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Influence of alloying on the passive behaviour of steels in bicarbonate medium

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Abstract

The electrochemical behaviour of passive films on carbon steel, chromium steel and high speed steel (HSS) was studied in 0.5 M $NaHCO_3$. The influence of the presence of 10 mM potassium chloride on passive film stability, and of the heat treatment of chromium steel and HSS on the respective film properties, was also investigated. Polarization curves showed that the alloy composition exerts a significant influence on the onset of passive film formation, chromium and HSSs passivating more easily as a result of the higher alloying content. Values of passive current, obtained both potentiodynamically and at fixed potential, were higher for HSS than for carbon and chromium steels, which was attributed to the contributions of Mo and W to the passive film composition. The presence of chloride ion delays the passivation of chromium and HSSs, but does not interfere with passive film stability, as shown by the chronoamperometric profile and passive current values. In the case of carbon steel, with no alloying elements, chloride ion diminishes film stability but does not influence passive film formation. Heat treatment, which alters the microstructure, does not alter the properties of the passive films except for a small effect on those formed potentiodynamically on HSS.

Keywords: Corrosion; Passivation; A. Steels; Bicarbonate; Chloride

1. Introduction

The passivation of steels is a subject of much interest due to its influence on the rate of corrosion. There is much work in the literature dealing with the influence of

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alloying elements, mainly W [1–3], Mo [2–4] and Cr [3,5], on the passivation (or repassivation) ability of stainless steels. Due to the presence of these elements, stainless steels are able to passivate even in solutions containing aggressive ions, and consequently have very positive pitting potentials. On the contrary, steels with lower contents of Cr, Mo and W cannot passivate and suffer from pitting corrosion as soon as they are immersed in solutions containing aggressive ions (e.g. high speed steel (HSS) in 0.1 M KCl solution [6]).

By promoting the formation of passive films on low-alloyed steels we can expect to be able to probe more clearly the influence of content and/or type of alloying elements on the electrochemical behaviour and in turn ascertain if this can be related to their different susceptibility to pitting. For this purpose we have used carbon steel, chromium steel and HSS, passivated in a bicarbonate solution at pH $\sim$ 8.5. The pitting corrosion of these types of steel has been studied in 0.1 M KCl solution [6,7], in which they do not show an anodic passive film region before pitting commences, as evidenced by the polarization curves. The bicarbonate passivating medium has been used by Brossard et al. to study the electrochemical behaviour of 1024 mild steel [8]; its localised corrosion was studied by adding chloride to bicarbonate and phosphate passivating media [9,10]. Cheng et al. [11,12] also used bicarbonate solution with and without chloride to study metastable pit formation in A516 carbon steel, as well as in chromate/bicarbonate mixtures [13]. A number of studies have been undertaken with regard to identifying the passive film formed on iron in bicarbonate solutions using electrochemical impedance [14,15], and by spectroscopy and spectroelectrochemistry [15–19]. The structure and chemistry of the passive film on iron have been extensively studied since 1790, but only recently has it been confirmed that spinel oxides form the basis of the passive film structure [20,21]. Nevertheless, the structure is not perfect [22], and defect sites remain, allowing localised corrosion to occur. The chemical breakdown of passivity on iron and consequent pit nucleation has also been investigated [23].

Passivation of mild steel electrodes as the potential becomes sufficiently positive is ascribed to the formation of a γ-Fe_2O_3/Fe_3O_4 film [24]. Simard et al. [8] showed that this film is not affected by the presence of HCO_3^-/CO_3^{2-} as long as the applied potential remains in the passive region, since the oxidation current is practically independent of the HCO_3^-/CO_3^{2-} concentration although other studies showed that this is pH and temperature dependent [25]. Pit nucleation and passivation of carbon steel [12,26] has also been assessed.

The effect of alloying on the passive film properties and film stability in the presence of chloride have been investigated, with the purpose of obtaining insight into the fundamental processes of passivation and the beneficial effects of alloying elements.

2. Experimental

The chemical composition of the three different types of steel—carbon steel, chromium steel and HSS—are shown in Table 1. Carbon steel was used as-received;

Table 1
Nominal chemical composition in wt% and area of the steel samples

Steel type	W	Mo	Cr	V	C	Mn	Si	Area/cm^2
Carbon steel 1015 (AISI)	–	–	–	–	0.17	<1.0	<0.4	3.1
Chromium steel CALMAX®	–	0.5	4.5	0.2	0.6	0.8	<0.4	2.0
HSS M2 (AISI)	6.4	5.0	4.2	1.9	0.9	<0.4	<0.4	1.8

chromium steel and HSS were used both as-received and after heat treatment, which consisted of the following steps:

(a) austenitizing at 950 °C (chromium steel) or at 1150 °C (HSS) for 10 min in argon atmosphere;
(b) quenching in oil down to room temperature and
(c) tempering for 2 h at 450 °C (chromium steel) and triple tempering for 2 h at 550 or 650 °C (HSS).

The samples were polished with silicon carbide papers of 600 and 1000 grit sizes and were then rinsed with water and ethanol. Electrodes were prepared by attaching a copper wire to the rear face with silver epoxy and covering it with epoxy resin, including the edges. Solutions of 0.5 M $NaHCO_3$ (pH 8.6) without and with 0.01 M chloride (pH 8.5) were used; they were prepared using analytical grade reagent and Millipore Milli-Q water. Solutions were not deaerated. Experiments were carried out at 25 ± 1 °C.

