http://dx.doi.org/10.5935/0103-5053.20140105

J. Braz. Chem. Soc., Vol. 25, No. 7, 1270-1274, 2014.
Printed in Brazil - ©2014 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Influence of Cold Deformation on Pitting Corrosion Resistance of ISO NBR 5832-1 Austenitic Stainless Steel Used for Orthopedic Implants

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O objetivo deste trabalho é avaliar o efeito da deformação a frio nas propriedades eletrônicas do filme passivo sobre o aço inoxidável austenítico ISO NBR 5832-1 e sua resistência à corrosão por pite. O aço testado foi laminado a frio até ocorrer a redução de espessura do mesmo para 50% da sua espessura inicial. As propriedades eletrônicas do filme passivo sobre este material foram avaliadas e comparadas com a do mesmo material como recebido, ou seja, sem deformação a frio. As propriedades eletrônicas do filme passivo foram caracterizadas pelo método de Mott-Schottky e a resistência à corrosão por pite, por curvas de polarização. O efeito da frequência adotada na análise de Mott-Schottky foi também investigado. Os resultados mostraram que o material deformado apresentou maior concentração de dopantes e maior suscetibilidade à corrosão por pite em comparação ao material sem deformação.

The aim of this work is to evaluate the effect of cold deformation on the electronic properties of the passive film on the ISO NBR 5832-1 austenitic stainless steel and its pitting resistance. The tested stainless steel was cold rolled to 50% of its initial thickness and the electronic properties of the passive film on this material were evaluated and compared with that of the same material as received, that is, without cold deformation. The electronic properties of the passive film were characterized by the Mott-Schottky approach and the pitting resistance by polarization curves. The effect of the frequency adopted in the Mott-Schottky analysis was also investigated. The results showed that the deformed material presented higher concentration of dopants, and higher pitting susceptibility compared with the material without deformation.

Keywords: austenitic stainless steel, cold deformation, pitting resistance, Mott-Schottky analysis, ISO NBR 5832-1

Introduction

Stainless steels are considered the backbone of modern industries due to the possibility of wide applications in chemical, petrochemical, offshore and power generation applications, among others.[1] Their corrosion resistance is strongly affected by their chemical composition.[2,3] Among the stainless steels, the austenitic types are considered one of the most corrosion-resistant stainless steels when exposed to aggressive environments.[4] The chromium content in the stainless steel is one of the most important factors for its corrosion resistance. Furthermore, the molybdenum content is another important aspect that contributes to the pitting corrosion resistance of the austenitic stainless steels in chloride-containing media.[5]

The influence of cold deformation on the pitting corrosion resistance, including its initiation, propagation and repassivation has also been reported.[6-8] Most studies indicated that cold deformation produces a harmful effect on the corrosion resistance of the material.[7,8] The effect of cold deformation on the higher susceptibility to pitting corrosion resistance of the material has been explained by different mechanisms.[7,9,10] The first associated it to the additional energy introduced to the material by deformation, decreasing the resistance of the material to localized corrosion.[6] A second related the increase in pitting susceptibility to the effect of cold working on the deformed material microstructure and its grain orientation (texture).[9,10]

The passive films formed on the stainless steel surface are mainly metallic oxides and these are treated like semiconductors. The conductivity properties of the passive

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film are of great importance to the protective character of the passive film against corrosion.[11] The Mott-Schottky analysis has been largely used to evaluate the concentration of donor and acceptor defects in passive films on different materials.[12-16] It shows the capacitive behavior of the charges inside the passive film.

The passive film on stainless steel is composed of a mixture of iron, nickel, chromium and molybdenum oxides, and this passive film shows semiconducting properties.[3,11,13] Consequently, its electronic properties must have an important role on the corrosion resistance of the material.[11,13] In the last decade, there has been increasing interest on the investigation of the electronic properties of passive films on stainless steel and the researches carried out led to important contributions to the understanding of the influence of this property on the corrosion resistance of stainless steels.

The aim of this work is to evaluate the effect of cold rolling on the electronic properties of the passive film formed on the ISO NBR 5832-1 austenitic stainless steel and its pitting resistance. This kind of stainless steel was studied due to its large use in Brazil for fabrication of orthopedic implants, mainly because of its fairly low price and high corrosion resistance.

