Semiconducting Properties of Passive Films Formed on AISI 420 Stainless Steel in Nitric Acid Solutions

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ABSTRACT

This study focuses on semiconductor properties of passive films formed on AISI 420 stainless steel immersed in four nitric acid solutions under open circuit potential (OCP) conditions. For this purpose, the passivation parameters and semiconductor properties of passive films were derived from potentiodynamic polarization and Mott–Schottky analysis, respectively. The OCP plots showed that the open circuit potential of AISI 420 stainless steel is directed towards positive amount, which is indicative of the formation of passive film and its role in increasing protectivity with time. The potentiodynamic polarization results showed that the corrosion current density of AISI 420 stainless steel increased with the increase in the concentration of solutions. Mott–Schottky analysis revealed the existence of a duplex passive film structure composed of two oxide layers of distinct semiconductivities (n-type and p-type). Also, Mott–Schottky analysis indicated that the donor densities are in the range 10^{21} cm^{-3} and increased with solution concentration.

1. Introduction

Martensitic stainless steels are mainly used for applications where high mechanical performance is required. However, due to their low chromium content, they are relatively sensitive to corrosion [1-3]. The corrosion resistance of stainless steel is due to the presence of passive films formed on the surface. Generally, the substrate (nature and content of alloying elements), the environment (temperature, aerated, deaerated, neutral, acidic or alkaline) and also specific experimental conditions (e.g. anodic polarization) affect both the chemical composition and the structure of the passive layer [3-5].

Passive films are mainly made up of metallic oxides or hydroxides which are envisaged as semiconductors. Consequently, semiconducting properties are often observed on the surfaces of the passivity metals [6-9]. To obtain a better knowledge of the passive films formed on stainless steels, many studies have been devoted to semiconducting properties by Mott–Schottky analysis. Mott–Schottky method has been widely used to study and characterize the semiconducting properties of the passive films on stainless steels [10, 11]. Passivity of stainless steel is usually attributed to the formation on the

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Table1. Chemical compositions of AISI 420 stainless steel

Elements	Cr	Ni	Mo	Mn	Si	C	P	Cu	S	Fe
AISI 420 / wt%	12.5	0.16	0.01	0.47	0.38	0.24	0.02	0.09	<0.003	Bal

metal surface of a mixture of iron and chromium oxide film with semiconducting behavior. In the last decade, increasing research on the electronic properties of passive films formed on stainless steels has given an important contribution to the understanding of the corrosion behavior of these alloys [12-15].

Generally, the chemical composition of passive film varies with the alloy composition and the pH of the solution, and this is expected to affect its semiconducting properties [16, 17]. In basic solutions, the main effect of an increasing pH on film formation is a thickening of the passive film, basically because iron oxides are more stable in alkaline solutions [18]. Conversely, in acid solutions a chromium-rich oxide film is formed due to slower dissolution of chromium oxide when compared to iron oxide [19].

The present study was designed to obtain a better knowledge of the semiconductor properties of a martensitic stainless steel in HNO_3 solutions. The aim of this work was to investigate the influence of solution concentration on passivation parameters and semiconductor properties of AISI 420 stainless steel (AISI 420) using potentiodynamic polarization and Mott-Schottky analysis.

2. Experimental

The chemical composition of AISI 420 used in the present research is shown in Table 1. All samples were polished mechanically by abrading with wet emery paper up to 2000 grit size on all sides and then embedded in cold curing epoxy resin. After that, the stainless steels were degreased with acetone, rinsed with distilled water and dried with a stream of air just before immersion. Acidic solutions (without purging oxygen or any gas) with four different concentrations were used and the compositions were 0.1, 0.8, 1.0 and 1.5 M HNO_3, respectively. All solutions were made from analytical grade 67% HNO_3 and distilled water, and the tests were carried out at 25±1 ◦C.

All electrochemical measurements were performed in a conventional three-electrode cell under aerated conditions. The counter electrode was a Pt plate, and all potentials were measured against Ag/AgCl in saturated KCl. All electrochemical measurements were obtained using METROHM AUTOLAB potentiostat/galvanostat controlled by a personal computer.

