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Low temperature nitriding of AISI 300 and 200 series austenitic stainless steels

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ABSTRACT

In this study the effects of low temperature plasma nitriding on the characteristics of different austenitic stainless steels, CrNi-based (AISI 304L and AISI 316L) and CrMn-based (AISI 202), were compared. Samples were nitrided at 400 and 430 °C, at 1000 Pa for 5 h, and their microstructure, phase composition, microhardness and corrosion resistance were evaluated. The characteristics of modified surface layers depended on both treatment parameters and alloy composition. For all the steels modified surface layers had a double layer microstructure. In the outer modified layer, mainly consisting of S phase, deformation (or shear) bands were observed in the grains, and nitrogen induced h.c.p. martensite, ε'_N, formed. The tendency to form shear bands and ε'_N was higher for AISI 202 samples, and decreased for AISI 304L and then for AISI 316L ones, influencing the modified layer thickness. When nitriding was performed at 430 °C, nitrides formed, and their amount was affected by steel composition. Nitriding treatments allowed to markedly increase surface microhardness and corrosion resistance, in comparison with the untreated alloys. When nitrides did not form, as for the 400-°C nitrided samples, the corrosion behaviour of the considered steels was comparable. Nitride precipitation affected corrosion resistance, increasing corrosion phenomena.

1. Introduction

Austenitic stainless steels are employed in many industrial fields thanks to their corrosion resistance, ease of formability and weldability. Their very good corrosion resistance in many aggressive environments is due to the presence of a surface passive film, mainly consisting of chromium oxide, which is self healing if damaged and protects the alloy from the surrounding medium [1]. The face centred cubic structure of these alloys is maintained owing to the presence of austenite stabilizing elements, like nickel, manganese and nitrogen. Fairly high amounts of nickel (usually 8 wt% or higher) are present in the so called AISI 300 series stainless steels, which are widely used. Nickel is partly substituted by manganese and nitrogen in the cheaper AISI 200 series stainless steels, which have higher strength; however, these alloys may show lower corrosion resistance than AISI 300 series steels, due to the lower chromium content [2].

The industrial applications of austenitic stainless steels may be limited by their low hardness and poor tribological properties, which may compromise the performance of components subjected to wear. Moreover, in spite of the very good resistance to general corrosion, these alloys suffer localised corrosion in specific environments, especially in chloride-ion containing solutions. Among the surface engineering techniques, employed to improve wear and corrosion resistance properties of austenitic stainless steels, low temperature nitriding has received increasing attention in the last years [1,3]. Treatment temperatures lower than 450 °C allow to avoid the precipitation of large amounts of chromium nitrides and the consequent decrease of corrosion resistance [4]. In this manner, a supersaturated solid solution of nitrogen in the expanded and distorted austenite lattice is produced, known as S phase [1,3,4] or expanded austenite [1,3,5], which has high hardness and improved corrosion resistance in chloride-ion containing solutions [3,4]. Many researches were devoted to study the structure [3,4,6–11] and the properties [3–5,12–15] of this phase, and the treatment techniques able to produce it [3,5,16–18]. These studies were usually carried out using a single steel type, in order to put in evidence the effects of different nitriding techniques [3,16–18] or treatment parameters [3,13,14,18–20]. The effect of steel composition was investigated especially regarding the influence of nickel

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[3,21–23], molybdenum [24–26], and chromium [3,21,23,27]. Recent studies also regarded steels with low amounts of alloy elements like copper and niobium [26], or the high nitrogen and nickel-free stainless steels with improved biocompatibility [28,29]. The analysis of the scientific literature shows that the used steels are mainly of the 300 series [3,5,6,25,26]; limited studies regarded low-nickel alloys, as 17Cr–15Mn–4N [30] and X50CrNiNbN 21 9 [31], or the nickel-free F2581 [29], which have a niche use. The direct comparison of the effects of nitriding on AISI 300 and 200 stainless steels has received little attention. Even if a comparison could be performed using the results obtained by different researches, it is hindered by the fact that different experimental conditions, and, in particular, nitriding parameters, were usually used.

In the present research a direct comparison of the effects of low temperature nitriding on the characteristics of the modified surface layers produced on AISI 300 and 200 series austenitic stainless steels was performed. Three steels of large commercial use were chosen, CrNi grades AISI 304L and AISI 316L, and the low-nickel CrMn grade AISI 202. Glow-discharge nitriding technique was used to perform nitriding treatments. The microstructure, phase composition, hardness and corrosion resistance characteristics of the nitrided samples were investigated and they were compared with those of the untreated alloys.

2. Experimental procedure

Three austenitic stainless steels were used, AISI 202, AISI 304L and AISI 316L, supplied by ThyssenKrupp Acciai Speciali Terni (Italy); the chemical composition of the steels is reported in Table 1. The steels, in the form of cold rolled, annealed and pickled plates, were cut in order to obtain prismatic samples (40 × 17 × 0.7 mm). The surface finishing of the samples was classified as 2D according to the EN 10088-2:2005 norm [32]. The surfaces, which had to be treated, were not ground and polished further; their average surface roughness, Ra, was 0.16 ± 0.02 μm, and their maximum height of profile, Rz, was 1.8 ± 0.1 μm. As an example, the surface morphology of an untreated AISI 202 sample is shown in Fig. 1.

