PHOTOELECTROCHEMICAL STUDY OF PASSIVE FILMS FORMED ON STAINLESS STEELS; INFLUENCE OF THE ALLOYING ELEMENTS.

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Abstract

The study of the electronic structure of the passive films formed on high purity Fe-Cr, Fe-Cr-Ni and Fe-Cr-Ni-Mo stainless steels was carried out by photoelectrochemical measurements. Bandgap energy and quantum efficiency are associated with the changes promoted by the alloying elements in the bilayer structure of the passive films. The analysis of the photocurrent as a function of the applied potential reveals a Poole-Frenkel effect. The donor densities extracted from photoelectrochemical measurements are compared to those obtained in previous works from capacitance measurements.

Keywords:Stainless steels, Passive films, Photoelectrochemistry, Electronic structure.

Introduction

Passive films formed on stainless steels have been intensively investigated in order to improve the corrosion resistance of these materials. It is well known that the films exhibit semiconductive properties and consequently their electronic structure can be described on the basis of the band structure model developed for semiconductors. Published data give valuable information about bandgap energies, conductivity type and flatband potentials of the films [1-8].

Unfortunately, the understanding of such films still needs further research. The films formed on stainless steels are generally composed by an internal chromium-rich oxide region, which plays the major role in corrosion resistance, and by an external iron-rich oxide region which controls the electrochemical properties of the film/electrolyte interface. These two regions form a duplex structure if both the chemical composition and the type of semiconductivity are considered [6].

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It is the purpose of this work to obtain more detailed information about the electronic structure of the films formed on stainless steels with particular emphasis in what concerns the influence of the main alloying elements (Cr, Ni, Mo). The study is conducted by photoelectrochemistry using high purity alloys with well-controlled chemical composition and structure.

In the present investigation it is considered that the crystallographic structure of the passive films can be compared to that of bulk well crystallized oxides. As a matter of fact, the degree of order concerning the passive films formed on stainless steels is still object of discussion, i.e., whether they are crystalline or amorphous. It is not easy to characterize the film from a structural point of view even when electron diffraction techniques of high efficiency are employed. However, the analysis of recent results [9] allows one to assume that at least a short-range order exists. This aspect is of crucial importance since the band structure is determined by the chemical bonding, the type of coordination and the type of short range order [10].

Theoretical aspects

When a radiation of sufficient quantum energy is absorbed by a semiconductor or an insulator a photocurrent is generated. The effect of light is primarily to increase the density of the free charge carriers. The photocurrent depends upon how long these carriers can remain free before recombining, i.e., upon their lifetime. Thus, the presence of electrical barriers promoted by space charges can facilitate or hinder recombination [11].

Assuming that the recombination of photogenerated charge carriers can be neglected, the photocurrent response of a semiconductor can be described quantitatively by the Gartner and Butler equation [12, 13]

$$I_{ph} = e\Phi_0 \left[1 - \frac{\exp(-\alpha\, w_{sc})}{1+\alpha\, L_p} \right] \qquad (1)$$

where I_{ph} is the photocurrent, e the charge of the electron, Φ_0 the incident photon flux, α the absorption coefficient, L_p the hole diffusion length and W_{sc} the space charge layer thickness. This parameter is related to the applied potential, U, and the flatband potential, U_{fb}, by

$$W_{sc} = (2\varepsilon\varepsilon_0/eN_d)^{½}\,(U-U_{fb})^{1/2} \qquad (2)$$

where ε and ε_0 are the dielectric constant and the vacuum permittivity, respectively, and N_d the donor concentration for a n-type semiconductor.

For $\alpha L_p << 1$ and $\alpha W_{sc} << 1$, i.e., a small hole diffusion length and a small space charge layer thickness, which is the case for the majority of passive and oxide films formed on metals and alloys, equation 1 can be simplified to

$$I_{ph} = e\,\Phi_0\alpha\,[L_p + W_{sc}] \qquad (3)$$

For many semiconductors it has been found that the relation between photon energy and the absorption coefficient α is given by

$$\alpha h\nu = A\,(h\nu - E_g)^n \qquad (4)$$

where E_g is the bandgap energy and n is 0.5 or 2 for direct and indirect optical transitions, respectively, and A is a constant.