A three-electrode cell containing a Pt foil auxiliary electrode and a saturated calomel reference electrode was employed, controlled by a EG&G PAR273A potentiostat with M352 Corrosion Analysis Software, also used for Tafel analysis of the polarization curves by curve fitting.

The points on the plots are the arithmetic mean and the error bars represent the standard deviation of the values obtained for at least three measurements for each steel sample.

3. Results and discussion

All electrochemical measurements were carried out in both 0.5 M $NaHCO_3$ and 0.5 M $NaHCO_3$ + 0.01 M KCl solutions. Polarization curves of the three different steels (carbon steel, chromium steel and HSS) were recorded first, since they allow the determination of the different regions of potential (dissolution, prepassivation, passivation and transpassivation) characteristic of each kind of steel. This was important in order that further experiments could be carried out at appropriately chosen values of potential, mainly in the passive region. Passivation current values and some qualitative information concerning the differences in the passive film formation, depending on the steel composition, were also obtained.

Carbon steel was used as reference, since it has the simplest chemical composition (see Table 1). The influences of composition, heat treatment and chloride ion on the passive film properties are the main factors exploited in the present work.

3.1. Polarization curves

3.1.1. Effect of alloying

Polarization curves for the three types of steels in $NaHCO_3$ solution without and with chloride ion are shown in Fig. 1. The effect of the alloying elements on the onset of the passive region can be clearly distinguished; the passive film on chromium steel and HSS is formed at more negative potentials than on carbon steel. The values of the primary passivation potential, E_{pp}, and critical anodic current density, I_{crit}, were obtained from the polarization curves in the way indicated in Fig. 1 (curve 1) and are shown in Fig. 2. For chromium steel values of E_{pp} and I_{crit} could not be obtained, since the prepassivation region is not observed in the polarization curves, as demonstrated in Fig. 1 (curves 2 and 3). There is a shift of almost 250 mV in E_{pp} in the negative direction for the HSSs compared to carbon steel (see Fig. 2a). At the same time, I_{crit} decreased significantly (see Fig. 2b) confirming the greater ability of HSS to passivate.

The passive current density, I_{pas}, is an important parameter because it is a measure of the corrosion resistance of the material in the passive state; a low passive current density indicates a high corrosion resistance. The I_{pas} values obtained from the polarization curves at specific potential values for the various steel samples are shown in Fig. 3. They were obtained at a potential within the passive zone of each steel sample: +0.7 V for carbon steel in the absence of chloride; +0.3 V for chromium steel and 0.0 V for HSS, both in the presence and absence of chloride. Carbon steel in the presence of chloride has a very narrow passive region (see Fig. 1, curve 1), and consequently a value of the passive current could not be obtained.

It is seen that the I_{pas} values are higher for HSS. In [2], it was found that the presence of Mo and W, which have similar electrical conductivities and electronegativities and are the dominant alloying elements of HSS, lead to beneficial effects on the passivity parameters of stainless steels. A quantitative relationship between passivation parameters and the Mo and W content was seen, although the reason for this was not clear. It does suggest, however, that the intrinsic properties of the passive film are directly related to the nature of the alloying elements, which will certainly alter the defect structure and vacancies in the films [20,27]. Another factor affecting the values of I_{pas} can be the different passive film thicknesses, according to the alloy composition.

Another interesting fact concerning the polarization curves is the appearance of one peak for chromium steel and two or three peaks in the case of HSS. Since none of these peaks appeared for carbon steel, they can be attributed to electrochemical reactions involving the transition to higher oxidation states of Cr in the case of chromium steel, and Cr, Mo and W for HSS. In fact, Pan et al. [28] observed a small