Low temperature glow-discharge nitriding treatments were carried out in a laboratory plasma equipment, previously described [33]. The treatment parameters were chosen on the basis of our previous results [13]. Before the treatments, the treatment chamber was evacuated up to a pressure of about 5 Pa; the required treatment pressure was maintained by a flow controlled dynamic vacuum system. Before the nitriding step, cathodic sputtering was performed in order to remove the natural passive film and enable a homogeneous nitriding process, operating at 130 Pa with 80 vol% N_2 and 20 vol% H_2 up to 310 °C. After this step, the temperature and pressure were increased up to their nominal values. Nitriding treatments were carried out at 400 or 430 °C, at a constant pressure of 1000 Pa, for 5 h, using a gas mixture of 80 vol% N_2 and 20 vol% H_2 in a 300 sccm total flow rate. The current density values depended on the treatment temperature, and they were 2.5 ± 0.1 mA cm^{-2} for the 400-°C treatment, and 2.8 ± 0.1 mA cm^{-2} for the 430-°C treatment; the voltage drop was 190 ± 10 V.

Table 1
Chemical composition (wt.%) of the used austenitic stainless steels.

Material	Composition							
	C	Si	Mn	Cr	Ni	Mo	N	Fe
AISI 202	0.065	0.40	7.7	17.0	4.1	–	0.15	Bal.
AISI 304L	0.028	0.30	1.7	18.0	8.0	0.27	0.065	Bal.
AISI 316L	0.029	0.34	0.9	16.6	10.3	2.01	0.049	Bal.

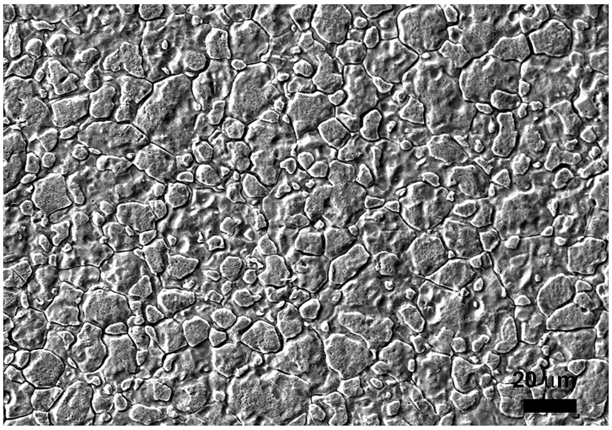

Fig. 1. Surface morphology of an untreated AISI 202 sample.

The microstructure of the nitrided and untreated samples was examined using light and scanning electron microscopies and energy dispersion spectroscopy (EDS) analysis. EDS analysis, performed on unetched samples using a 20 kV accelerating voltage for the electron beam, allowed to obtain a semi-quantitative evaluation of the amount of the alloy elements (Fe, Cr, Ni, Mo, Mn, Si) and of nitrogen in different zones of the samples. In order to observe the cross-section microstructure of the modified layers, samples were cut and mounted using glass-filled epoxy thermosetting resin. Tapered sections with a 1.5°-angle were obtained for selected samples by cold mounting them in epoxy resin. The microstructure of the modified surface layers and of the matrix was delineated by means of glyceregia etchant.

The phases present in the surface layers were identified by means of X-ray diffraction analysis (Cu Kα radiation). Diffraction patterns were collected in Bragg-Brentano configuration and with constant incident angles in the range 10–35°; in this latter configuration, the mean penetration depth (i.e. the depth at which the intensity drops by a factor of e) ranges from 0.6 μm ($\alpha = 10°$) to 1.47 μm ($\alpha = 35°$).

Roughness measurements were performed on the surface of the samples before and after the treatments by using a stylus profilometer tester (cut-off length: 0.8 mm). At least five measurements were taken at different locations on the surface. The average surface roughness Ra (arithmetical mean deviation of the roughness profile from the mean line) and the maximum height of profile Rz (sum of the largest profile peak height and the largest profile valley depth within a sampling length, according to EN ISO 4287-2009 norm) were recorded.

Surface microhardness measurements (load: 50 gf) and depth profiles (load: 10 gf) were performed on the samples using a Knoop indenter.

Corrosion resistance of untreated and nitrided samples was studied in aerated 5% NaCl solution at room temperature. A three-electrode electrochemical flat cell equipped with Ag/AgCl reference electrode (3.5 M KCl) and a platinum grid as counterelectrode was used. The sample surface area exposed to the electrolyte was 1 cm^2. Polarization measurements were performed potentiodynamically at a sweep rate of 0.3 mV s^{-1} after a delay period of 22 h. Three corrosion tests for each sample type were carried out for assessing the result.