Experimental

The chemical composition of the ISO NBR 5832-1 austenitic stainless steel used in this investigation is shown in Table 1.

The electrochemical tests in this study were carried out in a flat cell using a three electrode setup with an $Ag_{(s)}/AgCl_{(s)}/Cl^-_{(aq)}$ (3 mol L^{-1}) and a platinum wire as reference and counter electrodes, respectively. All potentials are referred to this reference electrode, $Ag_{(s)}/AgCl_{(s)}/Cl^-_{(aq)}$ (3 mol L^{-1}). The electrolyte used was a phosphate buffer solution (PBS) whose composition was: 58.41 g L^{-1} NaCl, 9.21 g L^{-1} Na_2HPO_4, and 17.65 g L^{-1} KH_2PO_4. All electrochemical tests were carried out in quiescent and naturally aerated PBS solutions at 37 °C.

The Mott-Schottky measurements were obtained at various frequencies (900 to 1050 Hz), using a 10 mV ac signal and a step rate of –50 mV. The measurements were carried out in the potential range from 0.7 V in the cathodic direction up to –1.5 V. Potentiodynamic polarization tests were performed at a scan rate of 1 mV s^{-1}. Polarization was carried from –20 mV relative to the open circuit potential (OCP) into the anodic direction. The direction of polarization was reversed when the current density reached nearly 10^{-3} A cm^{-2} and the polarization tested was ended when the final potential reached –150 mV. In order to investigate the reproducibility of the results, all tests were carried out at least three times at each investigated condition. The mean pitting potential (E_{pit}) was then estimated from the polarization results.

Results and Discussion

Figure 1 shows the Mott-Schottky plots for the stainless steel with cold rolling deformation corresponding to 50% of reduction in thickness and the same steel without deformation. According to equation 1, the donor density (N_D) can be estimated from the slope of the straight linear region of the 1/C *vs.* potential plot. The slope of the Mott-Schottky curve in the linear region corresponds to m in equation 1,

$$N_D = \frac{2}{q\varepsilon\varepsilon_0 m} \qquad (1)$$

where q is the charge (-1.602×10^{-19} or $+1.602 \times 10^{-19}$ C for electron or electron hole, respectively), ε is the dielectric constant (assumed as 15.6), ε_0 is the vacuum permittivity (8.854×10^{-14} F cm^{-1}).[17]

A lower concentration of p-type or n-type defects is associated with the stainless steel without deformation compared to that with 50% deformation, as indicated by the higher slopes of the positive or negative slopes associated with the material as received. These results are not supported by the literature, which indicated that deformation leads to decreased doping densities.[18] Deformation favors metal cation dissolution and, consequently, the increase in the concentration of p-type defects. As the n-type defects are created to compensate charge neutrality of the passive film, as the p-type defects increase, consequently the n-type defect concentration also increases. The Mott-Schottky plots in Figure 1 show that above the flat band potential the n-type defects show behavior typical of a parallel plate capacitor, whereas the p-type defects make ohmic contact. Therefore, for these potentials the results correspond to the n-type defects, while at potentials below the flat band potential, the results relate to the p-type defects.

Table 1. Chemical composition (wt.%) of ISO NBR 5832-1 austenitic stainless steel used in this study

Cr	Ni	Mo	Mn	S	Si	C	P	Fe
18.32	14.33	2.59	2.09	0.0003	0.378	0.023	0.026	Balance

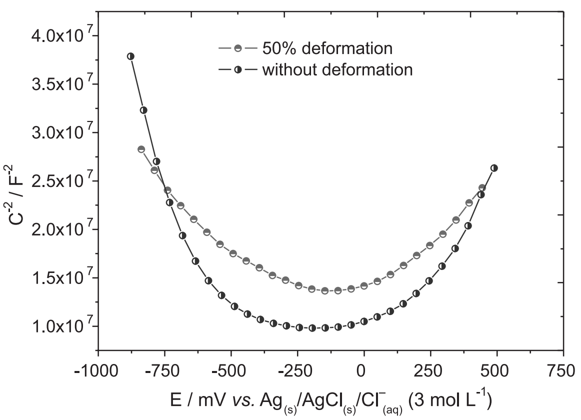

Figure 1. Mott-Schottky plots for the ISO NBR 5832-1 stainless steel, with cold deformation (thickness reduction corresponding to 50% of its original value) or without deformation (0%).

