HYBRID AND DUPLEX PLASMA SURFACE ALLOYING OF FERRITIC-AUSTENITIC DUPLEX STAINLESS STEEL[1]

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Abstract

Duplex stainless steels are of great technological importance as they possess high corrosion resistance and high mechanical properties as well as low cost. However, their low hardness and poor tribological properties have limited their wider applications in severe wear conditions. This research is directed at the response of ferritic-austenitic duplex stainless steel to plasma surface alloying with both carbon and nitrogen simultaneously (i.e. hybrid carbonitriding) and sequentially (duplex alloying treatment). It has been found that both hybrid and duplex plasma surface alloying treatments can produce a similar dual-layer case consisting of a surface nitrogen alloyed layer followed by a carbon alloyed layer; the dual-layer case is harder and thicker than the single layer produced by typical plasma nitriding or plasma carburising under the same temperature and time. After plasma surface alloying, while the original austenite grains in the duplex stainless steel can fully transform to S-phase, retained ferrite grains, expanded with interstitial solution alloying elements, carbon, nitrogen or carbon+nitrogen, were detected by TEM and XRD. The dual-phase S-phase/ferrite (expanded) structure will decrease the corrosion resistance of duplex stainless steel.

Keywords: Hybrid and duplex plasma surface alloying; Duplex stainless steel; S-phase; Expanded ferrite; Hardness; Corrosion.

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INTRODUCTION

Duplex stainless steels (DSS) are of great technological importance as they not only possess high corrosion resistance (in particular stress corrosion cracking resistance) and high mechanical properties but also low cost relative to austenitic stainless steels. Applications have been found in a range of industries, particularly the oil and gas, petrochemical, pulp and paper, and pollution control industries. However, their low hardness and poor tribological properties have limited their wider applications in severe wear conditions.

Research in the mid-1980s demonstrated that it was possible to effectively improve the surface hardness without loss of corrosion resistance of austenitic stainless steel by low temperature nitriding[1] or carburizing[2] to form a nitrogen or carbon S-phase. This has become one of the 'hot points' in surface engineering research - S-phase surface engineering.[3] Extensive scientific interests lead to - exploring the formation of S-phase in other Cr containing materials.

Some attempts have been made to introduce nitrogen and carbon into duplex stainless steels to combat - wear -, such as PI^3 nitriding at 400°C,[4] pulsed DC plasma nitriding at 350°C,[5] gaseous nitriding at 400°C[6] and gaseous carburizing at 470°C.[7] Based on XRD analysis these researchers claimed that the surface of duplex stainless steel was almost fully transformed into an S-phase layer during the treatments and the surface hardness was increased.

However, little research has been carried out on plasma surface alloying with both carbon and nitrogen simultaneously (i.e. hybrid alloying) or sequentially (i.e. duplex alloying); - furthermore limited work has been conducted on TEM characterisation of the structures and the corrosion resistance of the surface layers. This research is directed at the response of ferritic-austenitic duplex stainless steel to hybrid and duplex plasma surface alloying with carbon and nitrogen in terms of microstructure, mechanical and chemical properties.

EXPERIMENTAL

UNS31803 duplex stainless steel was used in the present work as the substrate material and the chemical composition is given in Table 1. Specimens were cut from hot rolled bars of 25.4 mm in diameter into discs of 6 mm thick. The flat faces of the discs were then manually ground using silicon carbide grinding papers down to 1200 grade to achieve a fine surface finish.

Table 1. Chemical compositions of investigated stainless steel

UNS number	**Composition wt %**							
	C	**Mn**	**Si**	**Cr**	**Ni**	**Mo**	**N_2**	**Fe**
S31803/39209	0.03	2.00	1.00	21.0-23.0	4.5-6.5	2.5-3.5	0.08-0.20	Balance

Plasma surface alloying was carried out using a plasma unit (Klockner Ionon GmbH, Germany) under a pressure of 4 mbar. The plasma alloying treatments included carburising, nitriding, hybrid (carbonitriding) and duplex (carburising followed by nitriding) treatments. Detailed treatment parameters and corresponding designation for the samples are summarised in Table 2.

