

# Enhancement in corrosion resistance of austenitic stainless steels by surface alloying with nitrogen and carbon

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## Abstract

In this work, attempts have been made to alloy the surfaces of austenitic stainless steels simultaneously with nitrogen and carbon in the glow discharge of a plasma at temperatures below 450 °C. As a result of such a low temperature hybrid treatment, a dual-layer structure is produced, which comprises a nitrogen-enriched layer on top of a carbon enriched layer. Both nitrogen and carbon are supersaturated in the austenitic face-centred cubic structure in the respective sublayer. Electrochemical corrosion tests have been conducted potentiostatically in a 3 wt.% NaCl aqueous solution to measure the anodic polarisation curves of the alloyed surfaces. The results show that this hybrid treatment can significantly improve the corrosion resistance of austenitic stainless steels by several orders of magnitude over a wide range of potentials.

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**Keywords:** Stainless steel; Surface alloying; Nitrogen; Carbon; Corrosion

## 1. Introduction

Austenitic stainless steels are a class of technologically important materials widely used in various sectors of industry. The problem associated with the poor tribological properties of these materials has recently been tackled by many investigators. These efforts have led to the development of two promising and industrial viable surface alloying techniques which do not compromise the good corrosion resistance of austenitic stainless steels. These include low temperature nitriding [1–6] and low temperature plasma carburizing [7–11]. The former is carried out at temperatures lower than 450 °C for up to several tens of hours, resulting in the incorporation of a large amount of nitrogen in the nitrided layer up to 20 µm thick to form an expanded austenite structure which is free from nitride precipitates. Such a low temperature nitrided layer possesses not only

a high hardness up to 1500 HV but also good corrosion resistance which is even better than untreated austenitic stainless steels [1,4,5]. Similarly, during plasma carburizing, which is carried out at temperatures between 400 and 500 °C, carbon, rather than nitrogen, is introduced into the surfaces of austenitic stainless steels, forming a precipitation-free, carbon supersaturated austenite layer up to 40 µm thick [8–10]. The carburized layer possesses a lower hardness (yet still as high as 1100 HV at the surface) but larger thickness than the low temperature nitrided layer [10].

A hybrid surface alloying process has recently been developed by the present author to integrate the low temperature plasma nitriding and carburizing processes by introducing nitriding and carburising species to the plasma media to effect the simultaneous incorporation of nitrogen and carbon into the surfaces of austenitic stainless steels, with the purpose to form a hybrid structure characteristics of both the nitrided layer and the carburized layer [12]. As a part of this new development, electrochemical corrosion tests have been conducted in 3.0% NaCl aqueous electrolyte on austenitic stainless steels surface

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alloyed by this hybrid process. This paper reports the results obtained and demonstrates that this hybrid process can produce a dual-layer structure which possesses superior corrosion resistance.

## 2. Experimental procedure

Three grades of austenitic stainless steel, AISI 304, 316 and 321, were used as the substrate materials. The chemical compositions of these steels are listed in Table 1. Disc specimens of 25 mm in diameter and 5 mm in thickness were cut from the as-received hot-rolled steel bars. The specimens were manually ground using SiC emery papers down to 1000 grade to achieve a fine surface finish.

The hybrid plasma surface alloying process is described in detail elsewhere [12]. Briefly, the process is similar to that of individual plasma nitriding and plasma carburizing. The major difference between the hybrid process and the individual processes lies in that in the hybrid process, both nitrogen and carbon species are introduced into the plasma chamber. The processing temperature is sufficiently low to avoid nitride and carbide precipitation in the alloyed zone, which will otherwise deteriorate the corrosion resistance of the alloyed zone. Although this process has similarity with the conventional nitrocarburising process for ferrous alloys, it is carried out at much lower temperatures. In this work, the hybrid process was carried out in a DC plasma nitriding unit at temperatures between 380 and 430 °C for 15 to 40 h. The gas mixture used is 95% N<sub>2</sub>+5% CH<sub>4</sub>, where N<sub>2</sub> acts as the nitriding species and CH<sub>4</sub> acts as the carburizing species.