In the present investigation, an evaluation on the effect of the frequency used in the Mott-Schottky analysis on the obtained result was also carried out. Figure 2 shows the Mott-Schottky plots obtained at three frequency ranges, for the stainless steel without cold deformation (0%).

The graphs shown in Figure 2 suggest that the inclination of the curve does not vary significantly at frequencies above 900 Hz and below 100 Hz. On the other hand, at the range of frequencies corresponding to 200-500 Hz, the slope of the straight line is not constant, consequently, it is not possible to estimate the defect concentration in the passive film, since it depends on the frequency adopted in the measurements.

The Helmholtz double layer might also alter the results since this layer presents a capacitive behavior. Hakiki *et al.*[3] reported that the Helmholtz contribution is negligible at high frequencies (1-3 kHz), since in this frequency range the capacitance of the interface passive film/electrolyte represents the main contribution of the results.

Figure 3 shows the Mott-Schottky plots obtained at various frequencies for the cold rolled stainless steel with deformation corresponding to 50% reduction in thickness. It can be seen that the behavior of this material was similar to that of the material without deformation, that is, for frequencies above 900 Hz and below 100 Hz no significant changes were found in the defect concentration in the passive film. On the other hand, for frequencies in the 200-500 Hz range, the curves show large slope variation within the frequency range tested.

The values of N_D in the passive film were estimated from the Mott-Schottky results obtained at 1000 Hz and the results are shown in Table 2.

The deformed material showed higher defect concentration, either p-type or n-type, than the material without deformation (as received).

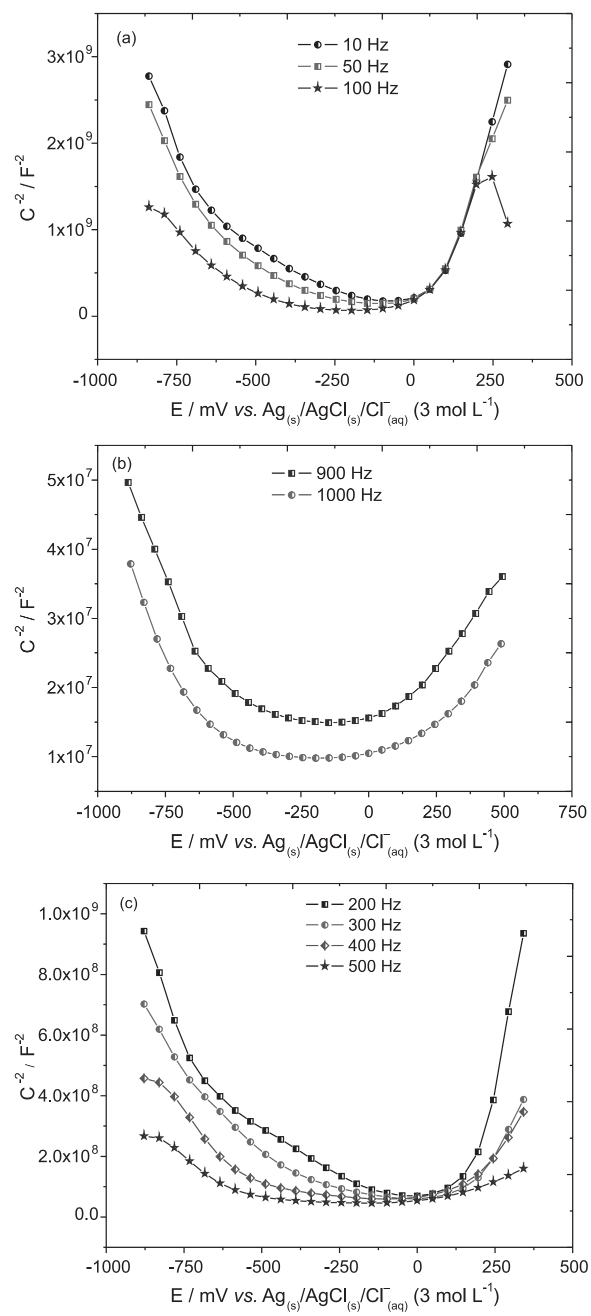

Figure 2. Mott-Schottky plots for the ISO NBR 5832-1 stainless steel as received, obtained at the frequency range: (a) 10-100 Hz; (b) 900-1000 Hz; (c) 200-500 Hz.