Table 2. Plasma alloying conditions and designation of the samples

Sample code	Plasma treatment	Parameters
N 42	Nitriding	420 °C, 20h, H2:N2 = 75:25
C42	Carburising	420 °C, 20h, H2: CH4 = 98:2
C46	Carburising	460 °C, 20h, H2: CH4 = 98:2
C52	Carburising	520 °C, 20h, H2: CH4 = 98:2
CN42	Carbonitriding	420 °C, 20h, H_2: N_2 :CH_4 =73:25:2
CN46	Carbonitriding	460 °C, 20h, H_2: N_2 :CH_4 =73:25:2
CN52	Carbonitriding	520 °C, 20h, H_2: N_2 :CH_4 =73:25:2
C46N42	Carburising + Nitriding	PC460(10h)+PN420(10h)
C52N42	Carburising + Nitriding	PC520(10h)+PN420(10h)

The - cross-section-view samples were etched using the Kalling's reagent. Optical micrographs were taken by the Leica 500 microscope. Chemical composition profiles were measured using the Leco GDS 750 QPD glow discharge optical spectrometer (GDOS). The microhardness of the samples was measured by - the Mitutoya MKV-H1 hardness tester with a Vickers indenter for surfaces hardness (load bearing capacity) and a Knoop indenter for cross-sectional hardness depth profiles. Corrosion tests were carried out using an electrochemical system, Solatron 1286 electrochemical interface and a working cell linked to a computer for data logging, collecting and presentation. All the tests were carried out in a 3.5 wt% NaCl solution at a scan speed of 1mV/sec. Before the test, a window of approximately 10mm×10mm was made in each specimen by masking the other areas with an appropriate paint.

Microstructural characterisation was conducted by the X'pert Philips X-ray Diffractometer (XRD) using a Cu-Kα radiation (wavelength 0.154 nm) and Jeol 1200 transmission electron microscope (TEM). Cross-section TEM sample was prepared by the focused ion beam (FIB) SEM, FEI Quanta-3D FEG Dual Beam System.

RESULTS AND DISCUSSION

Surface Layer Morphologies

After plasma alloying for 20 hours at temperatures of 420°C, 460°C and 520°C, a surface layer was formed on all the treated specimen surfaces. As can be seen from Figure 1, the surface layers alloyed with carbon show black and white contrasts (C42, CN42, C52, C52N42 and CN52) while the nitrogen alloyed layer on N42 sample show a much less contrast.