Prior to all electrochemical measurements, working electrodes were immersed at OCP for half an hour to form a steady-state passive film. Potentiodynamic polarization curves were measured potentiodynamically at a scan rate of 1 mV/s starting from -0.25 V (vs. E_{corr}) to 1.2 V. Mott-Schottky analysis was carried out on the passive films at a frequency of 1 kHz using a 10 mV ac signal and a step potential of 25 mV, in the cathodic direction.

3. Results and Discussion

3. 1. OCP measurements

In Fig 1, changes on OCP of AISI 420 in HNO_3 solutions are shown. At the start of immersion, the potential immediately reduces which shows the dissolution of oxide layer for all solutions. However, as time passes, the open circuit potential is directed towards positive amount. This trend is also reported for austenitic stainless steels in acidic solutions which are indicative of the formation of passive film and its role in increasing protectivity with time [20]. Fig 1 also indicates that after half an hour a complete stable condition is achieved and electrochemical tests are possible.

3. 2. Potentiodynamic polarization measurements

Fig 2 shows the potentiodynamic polarization curves of AISI 420 in HNO_3 solutions. For all curves, it was observed that before the electrode was transferred to a passive state an active current peak occurred, which could be attributed to the oxidation of Fe^{2+} to Fe^{3+} ions in the passive film [21, 22].

The corrosion potential and corrosion current density at different concentrations of HNO_3 solutions for AISI 420 are summarized in Table 2.

