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Glow-discharge nitriding of AISI 316L austenitic stainless steel: influence of treatment temperature

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Abstract

Nitriding treatments of austenitic stainless steels can be performed only at relatively low temperatures in order to avoid a decrease of corrosion resistance due to chromium nitride formation. These conditions promote the formation of the so-called S phase, which shows high hardness and good corrosion resistance. In the present paper, the influence of the treatment temperature of glow-discharge nitriding process on the microstructural and mechanical characteristics of AISI 316L steel samples was evaluated. Glow-discharge nitriding treatments were performed at temperatures in the range 673–773 K for 5 h at 10^3 Pa. The modified surface layer of the nitrided samples consists mainly of the S phase and, according to metallographic technique analysis, it seems to be essentially a modification of the austenite matrix. All the nitrided sample types show a peculiar surface morphology due to both plasma etching during nitriding and the presence of slip steps and relieves at grain boundaries, the latter features presumably due to the formation of the nitrided layer. X-ray diffraction analysis shows that for the samples nitrided at temperatures up to 723 K, besides the S phase, small chromium nitride precipitates are present at the surface, while using higher treatment temperatures both chromium (CrN) and iron (γ'-Fe_4N) nitrides precipitate along the grain boundaries and in the middle of the grains, and their amount increases as treatment temperature increases. High hardness values (from ~1450 to ~1550 $HK_{0.01}$, depending on nitriding conditions) are observed in the modified layer with a steep decrease to matrix values. Preliminary corrosion resistance tests, carried out in 5% NaCl aerated solution with the potentiodynamic method, show that with the used treatment parameters a substantial improvement of corrosion resistance can be achieved when glow-discharge nitriding treatments are performed at temperatures in the range 703–723 K.

Keywords: Glow-discharge nitriding; Austenitic stainless steel; AISI 316L; S phase

1. Introduction

Austenitic stainless steels have a widespread use in many industrial fields owing to their excellent resistance to general corrosion due to the formation of a passive surface film, but the low hardness and poor tribological properties of these materials can shorten the life of components if subjected also to wear. Wear resistance of steel components is usually improved by using surface engineering techniques, which modify the characteristics of the surface layers by means either coating processes, like physical vapour deposition, chemical vapour deposition or plasma spray, or diffusion processes, like carburizing or nitriding [1]. Nitriding is nowadays a well-assessed industrial practice for improving wear and corrosion resistance of steel components. However, if austenitic stainless steels are treated at temperatures generally used for nitriding of low-alloy steels or tool steels (about 773 K or higher), they suffer a significant decrease of corrosion resistance due to the precipitation of substantial amounts of chromium nitride, which depletes chromium from solid solution prejudicing the formation of the protective film [2,3]. Nitriding techniques are effective in improving both surface hardness and corrosion resistance of austenitic stainless steels only when they are performed at temperatures lower than about

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723 K. In fact, by using such low treatment temperatures the modified surface layer consists essentially of a metastable phase, known as supersaturated or expanded austenite γ_N [4–9], S phase [10–13], or *m* phase [14–16], which has proved to have high hardness and very good corrosion resistance. Many nitriding techniques were used to produce this phase, from plasma nitriding [10,12–14], to plasma immersion ion implantation [4,5,17], ion beam implantation [17], low-pressure arc discharge [6] and reactive magnetron sputtering [11]. Even if the first report on the so-called S phase by Ichii et al. [18] dates nearly two decades ago and the working conditions to form this phase are now outlined, its structure is still a matter of debate and has not completely clarified. Moreover, many studies are carried out also on the phases present in the modified layer, since they seem to be dependent on both the physical parameters and the used nitriding technique. For example, by using treatment temperatures of ~723 K or higher, besides the S phase, the presence of chromium nitride, CrN, and α-Fe was observed on plasma immersion ion-implanted samples [4,5] or on low-pressure plasma arc source ion nitrided samples [19]; on the other hand, in glow-discharge nitrided samples the presence of α-Fe was not detected, and only the S phase and chromium and iron nitrides were observed in the layer [20,21].