In terms of quantum efficiency, η, defined as the ratio of the photocurrent by the incident photon flux, the dependence of the photoresponse on the energy, $h\nu$, and the space charge layer thickness, W_{sc}, becomes:

$$\eta h\nu = A\,[L_p + W_{sc}]\,(h\nu - E_g)^n \qquad (5)$$

This relationship can be used to determine the optical bandgap E_g.

The Poole-Frenkel effect

The plots of Ln η vs U for passive films have been related to the Poole-Frenkel effect, which describes the influence of the electric field, F, on the escape probability, P_i, of the electron from a trap where it is bound by coulombic interactions. When an electric field is superimposed on the trap, the escape barrier is lowered by an amount $\beta F^{1/2}$ and P_i is given by the Poole-Frenkel equation [14]

$$P_i = \exp\ \frac{E_i + \beta F^{1/2}}{kT} \qquad (6)$$

where E_i is the ionisation energy, i.e. the energy difference between the lower edge of the conduction band and the trap. Since the photocurrent, I_{ph}, is proportional to the escape probability, it can be written as

$$I_{ph} = A'\exp\left(-\frac{E_i + \beta F^{1/2}}{kT} \right) \qquad (7)$$

where A' is a constant.

Assuming that the electric field, F, is related to the applied potential, U, and the flatband potential, U_{FB}, by

$$F = \frac{U - U_{fb}}{W_{sc}} \qquad (8)$$

where the space charge layer, thickness W_{sc}, is given by equation 2, the quantum efficiency is given by

$$\mathrm{Ln}\,\eta = \mathrm{Ln}\,\frac{A'}{e\Phi_0} - \frac{E_i}{kT} + \frac{1}{kT}\left(\frac{e^3}{\varepsilon\varepsilon_0\pi}\right)^{0.5}\left(\frac{eN_d}{2\varepsilon\varepsilon_0}\right)^{0.25}\left(U - U_{FB}\right)^{0.25} \qquad (9)$$

According to equation 9, the Ln η vs $(U-U_{FB})^{0.25}$ plots would reveal a linear variation, with a slope depending on the donor density, N_d, and the dielectric constant, ε.

Chemical and structural aspects of the passive films formed on stainless steels.

In order to correlate photoelectrochemical results with solid state properties, it is necessary to have an adequate description of the basic electronic structure of the passive films established by capacitance measurements (Mott-Schottky method).

The model presented in Fig.1 describes the film as an heterojunction, where the space charge regions are localized at the film-electrolyte and metal-film interfaces. Under the influence of anodic ($U \geq U_{fb}$) polarization the bands bend upwards at these two interfaces and promote, the development of depletion and accumulation space charge regions. For a polarization at potentials lower than the flatband potential, U_{fb}, the bands bend downward and the situation previously described is reversed. It is assumed that in this latter case ($U \leq U_{fb}$), at the film-electrolyte interface the accumulation process corresponds to a degeneracy of the iron oxide region of the film, which becomes a metal-like conductor. Thus, the capacitance measurements performed in this potential region can be related to the semiconducting properties of the internal chromium-rich oxide region.

At the interface situated between the inner p-type oxide region and the outer n type oxide region the films present an abrupt change in the concentration of electrons and holes as well as in the ionic lattice defects. This leads to the development of the interface at the p-n junction, which is a source of cationic and anionic vacancies. This kind of interface results from the development of distinct phases during the growth of the film. According to Vetter [15], during film formation under applied potential the

chemical potential, μ, and the electric potential, Ψ, vary in such a manner that the Fermi potential, E_F, remains constant. Thus, the following relationship must be verified.

$$E_F = \mu - e\Psi = \mathrm{const.} \qquad (10)$$

The chemical potential depends on the oxide phase formed, whereas the electric potential is particularly dependent of the flow of ionic defects through the film.