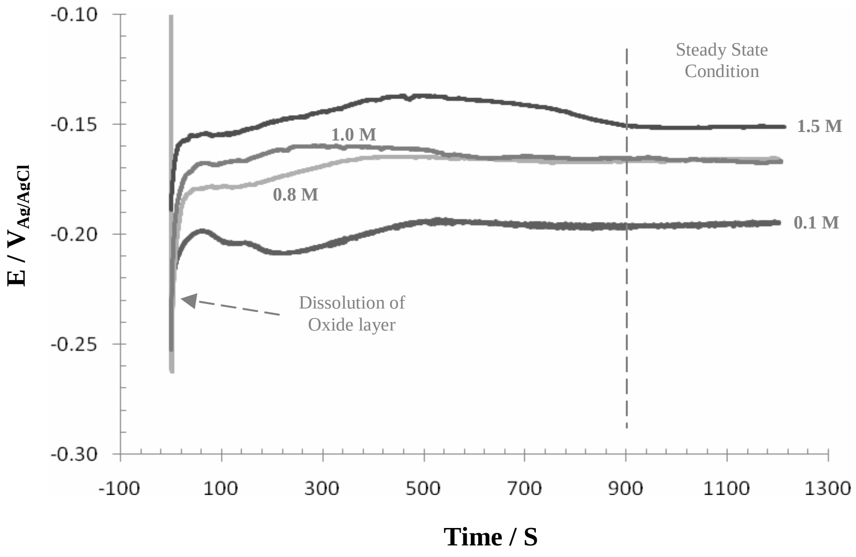

Fig. 1. OCP plots of AISI 420 in HNO_3 solutions

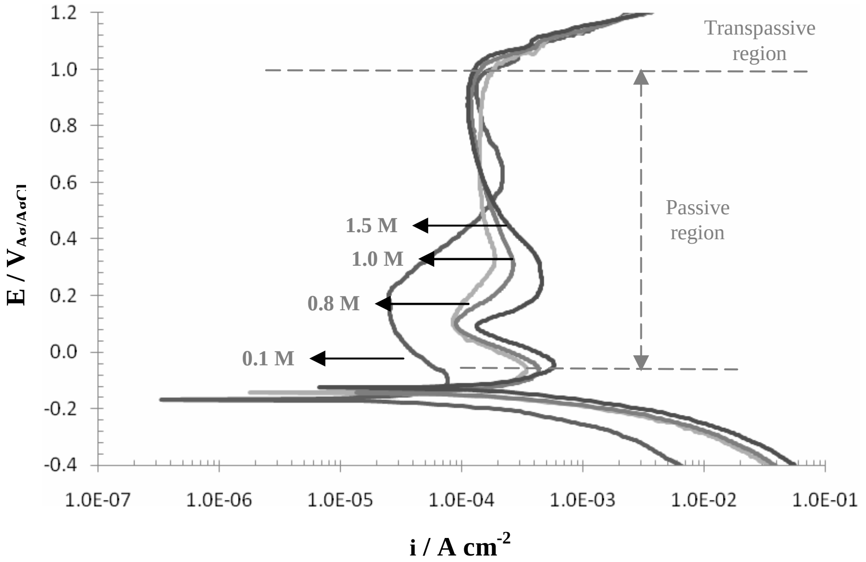

Fig. 2. Potentiodynamic polarization curves for AISI 420 in HNO_3 solutions with different concentration

It is evident from Fig 2 and the data in Table 2 that the corrosion potentials were found to shift slightly towards positive direction with an increase in solution concentration. Also, the results revealed that the corrosion current density increased with the increase in the concentration of HNO_3 solutions. It is also clear that in the low passive potential region (Figure 2), the passive current density increased with the increase in concentration of HNO_3 solutions.

3. 3. Mott-Schottky analysis

The outer layer of passive films contains the space charge layer and sustains a potential drop across the film. The charge distribution at the semiconductor/solution is usually determined based on Mott-Schottky relationship by measuring electrode capacitance C, as a function of electrode potential E [23-26]:

$$\frac{1}{C^2} = \frac{2}{\varepsilon\varepsilon_0 e N_D}\left(E - E_{FB} - \frac{kT}{e}\right) \qquad [1]$$

for n-type semiconductor

$$\frac{1}{C^2} = -\frac{2}{\varepsilon\varepsilon_0 e N_A}\left(E - E_{FB} - \frac{kT}{e}\right) \qquad [2]$$

for p-type semicondu

Table 2. Results of potentiodynamic polarization studies for AISI 420 in HNO_3 solutions

HNO_3 Solutions	Corrosion potential (E / $V_{Ag/AgCl}$)	Corrosion current density (A cm^{-2})
0.1 M	-0.163 ± 0.001	$4.7 \times 10^{-5} \pm 0.2 \times 10^{-5}$
0.8 M	-0.148 ± 0.001	$1.1 \times 10^{-4} \pm 0.2 \times 10^{-4}$
1.0 M	-0.145 ± 0.001	$2.1 \times 10^{-4} \pm 0.2 \times 10^{-4}$
1.5 M	-0.121 ± 0.001	$2.7 \times 10^{-4} \pm 0.2 \times 10^{-4}$

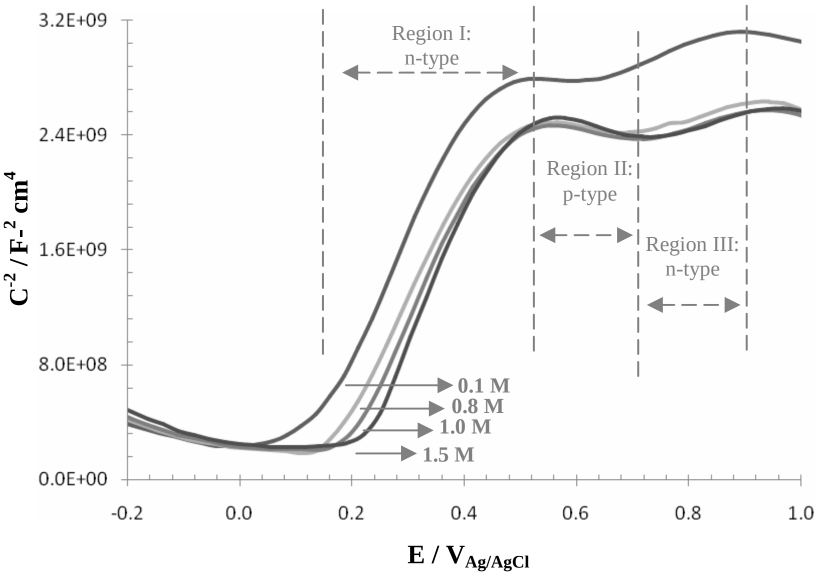

Fig. 3. Mott-Schottky plots of AISI 420 in HNO_3 solutions. The electrodes are immersed at OCP for 0.5 h to form a steady-state passive film

