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Effect of duplex treatments by plasma nitriding and triode sputtering on corrosion behaviour of 32CDV13 low alloy steel

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Abstract

This paper presents corrosion behaviour of duplex treated low alloy steel. Different kinds of samples were tested: non-treated, plasma nitrided, ZrBN-triode sputtered and ZrBN-duplex treated samples. The corrosion behaviour was evaluated by electrochemical techniques (corrosion potential and polarisation resistance evolutions versus immersion time, potentiodynamic curves). The corrosion tests were carried out in neutral aqueous saline solution (NaCl 30 g L^{-1}), naturally aerated. The composition and the structure of layers were determined by EDS and XRD, respectively, while the morphology was observed by SEM.

Experimental results showed that the corrosion current density I_{corr} increased with decreasing white layer thickness in plasma nitrided specimens. The nitrides ε-$Fe_{2-3}N$ and γ′-Fe_4N present in the white layer are nobler than the substrate but may promote, by galvanic effect, a localised corrosion through open porosity. The duplex treated specimens (nitriding + ZrBN coating) present better corrosion protection and enable to overcome the drawbacks of both techniques, mainly the porosity of the deposited films.
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Keywords: Triode sputtering; Plasma nitriding; Duplex; 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 nitrides and carbides of transition metal elements. Recently, increasing interest is paid on the corresponding borides [5]. However, even if the coatings allowed to increase the service lifetime of tools, their adhesion was not sufficient [6]. This could be a limit to their application. Nevertheless, in order to increase the adhesion of the films a previous nitriding treatment could be performed before the deposition [6]. That would mean making a duplex treatment.

Nitriding is a thermochemical process that is typically used to diffuse nitrogen into ferrous materials. This treatment can improve 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 wide application in industry [6,7].

However, the formation of porous compound layer affects the wear and corrosion resistance. Relatively few works were conducted concerning the combination of nitriding and PVD coatings to eliminate these disadvantages.

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

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2. Experimental

A series of experiments were 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 good toughness.

The substrate surface was prepared and polished with 1 μm 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 the samples is measured with the use of a thermocouple. The nitriding parameters were fixed similar to previous works [6,10]. The morphology of the sample's surfaces, nitrided layers and thin films were observed by Jeol 5900 Scanning Electron Microscope (SEM). X-ray diffraction analyses with Co K_α radiations were performed to determine their structure.

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

Corrosion tests were carried out in a neutral aqueous NaCl (30 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. The stirring was carried out using a rotating electrode (250 rev min^{-1}). In order to determine the corrosion behaviour of a specimen immersed in electrolyte, the curves $i(E)$ were plotted from −100 mV versus the corrosion potential up to 400 mV in the anodic side, using a sweep rate of 10 mV min^{-1}.

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

3. Results and discussion

Fig. 1 presents cross sections of 32CDV13 steel plasma nitrided at 500 °C in 80% N_2+20% H_2 gas mixture for 8 h. The top of the sample corresponded to the nitrided layer, indicating a thickness of about 5 μm (Fig. 1b). It appeared to be bright under optical microscope (Fig. 1a). EDS microanalysis showed that the nitrided layer contained a high amount of nitrogen on the surface and the nitrogen concentration decreased along with the increase of the distance from surface until the substrate value at a depth of about 100–150 μm. The compound layer formed on the surface does not contain micropores which is good for corrosion resistance.

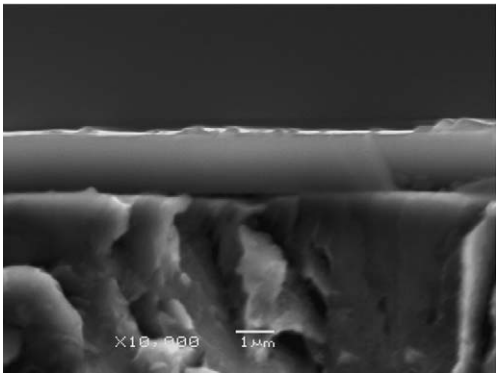

Fig. 2. Microstructure of ZrBN Coating ($f(N_2)$=12 sccm; substrate bias voltage=−100 V).