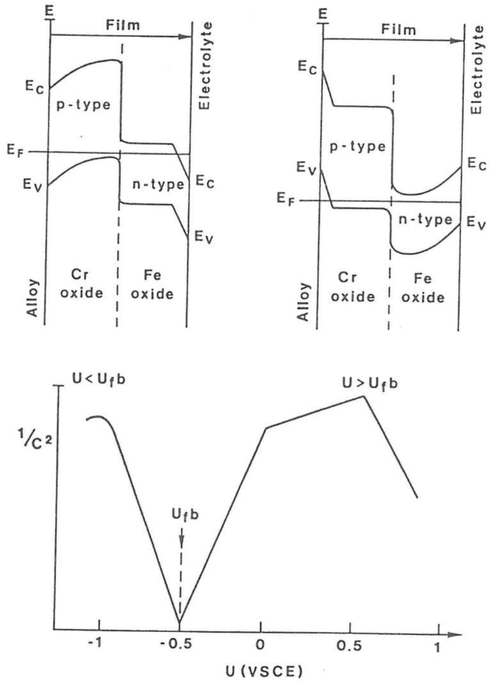

Fig. 1 – Model of the electronic structure of passive films formed on austenitic stainless steel (U > Ufb U < U_{fb}). Schematic representation of the Mott-Schottky plots ($^1/C^2$ vs. U)

Experimental

The very high purity Fe-Cr, Fe-17Cr-xNi and Fe-17Cr-25Ni-xMo alloys used as test specimens were prepared by a plasma furnace technique. In these alloys, the concentration of the non-metallic and metallic residual elements is very low (typically: 0.002C, 0.001N and lower than 0.002% for Si and Mn). The samples were annealed for 1hour at 900°C. The working electrodes were plate shaped ($1cm^2$) and mounted in an acrylic resin. The surface was abraded with wet SiC paper with 1200 grit size and was finally polished with alumina (2μm), rinsed in distilled water, ultrasonically cleaned and dried in air. A classical cell with three electrodes was used, with a platinum counter-electrode ($1cm^2$) and a saturated calomel electrode (SCE). All experiments were carried out at room temperature (22°C) under continuous deaeration with high-purity nitrogen in a buffer solution of composition H_3BO_3 (0.05 M) + $Na_2B_4O_7$. 10 H_2O (0.075 M) and pH = 9.2. The sample was cathodically prepolarized (~5 mA. cm^{-2}) for 5 min and then polarized for 2 hours at the film formation potential (+ 0.6 V, unless otherwise stated).

The photoelectrochemical measurements were performed using a 150 W xenon lamp and a 1200/mm grating monochromator (Jobin Yvon H25). The photocurrents were generated by focusing the light with a fused silica lens through the quartz window of the electrochemical cell onto the working electrode. The lock-in technique was applied, allowing the separation of the photocurrent from the passive current by chopping the light at a constant frequency (19 Hz) and feeding the signal as well as the current output of the potentiostat to a lock-in amplifier. The photocurrent versus the energy of the incident light were obtained by scanning the wavelength of the light in steps of 50 nm from 750 nm to 250 nm. The dependence of the photocurrent on the applied potential, U, was obtained at a fixed wavelength (350 nm) by scanning successively the applied potential in steps of 50 mV in the potential range 1V to –1.5V. The polarization was applied starting from the film formation potential in the cathodic direction in the potential range below the film formation potential and in the anodic direction in the potential range above this potential. The reported photocurrent action spectra were corrected for the lamp efficiency without taking into account the reflections at the film-solution interface. A potentiostat (EG&G 273) and a double phase synchronous detector (Brookdeal 5208 lock-in amplifier) with an internal oscillator working in a large frequency range (5Hz – 100 kHz) were used.

The measurements show an excellent reproducibility of the photocurrent spectra for the different alloys.

Results and Discussion

Chromium influence

In Fig. 2 the spectral data of the Fe-Cr alloys plotted according to equation 5 show that the photoresponse of the passive films decreases when the chromium concentration increases. The values of the bandgap energies E_g obtained from the intercept of the straight line with the photon energy axis show that the Fe-Cr alloys with chromium content lower than 15% have the same bandgap energy (about 2 eV) as the passive films formed on iron [12-15]. For Fe-Cr alloys with higher chromium content, the bandgap is about 2.3 eV.

