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Nitriding of 304 Steel by a Nitrogen Plasma: Increasing Corrosion Resistance†

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Exposure of a 304 stainless steel sample to an inductively coupled low pressure radio frequency (RF) nitrogen plasma leads to the formation of a nitriding layer. The protective properties of this layer are investigated by electrochemical methods. The corrosion potential of the steel in an aqueous solution depends on the working parameters of the plasma such as the time exposure and the distance between the steel sample and the high voltage (HV) coil of the treatment reactor.

Stainless steels are ion-based alloys containing at least 10.5% Cr. With increasing chromium content and the presence or absence of other elements stainless steel can provide an extraordinary range of corrosion resistance. There are many families of stainless steels (*i.e.* austenitic, ferritic) as defined by their crystallographic structure. Austenitic steel has desirable mechanical properties combined with ease of fabrication, which is why austenitic grades, especially type 304, are the most common of the stainless steel grades.

Surface treatment of steel to limit corrosion is continuously being developed because steel is ubiquitous in the construction industry. Metallic surface nitriding is applied to improve surface properties such as resistance to corrosion, increased hardness by the development of thin surface layers (1–10 μm) providing high resistance properties.[1]

Low pressure gas discharges are commonly used for steel surface nitriding in industrial reactors. The plasma-nitriding of steel is an important surface-hardening treatment carried out on a large scale in many industries. One of the strong points of this hardening method is the short treatment time compared with other techniques, such as gas-nitriding. The plasma-nitriding behavior of type 304 austenitic stainless steel in a DC glow discharge was studied at temperatures between 723 and 823 K.[2] The plasma-nitriding causes both a marked increase in hardness up to $H_V = 1200$ and the formation of a nitriding layer in which small particles of CrN precipitate in the matrix metal.[2] The thickness of the nitriding layer increases with nitriding time. It is concluded, therefore that plasma-nitriding is controlled by a diffusion process of nitrogen in the matrix metal.

This investigation was performed with a nitrogen plasma gas produced by a classical inductively coupled plasma generator under reduced pressure. In a plasma, a number of processes take place (*e.g.* ionization, dissociation by electron impact and attachment phenomena). These induce the formation of activated species such as, in the case of a nitrogen plasma, activated molecules [$N_2(C^3\Pi_g)$, $B^3\Pi_u$ and $A^3\Pi_u{}^+$], atomic nitrogen [$N(^2P)$ and ^4S] and ions ($N_2{}^+$, N^+) which are able to react at the steel surface and yield nitriding layers.[3]

The aim of this work was to investigate by electrochemical measurements the protective properties of the nitriding layers formed on 304 austenitic stainless steel by nitrogen plasma treatment. We recorded the polarization curves of the steel treated in the nitrogen plasma to determine the value of the corrosion potential of samples which provided us with information on the protecting power of the nitriding layer.

Materials and Experimental Procedures

The 304 steel samples used in this study are cylinders of diameter 1 cm and length 0.5 cm and composition as follows: 0.034% C, 0.36% Si, 1.76% Mn, 0.034% P, 0.012% S, 18% Cr, 9.23% Ni and 0.17% Cu. The samples are mechanically polished with different grinding SiC papers (400, 800 and 1200 grades), rinsed in absolute ethanol and air dried before being exposed to the nitrogen plasma.

The plasma-nitriding was carried out in a classical low pressure inductively coupled RF plasma reactor which has been used for others studies.[4–6] It comprises a tubular quartz reactor. The excitation is created by an RF discharge of 13.56 MHz. The input power is maintained in the range 100–2200 W and the pressure in the range 200–5000 Pa.

The 304 steel sample is positioned normal to the gas flow on a holder fitted with a stainless steel quenching head. The sample temperature T is monitored by a chromel alumel thermocouple whose hot junction is placed 0.3 mm under the sample.

The nitriding kinetics of the steel sample depend on the working parameters of the reactor. The injected power and pressure for the reactor were fixed respectively at 900 W and 1500 Pa. The distance between the steel target and the high voltage (HV) coil is kept constant ($d = 5$ cm). The nitrogen is injected into the reactor (flow rate: 0.35 N l min^{-1} in standard conditions) to maintain the desired constant pressure.

The potentiodynamic polarization curves were obtained on a Princeton Applied Research Model 273 potentiostat/galvanostat connected to the Model 342 Softcorr corrosion measurement software. The supporting electrolyte used was 10^{-2} M H_2SO_4 solution. It was deaerated by purging with nitrogen for 20 min. The steel sample was mounted in the electrochemical glass cell, with a platinum counter electrode and a saturated calomel reference electrode. The polarization curves were recorded using a potential sweep rate of 1 mV s^{-1}.

Results and Discussion

Potentiostatic polarization data were depicted as $\log(j\,\mu A\,cm^{-2})$ *vs.* applied potential E/mV. The corrosion potential E_{corr}, which is controlled by the nitriding layer formed at the surface of the 304 steel, depends on the plasma treatment conditions. Its evolution as a function of the treatment time is a good indicator of the changes occurring at the target surface.

