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Augmentation of crevice corrosion resistance of medical grade 316LVM stainless steel by plasma carburising

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ABSTRACT

Precipitate free carbon S-phase was produced on the surface of AISI 316LVM medical grade austenitic stainless steel with the use of low temperature direct current and active screen plasma carburising. The treated and untreated alloy was characterised and tested for pitting and crevice corrosion resistance. From this work it can be concluded that when compared to the untreated material, both treatments augment the pitting and crevice corrosion resistance. Using an active screen set-up results in a better surface composition and a higher crevice corrosion resistance than that produced using the direct current plasma carburising treatment.

1. Introduction

Austenitic stainless steels, such as AISI 316LVM (ASTM F138), are widely used in medical applications where biocompatibility and corrosion resistance are of utmost importance [1]. Currently the 316LVM alloy is mostly used for temporary implants which are designated to last 6–12 months in an intrahuman environment [2]. These temporary implants are generally bone plates and are locked in place using screws. Some austenitic stainless steel implants, such as hip joint replacement stems and intramedullary rods, are also implanted for up to 10 years. In such environments stainless steel suffers from crevice and pitting corrosion which can cause the implant to fail prematurely [2,3].

In the case of bone plates and screws, crevice corrosion can occur at the interface between the tightly contacted bone plate and the screw on the countersink. Corrosion results in ion release which, when enhanced by mechanical processes such as wear, cause the formation of debris allowing the prosthesis to grow loose and inevitably cause problems. Williams stated that "*The success of any implant is dependent on its bulk and surface properties, the site of implantation, tissue trauma during the surgery and motion at the implant/tissue interface*" [2]. Hence modifying the surface properties of austenitic stainless steel by enhancing their corrosion and wear resistance properties would in turn lead to an increased range of applications where they would be able to substitute the other more expensive alloys.

Surface engineering of austenitic stainless steel by the creation of a precipitate free carbon supersaturated layer called S-phase has improved both the pitting corrosion resistance [4–9] and tribological properties of these alloys [10,11]. A number of techniques can be used to form this layer three of them being: gas [5,7,9], direct current (DC) [1,10] and active screen low temperature plasma surface carburising [10,12–14].

In direct current plasma carburising a carbon bearing gas such as methane is introduced in a chamber and a voltage is applied between the chamber wall (anode) and the work table (cathode). Active screen plasma carburising uses of a cathodic cage also know as a screen, which surrounds the work to be treated. The cage is constructed of a mesh which is subject to a highly cathodic potential and on which plasma is formed. In this case the work table is given a bias, which is a fraction of the potential used to generate the plasma [10,12,13].

Direct current plasma treatments present a number of surface defects and process instabilities such as surface arcing, hollow cathode and edge effects. Active screen low temperature plasma surface alloying is advantageous in so much as many of the defects generated by direct current treatments are minimised or completely eliminated by its application. Its use also results in improved treatment temperature control, material properties and surface quality [12]. Although the effectiveness of the active screen plasma surface treatment is evident, limited work has been

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conducted to compare the corrosion properties of direct current and active-screen treated austenitic stainless steels.

Extensive research on S-phase surface engineering of austenitic stainless steel have shown many promising results in terms of effectively improved biocompatibility [1,10], fatigue [10], wear-corrosion [10], fretting-wear [10] and localised corrosion properties [4,10]. These very promising results could pave the way towards long-life, high-performance medical devices [10].

The research work which is related to the localised corrosion resistance of low temperature carburised industrial grade stainless steel in chloride containing environments was carried out by the following authors: Martin et al. [5,9], Heuer et al. [7,8], Sun [6] and García Molleja et al. [15].

In his work Sun [6] concludes that in order to augment the localised corrosion resistance carbon S-phase must have a critical carbon concentration of about 0.25 wt.%. García Molleja et al. [15] carburise an AISI 316L alloy and perform immersion tests in a 5.85 wt.% NaCl solution. Contrary to other findings they report that the carbon S-phase layer had a reduced corrosion resistance when compared to the untreated material. In the works by Martin et al. [5,9] and Heuer et al. [7,8] the enhanced localised corrosion resistance in both 0.6 M NaCl and sea water of carbon S-phase has been reported. Heuer et al. [7,8] challenges the widely accepted theory given by Jargelius-Pettersson [16] by proposing a chemo-mechanical model of passive film breakdown in order to credit carbon or nitrogen interstitials for this enhanced resistance to localised corrosion. While the theory given by Jargelius-Pettersson [16] can only explain the benefits of nitrogen; on the other hand, the model by Heuer et al. [7,8] includes the beneficial effects of both nitrogen and carbon.