For photon energies lower than E_g, i.e., in the sub-bandgap region, the plots of η as a function of hν show for films formed on the same alloys (Fig. 2b) the existence of a peak of photocurrent at 1.9 eV. This peak is thus situated at 0.1 V or 0.4 eV below the conduction band. This means that excitation is possible from the valence band to localized states in the bandgap of the passive film. It also appears that the quantum efficiency for sub-bandgap photon energies decreases with increasing chromium content.

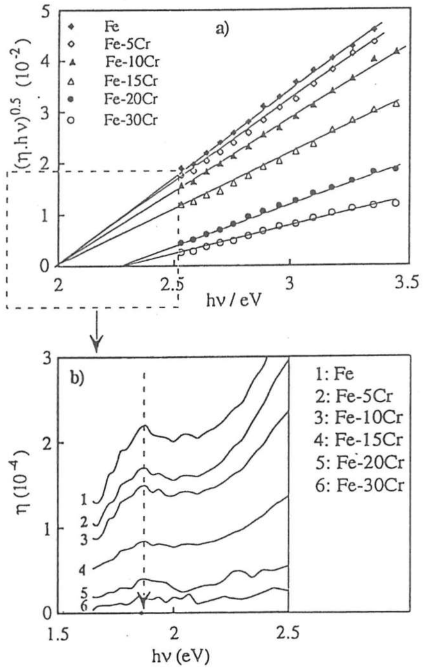

Fig. 2 – Photoresponse of passive films formed on Fe-Cr alloys for photon energies higher (a) and lower (b) than that of the bandgap energy E_g.

Figure 3 depicts the values of both the bandgap, E_g, and the quantum efficiency, at 1.9 eV, η, obtained by measurements on passive films formed on Fe-Cr with increasing Cr concentrations. A discontinuity in the data can be observed for chromium concentrations at which the alloys become stainless steels (~15%Cr).

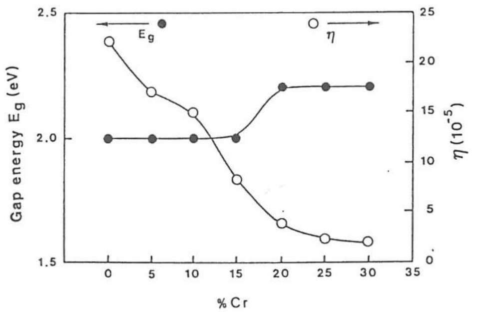

Fig. 3 – Evolution of the quantum efficiency and bandgap as a function of the chromium concentration.

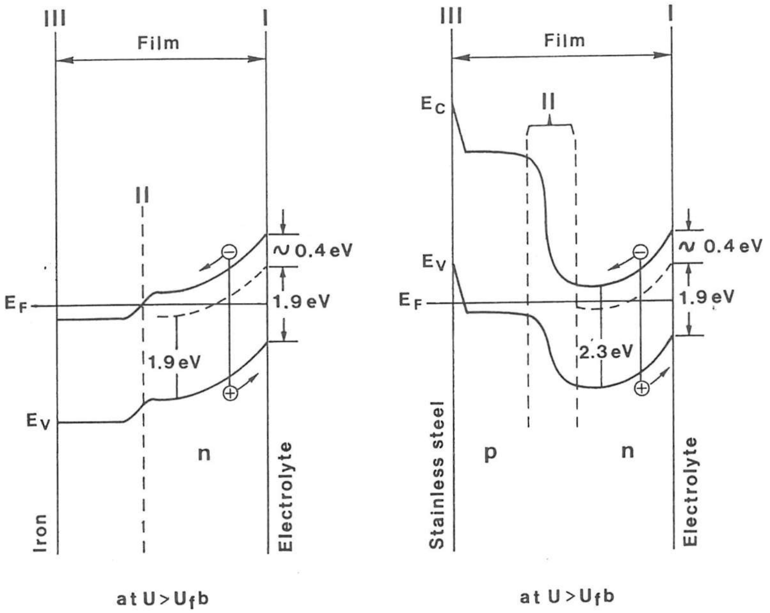

Fig. 4 – Energy band pictures for the passive films formed on iron and stainless steels (Cr>15%). In both cases the photocurrent is produced at the film-electrolyte interface and in both cases the electrons will move towards the metallic substrate and the holes will move toward the electrolyte, i.e., the photocurrent is anodic. The flow of electrons meets only ohmic contacts (interfaces II and III) in the case of the film formed on iron but can be strongly affected by potential barriers existing in region II of the film formed on stainless steel.

