



Effect of alloying elements on the electronic properties of thin passive films formed on carbon steel, ferritic and austenitic stainless steels in a highly concentrated LiBr solution



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ABSTRACT

The influence of alloying elements on the electrochemical and semiconducting properties of thin passive films formed on several steels (carbon steel, ferritic and austenitic stainless steels) has been studied in a highly concentrated lithium bromide (LiBr) solution at 25 °C, by means of potentiodynamic tests and Mott–Schottky analysis. The addition of Cr to carbon steel promoted the formation of a *p*-type semiconducting region in the passive film. A high Ni content modified the electronic behaviour of highly alloyed austenitic stainless steels. Mo did not modify the electronic structure of the passive films, but reduced the concentration of defects.

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1. Introduction

Stainless steels are the most widely known metallic materials, and their demand has increased dramatically in recent years [1–3]. Stainless steels owe their widespread use to a combination of unique properties that have advantage over those of other steels and nonferrous metals for many applications. The main characteristics are their resistance to corrosion in different environments, their good mechanical properties over an extremely wide range of temperatures, and their resistance to oxidation and scaling at very high temperatures [1,3]. The corrosion resistance of stainless steels is provided by a very thin and protective surface oxide film, known as passive film. It is generally accepted that passive films formed on stainless steels have a duplex structure which consists of an inner region rich in chromium and an outer region rich in iron [4–9]. Some authors have also observed that when the amount of molybdenum in a stainless steel is high enough, it is incorporated into the passive film, showing complex oxide chemistry with different states of oxidation [7, 10,11]. Depending on the nickel content in the stainless steel, Ni may or may not appear in the chromium and iron oxide layers [8,9].

One of the main factors that control the behaviour of a passive film is its electronic properties [4–6,12–22]. However, there is some controversy as to the electronic structure of the layers which make up the passive films formed on stainless steels, especially on those with high Ni

content, and no general agreement exists on this topic yet. Some studies that used Mott–Schottky analysis [18,19,23–26] claimed that passive films formed on stainless steels are *n*-type semiconductors due to a protective barrier layer of Cr₂O₃; however, it is interesting to note that in the references mentioned above, only limited information has been obtained, since capacitance measurements have been generally restricted to the more anodic potential range. According to Sato [12,21], the passive film comprises an anion-selective and *n*-type semiconductive inner layer, and a cation-selective and *p*-type semiconductive outer layer. In other studies [4–6,17,27,28] the electronic structure of passive films formed on stainless steels has been described as a *p*-type inner layer (rich in Cr-species) and an *n*-type outer layer (rich in Fe-species).

Highly concentrated aqueous LiBr solutions are widely used as a refrigerant for absorption-type air-conditioning and industrial drying systems due to its good thermodynamic properties [29–32], but these solutions are highly corrosive and attack the copper and ferrous (austenitic and duplex stainless steels) parts of the system [33–40]. Stainless steels are susceptible to several forms of localised corrosive attack, especially in the presence of halides, such as bromides. The general and localised corrosion behaviour of passive films can be related to their semiconducting properties, so it is essential to understand these semiconducting properties to correlate them with the corrosion behaviour of stainless steels. However, the interpretation of the electronic properties of passive films formed on stainless steels is difficult because of the complexity of the bilayer structure of the films. Since the alloying elements can modify the semiconducting behaviour of the different oxide layers, their influence must be taken into account when studying passive films semiconductivity, especially in highly alloyed materials.

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In the present work, the influence of alloying elements on the semi-conducting properties of passive films formed on several steels (carbon and stainless steels) has been studied in a highly concentrated LiBr solution (992 g/l, commonly used in absorption machines) at 25 °C, by means of Mott–Schottky analysis. Potentiodynamic polarisation experiments have also been carried out to establish a connection between the electrochemical and electronic behaviours.

2. Experimental details

2.1. Materials, solution and electrochemical cell

Experiments were performed in a deaerated and highly concentrated LiBr solution (992 g/l, 11.42 M), at 25 °C. The deaerated atmosphere was created by bubbling N₂ in the solution for 1 h before the tests, and over the electrolyte solution during the tests.

The materials tested were different steels (carbon and stainless steels), with variable Cr, Ni and Mo content (Table 1). The electrodes were cylindrically shaped (8 mm in diameter and 55 mm long) and covered with a polytetrafluoroethylene coating. The area exposed to the solution was 0.5 cm². All specimens were wet abraded from 500 to 4000 SiC grit, and finally cleaned with ethanol, rinsed with distilled water and air-dried.

The electrochemical measurements were carried out with an Autolab PGSTAT302N potentiostat. An Ag/AgCl (3 M KCl) electrode served as the reference electrode and a platinum wire served as the counter electrode. In all cases the tests were repeated at least three times in order to verify reproducibility.

2.2. Potentiodynamic polarisation tests

Potentiodynamic polarisation tests began at a potential value of –250 mV with respect to the open circuit potential and the potential was subsequently scanned anodically at 0.5 mV s^{–1} until the current density reached 1 mA/cm². The pitting potential (E_p) has been defined as the potential at which current density reaches a value of 100 μA/cm² [40–42].