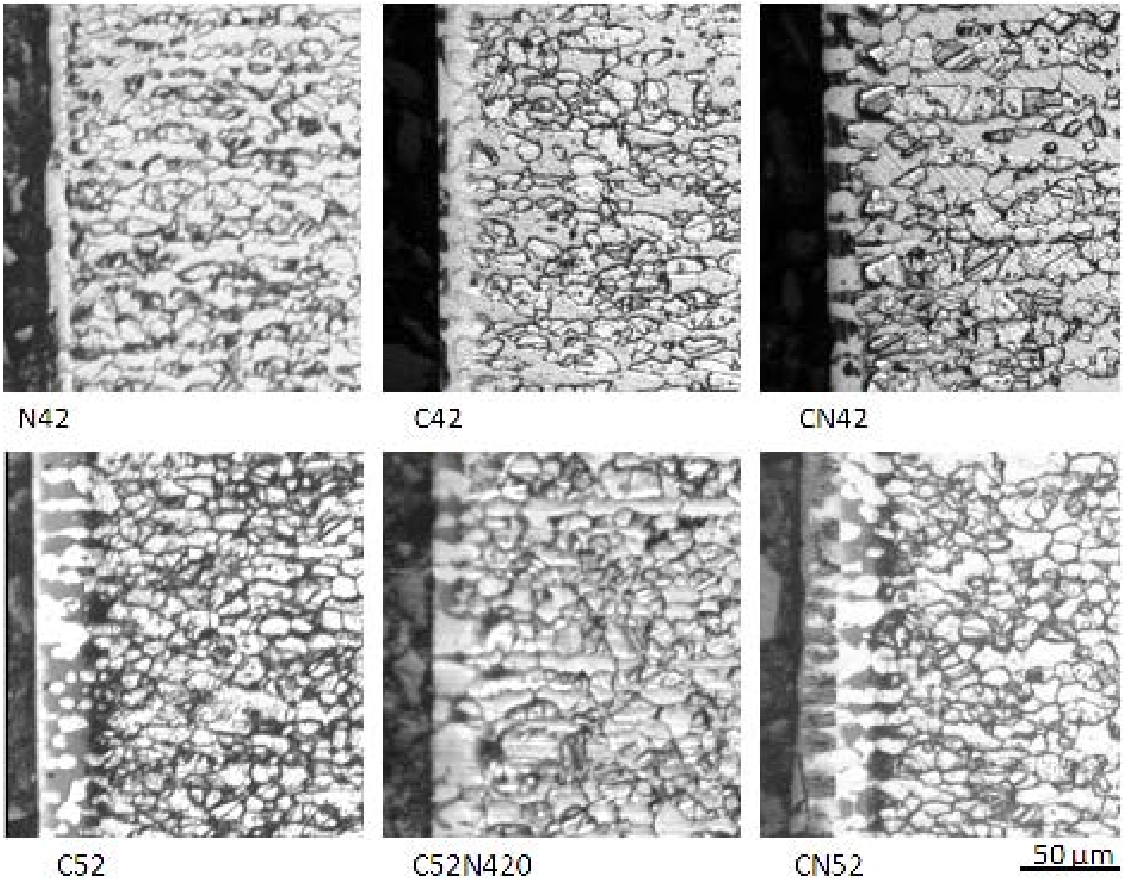


Figure 1. Typical optical microstructures of surface alloyed layer under different treatment conditions.

These black and white contrasts are believed to be connected with the original FCC austenite grains and BCC ferrite grains, which is supported by the continuality of the grains across the surface layer/substrate interface (e.g. C52). Sample CN52 revealed a clear two-layer structure with more dark grains in the outer layer than the inner layer.

This black and white contrast implies that some grains are more resistant to the etchant than the others. This is probably because the microstructure of DSS consists of both FCC austenite grains and BCC ferrite grains and the high chromium and low nickel contents in BCC ferrite grains made them less corrosion resistant than the austenite grains. Furthermore, as will be discussed later, the formation of such contrast could be related to the different response of these two phases to the alloying elements.

Hardening Effect

The surface layer thickness and hardness of the treated samples are plotted in Figure 2 and several observations can be made. Firstly, the thickness and hardness of the layer increased with increasing plasma treatment temperature for carburised (C42, C46 and C52), hybrid (CN42, CN46 & CN52) and duplex (C46N42 & C52N42) group samples; secondly, for the same treatment temperature, plasma carburising produced a thicker layer than nitriding but with a lower hardness, N42 verses C42; thirdly, hybrid treatment promoted a thicker surface layer than duplex treatment as evidenced by the fact that CN42 is 4μm thicker than C46N42 and that CN46 has the similar thickness as C52N42; fourthly, hybrid treatment (e.g. CN42) produced a thicker surface layer than did by nitriding (e.g.N42) or carburizing (e.g.C42) when treated at the same temperature (420°C) for 20 hours. This implies that interaction between C and N must have occurred, which promoted the formation of a thicker layer.