Crevice corrosion work on untreated austenitic stainless steel has been researched extensively [17] but the same testing on S-phase treated stainless steel has not been performed. In fact the only reference to crevice corrosion testing of low temperature carburised alloys is related to a Ni-base super alloy rather than stainless steel [18]. Some work has been conducted in the investigation of the hardness and localised corrosion resistance of low temperature plasma surface alloyed biomedical austenitic stainless steels [4,10]. However, most of this work is applied only to the nitrogen S-phase and the crevice corrosion resistance of the S-phase layer created by active screen technology on biomedical stainless steels has never been explored [10].

This study attempts to fill this gap by investigating the pitting and crevice corrosion resistance of untreated and carburised 316LVM stainless steel. The carburising treatments used in this study use the well documented direct current carburising treatment [1,10] and the new active screen carburising treatment [10,12–14].

2. Materials and methods

2.1. Material and surface treatments

The material used in this study was an ASTM F138 (Sandvik Bioline 316LVM) austenitic stainless steel which was supplied in the form of an annealed bar of 25 mm in diameter. Its composition can be found in Table 1.

Coupon samples of 6 mm in thickness were cut from the bar and one of the flat surfaces was wet ground using silicon carbide paper from 120 down to 1200 grit. Prior to plasma surface alloying treatments, samples were ultrasonically cleaned in acetone and dried with hot air.

Low temperature plasma surface alloying with carbon (carburising) was carried out using a DC 40 kW Klöckner Ionon and a 75 kW Plasma Metal Active Screen plasma furnace. The treatments will be referred to as direct current plasma carburising (DCPC) for the former and active screen plasma carburising (ASPC) for the latter.

The coupons were treated in a specially designed sample holder made from a 13 mm thick disc that has a diameter of 200 mm. A thermocouple sheath was radially inserted into the side of the holder. The samples, 25 in total, were placed in recesses machined in the sample holder with their upper surface flush to its surface. Thus the specimens and holder presented a uniform surface with just one edge (the holder circumference) on which the edge effect could occur, and a continuous bulk which allowed a uniform temperature to be attained.

Surface treatment conditions and the codes for the samples are given in Table 2. The chosen treatment parameters were based on previous work for producing precipitate free S phase layers on the AISI 316 alloy by DCPC [1] and ASPC [12]. Following the surface treatments, all treated and untreated samples were polished due to the presence of a back-deposited superficial layer as explained in Ref. [19]. Transmission electron microscope observation in our previous work [19] revealed that this back deposited layer consisted of extremely fine equiaxed grains with a diameter of 5–10 nm and with a thickness of 50 nm. Its structure can be assigned to an fcc structured M(N,C) where M = Fe, Cr, Ni, Mo and Mn. Polishing was conducted on a Streurs LaboPol-5 automatic polisher using 6 μm diamond paste with a medium force (mark 3) for 3 min. This was followed by a final polishing at a low force (mark 1) using 1 μm diamond paste for another 3 min. In order to gauge the thickness of material removed a 5 μm GDOES hole was sputtered, measured with a profilometer and then the sample was polished until the mark was no longer visible. Using this polishing technique for all the samples, made sure that less than 5 μm of the layer was removed and the surface finish (Ra) of all the polished samples was between 0.06 and 0.10 μm.

2.2. Characterisation

Standard procedures were followed to prepare metallographic specimens to be examined under a Nikon OPTIPHOT-100 optical microscope. This included cross-sectioning normal to the surface, mounting in phenolic resin, wet grinding with silicon carbide paper, polishing and etching in a solution containing 50 ml of HCl (39% conc.), 25 ml of HNO_3 (69% conc.) and 25 ml of distilled water [20].

Composition depth-profile analysis was carried out using a LECO GDS-750 QDP Glow Discharge Optical Emission Spectroscopy (GDOES). This equipment was calibrated for all the alloying elements found in stainless steel with special attention to carbon.

The surface hardness of the samples was measured using a Mitutoyo MVKH2 micro-hardness tester with a Vickers indenter. A constant load of 0.05 kgf was used, with 10 repeats for each measurement.

Table 1
Composition of the 316LVM material, wt.%.

Material	Composition											
	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	N	Nb	Fe
ASTM F138	0.019	0.5	1.87	0.018	0.001	17.43	13.75	2.72	0.06	0.08	–	Bal.