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In-vitro long term and electrochemical corrosion resistance of cold deformed nitrogen containing austenitic stainless steels in simulated body fluid

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ABSTRACT

This work was focused on the evaluation of the corrosion behavior of deformed (10% and 20% cold work) and annealed (at 1050 °C for 15 min followed by water quenching) Ni-free high nitrogen austenitic stainless steels (HNSs) in simulated body fluid at 37 °C using weight loss method (long term), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization. Scanning electron microscopy (SEM) was used to understand the surface morphology of the alloys after polarization test. It has been observed that cold working had a significant influence on the corrosion resistant properties of these alloys. The weight loss and corrosion rates were observed to decrease with increasing degree of cold working and nitrogen content in the alloy. The corrosion resistance of the material is directly related to the resistance of the passive oxide film formed on its surface which was enhanced with cold working and nitrogen content. It was also observed that corrosion current densities were decreased and corrosion potentials were shifted to more positive values. By seeing pit morphology under SEM, shallower and smaller pits were associated with HNSs and cold worked samples, indicating that corrosion resistance increases with increasing nitrogen content and degree of cold deformation. X-ray diffraction profiles of annealed as well as deformed alloys were revealed and there is no evidence for formation of martensite or any other secondary phases.

1. Introduction

Stainless steels (e.g. AISI 316L), cobalt-based alloys, pure titanium (CP-Ti) and Ti–6Al–4V alloy are the most extensively used metallic biomaterials. There is growing attention in Ti and its alloys, particularly as dental and orthopedic implants because of their relatively lower modulus of elasticity, superior biocompatibility and higher corrosion resistance [1]. 316L grade of austenitic stainless steel (SS), however, is still a broadly used material for internal fixation devices like fracture plates, screws, hip nail and artificial joints because of their good mechanical properties, corrosion resistance, easy processing, acceptable biocompatibility and very low cost as compared with those of other metallic implant materials [2,3]. These conventional SSs contain nickel (12.0–15.0%) which causes negative reactions in the body at normal physiological conditions [4]. Therefore, the austenitic stabilizing property of nitrogen allows the nickel content in steel to be reduced practically to zero, offering additional advantages such as lower production costs, higher strength, higher corrosion resistance and also excellent biocompatibility. Up to now, all *in-vivo* and *in-vitro* studies strongly suggested that HNSs would be a class of promising biomaterials for clinical applications [5–8].

Pitting corrosion is one of the most severe types of localized attack on SSs, which can limit their applications in the bio-system. Pitting corrosion can adversely affect both biocompatibility and mechanical strength of the implant [9]. The pitting corrosion resistance of SS is significantly affected by metallurgical parameters [10–12] like, cold working, alloy composition, inclusions, heat treatment, grain size, sensitization, and secondary precipitates. SSs are exposed to different levels of cold work during the final manufacturing stages of components for orthopedic applications. Cold work might affect the pitting corrosion resistance of SSs because deformed substructures like planar dislocation arrays [13,14] and deformation twinning [15] could be introduced. It was predicted that on cold working strain-induced martensite and residual stresses are significantly introduced on the surface, which affects the localized corrosion resistance by increasing the number of active anodic sites on the surface [16,17]. Barbucci et al. [18] reported that the passive currents of 304 SS in sulfate + chloride solutions significantly increased with the degree of cold work. In addition, the pitting corrosion resistance was observed to decrease with increasing cold work in a 3.5% NaCl solution [19]. The susceptibility of cold worked 18Cr–10Ni–2Mo steel to pitting corrosion in a NaCl solution was

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Table 1
Composition of stainless steels (wt.%).

Sample	C	Cr	Mn	Ni	Si	Mo	S	P	N	Fe
316LVM	0.02	17.24	1.68	14.42	0.24	2.83	0.004	0.007	0.07	Bal.
$316MnN_1$	0.48	19.32	12.77	0.05	0.26	3.32	0.006	0.009	0.34	Bal.
$316MnN_2$	0.08	19.11	11.85	0.08	0.25	3.02	0.004	0.010	0.43	Bal.
$316MnN_3$	0.017	18.28	11.92	0.04	0.07	3.24	0.003	0.008	0.52	Bal.

observed with the number of pits generally increasing with an increase in the deformation, except in the 15% deformation where low pit count and large average pit size were reported [10]. Forchhammer and Engell [20] studied the effect of cold work on the pitting potential of different austenitic SSs; 18Cr–10Ni, 25Cr–10Ni, 17Cr–10Ni–2.4Mo and 16Cr–14Ni–Mo. They found that in a 30% NaCl solution pitting potential was not greatly affected by cold work, but for the cold worked specimens the number of pits was higher and the pits were smaller. According to Randak and Trautes [17], the quasimartensite produced in 18Cr–8Ni steels by cold working does not change the pitting potential value in chloride solutions, but they have also observed increasing pit density with increasing cold work level. Kamachi Mudali et al. [21] have reported that pitting and crevice corrosion resistances of ferritic SSs were not affected by cold working up to 20% in a 0.5 M NaCl solution irrespective of the defect structure containing deformation bands.

