Corrosion resistance of low-carbon steel modified by plasma nitriding and diamond-like carbon

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ABSTRACT

In this paper, the corrosion resistance of nitrided and diamond-like carbon (DLC)-coated SAE 1020 steel samples was investigated. The DLC coating was deposited after plasma-nitriding. The structure and composition of different phases of the samples were characterized by Vickers micro-hardness, scanning electron microscopy, X-ray diffraction, and Raman spectroscopy. The corrosion behavior of the samples was investigated by electrochemical methods using a 0.1 mol L^{-1} H_2SO_4 solution. The results obtained from sample characterization agreed well with those obtained from electrochemical corrosion methods. The 500-W DLC coating exhibited the best corrosion-resistance. The DLC-coated samples showed better corrosion-resistance than uncoated samples.

1. Introduction

Protective surface coatings are widely employed to improve electrochemical and mechanical properties such as corrosion resistance, wear, and hardness. Techniques using plasma atmosphere are employed in material coating processes to improve the surface energy, friction, and hardness, along with the adhesion to other materials or coatings.

During plasma nitriding, nitrogen atoms are introduced into the surface of a sample, thus producing a compound layer and a diffusion layer.

The characteristics of a nitrided steel surface depend on the chemical composition of the substrate and process parameters such as time, temperature, and especially the nitriding potential of the treatment medium [1]. Therefore, according to Colijin et al. [2] and Lampe et al. [3] the microstructure of nitrided layers can be subdivided into two distinct regions: a compound layer and a diffusion zone.

Compound layer is the outermost layer and may be either single-phase (γ'-Fe_4N or ε-$Fe_{2-3}N$) or polyphase (γ'-Fe_4N + ε-$Fe_{2-3}N$ nitrides of alloying elements). It is very hard, and hence contributes to the wear and corrosion resistance of nitride layers.

Diffusion zone lies below the compound layer and is formed by the saturation of ferrite by nitrogen, precipitation of very thin and coalescence-resistant nitrides (α''-$Fe_{16}N_2$ and γ'-Fe_4N), and generation of residual stresses. It contributes significantly to the improvement of the wear resistance and fatigue properties [4] of nitride layers.

Low-nitrogen and carbon-free atmospheres favor the formation of the γ'-Fe_4N phase. This phase has a face-centered cubic (FCC) crystal structure and exhibits a narrow solubility range for nitrogen (5.7–6.1%) [5,6].

The ε-$Fe_{2-3}N$ phase starts precipitating when the nitrogen content is ~6.1% by weight. Hence, high nitrogen content and the presence of carbon favor the precipitation of ε-$Fe_{2-3}N$. This phase can dissolve up to 11.5% (by weight) of nitrogen at temperatures below 500 °C and has a packed hexagonal crystal structure [1,6].

However, a brittle and porous compound layer affects the characteristics of nitride layers adversely, thus limiting their applications [7,8].

To eliminate the effect of the brittleness and porosity of compound layers, nitride layers are coated with diamond-like carbon (DLC) films, which are amorphous carbon composite films that have carbon-carbon and carbon-hydrogen bonds, the carbon atoms being sp^2 and sp^3 hybridized. These bonds impart diamond-like characteristics such as hardness and chemical inertness to these films [9]. These films can be classified into various types depending upon the amount of hydrogen and the ratio between the sp^2 and sp^3 bonds [10].

DLC coatings have good chemical stability in acidic and alkaline solutions at room temperature, which makes them corrosion-resistant [11–13]. However, DLC films cannot be deposited directly onto SAE 1020 steel, because it is a ductile substrate, and their modulus of elasticity difference is not adequate for mechanical stresses. Thereby, a

nitride layer is a good intermediate layer to sustain the DLC film [14–16]. When DLC film is used, it is necessary two additional layers: nitrided layer acts as a mechanical support, and a Si-rich layer improves chemical adhesion.

Owing to their versatility, these surface coatings have been used in a number of engineering applications and have attracted the attention of many researchers. These coatings can be applied to magnetic and optical discs, video recording drums, engine parts, razors, bar code scanners, glass lenses, biomedical devices, etc. [17–24].

Generally, these coatings are applied to the materials that exhibit excellent mechanical properties to minimize the wear. Indeed, it is necessary to investigate the properties of these coatings in order to use them for a wide range of applications [17].

In recent years, much research has been carried out on corrosion resistance of materials using thin films such as DLC, which are known for their excellent corrosion resistance, to meet the demands of new technological applications [17,25]. In this work, a 0.1 mol L^{-1} H_2SO_4 solution was used to investigate the corrosion behavior of SAE 1020 mild steel with and without plasma nitride layer and DLC coatings. The protective effect was investigated by open-circuit potential (OCP) measurements, linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization.

2. Experimental

2.1. Plasma nitriding and DLC deposition

Cylindrical coupons of SAE 1020 mild steel (28 mm in diameter and 7.5 mm in thickness) were used for plasma nitriding, deposition of DLC films, and the corrosion tests. Nitriding and DLC deposition were performed in a plasma reactor with an internal volume of 1 m^3 in a mounting configuration as shown in Fig. 1. The DLC deposition was performed using an MKS RPG-100 10 kW plasma source. A pulse frequency of 100 kHz was used throughout the cycle time, and a + 50 V voltage was used to maintain process stability.