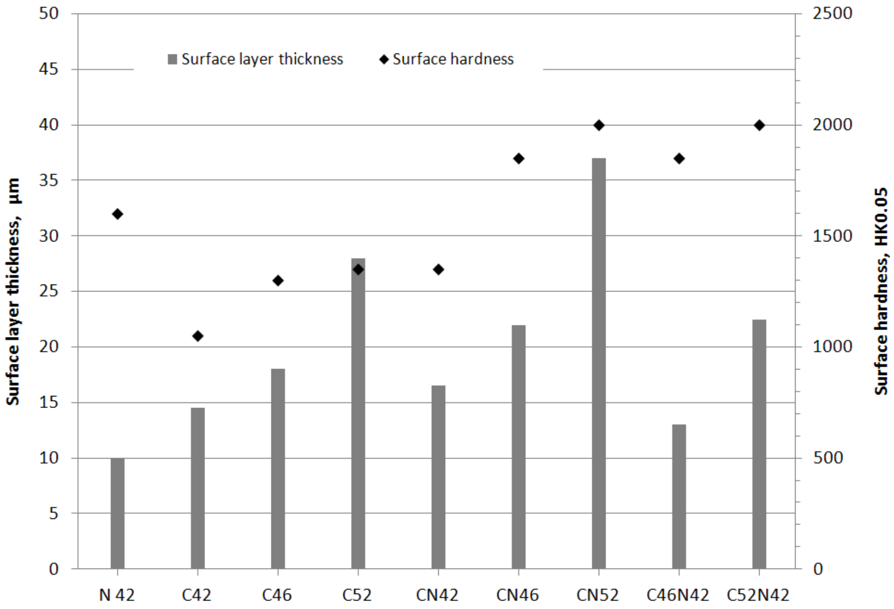
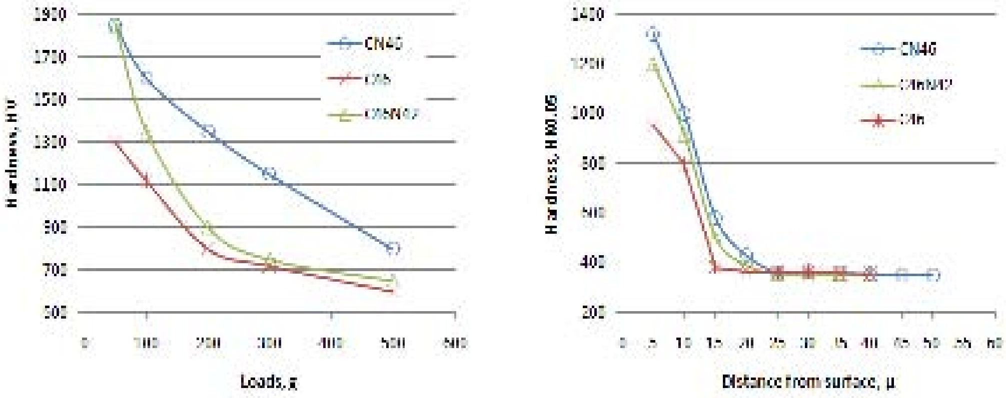


Figure 2. Surface layer thickness and hardness of treated samples.

The load bearing capacity and hardness depth profiles for carburised C46, hybrid CN46 and duplex C46N42 samples are compared in Figure 3. It can be seen that the order of the load bearing capacity and the hardened layer thickness from higher to lower follows hybrid, duplex and single treatment, i.e. CN46>C46N42>C460, for the group. This further confirms that the hybrid treatment can promote the diffusion of the alloying elements carbon and nitrogen, resulting a thicker and harder surface layer than that produced by duplex and single element treatments under similar treatment temperature and time.



a b

Figure 3. Load bearing capacity, a) and hardness depth profiles, b) for C46, hybrid CN46 and duplex C46N42 samples.

Chemical Composition

GDS analysis of alloying elements on treated sample surfaces revealed two types of depth profiles as show in Figure 4. For plasma treatment with single element at different temperatures, carbon or nitrogen can be introduced into the surface to the range of 3-6 wt% and the depth profiles presented typical diffusion curves. The surface content of nitrogen is double that of carbon but the later can diffuse much deeper than the former (Figure 4a) under the same treatment conditions. The second kind of carbon and nitrogen depth profiles is shown in Figure 4b. It can be seen that regardless of the treatment methods, hybrid or duplex, the alloying element of nitrogen always distributed at the outer surface and carbon distributed in the inner layer. However, the hybrid treatment introduced more nitrogen than duplex treatment did (Figure 4b).

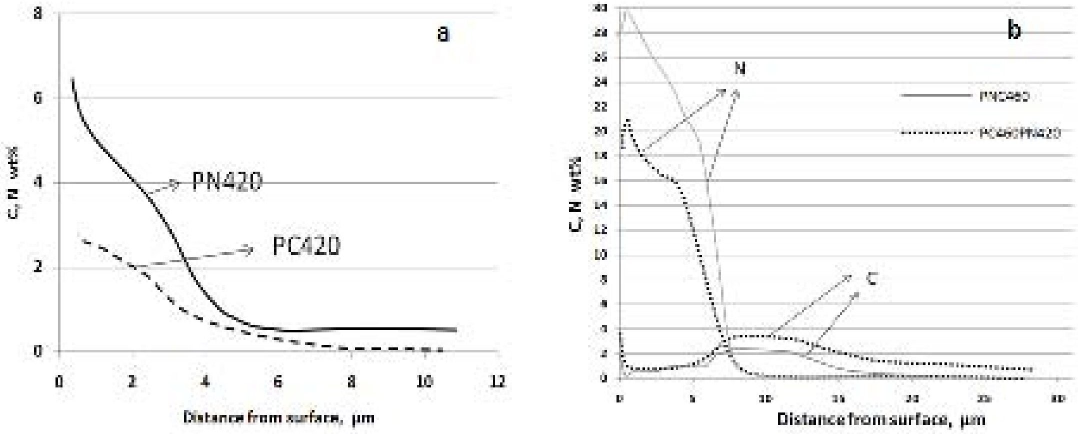


Figure 4 Typical GDS depth profiles of carbon and nitrogen, a)plasma alloying with single element, b) both carbon and nitrogen introduced into sample surfaces