This research was planned with the aim of studying the effects of glow-discharge nitriding on the characteristics of AISI 316L austenitic stainless steel, particularly related to the formation conditions of the so-called S phase. In the present paper, the influence of the treatment temperature on the microstructural and mechanical characteristics of the modified surface layer of the nitrided samples is discussed. Preliminary results of the corrosion behaviour of untreated and nitrided samples in 5% NaCl solution are also reported.

2. Experimental procedure

Prismatic samples (40×18×4 mm) were obtained from an annealed A151 316L steel bar (diameter: 60 mm) by cutting, grinding and polishing up to 6-μm diamond suspension; the mean surface roughness (R_a value) of the samples after polishing was ~ 0.3 μm.

Glow-discharge treatments were performed in a laboratory plasma equipment at a working pressure of 10^3 Pa using a dc power supply. Nitriding treatments were carried out at temperatures in the range 673–773 K, for 5 h, using a gas composition of 80 vol.% N_2 and 20 vol.% H_2 and after a cathodic sputtering cleaning.

The microstructure of the untreated and treated samples was examined by optical metallographic, scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS) analysis techniques. X-ray diffraction analysis (Cu Kα radiation) was performed in order to identify the phases present in the surface layers. Diffraction patterns were collected in Bragg–Brentano configuration and were analysed by means of the program MAUD using the Rietveld method [22]. Additional X-ray diffraction analysis was performed collecting the diffraction patterns in glancing angle configuration by using constant incident angles varied in the range 5–20° in order to identify the phases present in different parts of the nitrided layer. Under these conditions, the mean penetration depth (i.e. the depth at which the intensity drops by a factor of e) ranges from 0.32 μm ($\alpha=5°$) to 1.03 μm ($\alpha=20°$).

Microhardness profile measurements (Knoop indenter, 10 gf) were carried out on the modified layers and on the matrix. Roughness analysis was performed on the surface of the samples before and after the treatments by using a stylus surface tester (measuring range: 0.01÷10 μm).

Corrosion behaviour was preliminarily studied in 5% NaCl aerated solution using the potentiodynamic method. The solution was prepared with doubly distilled water and reagent grade chemicals, and the tests were carried out at room temperature. Polarization curves were performed using a Pyrex cell equipped with an Ag/AgCl reference electrode (KCl saturated) and a platinum grid as counter-electrode. The sample surface area exposed to the electrolyte was 1 cm^2. The linear voltammetries were performed at a potential scan rate of 0.3 mV s^{-1} after a delay period of 24 h. Three corrosion tests for each sample type were carried out in order to assess the result.

3. Results and discussion

3.1. Morphology and microstructure

After the treatments, the surface of all the samples types shows a peculiar morphology, as shown in Fig. 1a. The surface appears to be plasma etched, and this etching, observed also by other authors [9,16,23], can be ascribed to both the cathodic sputtering performed before the nitriding process and the treatment itself, since it was observed interrupting the treatment after the sputtering and it has enhanced features as the treatment temperature increases. The surface of the treated samples, as delineated by this plasma etching, still shows an austenitic structure with the characteristic twins, as commonly revealed by chemical etching with glyceregia on untreated samples (Fig. 1b). Moreover, as a new feature, slip bands are delineated within the grains of the treated samples. SEM analysis shows that at grain boundaries high relieves are present, and some grain boundaries leaning forward on adjacent grains are observed, as shown in Fig. 2. The presence of slip steps and grain boundary relieves cannot be ascribed to the plasma etching and suggests that the formation of the nitrided layer is accompanied by high compressive stresses which cause a plastic deformation in the material; this effect is more enhanced as treatment temperature increases, as shown also by the increase of surface roughness, ranging from 0.4 μm (673 K) to 0.75 μm (773 K). These features of