

## **Nanocomposite nitride thin films for hard coatings: Application to wear and corrosion resistance**

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### **Abstract**

New simple and duplex coatings were elaborated by triode sputtering and ionic nitriding, imposed to low alloy steel and characterized by the mean of various experimental techniques (EDS, XPS, XRD, SEM, TEM, FTIR, ...). Their ability to protect substrate against corrosion and wear has been evaluated.

These deposits are either CrN or ZrN monolayer, or nanocomposite deposits formed by the dispersion of BN into ZrN matrix.

The experiments show the good physical, chemical and mechanical properties of the films. The tribological analysis permitted us to define the optimal conditions of triode sputtering and the ionic nitriding ones used in the duplex treatments. A great amelioration in the tribological properties was observed and was explained by the good stress repartition into the layers.

Simples and duplex treatments were imposed to low alloy steel cutting tools. Their application in peeling of wood and corrosion shows their efficiency.

**Keywords:** triode sputtering, nitriding, duplex, nanocomposite, microstructure, tribology, peeling, corrosion.

### **1. Introduction**

The nitride coatings deposited by Physical Vapour Deposition (PVD) techniques have some excellent properties, such as high hardness, good wear resistance, chemical stability, corrosion resistance and attractive colours, and therefore, are widely used in industry [1-5]. These coatings are mainly based on the nitrides and carbides of the transition metal elements. Recently, increasing interest is laid on the corresponding borides [5]. However, even if the coatings allowed increasing the service life of tools, their adhesion is not sufficient [6]. This could be a limit to their employment. Nevertheless, the solution to increase the adhesion of the films was to realise a previous nitriding treatment before the deposition [6]. That means to make a duplex treatment.

Nitriding is a thermochemical process that is typically used to diffuse nitrogen into ferrous materials. This treatment can improve the surface hardness, fatigue strength, wear and corrosion resistance [6-9]. Plasma nitriding owing to a number of advantages such as a lower process temperature, a shorter treatment time, minimal distortions and low energy use compared to conventional techniques has found increasing applications in industry [6, 7].

However the formation of porous compound layers affect the wear and corrosion resistance. Relatively little works have been done concerning the combination of nitriding and PVD coatings to remove these disadvantages.

The aim of the present study is to investigate the corrosion resistance of 32CDV13 low alloyed steel duplex treated by using ion nitriding and PVD triode process. The effect of the different parameters of nitriding and coating is evaluated.

### **2. Experimental**

A series of experiments have been carried out to investigate the plasma nitriding and triode PVD sputtering responses of 32CDV13 low alloyed steel. The chemical composition of 32CDV13 is: 0.3% C; 0.31% Si; 0.5% Mn; 3.25% Cr; 0.44% Mo; 0.11% Ni; 0.1% V. This steel commonly used for nitriding, presents a good toughness and provides the ability of hardness gradient from the treated surface layer down to the bulk.

The substrate surface was prepared and polished with 1  $\mu\text{m}$  diamond paste. Specimens were nitrided in a vacuum furnace pumped down to low pressure ( $10^{-3}$  mbar) to minimise the oxygen contamination. The temperature of samples is followed thanks to a thermocouple very closed to them. The nitriding parameters were fixed referred to previous works [6, 10]. The morphology of samples surfaces, nitrided layers and thin films were observed by Jeol 5900 Scanning Electron Microscope (SEM). X-ray diffraction analyses with Co  $K_{\alpha}$  radiations were performed to determine their structure.

The ZrBN films were deposited by reactive triode sputtering. The deposition parameters are defined in a previous works [10, 11].

The corrosion tests were carried out in a neutral aqueous NaCl ( $30 \text{ g L}^{-1}$ ) solution, naturally aerated. The test device was composed of an EGG 273 potentiostat and a 1 L cell containing electrolyte, into which three electrodes were plunged: the calomel reference electrode saturated in KCl (SCE), the graphite counter electrode and the specimen as the working electrode. Stirring was carried out at  $250 \text{ rev. min}^{-1}$  using rotating electrode. In order to determine the corrosion behaviour of a specimen immersed in electrolyte, the curves  $i(E)$  are plotted from -100 mV versus the corrosion potential up to 400 mV in the anodic side, using a sweep rate of  $10 \text{ mV min}^{-1}$ .

Prior to electrochemical tests, the specimens were ultrasonically cleaned in acetone. The potentiodynamic polarization tests were performed on all specimens: plasma nitrided, ZrBN coated and duplex treated ones. An untreated sample was also used as reference.