Phase Composition

XRD diffractions from surface alloyed layers show three different patterns for samples treated using different treatment parameters. For samples treated at 420°C with the single alloying element, carbon or nitrogen, the X-ray pattern composed of strong S_C or S_N phase peaks and weak carbon or nitrogen expanded ferrite, α_C or α_N, peaks (see C42 sample in Figure 5 as an example). XRD patterns for samples plasma carburized at 460°C and 520°C show carbides of $Cr_{23}C_6$ + Cr_7C_3 and S_c-phase peaks, as can be seen in Figure 5 for sample C46 and C52. The higher intensity of the carbides peaks for C52 sample than for C46 implies that more carbide precipitated at 520°C than at 460°C. XRD patterns from hybrid (e.g. CN46 in Figure 5) and duplex (e.g. C52N42 in Figure 5) treated samples showed a very different phase composition: strong C/N or C+N expanded ferrite peaks (α_N,α_C or α_{C+N}), ε-M_3(C,N), (M=Fe, Cr) and weak $S_{C,N}$ peaks. CrN peaks superimposed with other peaks, which may be also present in the layer. Clearly, it is difficult, if not impossible, to conclusively identify the phases formed during the plasma alloying of duplex stainless steels in particular for hybrid and duplex treated samples.[8]

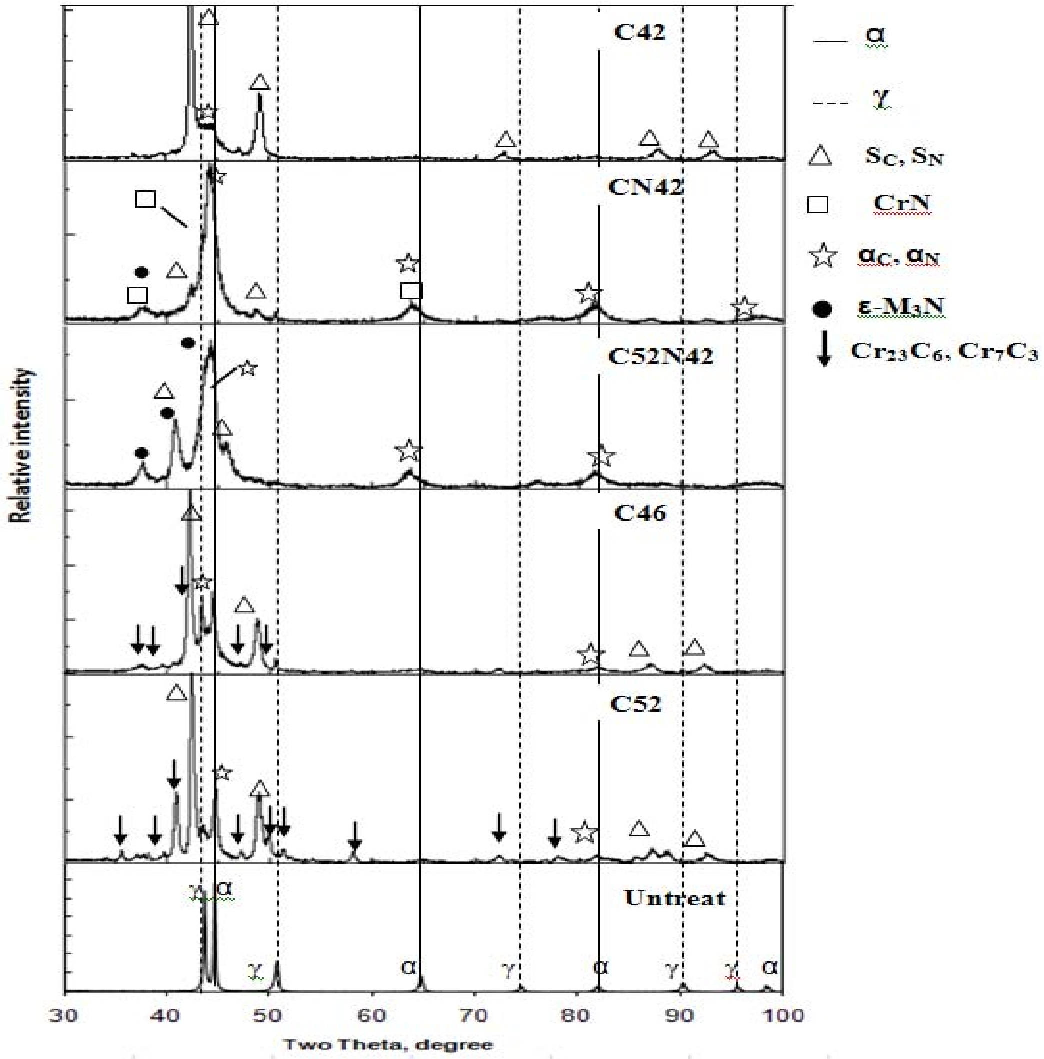


Figure 5. XRD patterns for surface treated samples.