Fig. 1 shows the anodic and cathodic polarization curves: (1), for an untreated steel sample; (2), for a treated steel sample during 3 h in the nitrogen plasma. The corrosion

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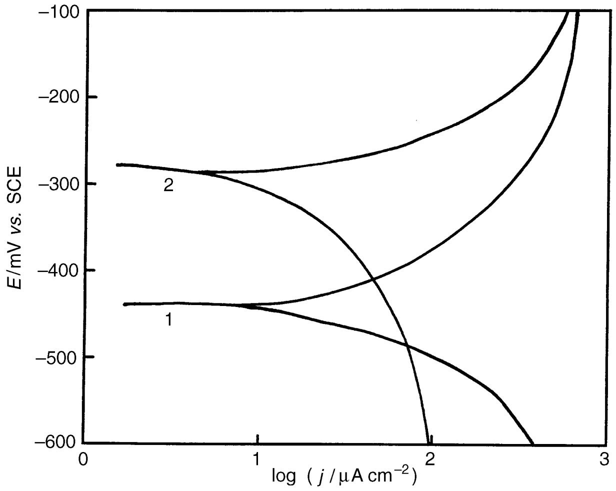

Fig. 1 Anodic and cathodic polarization curves of 304 steel in 10^{-2} M H_2SO_4 (1 mV s^{-1}). (1) Untreated steel. (2) Nitrogen plasma treated steel for 3 h (injected power: 900 W, pressure: 1500 Pa, $d = 5$ cm, $T = 525$ K)

potential values of untreated and treated samples were found at –438 and –290 mV *vs*. SCE, respectively. The E_{corr} of the treated sample moves towards positive potentials and its anodic current decreases. This effect is related to the nitriding layer formed at the sample surface which makes the dissolution of the steel in the 10^{-2} M H_2SO_4 solution more difficult.

We operated the nitrogen plasma in the standard working conditions but varied the exposure time between 1 and 6 h. The anodic and cathodic polarization curves of all the plasma treated samples were recorded in the same conditions. Fig. 2 shows the evolution of the corrosion-potential as a function of the treatment time. The E_{corr} values provide evidence that the corrosion potential is an increasing function of the treatment time: for a 4 h treatment, E_{corr} increases from –438 to –123 mV *vs*. SCE after an induction period close to 2 h. This may be related to an increase in the nitriding layer thickness constituted of small particles of CrN.[2] For plasma treatments longer than 4 h and shorter than 6 h, E_{corr} tends to a limiting value close to –100 mV *vs*. SCE which may be related to insignificant evolution of the thickness and the composition of the nitriding layer.[2,7]

The influence of the electric power was investigated. The maximum E_{corr} value (≈ -100 mV *vs*. SCE) is reached more rapidly the higher the electric power P for other given working parameters. For example, the maximum E_{corr} is reached after 3 h for $P = 1100$ W. This result reflects the high efficiency of the nitrogen plasma treatment as the power increases.

In conclusion, the potentiodynamic polarization curves can be used to study the protective properties of the nitriding layers formed on the 304 stainless steel after a nitrogen plasma treatment. This work shows that the E_{corr} of the treated samples moves towards positive potentials depending on the working parameters of the plasma. The increase of the nitriding layer thickness makes the corrosion of the 304 stainless steel in an aqueous solution more difficult.

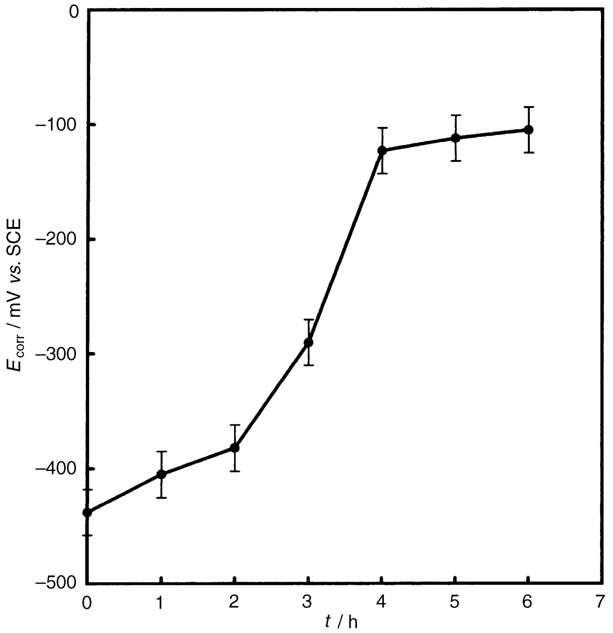

Fig. 2 Variation in E_{corr} for 304 steel treated by a nitrogen plasma (injected power: 900 W, pressure: 1500 Pa, $d = 5$ cm, $T = 525$ K) as a function of the plasma treatment time

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