where e is the electron charge (-1.602×10^{-19} C),), N_D is the donor density for n–type semiconductor (cm^{-3}), N_A is the acceptor density for p–type semiconductor (cm^{-3}), ε is the dielectric constant of the passive film (usually taken as 15.6), ε_0 is the vacuum permittivity (8.854×10^{-14} F cm^{-1}), k is the Boltzmann constant (1.38×10^{-23} J K^{-1}), T is the absolute temperature and E_{FB} is the flat band potential. Flat band potential can be determined from the extrapolation of the linear portion to $C^{-2} = 0$ [23-26].

Fig 3 shows the Mott-Schottky plots of AISI 420 in HNO_3 solutions. Firstly, it should be noted that for all concentration, C^{-2} clearly decreases with solution concentration. Secondly, all plots show three regions in which a linear relationship between C^{-2} and E can be observed. The positive slopes in the region I (main passive region) are attributed to an n-type behaviour, probably due to the presence of Cr_2O_3 and FeO on the passive films [27]. Region II presents negative slopes, which depicts a p-type semiconducting behaviour. Finally, the positive slopes in region III are attributed to n-type behaviour. This feature is usually explained in terms of a strong dependence of the Faradaic current on potential in the transpassive region. In this sense, the behaviour of capacitance at high potentials near the transpassive region is attributed to the development of an inversion layer as a result of an increasing concentration in the valence band [27].

In all plots, straight lines with a positive and negative slope show that the passive films formed on this stainless steel behave as n-type and p-type semiconductors. This behavior implies that the passive films have a duplex structure. Early studies of the bipolar duplex structures of passive films on stainless steels are attributed to Sato [28], and since then, other investigations have given credence to this observation [29, 30]. It is widely accepted that the inner part of the passive film, which has a p-type behavior, consists mainly of Cr oxides, whereas the outer region, with the features of

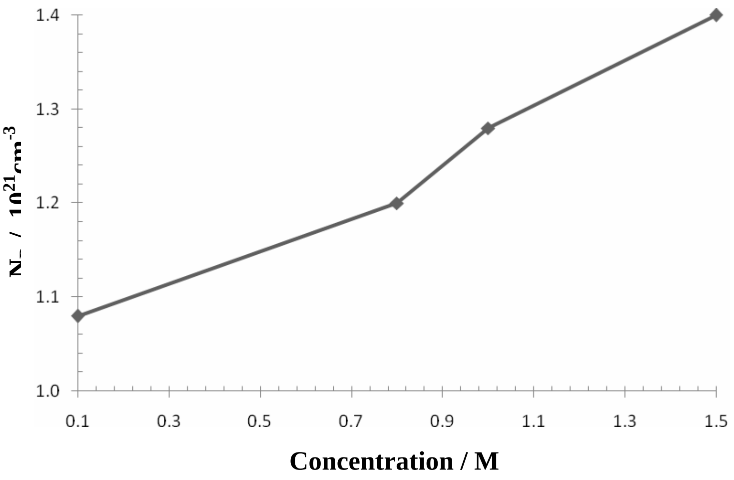

Fig. 4. Donor density of the passive films formed on AISI 420 in HNO_3 solutions as a function of concentration