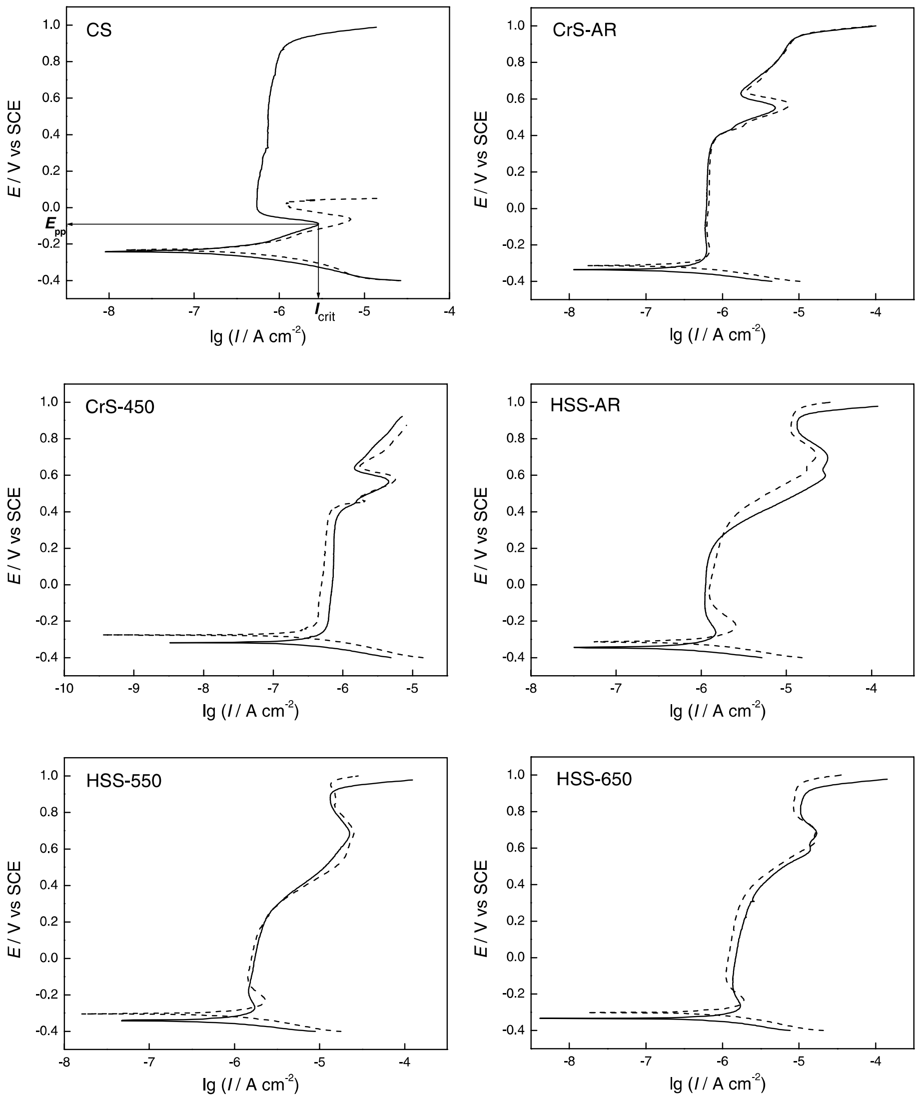

Fig. 1. Polarization curves of the steel samples in solutions of (—) 0.5 M $NaHCO_3$ and (- - -) 0.5 M $NaHCO_3 + 0.01$ M KCl; scan rate: 0.2 $mV\,s^{-1}$. CS: Carbon steel; CrS-AR: Chromium steel as-received; CrS-450: Chromium steel tempered at 450 °C; HSS-AR: HSS as-received; HSS-550: HSS tempered at 550 °C; HSS-650: HSS tempered at 650 °C.

current peak at about 0.65 V vs. SCE in the passive region of both austenitic high-N and duplex SAF2507 stainless steels, whose dominant alloying elements are Cr and Ni, and attributed this to the electrochemical oxidation Cr(III) → Cr(IV). As for the steels studied here (especially HSS), Pan et al. [28] found that the steels still remain in a passive state above the peak potential(s).

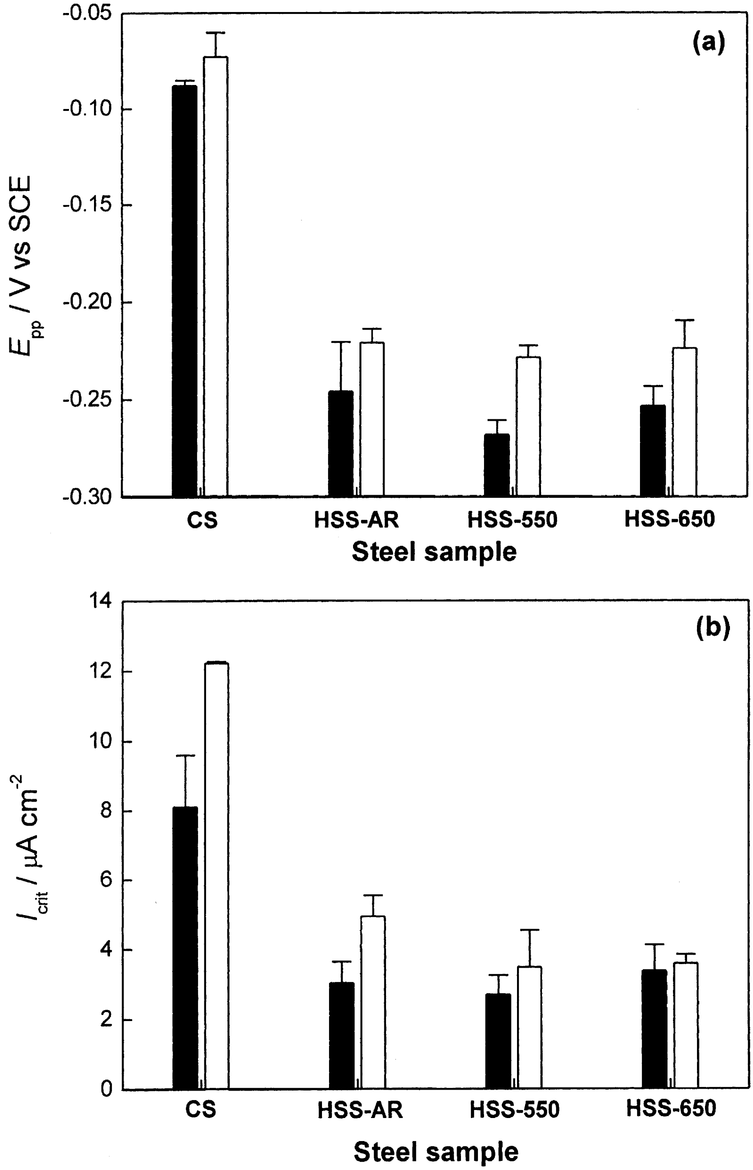

Fig. 2. Values of primary passivation potential, E_{pp}, and critical anodic current density, I_{crit}, for the steel samples obtained from the prepassivation zone of the polarization curves. (■) 0.5 M $NaHCO_3$; (□) 0.5 M $NaHCO_3$ + 0.01 M KCl. Sample designation as in Fig. 1.