The aspect of cold working has not been yet related clearly to the influence on the corrosion resistance of HNSs in simulated body fluid (SBF) especially for long term applications. In the present work, an attempt was made to study the effect of cold working on the long term and electrochemical corrosion resistance of HNSs with different nitrogen contents in SBF. The SBF used in this study was Hank's solution. Usually SS which is used for biomedical applications contains low carbon ($\leq$0.03%). But some newly developed high nitrogen medical grade SSs also contain carbon. For example P558 alloy contains about 0.20 wt.% carbon and F2581 contains 0.15–0.25 wt.% carbon [22,23]. To analyze the effect of carbon having nitrogen in the alloy on corrosion behavior, one alloy which contains high nitrogen (0.34 wt.%) as well as carbon (0.48 wt.%) was also selected for the present study. The results were compared with conventionally used 316LVM. The techniques used in this study for the characterization of the corrosion resistance were weight loss method, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization. Structural evolution of passive films was also discussed with the help of EIS. Finally, scanning electron microscopy (SEM) was used to understand the surface morphology of the alloys after polarization test. Optical microscopy was employed to study the microstructural changes produced after cold working. X-ray diffraction (XRD) and macrohardness measurements of the samples were also carried out.

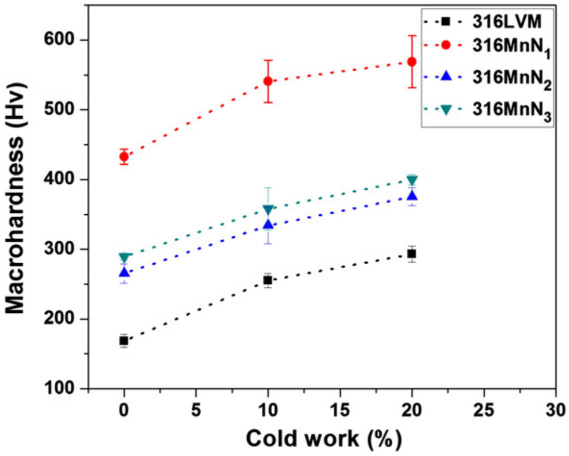

Fig. 2. Macrohardness values of alloys against cold working levels.

2. Experimental

2.1. Materials

Three HNSs ($316MnN_1$, $316MnN_2$ and $316MnN_3$,) with different nitrogen contents were prepared in the form of ingots respectively by melting Armco iron and ferro alloys (Cr, Mo, Mn, high nitrogen ferrochrome etc.) in appropriate proportions to meet the aimed composition of alloy in an induction furnace. These ingots were solutionized at 1050–1070 °C to avoid segregation. Then samples as slices of 80 × 20 × 6 mm were cut from ingot, hot-rolled at 1050 °C to reduce thickness by 50–80%, the solution treated at 1050–1070 °C for 15 min, and then water quenched respectively. 316LVM SS was obtained from Mishra Dhatu Nigam Ltd. (MIDHANI), Hyderabad, India. This steel was received in hot rolled & annealed condition and used for study in similar condition. The chemical compositions of all four austenitic SSs are shown in Table 1.

2.2. Cold working and microstructural observation

The annealed specimens of 80 × 12 × 2 mm were cut and cold rolled to 10% and 20% reductions in thickness values. Specimens of 10 mm × 10 mm size were cut from them and abraded successively with emery papers 600–800–1000–1200 grades. The surface was then mirror polished using alumina of 0.3 μm and etched in aquaregia until grain boundaries were revealed for observing the changes in the microstructure due to cold working. To identify the phases present after cold working, XRD of the annealed and cold worked (c.w.) samples were carried out using a Rigaku Miniflex II X-ray diffractometer. The macrohardness

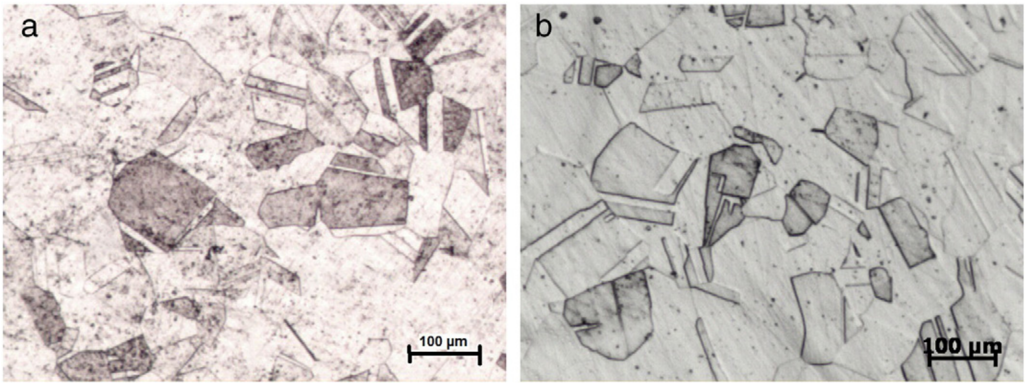

Fig. 1. Optical micrographs of 316LVM showing an austenitic microstructure. (a) 0% c.w. (b) 20% c.w.