### 3. Results and discussion

Figure 1 presents cross sections of 32CDV13 steel plasma nitrided at  $500^{\circ}\text{C}$  in  $80\%\text{N}_2+20\%\text{H}_2$  gas mixture during 8 hours. The top of the sample corresponds to the nitrided layer, indicating a thickness of about  $5 \mu\text{m}$  (Fig. 1.b). It appears to be bright under optical microscope (Fig. 1.a). EDS microanalysis showed that the nitrided layer contains a high amount of nitrogen in the surface and the nitrogen concentration is gradually reducing with increasing distance from surface until the substrate value at a depth of about  $100\text{-}150 \mu\text{m}$ . The compound layer formed on the surface does not contain micropores which is good for corrosion resistance.

The morphology of selected coatings deposited on low alloyed steel is shown in the SEM photograph (Fig. 2). It appears that Zr-B-N coatings exhibit a very dense structure, without columns or grains. Mitterer and al. [12] obtained similar results using non reactive and reactive d.c. magnetron sputter deposition.

The XRD analysis shows that the compound layer of the plasma nitrided specimens consists in  $\epsilon\text{-Fe}_{2.3}\text{N}$  and  $\gamma'\text{-Fe}_4\text{N}$  phases (Fig. 3.a). The ZrBN films were also examined by glancing angle X-Ray diffractometry and the results for a  $2\theta$  range between  $20^{\circ}$  and  $100^{\circ}$  are shown in Fig. 3.b. Owing to the fact that boron nitride may be not crystallised and is almost transparent to X rays at thicknesses down to  $1 \mu\text{m}$ , the spectrum is expected to reflect only ZrN reflection peaks as reported by Gibson et al. [13] for the Ti-B-N system.

Indeed, a major peak at an angle  $2\theta \approx 34^{\circ}$  characteristic of ZrN (111) reflections appears, which can be attributed to  $\text{ZrN}_{1-x}\text{B}_x$  compounds. In addition, minor signals from ZrN, corresponding to (220) and (311) orientations, are also detected.

Figure 4 shows the surface morphology of the specimens after corrosion tests in NaCl  $30 \text{ g.L}^{-1}$  solution. The pictures (Fig. 4) clearly delineate the increase of corrosion resistance from ZrBN coated sample (Fig. 4.a) to the plasma nitrided sample (Fig. 4.b) and to the duplex treated one (Fig. 4.c).

ZrBN coated steel samples reveal defects, which appear as craters or droplets. M. Ürgen et al. [14] have also observed that the Zr-B-N layers on steel substrate exhibited various types of defect which decreased the protective properties of the coating. A recent study conducted on arc PVD TiN and CrN coatings showed that the droplets were identified as important defect sites [5].

Potentiodynamic curves for nitrided steel surfaces and duplex treated ones, recorded after immersion in the corrosive solution, are shown in Fig. 5. The plasma nitriding considerably changed the polarisation properties of 32CDV13 steel as can be seen in Fig. 5.a. Firstly, the corrosion potential  $E_{corr}$  was shifted to higher values, e.g. from -610 mV/SCE for the untreated sample to -350 for 80%N<sub>2</sub>+20%H<sub>2</sub> plasma nitrided sample. Moreover, the latter part denotes from a passive interesting behaviour, on more than 200 mV. Secondly the current densities were reduced e.g.  $I_{corr}$  was decreased from 8  $\mu\text{A}/\text{cm}^2$  for the untreated sample to 0.7  $\mu\text{A}/\text{cm}^2$  for 80/20 nitrided one. These results are in good accordance with those of A. Alsaran et al. [9] who had studied the corrosion behaviour of plasma nitrided AISI 5140 steel and found that the dense compound layer formed after plasma nitriding can significantly improve the corrosion characteristics. In the same way, enhanced protection properties were also reported by Steyer et al. for gas nitrided steels [15]. Nevertheless, some authors [2] found that when plasma nitriding is carried out at high temperature, e.g. 500 °C, chromium nitrides may form in the nitrided layer so that the bulk of the nitrided case had very poor corrosion resistance. In our case, this phenomena was not observed, probably owing to the steel composition.

ZrBN coated samples indicates the same potentials value as substrate one (Fig. 5.b), which confirm the fact that it does not cover totally steel part (Fig. 4.a). Nevertheless, despite of an unfavourable anodic/cathodic (steel/coating) areas ratio, ZrBN coating affords a beneficial effect on corrosion protection, by decreasing, of more than one decade, the corrosion rate of steel. This result is in accordance with [14, 16-17].