To this end, preliminary TEM work has been conducted on two samples, N42 and C46, to further characterise the microstructures produced. It has been found that two phases of N/C supersaturated FCC austenite (i.e. S_N/S_C-phase) and BCC ferrite (i.e. α_N/α_c) presented in the surface layers, as evidence in Figure 6 for sample N42 and C46. It is evident that the original ferrite was retained rather than fully converted into austenite as claimed by some researchers.[5,9] Further study is undertaking to quantitatively characterise the response of ferrite to carbon and nitrogen during plasma alloying treatments.

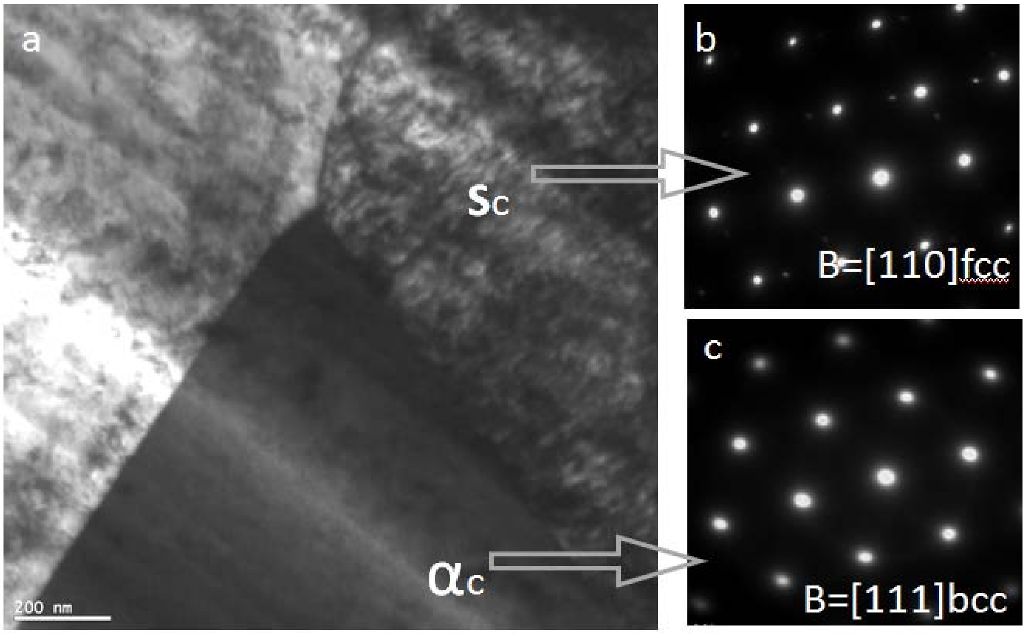


Figure 6. Cross-section TEM microstructure and corresponding SAD patterns of sample C46, showing carbon supersaturated a) austenite, or Sc-phase, and b) ferrite, or α_c within surface hardened.

Corrosion Resistance

Electrochemical polarisation curves were measured for treated samples as well as the untreated samples for comparison, and some typical curves are shown in Figure 7. It was found that all single element (C or N) treated samples showed reduced corrosion resistance in 3.5 wt% NaCl solution compared with the untreated sample. The order of the deterioration in corrosion resistance from the worst is C52, C46, N42 and C42 and some examples are shown in Figure 7a). Similar observation was reported by Blawert[10] for nitrogen PI^3 treated DSS samples. It was found the corrosion resistance of 400 and 500°C treated samples were poorer than the untreated one in electrochemical polarization tests in 0.5M H_2SO_4 solution.

