

A COMPARISON OF THE CORROSION RESISTANCE OF DIN W. NR. 1.4460 HIGH NITROGEN AND F-138 STAINLESS STEELS FOR BIOMEDICAL APPLICATIONS

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ABSTRACT

The ASTM F-138 stainless steel (SS) is widely used for several biomedical applications, including both temporary and permanent implants. The presence of delta-ferrite in SS implants is known to produce adverse interactions between magnetic fields and the implant material because they may lead to magnetic resonance if the patient is undergoing an MRI test. The DIN W Nr 1.4460 SS high N does not form any ferromagnetic phases, like delta-ferrite or martensite, and due to this property it can be considered as a potential material for biomedical applications. However, the corrosion resistance of this steel has not yet been evaluated with this purpose of use. In this work, the resistance of localised corrosion of 1.4460 high N SS was investigated by electrochemical methods, including potentiodynamic polarization and electrochemical impedance spectroscopy measurements in a phosphate-buffered solution. The F-138 SS was also tested in the same solution for comparison reasons.

Keywords: Biomaterials, DIN W. Nr. 14460 high N, ASTM F-138, corrosion

INTRODUCTION

Some metallic materials are suitable for body implants because they combine good mechanical properties in static and dynamic conditions with an inert behaviour. However, their most important characteristic must be a high corrosion resistance. Milosev and Strehblow ⁽¹⁾ studied the corrosion behaviour of stainless steels in a physiological solution and concluded that the presence of chromium and molybdenum in the passive layer, associated with the depletion of iron in the metallic surface under the passive layer account for the corrosion resistance of stainless steels orthopedic implants. The electrochemical behaviour of ASTM F-138 in physiological solutions is widely reported in literature ⁽²⁻⁴⁾. Also, the susceptibility of this steel to localized attack, as a consequence of the salts present in these solutions ⁽⁵⁻⁷⁾. Corrosion may result in toxic corrosion products and these may cause infectious or allergenic responses which in turn may cause premature implant failure. Despite of these shortcomings, stainless steel implants are still currently used due to a combination of mechanical strength and easy fabrication at low cost.

Among the stainless steels, the ASTM F-138 has been extensively used for biomedical applications, including both temporary and permanent implants. The presence of delta-ferrite or other ferromagnetic phases in stainless steel implants is known to produce adverse interactions between magnetic fields and the prosthesis. These interactions may lead to magnetic resonance if the patient is undergoing a magnetic resonance imaging (MRI) test ⁽⁸⁾.

In this study, the corrosion resistance of a 25Cr-5.5Ni-2Mo (wt%) SS, which originally had a ferritic-austenitic duplex microstructure (DIN W. Nr. 1.4460), and to which 0.87% (in mass) nitrogen was added to become fully austenitic, ⁽⁹⁾ was investigated in a phosphate-buffered solution (PBS) naturally aerated and at 25 °C. The aim of this investigation was to evaluate the potential of this material for applications as biomaterials. The results of this steel were compared to those of the ASTM F-138 steel, which is employed as implant materials.⁽⁸⁾ The techniques used in this study to characterize the electrochemical behaviour of both materials were electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization.

EXPERIMENTAL

The chemical compositions of the steels investigated in this study are shown in Tab. 1. The ATSM F-138 samples were tested in solubilized condition, and the high N DIN W. Nr. 1.4460, as-received. All specimens were ground with silicon carbide paper up to #600, and then washed with deionized water, degreased with acetone and immersed in the PBS solution at room temperature for 24 hours, prior to carrying out the electrochemical measurements. The composition of the PBS solution is given in Tab. 2.

Table 1 - Chemical compositions of F-138 and DIN W. Nr. 1.4460 high N stainless steels (% mass).

Steel	C	Cr	Ni	Mo	Si	Mn	Others	Fe
F-138	0.007	17.40	13.50	2.12	0.37	1.78	-	Balance
1.4460 high N	0.03	25.10	5.50	1.90	1.50	1.20	N=0,87	Balance

Table 2 - Composition of PBS solution

Compound	g L ⁻¹
NaCl	8.77
Na ₂ HPO ₄	1.42
KH ₂ PO ₄	2.72

The corrosion tests were performed using a three electrode-cell set-up, with a platinum wire and a saturated calomel electrode (SCE) as counter and reference electrodes, respectively. Electrochemical impedance spectroscopy (EIS) measurements were taken with a 1255 Solartron frequency response analyzer coupled to an EG&G 273A potentiostat. All EIS data were performed in potentiostatic mode at the open-circuit potential. The amplitude of the perturbation signal was 10 mV and the investigated frequency range varied from 100 kHz to 10 mHz with an acquisition rate of 6 points per decade.