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

The XRD analysis showed that the compound layer of the plasma nitrided specimens consists in ε-$Fe_{2-3}N$ and γ′-Fe_4N phases (Fig. 3a). The ZrBN films were also examined by glancing angle X-ray diffractometry and the results for a 2 θ range between 20° and 100° are shown in Fig. 3b. Owing to the fact that boron nitride may not be crystallised and is almost transparent to X-rays at thicknesses down to 1 μm, 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 $\theta \approx 34°$ characteristic of ZrN (111) reflections appears, which can be attributed to $ZrN_{1-x}B_x$ compounds. In addition, minor signals from ZrN, corresponding to (220) and (311) orientations, were also detected.

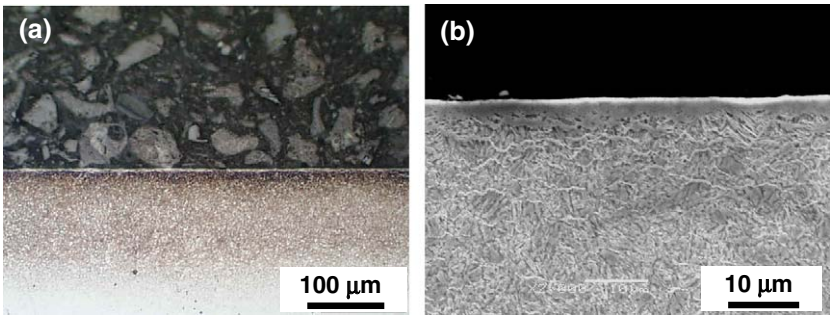

Fig. 1. Cross sections of 500 °C plasma nitrided low alloyed steel (80% N_2+20% H_2 gas mixture; 8 h) (a) optical micrograph; (b) SEM image.

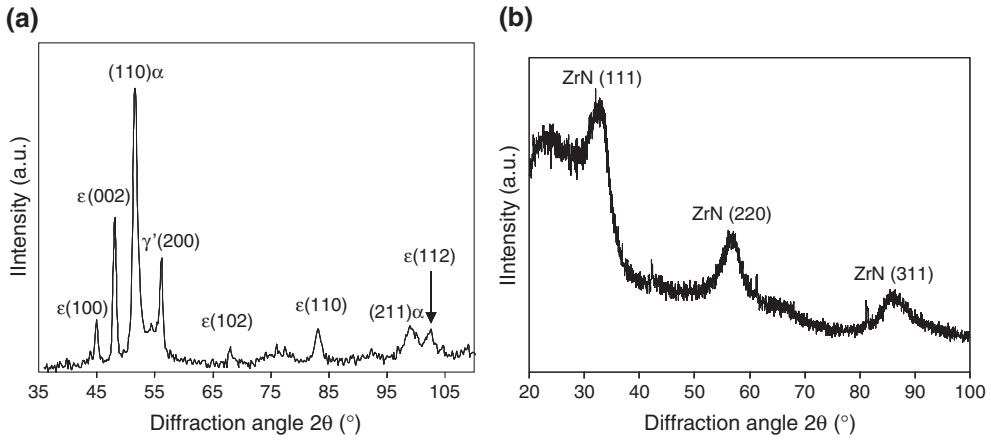

Fig. 3. XRD patterns of plasma nitrided layer (80% N_2+20% H_2; 8 h; 500 °C) (a) and ZrBN coating layer (b).

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

ZrBN coated steel samples reveal defects, which appear as craters or droplets. Ürgen et al. [14] also observed that the Zr–B–N layers on steel substrate exhibited various types of defects 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 untreated, nitrided steel surfaces, ZrBN coated and duplex treated samples, recorded after immersion in the corrosive solution, are shown in Fig. 5 (a and b). The plasma nitriding considerably changed the polarisation properties of 32CDV13 steel as can be seen in Fig. 5a. 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_2+20% H_2 plasma nitrided sample. Secondly, the current densities were reduced, e.g. I_{corr} was decreased from 8 μA/cm^2 for the untreated sample to 0.7 μA/cm^2 for 80/20 nitrided one. These results are in good accordance with those of Alsaran et al. [9] who 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. Similarly, enhanced protection properties were also reported by Steyer et al. for gas nitrided steels [15]. Nevertheless, the reduction of corrosion resistance due to chromium nitride precipitation can be only observed for high chromium steel (above 12 wt.% of chromium) [2] and in the present study, the used steel has chromium content lower than 12 wt. %. In the case of ZrBN coated samples (Fig. 5b) they indicated nearly the same values of the potentials as substrate one, which may be due to the fact that the coating does not totally cover steel part. Nevertheless, despite 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 anodic current. This result is in accordance with Refs. [14,16,17]. Concerning the duplex treated samples (Fig. 5b), they showed better electrochemical corrosion behaviour when compared with the ZrBN coated samples, and even the nitrided ones, by decreasing the active corrosion rate and the current density. Indeed, they show the highest corrosion potential (−338 mV) and the lower anodic current (~0.13 μA/cm^2). 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.