The pitting resistance of the stainless steel in the two conditions tested was evaluated by potentiodynamic polarization curves and the results are shown in Figure 4. It is clearly seen that the material without cold deformation presents superior pitting resistance than the cold rolled material. The pitting potential is affected by various factors, such as chemical composition of the material, electronic properties and thickness of the passive film.

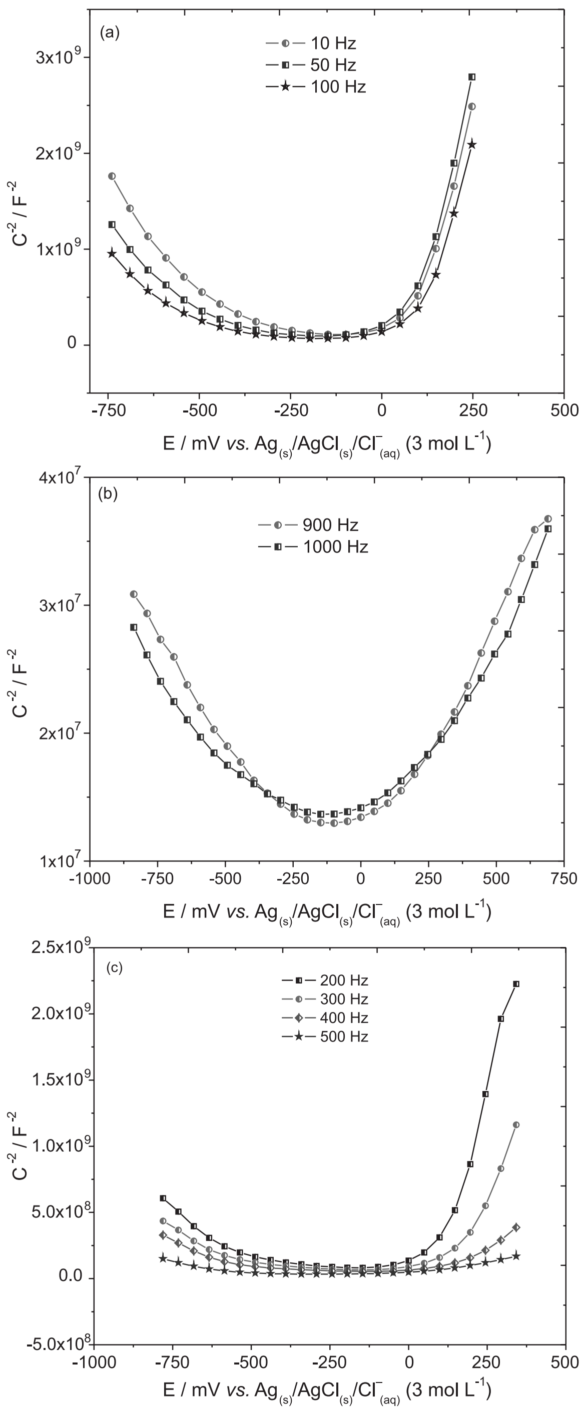

Figure 3. Mott-Schottky plots for the ISO 5832-1 austenitic stainless steel withcold deformation (50% reduction in thickness) obtained at (a) 10-100 Hz; (b) 900-1000 Hz; (c) 200-500 Hz.

Table 2. Defect concentration (ND) in the passive film of ISO NBR 5832-1, with and without cold deformation for tests carried out at 1000 Hz

Type of defect	Material without any deformation	Material with 50% of cold deformation
p-type	9.04×10^{21}	2.26×10^{22}
n-type	1.8×10^{22}	3.01×10^{22}

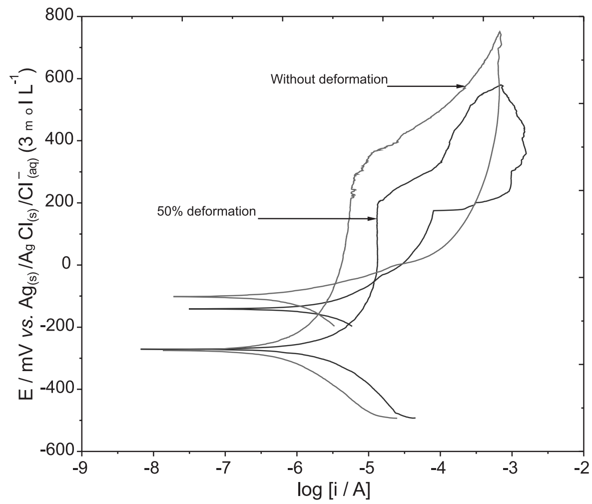

Figure 4. Potentiodynamic polarization curves for the ISO NBR 5832-1 stainless steel with cold deformation (50% reduction in thickness) or without deformation (0%) obtained at a scan rate of 1 mV s^{-1} in PBS at 37 °C.