Table 1 lists the plasma process parameters. The total gas flow was kept constant at 1000 sccm throughout the process. A small amount of methane was added during the nitriding process in order to keep the ε-$Fe_{2–3}N$ phase stable. A Si-rich phase (interlayer) was deposited using a mixture of hexamethyldisiloxane (which acted as the precursor), hydrogen gas, and methane to improve the chemical adhesion and minimize the residual stress between the nitrided layer and the DLC coating [14,26,27]. Methane was used as the only source of carbon and hydrogen during the deposition of the DLC films.

From now on, the following nomenclature will be used for various samples used in this study: Bare SAE 1020 will be denoted by BS, nitrided SAE 1020 will be denoted by NS, nitrided SAE 1020 with DLC coatings will be denoted by 500 W - NS or 700 W - NS depending upon the polarization power used during the coating process, as shown in
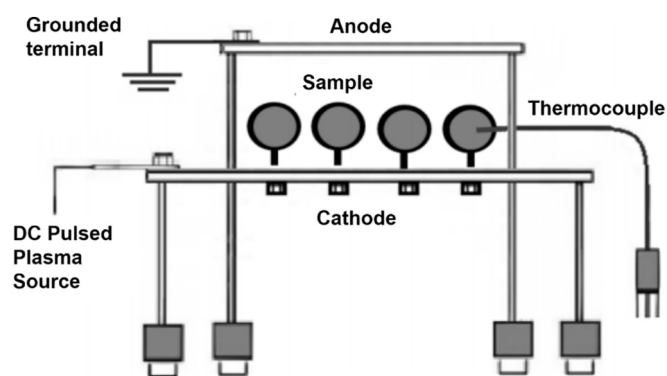

Fig. 1. Plasma Enhanced Chemical Vapor Deposition (PECVD) processing configuration on industrial scale.

Table 1
Processing parameters for the nitride layer, interlayer, and DLC (a-C:H) coating.

Sample (DLC/ 500 W)	T (°C)	P (Torr)	Bias (V)	Gas mixture	Time (min)
Nitride layer	550	2	350	90% N_2 + 9% H_2 + 1% CH_4	90
Interlayer	250	1	400–500	HMDS + H_2 + CH_4	35
a-C:H	250	1	400–500	H_2 + CH_4	10

Sample (DLC/ 700 W)	T (°C)	P (Torr)	Bias (V)	Gas mixture	Time (min)
Nitride layer	550	2	350	90% N_2 + 9% H_2 + 1% CH_4	90
Interlayer	250	1	420–520	HMDS + H_2 + CH_4	35
a-C:H	250	1	420–520	H_2 + CH_4	10

Table 2
Identification of the samples.

Sample	Identification
SAE 1020 Steel	BS
Nitrided SAE 1020 Steel	NS
Nitrided SAE 1020 Steel + DLC film deposition with power of 500 W	500 W - NS
Nitrided SAE 1020 Steel + DLC film deposition with power of 700 W	700 W - NS

Table 2.

2.2. Characterization

A Philips XL-30 scanning electron microscope (SEM) was used to study the microstructure of the samples. An Energy-dispersive analysis by X-rays (EDAX) microprobe was coupled to the SEM to carry out the energy dispersive X-ray analysis (EDX) of the samples.

The image of the cross sections was made in an optical microscope Leica DM4000/DFC450, with up to 3000 × increase in capacity (associating an objective lens with 150 ×).

The surface structure of NS was examined by X-ray diffraction (XRD) using a Philips X'Pert MPD diffractometer using a Kα radiation (λ = 1.5418 Å) at a power of a 40 kV and a current of 30 mA. We used the divergent slits of 1° ¼° Soller that refer to the optical path of the X-ray diffraction. 2θ was varied from 30 to 120° and scanning was done at a resolution of 0.02° X'Pert High Score Plus 2.2-Panalytical B.V software was used along with the JCPDS-ICDD PDF-2 2004 (ICDD, 2004) and ICSD (ICSD, 2012) databases to analyze the diffractograms.

The chemical structure of the samples was investigated by using a Raman spectroscope (Renishaw model 2000) using a 514.5 nm Ar excitation.

The micro-hardness profile of the samples was evaluated with a Leco LM100AT analyzer using a 10 g charge for 15 s. Norm ASTM E 384-11^{ε1} [28] was adopted as the standard. However, 15 micro-indentations were performed to obtain the micro-hardness profile at different points on the sample surfaces. Four successive measurements were performed on each sample. The first indentations were measured on the surface of the compound layer. The distance between successive indentations was 20 μm.

2.3. Cell, electrodes, and coupons

The corrosion tests were performed in a horizontal glass electrochemical cell using three electrodes. SAE 1020 (treated and untreated) was used as the working electrode (0.785 cm^2 in area). For untreated samples, the working electrode was mirror-polished with a 1200 emery