Above 1.0 V all the steel samples show a sudden increase in anodic current, related to oxygen evolution, as seen elsewhere [29].

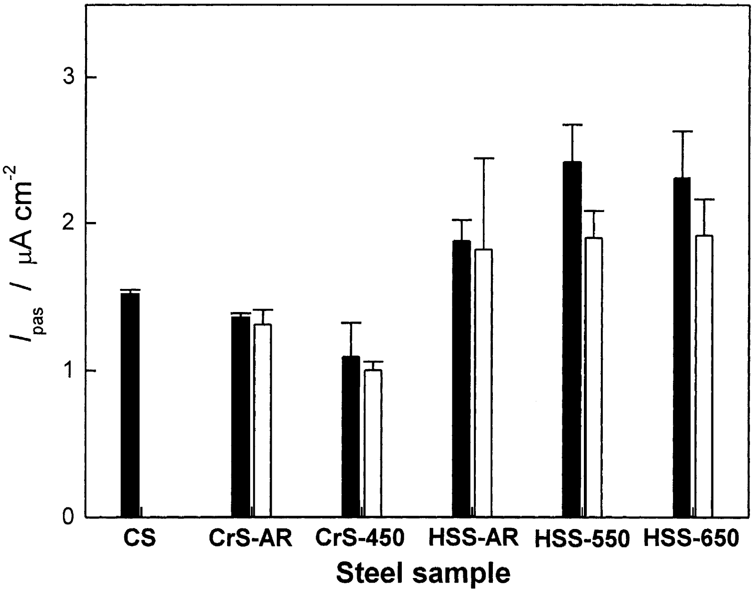

Fig. 3. Values of passive current, I_{pas}, for the steel samples obtained at specific potential values in the passivity region of the Tafel plots. (■) 0.5 M $NaHCO_3$; (□) 0.5 M $NaHCO_3 + 0.01$ M KCl. Sample designation as in Fig. 1.

3.1.2. Effect of chloride ion and heat treatment

The addition of 0.01 M chloride ion to 0.5 M $NaHCO_3$ caused a significant change in the passivity region of carbon steel (see Fig. 1, curve 1): the film is easily ruptured and pitting corrosion takes place. On the other hand, the potentiodynamic behaviour of alloyed steels (chromium steel and HSS) does not change, showing—as would be predicted—that they are more resistant to pitting corrosion than is carbon steel. Nevertheless, in the case of HSS a small shift of E_{pp} in the positive direction is observed, together with higher I_{crit} values, which means that the formation of the anodic passive film is delayed even in the presence of such a small chloride concentration (see Fig. 2). The same effect is observed for chromium steel, although it was not possible to determine E_{pp} and I_{crit} values.

There is some similarity between the I_{pas} values in the presence or absence of chloride, although the average values of I_{pas} in the presence of chloride are always lower than those obtained when it is absent (see Fig. 3). However, further evidence is necessary to confirm that this low anion concentration really affects the passive film current value. One study using secondary ion mass spectroscopy (SIMS) found that there was no difference in oxide thickness on Fe samples prepassivated in borate solution and galvanostatically anodised at 5 μA/cm^{-2} in solutions with or without Cl^- [30]. No Cl^- was incorporated into the oxide during this treatment.

From analysis of the polarization curves in the Tafel region, the corrosion potential, E_{cor}, and corrosion current density, I_{cor}, were obtained, as shown in Fig. 4.