2.3. Capacitance measurements

Before passivation, the electrode potential was kept at a cathodic value of –800 mV_{Ag/AgCl} for 15 min, to create reproducible initial conditions. Afterwards, the working electrodes were polarised at the film formation potentials of –300 mV_{Ag/AgCl} for 1 h. A film formation potential of 100 mV_{Ag/AgCl} was also used in the case of Alloy 33 and Alloy 31. Capacitance measurements were performed once a stable passive film was formed on the surface of the samples. The capacitance of the interface was calculated at a constant frequency of 5 kHz using a 10 mV amplitude signal and scanning the potential from the formation value in the negative direction at a rate of 50 mV s^{–1}. A high scanning rate was used to avoid electroreduction of the passive film and changes in film thickness during the measurements. At a sufficiently high scanning rate, the defect structure within the passive film is “frozen-in”, which avoids the defect density from being affected by potential [43–45].

3. Results and discussion

3.1. Potentiodynamic polarisation curves

Fig. 1 shows the potentiodynamic polarisation curves for the six steels studied in the 992 g/l LiBr solution at 25 °C. As tests were reproducible, the curves illustrate one of the recorded measurements. A passive region where current density is almost constant is observed in all the curves. Polarisation curves also show that, once the pitting potential is reached, the current density increases sharply. The standard electrode potential of the pair Br₂/Br[–] ($E^0 = 882 \text{ mV}_{\text{Ag/AgCl}}$) is higher than the potential values at which current density increases abruptly, so this increase indicates the breakdown of the passive film. Moreover, visual inspection of the electrodes after the potentiodynamic tests revealed clear pits throughout the samples surface.

Before the sharp increase in current density due to the onset of pitting corrosion, a slight increase in current density can be observed in the potentiodynamic polarisation curves of the different stainless steels. This steady increase of current density can be associated with the transpassive dissolution of Cr-containing species and is closely related to the passive film breakdown and localised corrosion phenomena [22].

Carbon steel S355J2G3 presents the highest values of current density within the passive region, as well as the lowest pitting potential, E_p . This displacement of the pitting potential towards more negative values makes the extent of the passive region significantly lower for the carbon steel than for the stainless steels.

The curves of stainless steels show lower passive current densities compared with the values recorded for the carbon steel, due to the influence of Cr [33]. The main difference between the curves of the different stainless steels is the value of the pitting potential. The value of the pitting potential is affected by several parameters, such as temperature, concentration of aggressive ions or alloy composition. In this case, the differences in E_p between stainless steels are caused by the alloying elements. When alloying the carbon steel with 17 wt.% Cr (AISI 430), the pitting potential increases dramatically. Therefore, the positive influence of Cr on the pitting corrosion resistance of stainless steels is evident from Fig. 1, due to the formation of Cr(III) oxides and hydroxides. The addition of 10 wt.% Ni (AISI 304) modifies the value of E_p to some extent, whereas the addition of 2.3 wt.% Mo (AISI 316) has a more clear influence. Finally, a considerable increase in Cr and Ni content (Alloy 33) as well as in Mo content (Alloy 31) enhances the resistance to pitting corrosion even more. The main influence of Ni in the curves shown in Fig. 1 is the reduction of the passive current density, which decreases for AISI 304 if compared with AISI 430. It can also be observed that Mo enhances the passivity of AISI 316 in comparison with AISI 304, and Alloy 31 in comparison with Alloy 33, shifting the pitting potential towards more positive values, having therefore a beneficial influence on the pitting resistance of stainless steels, as also reported by other authors [10,36,46–48].

The relative resistance of a stainless steel to pitting corrosion in the presence of aggressive anions, such as bromides, can be related to an alloy composition by an empirical formula called the Pitting Resistance Equivalent Number (PREN). The most commonly used PREN expression is [49]:

$$\text{PREN} = \% \text{Cr} + 3.3[\% \text{Mo} + 0.5\% \text{W}] + x \cdot \% \text{N} \quad (1)$$

Table 1

Compositions of the different steels used in this study (in wt.%).

Steel	Description	C	Cr	Ni	Mo	Si	P	Cu	N	S	Fe
S355J2G3	Carbon steel	0.24	–	–	–	–	–	–	–	–	Bal.
AISI 430	Ferritic SS	0.07	17	–	–	<1	<0.04	–	–	<0.03	Bal.
AISI 304	Austenitic SS	0.05	18	10	–	<0.8	–	–	0.1	–	Bal.
AISI 316	Austenitic SS	0.05	17	11	2.3	<0.8	<0.04	–	0.1	<0.03	Bal.
Alloy 33 (UNS R20033)	Superaustenitic SS	0.015	32.8	30.9	1.7	0.3	0.01	0.6	0.4	<0.01	Bal.
Alloy 31 (UNS N08031)	Superaustenitic SS	0.015	26.7	31.8	6.6	0.1	0.02	1.2	0.2	<0.01	Bal.

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