Influence of Cold Deformation on Semiconducting Properties of the ISO NBR 5832-1 Austenitic Stainless Steel

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Introduction

Stainless steels are widely used in different types of industries due to their properties[1]. Depending on the final applications, many alloying elements, besides nickel and chromium, are used to increase their mechanical and corrosion properties since the corrosion resistance of stainless steels is strongly affected by their chemical composition[2,3]. The passive films formed on stainless steels surface are mainly metallic oxides and these are treated like semiconductors. The conductivity properties of the passive film are of great importance to the protective character of the passive film against corrosion[4]. The Mott-Schottky analysis has been largely used to evaluate the concentration of donors and acceptors defects in passive films on different materials, such as: chromium[5,6], nickel[7,8] , and titanium[9,10]. The passive film on stainless steel is composed of a mixture of iron, nickel and chromium oxides, and this passive film shows semiconducting properties[11]. 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 contribution to the understanding of the influence of this property on the corrosion resistance of stainless steels**Erro! Indicador não definido.**.

Experimental

The material used in this investigation consisted of ISO NBR 5832-1 stainless steel (SS) and its chemical composition is shown in **Erro! Fonte de referência não encontrada.**. This SS is used for biomedical applications, mainly for fabrication of metallic implants.

Table 1. Chemical composition (wt. %) of ISO NBR 5832-1 stainless steel tested.

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	Bal.

Prior to test, the surface all specimens was prepared by wet ground with silicon carbide paper up to 1200 mesh, degreased with ethanol and rinsed with deionized water. The electrochemical tests were carried out in a flat cell with an Ag/AgCl as reference electrode and a platinum wire as counter electrode. The test solution (electrolyte) was composed of 58.41 g/L of NaCl, 9.21 g/L of Na_2HPO_4, and 17.65 g/L of KH_2PO_4. All tests were carried out at 37 ^oC. The capacitance 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.

Results and Discussion

Figure 1(a) and (b) shows the variation of $1/C^2$ as a function of applied potential at frequency ranges of 900 to 1050 Hz.

Figure 1 shows both, positive and negative slopes, related to the capacitive behaviour of a system with a duplex character, namely, an inner p-type semiconducting region where chromium oxide prevails and an outer n-type semiconducting region where iron oxide predominates**Erro! Indicador não definido.**. The flatband potential is estimated from the potential where $1/C^2$ tends to zero. Below the flatband potential, the ionic vacancies (due passive film dissolution) acts like a Schottky barrier, therefore a p-type semiconductivity is revealed, whereas above the flatband potential, the cationic vacancies (due passive film growth) is in a condition of depletion (act like Schottky barrier), therefore a n- type semiconductivity is shown[12].

Figure 1 shows the influence of frequency on the capacitance associated to the austenitic stainless steel, with and without cold deformation. It is important to highlight that the curves present slopes that are nearly parallel at all frequencies used (900-1050 Hz). This type of behaviour is appropriate to estimate the N_d in the passive film, since the defects concentration does not change with frequency. The data presented on the $1/C^2$ *vs.* potential plot can describe the semi conductive behaviour of the passive film in the depletion zone. Figure 1 also shows that the flatband potential is not affected by the measuring frequency, and that the slopes of the $1/C^2$ are not strongly affected by variation of frequency.

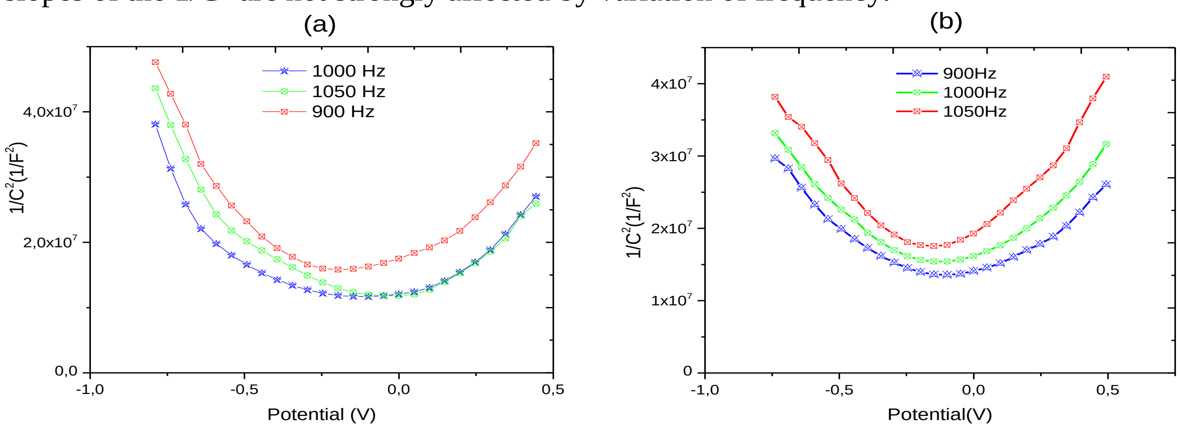

Figure 1 – Influence of the test frequency on the concentration of donors and acceptors in the passive film of the ISO NBR 5832-1 austenitic stainless steel, (a) without deformation and (b) with 70% deformation.

Figure 2 compares the results obtained with SS samples with 70% cold deformation and without any cold deformation. The influence of cold deformation is clearly seen, since it leads to lattice elongation as well as atoms bonding breakdown. These effects increase the metal/passive film dissolution, and consequently, the concentration of oxygen vacancies. The effect of cold deformation might be explained by a more disordered structure once the bonding between the atoms inside the passive film is weakened, favoring the metallic ions dissolution, and, consequently, increasing the amount of defects in the passive film.

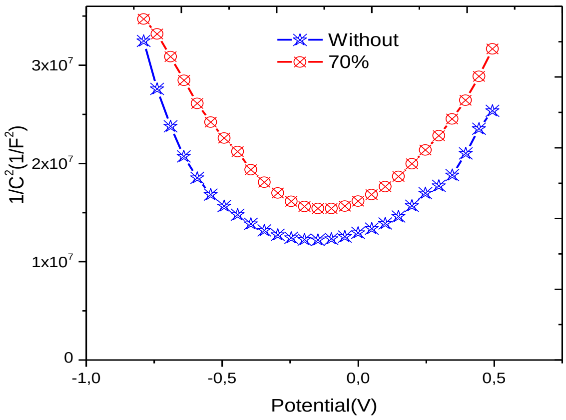

Figure 2 – Effect of cold deformation on conductivity of ISO NBR 5832-1 SS at 1 kHz.

Table 2 shows the N_d in the passive film. It is possible to observe that deformed material has lower concentration of p-type defects than the material without any deformation. On the other hand, the concentration of n-type defects of the material with 70% of deformation was higher than the material without deformation (oxygen vacancies).

Table 2. Amount of defects in the passive film of ISO NVR 5832-1, with and without cold deformation.

Type of defect	Material without any deformation	Material with 70% of cold deformation
p-type	$3.92x10^{21}$	$2.35x10^{21}$
n-type	$1.68x10^{21}$	$1.96x10^{21}$

Conclusions

The effect of the frequency of test for the frequency range used on the Mott-Schottky analysis was not found leading to the conclusion that N_d is not affected with variation of frequency. Consequently, the Mott-Schottky can be carried out at frequencies around or above 1 kHz. The cold deformation of the ISO NBR 5832-1 stainless steel increased the number of n-type defects in the passive film (increasing of the passive film), although, the number of p-type defects was lower, and as outcome of this, the protective property of the passive film is better, increasing the pitting corrosion resistance of material.

Acknowledgements

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