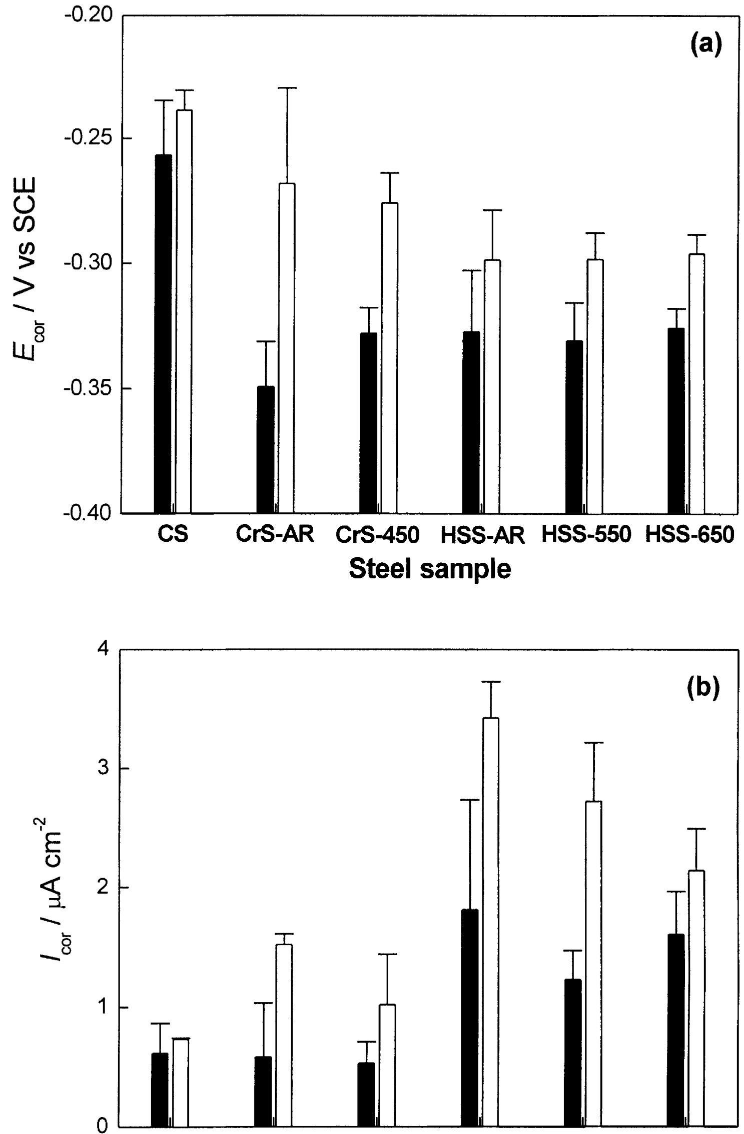

Fig. 4. Values of corrosion potential, E_{cor} and corrosion current density, I_{cor} for the steel samples obtained from the Tafel region of the polarization curves. (■) 0.5 M $NaHCO_3$; (□) 0.5 M $NaHCO_3$ + 0.01 M KCl. Sample designation as in Fig. 1.

The influence of chloride ion is evident, since E_{cor} values are shifted in the positive direction, as happened with the E_{pp} values. Additionally, the I_{cor} values are significantly higher when chloride is present. Thus a concentration of 0.01 M chloride is already able to increase the corrosion rate. It is interesting to note that the I_{cor} values of the steel samples follow the same trend as the I_{pas} values.

In order to determine the pitting potentials of both chromium steel and HSS the chloride content was increased to 0.1 M (Fig. 5 shows the polarization curves). It can be seen that under these conditions chromium steel and HSS suffer from pitting corrosion after the passive anodic region. Additionally, HSS samples have more positive pitting potentials than chromium steel (except in the case of HSS tempered at 550 °C), which is probably related to their higher degree of alloying and different microstructure. The presence of a higher quantity of Mo can be responsible for the better corrosion resistance of HSS.

The samples of heat-treated HSS have higher values of passive current than as-received samples, suggesting that heat treatment exerts some influence on the passive film properties, as found for HSS in the absence of passive film in chloride solution

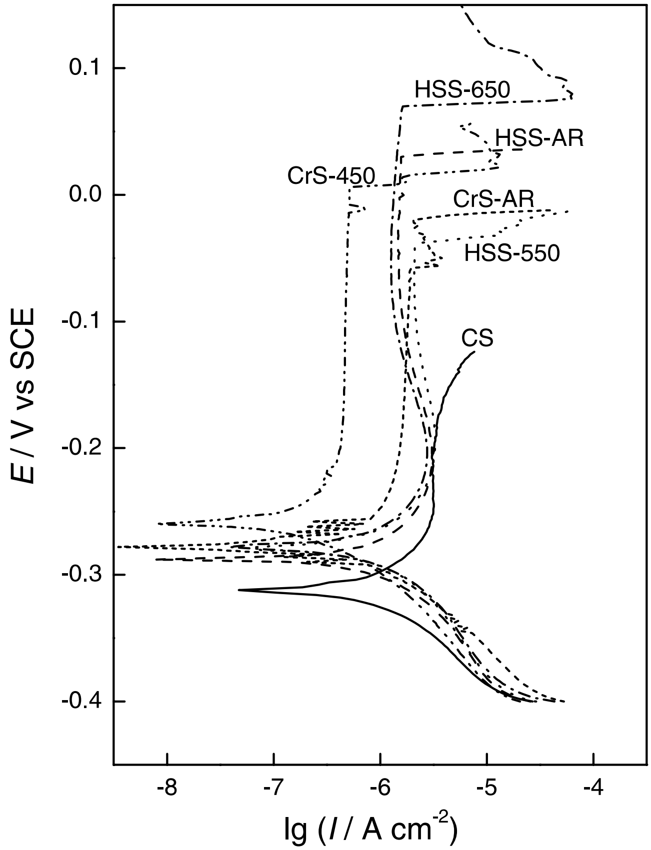

Fig. 5. Polarization curves of the steel samples in 0.5 M $NaHCO_3$ + 0.1 M KCl; scan rate: 0.2 mV s^{-1}. Sample designation as in Fig. 1.

[6]. In as-received HSS all the carbon is present as carbides, there being none present in the ferritic matrix. Transformations which occur on tempering are changes in the microstructure due to the formation of submicrometre particles of different carbides. At 550 °C there is already formed some M_4C_3, very rich in V and Cr, and also $M_{23}C_6$. By 650 °C, the M_4C_3 and some of the $M_{23}C_6$ are beginning to dissolve into the ferritic matrix. Further details may be found in [6].

In the case of chromium steel, the main change in the microstructure is the formation of chromium carbides, such as Cr_7C_3. Heat treatment at 450 °C did not significantly influence anodic passive film formation (see Figs. 1 and 3).

3.2. Open circuit behaviour as a function of time

3.2.1. Effect of chloride

Since chloride ion showed some influence on the onset of formation of the anodic film on the steels studied, especially alloyed steels, uncorroded samples were immersed in solutions without and with 0.01 M chloride and the open circuit potential, E_{ocp}, was measured during 2 h (see Fig. 6). In both media, the general shape of the curves is the same for all samples; the potential shifts to the positive direction with increasing immersion time, owing to the steel surfaces becoming passivated.