4. Conclusion

The corrosion behaviour of plasma nitrided, ZrBN coated and duplex treated 32CDV13 low alloyed steel was studied

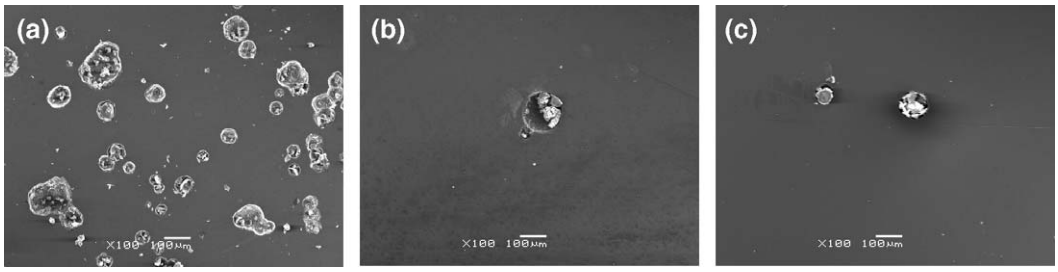

Fig. 4. Surface morphology after potentiodynamic test in NaCl 30 g L^{-1} of ZrBN coated part (a), plasma nitrided (80% N_2+20% H_2; 8 h; 500 °C) steel (b) and duplex treated steel (c).

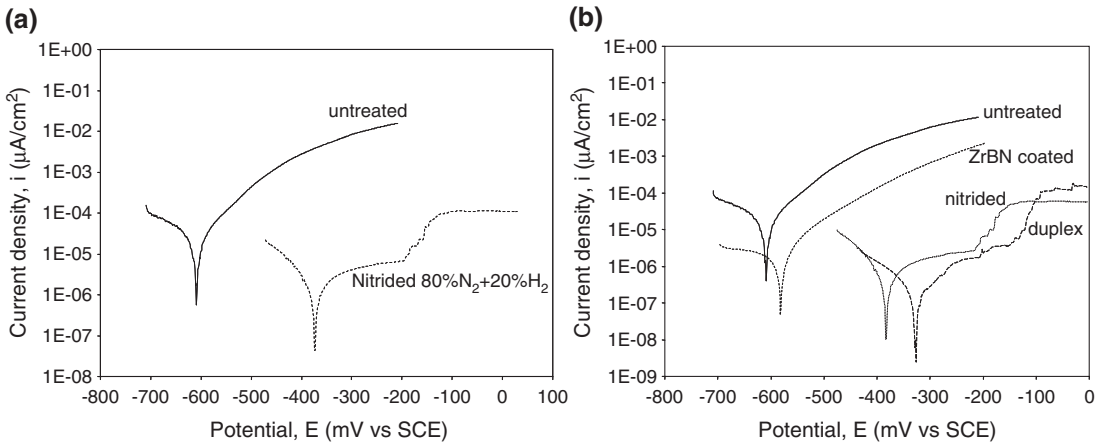

Fig. 5. Potentiodynamic polarisation curves in NaCl 30 g L^{-1} for untreated and nitrided samples (a) and all samples, untreated, nitrided, ZrBN coated and duplex treated (b).

using potentiodynamic techniques in NaCl solution. The results obtained can be summarized as follows:

- After plasma nitriding, the compound layer corresponds mainly to $Fe_{2-3}N$ and Fe_4N iron nitrides, which present good corrosion properties. This layer is dense and contains few 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, small anodic area (steel exposed through open porosities) against large cathodic one (ZrBN film) may provoke severe localised 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, exhibiting, at the same time, passive ability.

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