Figure 4 gives a schematic representation of the band structure of the passive films formed both on iron and stainless steel. In the case of iron the inner Fe_3O_4 layer is generally considered an electronically conducting layer and consequently the consequently the semiconductivity of the film is that of the γ Fe_2O_3 outer layer. For the passive films formed on stainless steels, the band structure is determined by the existence of a bilayer formed by p-type and n-type regions [6]. The decrease in the quantum efficiency observed for these alloys can be related to the development of the inner chromium oxide region and most particularly to the development of an interface situated between the p-type and n-type regions. In fact, to reach the metallic substrate (anodic current) the photoelectrons created by the incident light must flow from the external n-type region to the internal p-type region of the film. However, if potential barrier is small enough, then electrons can tunnel from the conduction band to the valence band and it can be assumed that the magnitude of the photocurrent is controlled by the hole transport, since this is the slower process. This situation is different from that found in the passive film formed on iron where the interface between the n-type outer region and the inner region of the film can be considered as an ohmic contact.

- Nickel and molybdenum influence

The presence of 8% Ni in an alloy containing 17%Cr does not lead to a significant increase of the photocurrent. However the influence of this alloying element is very important in the case of the alloy with 25% Ni (Fig. 5). It should be noted that nickel in the oxidized state, is generally detected in the iron oxide region [6, 16]. Nickel oxide also affects the capacitance values in the potential range near the flatband potential [16]. This can be interpreted as the consequence of the influence of nickel on the potential difference at the interface formed by the regions of p-type and n-type semiconductivity.

The photoelectrochemical study of stainless steels with molybdenum addition shows that the photoresponse is closely related to the molybdenum concentration (Fig. 6a). In fact, the value of the quantum efficiency increases with increasing molybdenum content. However, the value of the bandgap energy is always 2.3 eV, whatever the molybdenum concentration. For photon energies lower than E_g, i.e. in the subband gap region, the plots of η as a function of $h\nu$ shown in Fig. 6b, reveal also the existence of a peak of photocurrent. It is also apparent that for the subband gap photon energies the quantum efficiency increases with increasing molybdenum content.

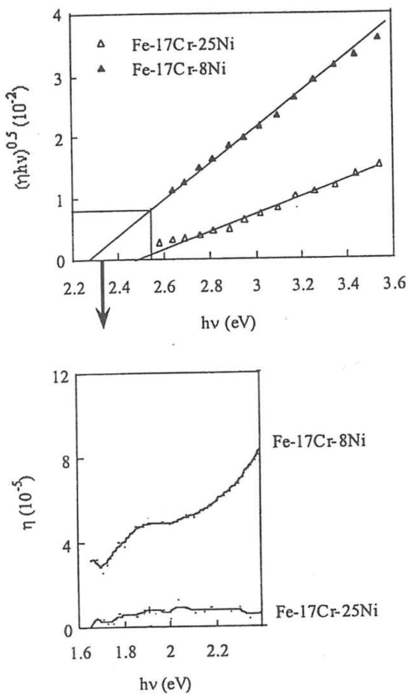

Fig. 5 – Photoresponse of passive films formed on Fe-Cr-Ni alloys for photon energies higher (a) and lower (b) than that of the band gap energy E_g.

- *Space charge effects*

At fixed wavelength and variable potential, the photoresponse is governed by the band bending created by the electrochemical polarization and reflects the behaviour of the space charge layer under illumination. Experimentally, this kind of information can be obtained only if the energy of the incident light is greater then the bandgap energy.