The passivation behaviour of carbon steel is chloride independent and the E_{ocp} values become almost constant after the first half-hour of immersion. This is in agreement with the fact that E_{pp} is also chloride independent (Fig. 2a). The effect of chloride is more pronounced in the case of the alloyed steels (chromium steel and HSS). With the exception of HSS as-received, all curves are shifted in the positive direction in the presence of chloride, confirming it interferes with passivation, as already observed from the E_{pp} values measured under potentiodynamic conditions.

3.2.2. Effect of alloying elements and heat treatment

The presence of the alloying elements Cr, Mo, W in the steels causes a lowering of the potential at which the steel is able to passivate, as revealed by the E_{ocp} values (see Fig. 7). HSS and chromium steel are more easily passivated than carbon steel, in agreement with the E_{pp} values. The values of E_{ocp} of heat-treated HSS are always more negative than those of as-received HSS, both in the presence or absence of chloride (with the exception of HSS as-received in the presence of chloride), indicating that the heat treatment alters the film properties, since these samples are more easily passivated. However, the heat treatment does not change the passivation behaviour of chromium steel. These results are in agreement with those obtained from the polarization curves.

3.3. Chronoamperometric measurements

After prepassivating the steel samples during 2 h at open circuit in 0.5 M $NaHCO_3$, or in 0.5 M $NaHCO_3 + 0.01$ M KCl, chronoamperometric curves were recorded during application of a fixed applied potential localised in the passive zone (identical to that at which I_{pas} values were obtained in the polarization curves). The

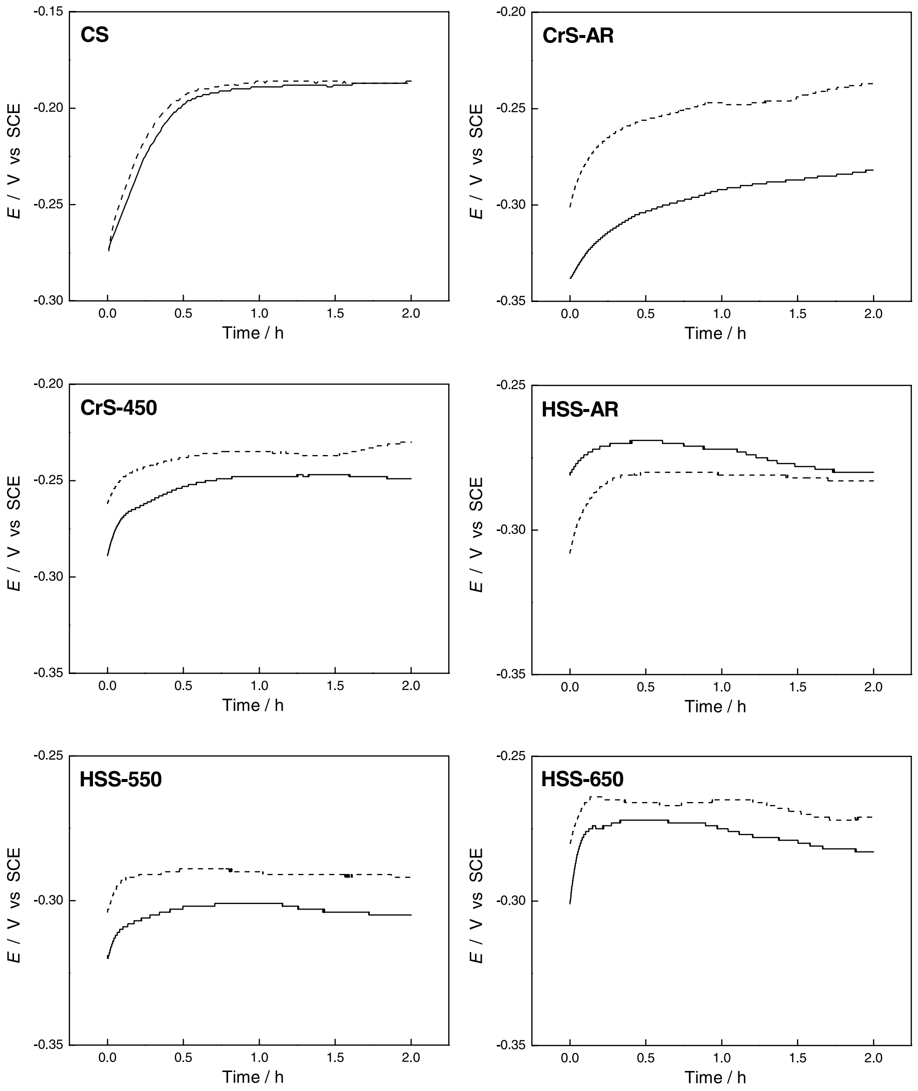

Fig. 6. Open circuit potential as a function of time of the steel samples in solutions of (—) 0.5 M $NaHCO_3$ and (- - -) 0.5 M $NaHCO_3$ + 0.01 M KCl. Sample designation as in Fig. 1.

objective was to examine if anodic current transients related to metastable pitting processes, which include pit initiation, growth and repassivation, could be observed and to gain information concerning the passive film stability of the different steels. The current was measured at a sampling rate of 1 point every 1.2 s. For all steel samples investigated, the general variation of anodic current with time indicated a passivation process (see Fig. 8). The values of passive current after 1 h immersion are shown in Fig. 9.