Potentiodynamic polarization was performed with a scan rate of 1 mV.s⁻¹ from -800mV_{SCE} until a current density of 10⁻³ A/cm². The passive and corrosion current

densities were determined for both SS, ASTM F-138 and high N DIN W. Nr. 1.4460. The samples' surface was observed after the electrochemical tests using a scanning electron microscope Philips XL30.

RESULTS AND DISCUSSION

The EIS results are shown in Figs. 1 and 2 as Bode phase angle and Nyquist diagrams for ASTM F-138 and high N DIN W. Nr. 1.4460 stainless steels in PBS solution at 25°C. The high N DIN W. Nr. 1.4460 presented a highly capacitive behaviour in the investigated frequency range, with phase angles close to -80° , and higher impedance values than the F-138 SS, indicating that the oxide layer is very protective affording good corrosion protection to the underlying metal. The Bode phase angle diagrams depressed at low frequencies for both steels suggest two time constants.

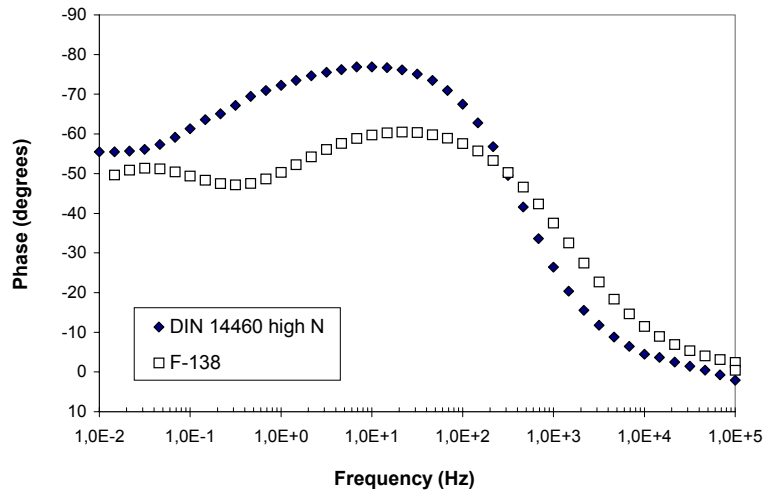


Figure 1: Bode phase angle diagrams for ASTM F-138 and DIN W. Nr. 1.4460 high N after 24 h of immersion in PBS solution.

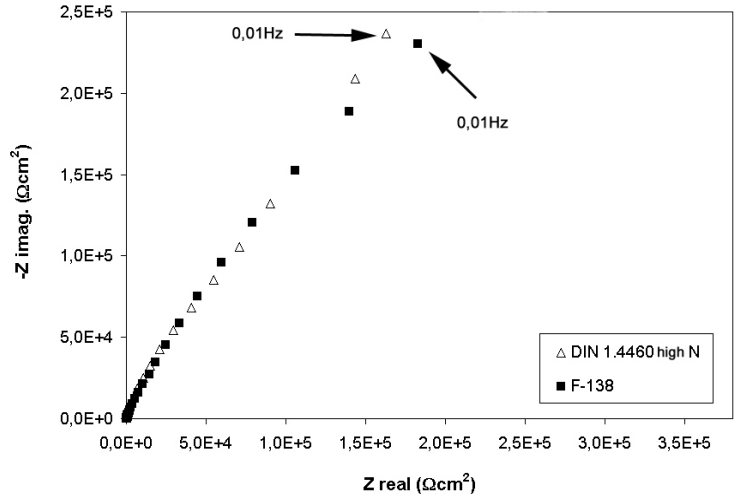


Figure 2: Nyquist diagrams for ASTM F-138 and high N DIN W. Nr. 1.4460 after 24 h of immersion in PBS solution.