The duplex treated samples showed far better electrochemical corrosion behaviour when compared with the plasma nitrided or the ZrBN coated ones by decreasing the active corrosion rate and the current density. The specimens duplex treated shows higher corrosion potential (-338 mV) than the plasma nitrided specimen. A lower anodic currents ( $\sim 0.13 \mu\text{A}/\text{cm}^2$ ) are also observed. The nobler electrochemical behaviour of duplex treated specimens can be explained by a conjunction of the good properties of ZrBN films and the protection of the nitride layer which eliminates the drawbacks due to the droplets and the discontinuities of the ZrBN coating.

## Conclusion

The corrosion behaviour of plasma nitrided, ZrBN coated and duplex treated 32CDV13 low alloyed steel was studied using potentiodynamic techniques in NaCl solution. The results obtained can be summarized as follows:

- After plasma nitriding, the compound layer corresponds mainly to Fe<sub>2-3</sub>N and Fe<sub>4</sub>N iron nitrides, which present good corrosion properties. This layer is dense and contains little defects.
- ZrBN layers on steel exhibit various types of defect (droplets, physical discontinuities) which decrease the protective properties of the coating. Moreover, due to a galvanic effect, the small anodic area (steel exposed through open porosities) against the large cathodic one (ZrBN film) may provoke severe localized corrosion.
- The corrosion protection properties depend on the porosity of the protective layer. The conjunction of nitriding and deposition processes enables to overcome the drawbacks of the two techniques and mainly the porosity of the deposited films. Therefore, the duplex treated specimens (nitriding + ZrBN coating) present the better corrosion protection, with, in addition, passive ability.

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## Figure captions

Fig. 1: Cross sections of the 500 °C plasma nitrided low alloyed steel (80%N<sub>2</sub>+20%H<sub>2</sub> gas mixture; 8h) (a) optical micrograph; (b) SEM image.

Fig. 2: Microstructure of ZrBN Coating (f(N<sub>2</sub>)=12 sccm; substrate bias voltage = -100 V).

Fig. 3: XRD patterns of plasma nitrided layer (80%N<sub>2</sub>+20%H<sub>2</sub>; 8h; 500 °C) (a) and ZrBN coating layer (b).

Fig. 4: The surface morphology after potentiodynamic test in NaCl 30 g/L of ZrBN coated part (a), plasma nitrided (80%N<sub>2</sub>+20%H<sub>2</sub>; 8h; 500 °C) steel (b) and duplex treated steel (c).

Fig. 5: Potentiodynamic polarization curves in NaCl 30g/L for nitrided samples (a), ZrBN coated and duplex treated parts (b).