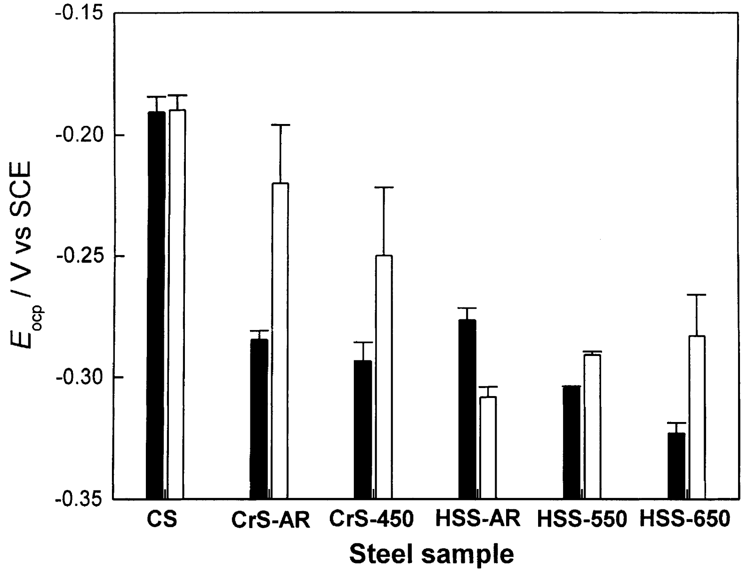

Fig. 7. Values of open circuit potential, E_{ocp}, for the steel samples obtained at the end of 2 h immersion in (■) 0.5 M $NaHCO_3$ and (□) 0.5 M $NaHCO_3$ + 0.01 M KCl. Sample designation as in Fig. 1.

Carbon steel (Fig. 8, curve 1) exhibited large anodic current transients in the presence of chloride ion, although they were also observed, to a lesser extent, in chloride-free solution. The latter can be associated with the dissolution of sulphide inclusions, as for stainless steels in Cl^--free solutions [31]. Sulphur was detected by EDX in this carbon steel, and inclusions were visible by optical microscopy. Such a type of current transient, characterized by a quick rise followed by exponential decay, has also been observed during metastable pitting in other carbon steels [11,12] and in pure iron [32].

The presence of chloride caused a lowering of the carbon steel passive currents (Figs. 8, curves 1 and 9). This can be explained through specific adsorption of chloride ions on the steel surface leading to the local thinning of the passive film via formation of an iron (III) hydroxychloro-complex [33].

Chromium steel and HSS show a more stable general variation of passive current with time compared with carbon steel, indicating a higher resistance of the passive films towards metastable pitting. The general chronoamperometric behaviour did not show significant differences in the presence of chloride ion; this is also seen from the passive current values obtained at the end of the current versus time curves (see Fig. 9). This is unlike what was found with the I_{pas} values obtained from the polarization curves (Fig. 3) which were systematically slightly lower in the presence of chloride. One of the reasons for this difference is that the passive current values were obtained when the systems were in steady-state conditions, while under potentiodynamic conditions this was not the case. Again, the I_{pas} values are systematically