The potentiodynamic polarization curves for both tested steels in PBS solution are shown in Fig. 3. Very low corrosion current densities (around 10^{-6} and 10^{-5} A.cm⁻²), typical of passive metals, were obtained for both steels at the corrosion potential. The results suggest that both steels tested present susceptibility to localized corrosion. However, the breakdown potential of the F-138 is lower than that of the high N DIN 1.4460 SS (around 100mV/ECS and 700mV/ECS, respectively).

The results of electrochemical impedance spectroscopy and potentiodynamic polarization curves indicated that both steels are susceptible to localized attack in the test medium used; however, higher localized corrosion resistance was related to the high N DIN W. Nr. 1.4460 SS comparatively to the ASTM F-138.

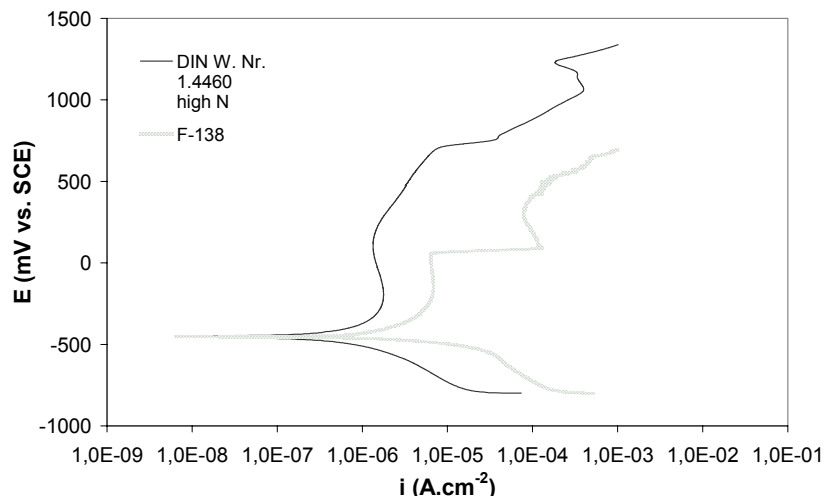


Figure 3: Potentiodynamic polarization curves for F-138 and high N DIN 1.4460 SS after 24 h of immersion in PBS solution at 25°C.

Micrographs of ASTM F-138 and high N DIN W. Nr. 1.4460 specimens after potentiodynamic polarization test in PBS solution at 25°C are shown in Figs. 4 and 5. As stated in the interpretation of the potentiodynamic data, the susceptibility of both materials to localized attack is confirmed by the SEM micrographs. Pits are present on both steels' surfaces, being easily seen on the ASTM F-138 SS but not on the high N DIN 1.4460 SS to their very small size. Fig. 5 also reveals the presence of a large number of precipitates on this last steel, and that corrosion initiation occurred at the interface precipitate/matrix; some of the precipitates being removed from the sample. EDS analysis confirmed that these precipitates are rich in chromium and, according to the literature, they are chromium nitrides.⁽¹²⁾ Despite of the large amount of precipitates shown in Fig. 5a, the corrosion resistance of the high N DIN 1.4460 steel was still slightly higher than that for the ASTM F-138. These findings support the electrochemical results obtained from EIS and polarization data that indicated the more protective character of the oxide layer on the surface of the high N DIN W. Nr. 1.4460 SS comparatively to ASTM F-138.