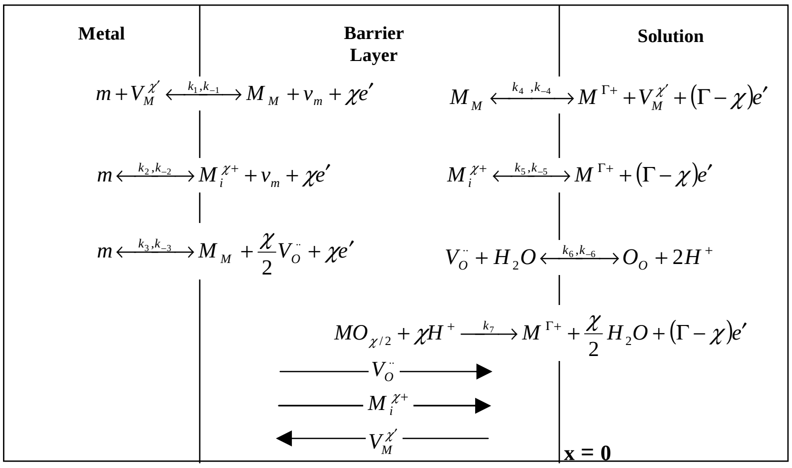

Fig. 5. Interfacial defect generation-annihilation reactions that are postulated to occur in the growth of passive films according to the PDM (m = metal atom, M_M = metal cation on the metal sublattice, O_O = oxygen anion on the oxygen sublattice, $M^{\Gamma+}$ = metal cation in solution) [31, 32]

an n-type behavior, is predominantly Fe oxides [31].

According to Eq. (1), donor density has been determined from the positive slopes in region I of Fig 3. Fig 4 shows the calculated donor density for the passive films formed on AISI 420 in 0.1, 0.8, 1.0 and 1.5 M HNO_3. The orders of magnitude are around 10^{21} cm^{-3} and are comparable to those reported in other studies. According to Fig 4, the donor density increases with solution concentration. Changes in donor density correspond to non-stoichiometry defects in the passive film. Therefore, it can be concluded that the passive film on AISI 420 is disordered and becomes more visible at higher concentration. Based on Point defect model (PDM) [31, 32] the donors or acceptors in semiconducting passive layers are point defects, as explained briefly in part 3.4.

3. 4. Point defect model

The PDM postulates that the point defects present in a barrier layer are, in general, cation vacancies ($V_M^{\chi'}$), oxygen vacancies ($V_O^{\cdot\cdot}$), and cation interstitials ($M_i^{\chi+}$), as designated by the Kroger-Vink notation. The defect structure of the barrier layer can be understood in terms of the set of defect generation and annihilation reactions occurring at the metal/barrier layer interface and at the barrier layer- solution interface, as depicted in Fig 5 [31, 32].

On pure metals, the passive film is essentially a highly doped, defect semiconductor, as demonstrated by Mott-Schottky analysis. Not unexpectedly, the situation with regard to alloys is somewhat more complicated than that for the pure metals, because substitution of other metal cations, having oxidation states different from the host, on the cation sublattice may also affect the electronic defect structure of the film.

According to the PDM, the flux of oxygen vacancy and/or cation interstitials (Cr^{2+}, Cr^{3+}, $Ni^{2+}$and Fe^{2+}) through the passive film is essential to the film growth process. In this manner, the dominant point defects in the passive film (main passive region) are considered to be oxygen vacancies and/or cation interstitials acting as electron donors.

4. Conclusions

The electrochemical behaviour of AISI 420 in HNO_3 solutions under OCP conditions were investigated in the present work. Conclusions drawn from the study are as follows

1. The OCP plots showed that open circuit potential is directed towards positive amount, which is indicative of the formation of passive film and its role in increasing protectivity with time.
2. The potentiodynamic polarization curves suggested that AISI 420 showed comparable passive behaviour in HNO_3 solutions. Also, the potentiodynamic polarization curves revealed that the corrosion current densities increase with the increase in the concentration of HNO_3 solutions.
3. Mott–Schottky analysis revealed the existence of a duplex passive film structure composed of two oxide layers of distinct semiconductivities (n-type and p-type).
4. Based on the Mott–Schottky analysis, it was shown that donor densities are in the range of 10^{21} cm^{-3} and increased with solution concentration.

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