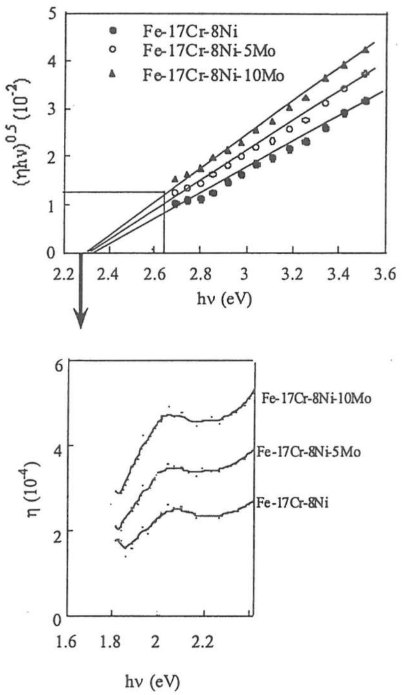

Fig. 6 – Photoresponse of passive films formed on Fe-Cr-Ni-Mo alloys for photon energies higher (a) and lower (b) than that of the band gap energy E_g.

At a fixed wavelength of (λ = 370 nm), at which the photocurrent spectra present their maximum intensities i.e., I_{ph} as a function of the applied potential was measured. In Fig. 7 the photoresponse of passive films formed on three stainless steels of different compositions is compared to their capacitance behaviour (C^{-2} vs U plots). The main factor in the intensity of the photoresponse is the thickness of the by the depletion layer according to equation 2. The photoresponse behaviour is also modified at the potential of about 0 V, i.e., at the potential where the doping density of the film changes as a consequence of the ionization of the deep donor level [6,8].

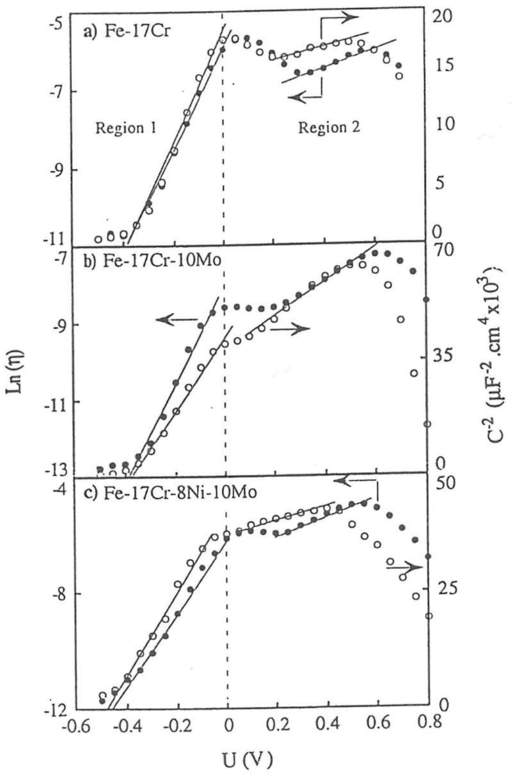

Fig. 7 – Plots of Ln (η) vs U for passive films formed on the various stainless steels (at 370 nm). The photoelectrochemical behaviour is compared to the capacitance behaviour observed in the same experimental conditions [6].

- *Poole-Frenkel behaviour*

Figure 8 shows the Ln (η) vs $(U-U_{fb})^{0.25}$ plots for the passive films formed on Fe-Cr, Fe-Cr-Ni and Fe-Cr-Ni-Mo alloys. The straight lines indicate a behaviour according to the Poole-Frenkel effect. This phenomenon can be related to a classical potential barrier process. The contribution of different possible tunneling processes is most probably negligible [14].

