we can notice the corrosion behavior in the form of active dissolution of the substrate and of the monolayer coating. The corrosion behavior improves greatly when using multilayer 4. As for this coating, thanks to a barrier effect, we can see the movement of the curves towards lower currents, the applied potential being equal. The multilayer 8 coating shows a passive behavior, characteristic of the superficial chromium layer. The disappearance of the barrier effect when using multilayer 8 coating can be explained as follows: the increase of the thickness causes a greater brittleness because of the rise of the tensions inside the coating plus the tensions accumulated by the steel during the electroerosion process. The images of the working areas show the widespread attack of the substrate, the localized attack of the monolayer, multilayer 4 and 8 coatings.

The corrosion behavior of the coatings applied on a sandblasted finish does not improve in a significant way even when a multilayer 8 coating is used. However, as for this coating we notice a shift of the curves at lower currents by keeping an active behavior.

SEM analysis

As is possible to notice in picture 4 the coatings applied on mirror finish show a homogeneous surface and defect less with the exception for the presence of droplets. From the working areas of the monolayer we can notice that the corrosive attack and the breakdown of the coating take place next to the droplets. The working areas of the multilayer 4 and 8 are practically intact, but there is an increase of porosity in the areas next to the droplets.

As far the ground finish substrate we can see a corrosive attack following the grinding crests and it spreads as generalized corrosion. As for the coatings applied on this finish we can notice that the droplets are located on the grinding crests. The same corrosion behavior of the substrate is observed for the monolayer and the multilayer 4. The multilayer 8 shows a localized corrosive attack which does not depend on the morphology of the ground lines. By observing the coated samples of the electroeroded finish surfaces, the concentration of droplets is greatest in the areas between crests and depressions while it is lowest on the crest tops. The working area of the substrate shows a localized corrosive attack in the areas between crests and depressions where the white layer is lower, as seen after the metallographic analysis. As far the monolayer and multilayer 4, the corrosive attack and the resulting coating breakdown are located in the same critical areas of the substrate. The multilayer 8 shows a surface characterized by the presence of cracks.

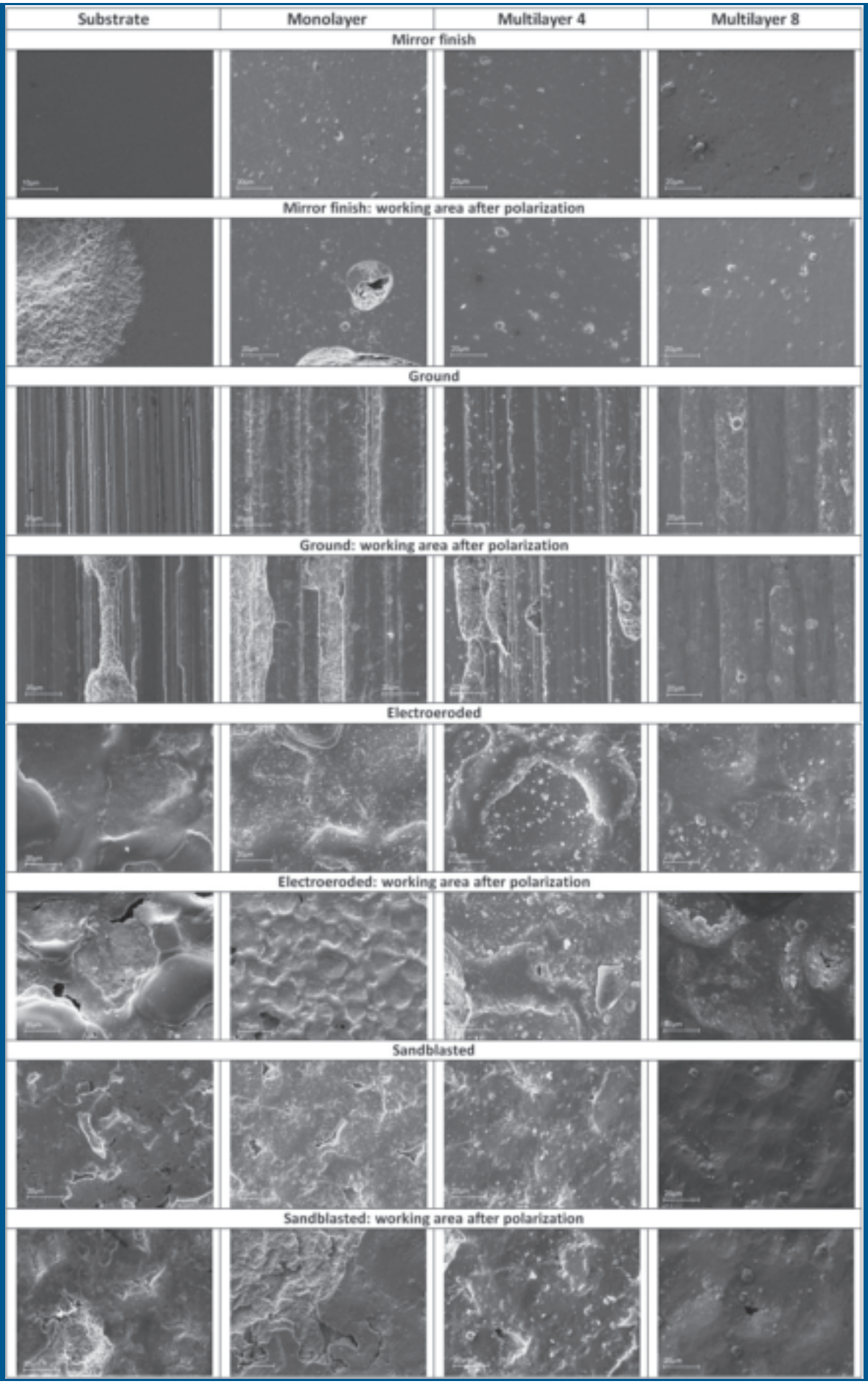
The surface of sandblasted finish substrate shows a great number of sharp holes and crests which cannot be covered by monolayer and multilayer 4. The substrate working area shows the localized corrosive attack which tends to widespread. This takes place next to the holes of the surface. As for monolayer and multilayer 4 the corrosive attack and the resulting coating breakdown are localized in the same critical areas already observed in the substrate. The multilayer 8 shows a localized corrosive attack at less density compared to the previous coatings applied on this finish.