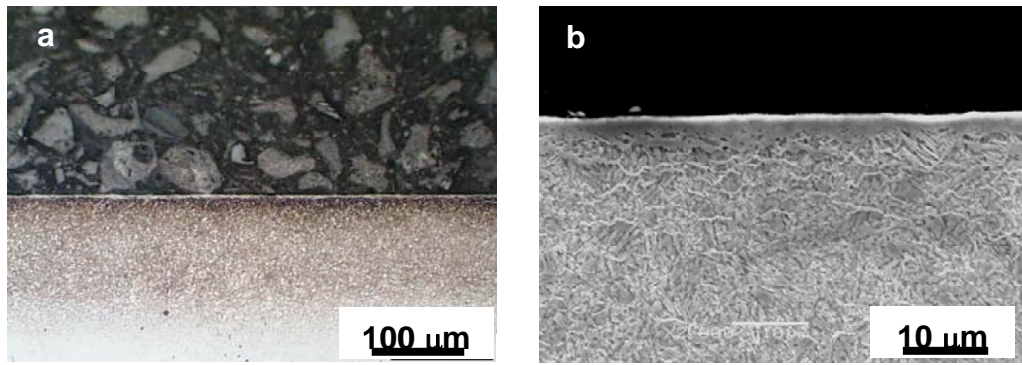


Figure 1

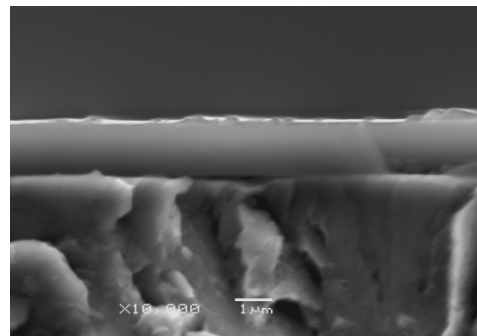


Figure 2

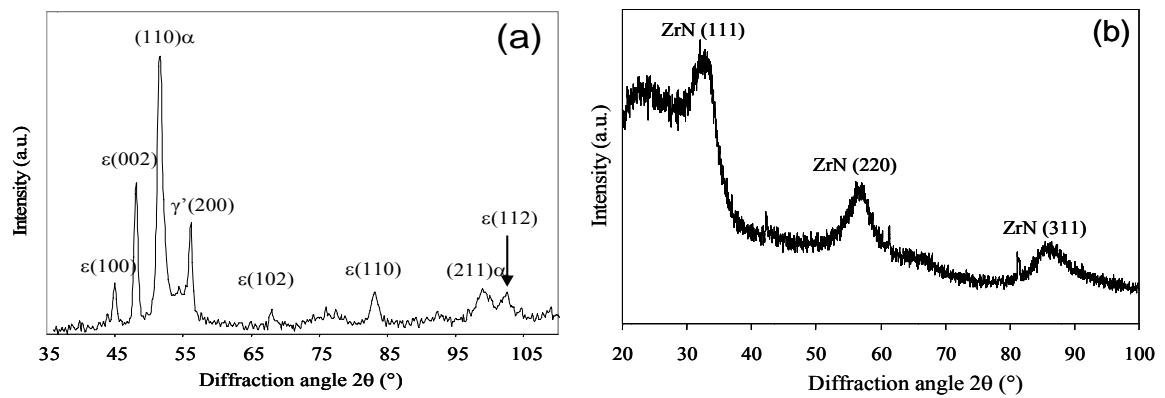


Figure 3

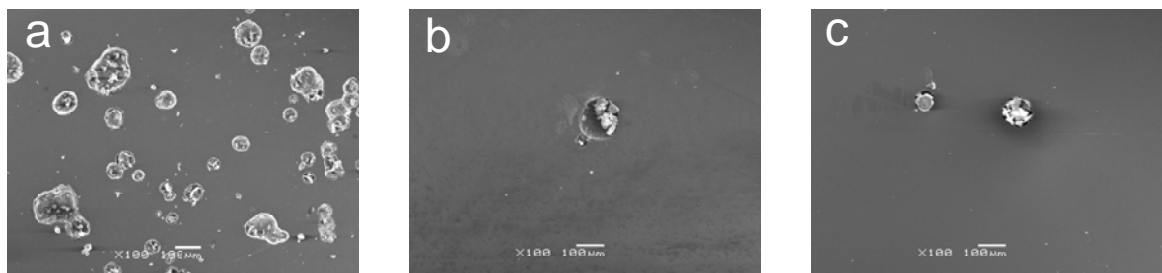


Figure 4

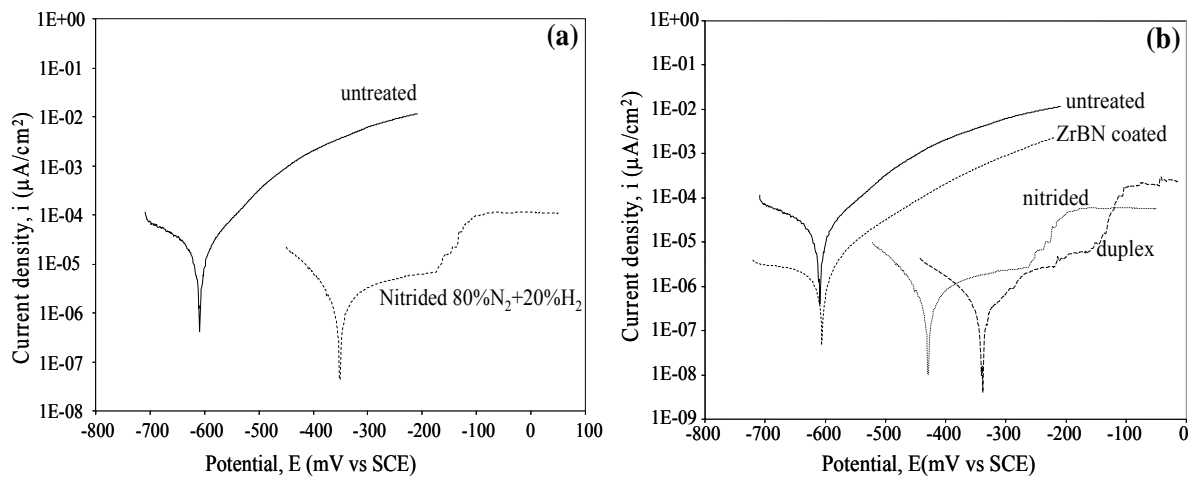


Figure 5