McBee and Kruger[19] showed that chloride ions might be incorporated inside the passive film. It is reasonable to assume that this occurs due to oxygen vacancies filled by chloride ions,[13] as indicated in equation 2:

$$V_O + Cl^-_{(aq)} \rightarrow Cl_O \qquad (2)$$

where V_O are oxygen vacancies, Cl^- are chloride ions and Cl_O are vacancies occupied by chloride ions.

Considering that the deformed material presents higher defect concentration compared to the material without cold deformation, either of p-type or n-type, the aggressive chloride ions are incorporated in the oxygen vacancies. This explains the higher susceptibility to corrosive attack by chloride ions and, consequently, to pitting corrosion of the cold rolled steel.

The point defect model proposes that n-type defects are created in the metal/film interface, however, these are annihilated in the passive film/electrolyte interface through either the adsorption of water molecules or Schottky pair (chloride ion adsorption). When water molecules are adsorbed, the oxygen of these molecules (H_2O) is incorporated in the oxygen vacancies at the film/electrolyte interface and hydrogen ions (H^+) are released to the electrolyte, causing a local acidification and, consequently, increasing the susceptibility of the passive film to be attacked.[20]

The hysteresis observed in the cyclic polarization tests is an experimental evidence of pitting occurrence and this was supported by surface observation of the stainless steel (deformed or undeformed) after the polarization test, as shown in Figure 5. Scanning electron microscopy (SEM) of the polarized surface shows a pit nucleated on the NBR ISO 5832-1 stainless steel, which was formed during the polarization test in the PBS solution. This result supports the hypothesis that the increase in current that occurred at approximately 200 and 400 mV for the stainless steel with or without cold deformation was due to pitnucleation of the tested stainless steel. The pit shows a hemispherical morphology and thin grain boundaries seemed to be revealed by the anodic polarization test.

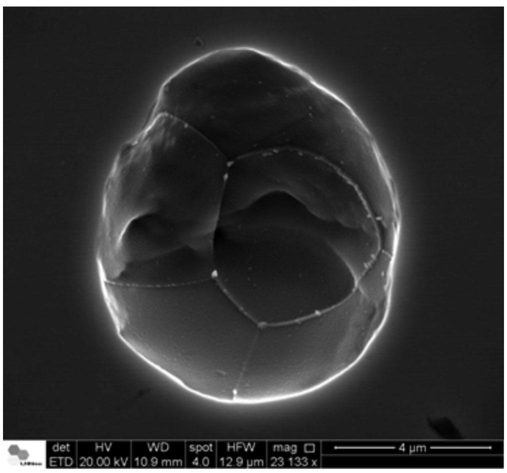

Figure 5. Scanning electron microscopy image of secondary electrons of the ISO NBR 5832-1 stainless steel surface without deformation showing a pit nucleated during the polarization test.

Conclusions

The results of the present study showed a detrimental effect of cold deformation on the pitting resistance of the ISO NBR 5832-1 stainless steel. The Mott-Schottky data showed that cold rolling deformation that caused a thickness reduction of 50% of its initial value led to increased concentration of p-type and n-type defects in the passive film. The polarization results also showed that the cold deformation decreased the pitting resistance of the stainless steel tested. The analysis of the effect of frequency adopted in the Mott-Schottky approach on the estimation of the defect concentration showed that the frequency range might affect the evaluation of defect concentration. Consequently, the frequency adopted in Mott-Schottky tests should be selected after evaluation tests in order to delineate the frequency range that does not interfere with the defect concentration estimation.

Acknowledgments

Acknowledgments are due to FAPESP (Processo No. 2012/50187-7) for the financial support provided to this research.

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Submitted: October 27, 2013
Published online: May 16, 2014

FAPESP has sponsored the publication of this article.