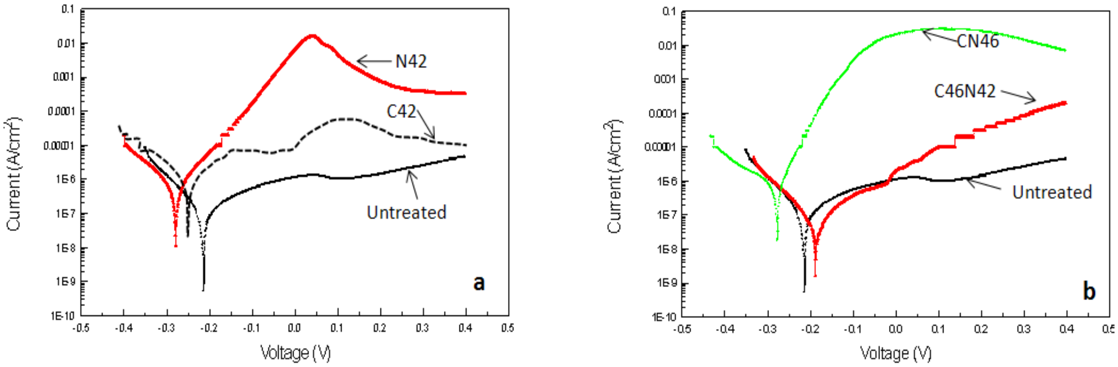


Figure 7. Anodic polarisation curves for 420°C single element treated a) and both C and N treated samples in 3.5% NaCl, untreated sample used as comparison.

The observed poor corrosion resistance of the medium (460°C) and high (520°C) temperature carburised C46 and C52 could be related to the formation of chromium carbides as evidenced in Figure 5. It is understandable for the samples with chromium carbide precipitation that the corrosion resistance was impaired because of the chromium depletion regions in the matrix around the precipitates, where acted as sites for preferential attack.[11] This is also supported by slightly better corrosion behaviour of the low-temperature carburised C42 sample relative to that of medium-to-high temperature carburised C46 and C52 samples. However, the corrosion resistance was still inferior to that of the untreated materials (Figure 7a) although no peaks of such chromium carbides were detected from C42 sample. This could be attributed to the two-phase microstructure of ferrite/S-phase, in which the S-phase possessed a much better corrosion resistance than the ferrite phase.

For the hybrid and duplex treated samples, which were alloyed with both nitrogen and carbon, significant decrease in corrosion resistance was also observed except for C46N42 duplex treated sample (Figure 7b). Again, higher temperature treated samples revealed poorer corrosion resistance than the lower temperature treated ones. It is of interest that sample C46N42 showed similar corrosion resistance to the untreated sample below minus voltage although the mechanism is not clear.

CONCLUSIONS

Systematic plasma surface alloying of UNS31803 duplex stainless steel with both carbon and nitrogen simultaneously (hybrid) or sequentially (duplex) was investigated. Based on the experimental results, the following conclusions can be drawn from this research.

- UNS31803 duplex stainless street can be significantly hardened by plasma surface alloying with carbon (carburising), nitrogen (nitriding), and both carbon and nitrogen simultaneously (hybrid carbonitriding) or sequentially (duplex alloying).
- Both the thickness and the hardness of the surface layers increase with the treatment temperature for carburised, hybrid carbonitrided and duplex alloyed samples.
- When treated at 420°C for 20h, hybrid carbonitriding can produce a thicker surface layer than that produced by single carburising or nitriding.
- Except for 420°C/20h nitrided sample, all the plasma surface alloyed surfaces show a mixed microstructure with black and white grains. A dual layer structure was formed during 520◦C/20h hybrid carbonitriding treatment.
- Both XRD and TEM studies reveal that the original ferrite cannot be fully converted into S-phase during plasma surface alloying with carbon, nitrogen, or both carbon and nitrogen.
- All these surface alloying processes, carburising, nitriding, hybrid carbonitriding or duplex alloying, will more or less reduce the corrosion resistance of UNS31803 duplex stainless street.

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