CONCLUSIONS

According to the results, we can state that the improvement of the anticorrosive properties of a coating through the introduction of a multilayer structure with an increasing thickness is a valid approach even if not always suc-

Fig. 4 - SEM images of the sample surfaces at different finish and coatings before and after polarization.

Fig. 4 - Immagini SEM delle superfici dei campioni a diversa finitura e diverso rivestimento prima e dopo polarizzazione.


Substrate
Monolayer
Multilayer 4
Multilayer 8
Mirror finish
Mirror finish: working area after polarization
Ground
Ground: working area after polarization
Electroeroded
Electroeroded: working area after polarization
Sandblasted
Sandblasted: working area after polarization

cessful. This happens because it is not possible to think about coating and substrate as two separated items, but we need to consider the whole system substrate-coating. By changing the substrate finish followed a different corrosive behavior of the sample:

- As for the mirror finish, without defects, the barrier effect is already present for multilayer 4 coating and it may be compared to the performances provided by multilayer 8 which is thicker and with a higher numbers of layers.
- As for ground and sandblasted finish, due to the hard finish, only multilayer 8 coating can make the surface uniform and protect the substrate against corrosion.
- Electroerosion leads to tensions on the material surface and to changes in the composition of the alloy elements of the superficial layers of the steel. So the increase in the coating thickness is not linked to the improvement of protection against corrosion. We need to find a compromise by applying a coating as multilayer 4 characterized by less tension than the thicker multilayer 8.

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Rivestimenti multistrato a base di CrN/Cr per stampi di materie plastiche

Parole chiave: Acciaio - Corrosione - Rivestimenti - Caratterizz. materiali - Microscopia elettronica

Molti problemi legati all'efficienza tribologica e al comportamento a corrosione di substrati in acciaio sono stati migliorati grazie all'introduzione di coatings ceramici a base di nitruri di metalli di transizione(TiN, CrN, ZrN, TiCN, AlTiN), applicati tramite deposizione fisica di vapori (PVD, Physical Vapor Deposition) [1]. Attualmente, dal punto di vista industriale si stanno sviluppando coating PVD multistrato in modo tale da giungere ad un ulteriore aumento delle performance sia in campo tribologico che di resistenza a corrosione. Il principio del metodo sta nel creare un'architettura del coating caratterizzata da strati impilati in modo tale da bloccare sia la crescita della struttura colonnare ad elevata porosità che la formazioni di difetti come pori e punte di spillo. La presenza di tali difetti causa un esposizione del substrato e costituisce il punto di innesco di failure [2, 3]. Per questo lavoro sono stati presi in considerazione una serie di rivestimenti mono e multistrato costituiti da CrN e Cr realizzati in una camera di deposizione PVD tramite arco catodico presso la società CRT. Come acciaio substrato è stato scelto l'AISI H11 a finitura a specchio, elettroerosa, sabbiata e rettificata. I rivestimenti realizzati sono stati caratterizzati dal punto di vista morfologico, chimico ed elettrochimico.