The treated specimens were characterized by X-ray diffraction for phase identification, metallography for layer morphology and thickness examination, glow discharge optical spectrometry (GDS) for composition profiling, and microhardness tests for hardness measurements. Electrochemical corrosion tests were performed using an EG and G Parc three electrode electrochemical flat cell connected to an ACM GILLAC potentiostat equipped with a computer data login, requisition and analysis system. The specimen was clamped to the cell, sealing against a PTFE knife-edge gasket which expose 1.0 cm<sup>2</sup> of the specimen surface to the electrolyte. The electrolyte used for the tests was 3.0 wt.% NaCl in de-ionised water. DC polarization was performed potentiodynamically and anodically. The anodic polarization curves were recorded with a sweep speed of 2 mVs<sup>-1</sup>.

Table 1  
Chemical compositions of the austenitic stainless steels investigated (wt.%)

AISI	Cr	Ni	Mo	Ti	Mn	C
316	19.23	11.26	2.67	0.00	1.86	0.07
304	18.45	10.54	0.00	0.00	2.00	0.07
321	18.78	11.04	0.00	0.45	1.91	0.10

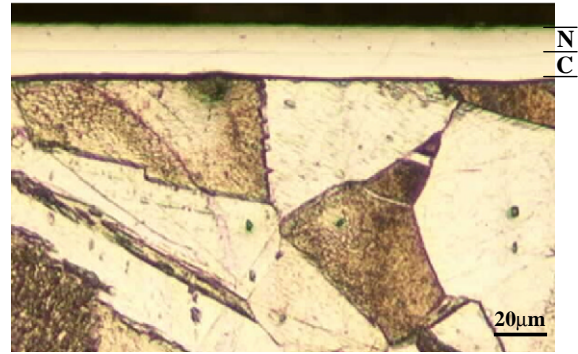


Fig. 1. Optical micrograph of the cross sectional morphology of the alloyed zone produced by the hybrid treatment on AISI 316 steel at 415 °C for 15 h, showing the dual layer structure comprising a nitrogen-enrich layer on top of a carbon-enriched layer.

All the tests were carried out at room temperature (24 °C), open to the air.

## 3. Results and discussion

The alloyed zones produced on the three investigated steels by the hybrid treatment exhibit similar layer structure and morphology. Fig. 1 shows the cross sectional morphology of a typical alloyed zone on AISI 316 steel produced by the hybrid treatment. The corresponding nitrogen and carbon concentration profiles measured by GDS across the alloyed zone are given in Fig. 2. It can be seen that the alloyed zone comprises a dual-layer structure: the outer layer is rich in nitrogen and the inner layer is rich in carbon. The hybrid process thus successfully integrates the low temperature nitriding and carburizing processes and results in the formation of an alloyed zone characteristic of these two individual processes. Both the N-enriched layer and the C-enriched layer are resistant to the etchant (50% HCl+25% HNO<sub>3</sub>+25%H<sub>2</sub>O) used to reveal the microstructure of the substrate material, such that the two sublayers appear “bright” under optical microscopy. X-ray diffraction could not detect any nitride and carbide formation in the alloyed zone, instead two expanded austenite phases,  $\gamma_N$  and  $\gamma_C$ , were detected (Fig. 3). The former ( $\gamma_N$ ) is obviously from the N-enriched layer and is similar to that produced by low temperature

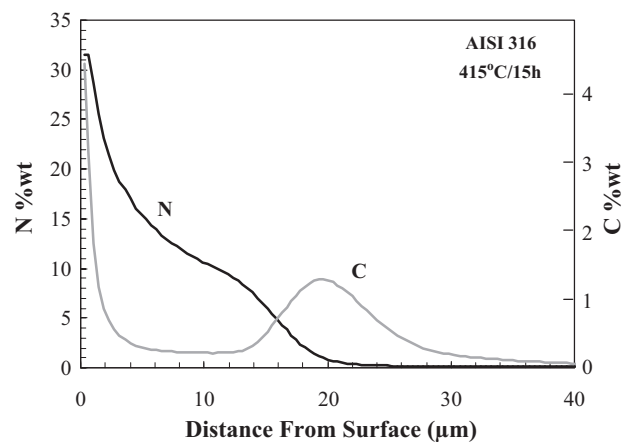


Fig. 2. Nitrogen and carbon concentration profiles measured by GDS across the alloyed zone shown in Fig. 1.

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