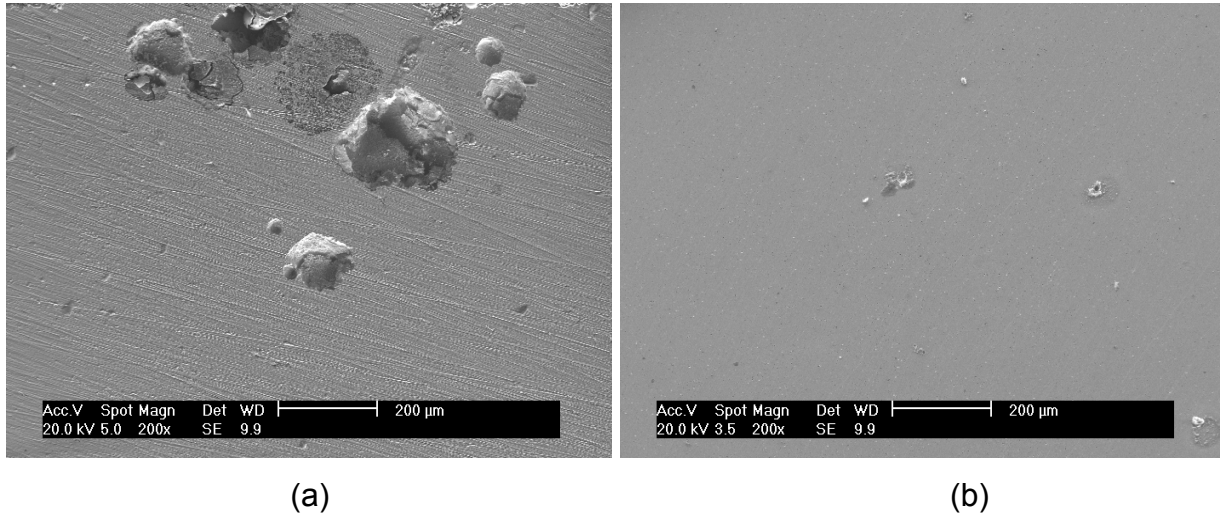


Figure 4: SEM micrographs of a) ASTM F-138 and b) high N DIN W. Nr. 1.4460 stainless steels after polarization test in PBS solution.

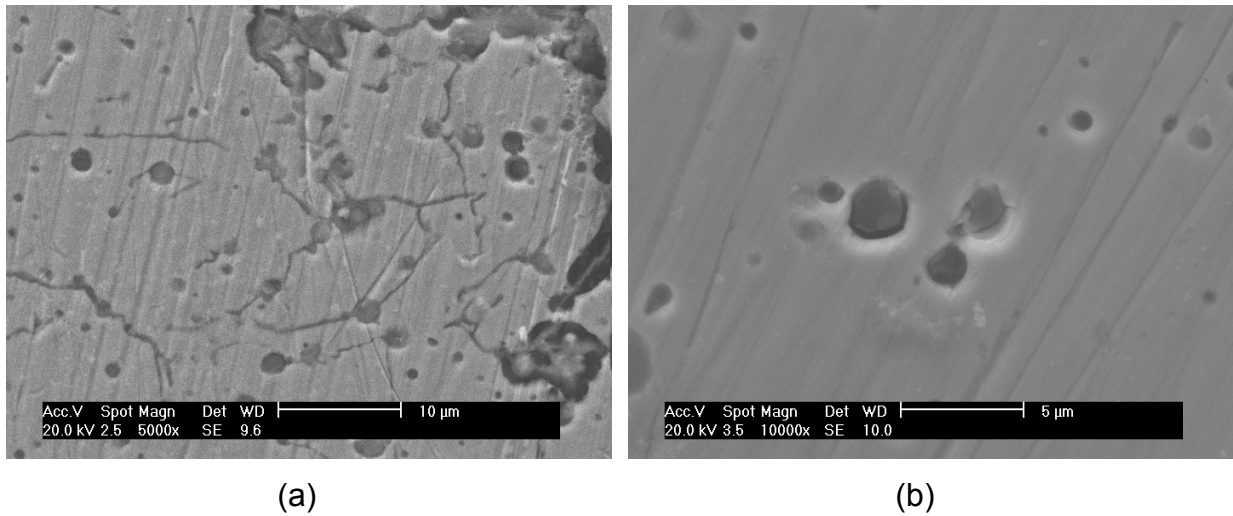


Figure 5: SEM micrographs of the high N DIN W. Nr. 1.4460 stainless steel after polarization test in PBS solution. Showing localized attack at the precipitate/matrix interface. (a) Large amount of precipitates. (b) Localized attack at the interface.

CONCLUSIONS

The corrosion resistance of the high N DIN W. Nr. 1.4460 is higher than that of the ASTM F-138 as indicated by electrochemical impedance spectroscopy and potentiodynamic polarization results. Both steels are prone to localized attack but a

smaller number of pits are formed on the high N DIN W. Nr. 1.4460 comparatively to the ASTM F-138 SS. Taking only corrosion resistance of the high N DIN W. Nr. 1.4460 SS into account, it can be concluded that it is a potential candidate for use as biomaterial. Indeed, this result outlines its main attractive feature, that is, the total absence of magnetic phases.

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