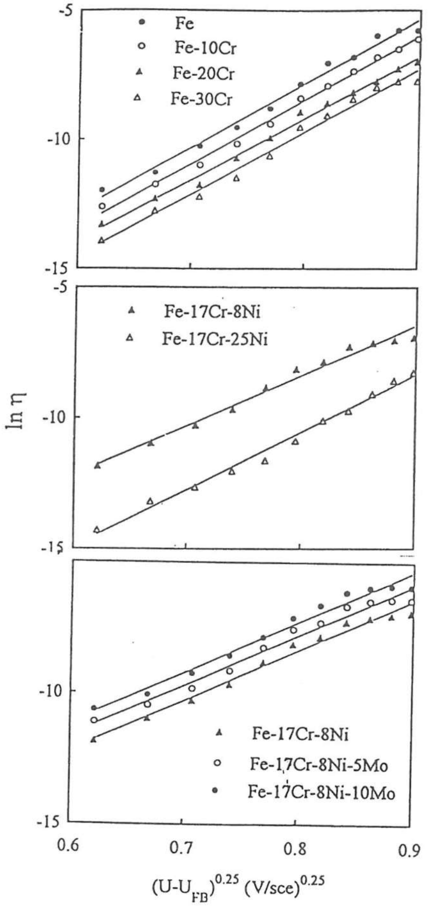

Fig. 8 – Poole-Frenkel plots for passive films formed on different stainless steels.

From the slopes of Ln (η) vs $(U-U_{fb})^{0.25}$ plots and using equation 9 the donor densities of the passive films can be evaluated quantitatively. In Fig. 9 the donor densities obtained by this method for Fe-Cr (Fig. 9a) and Fe-17Cr-8Ni- xMo (Fig. 9b) alloys (using $\varepsilon = 12$) are compared to those obtained in previous work [6] by capacitance measurements.

The values of N_D obtained by the photoelectrochemical methods are lower than those determined by capacitance measurements. Nevertheless, the ratio of the donor densities obtained by both methods is approximately constant. Many effects can be suggested to explain the difference between the values of N_d determined by the two types of techniques. One explanation could be that capacitance and photocurrent are frequency dependent and the range of frequencies used to determine the donor densities differed from are method to the other. Another interpretation is based on the fact that the electric field present in the space charge developed in the dark is disturbed under illumination because a counter field is formed by the processes of charge separation. This phenomenon may reduce the quantum efficiency of the electron-hole pairs generated by the incident light.

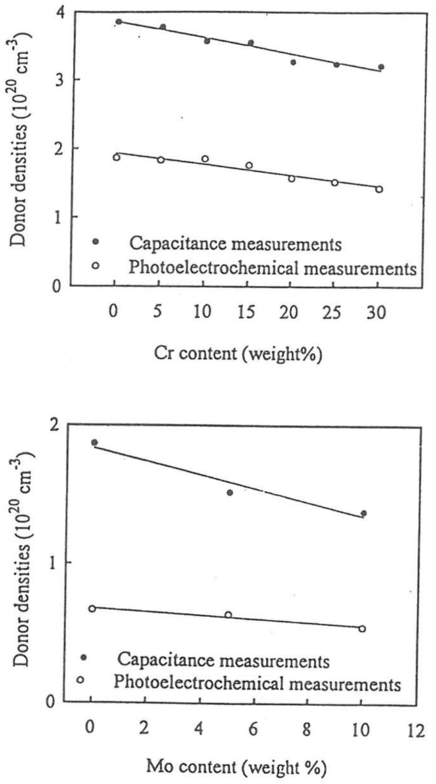

Fig. 9 – Doping densities of passive films formed on alloys with different chromium and molybdenum concentrations. Comparison is made between two experimental methods.

Conclusions

The photoelectrochemical study gives a more detailed picture of the electronic structure of the p-n heterojunction present in the passive films formed on stainless steels. Due to the different semiconducting properties of the constitutive oxides, the passive films develop under the influence of polarization, space charge regions localized at the metal-film and film-electrolyte interfaces [17]. There is also an interface between the p-type and n-type regions, created during film growth, which is obviously extremely thin and can be described as a boundary of the two different phases. Like the internal and external interfaces this "boundary" is a defect source of anionic and cationic vacancies.

This study allows the discussion of the manner in which the principal alloying elements affect the structure of the passive films. Chromium promotes the development of film with a duplex character. Consequently the semiconducting properties of a the film are dependent of the two constitutive oxides; the internal chromium oxide region and the external iron oxide region.

Nickel influence probably occurs more significantly in the intermediate/outer layers of the film, since it is there that the nickel is usually located [17]. Like nickel, the presence of molybdenum in the alloy does not affect the basic structure of the heterojunction but decreases the doping density of the external Fe oxide layer. Molybdenum also enhances the contribution of a second donor level situated in the bandgap.

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