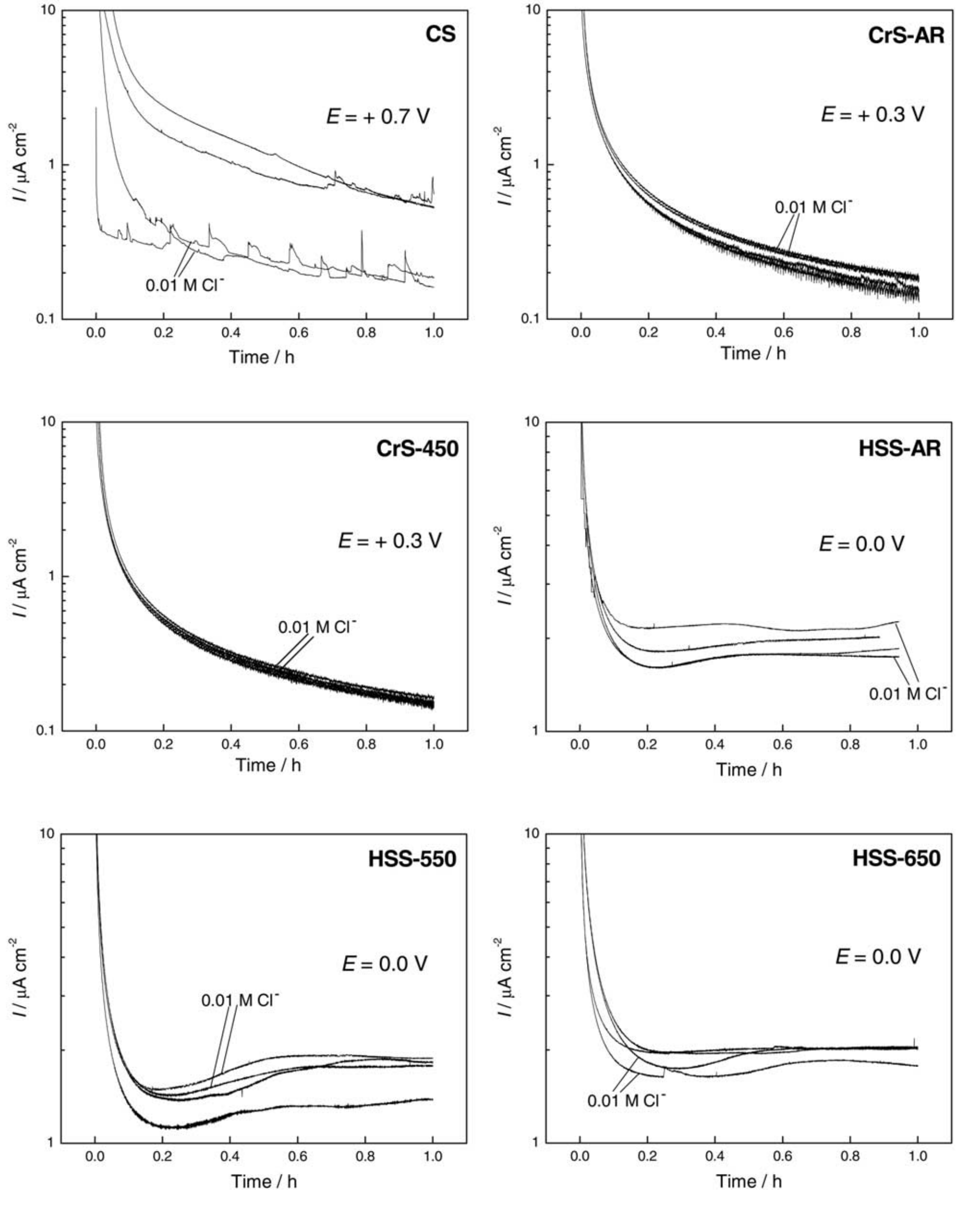

Fig. 8. Chronoamperometric behaviour for passivated steel samples in 0.5 M $NaHCO_3$ and 0.5 M $NaHCO_3$ + 0.01 M KCl held at the potentials specified in the figure within the passivity region. The results of two separate experiments for each of the two bathing solutions are shown. Sample designation as in Fig. 1.

higher for HSS, in comparison with those of carbon and chromium steels, as obtained potentiodynamically (see Fig. 3).

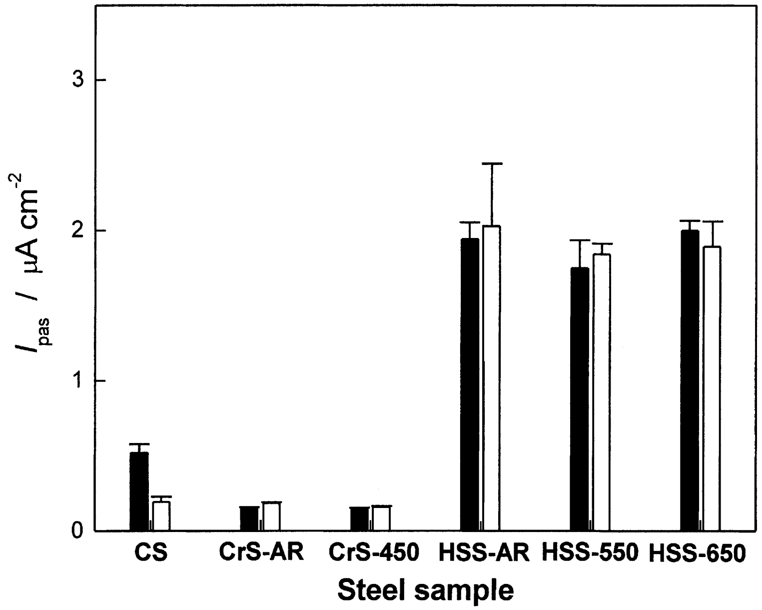

Fig. 9. Values of passive current, I_{pas}, for the steel samples obtained at the end of the current versus time curves exemplified in Fig. 8. (■) 0.5 M $NaHCO_3$; (□) 0.5 M $NaHCO_3$ + 0.01 M KCl. Sample designation as in Fig. 1.

The I_{pas} values for heat-treated samples are not significantly different from those for as-received samples. For HSS this is in contrast with the results obtained potentiodynamically. Once again, the explanation for this difference is that data obtained potentiodynamically were not steady state, as was the case for those obtained by chronoamperometry.

The phenomena causing the anodic current transients is a sudden failure of the protective layer, followed by a slow repassivation process [34]. The rate of repassivation is influenced by the presence of alloying elements in the steel, which are assumed to accelerate it. It was recently demonstrated that increasing contents of Cr, Mo and W in ferritic stainless steels lead to an increase in the repassivation rate of scratched alloys [3], which was clearly seen through the current transients generated. However, stainless steels show a different type of current transient, which is a slow rise followed by a quick drop in current [32]. The results obtained in this work are in agreement with an abrupt localised failure of the passive layer followed by a slow repassivation process.

3.4. Comparative remarks

All the electrochemical results are in agreement that the higher-alloyed steels (chromium steel and HSS) are more easily passivated than carbon steel in 0.5 M $NaHCO_3$.

This is clearly seen by the more negative values of E_{ocp} and E_{pp} for these steels, compared to carbon steel. This is ascribed to the presence of the alloying elements in the passive film as described above; other studies have also shown changes to the passive film structure and properties [27,35].

The I_{pas} values were obtained both from the polarization curves and by chronoamperometry. Independently of the methodology used, the values were systematically higher for HSS in comparison with those for chromium steel and carbon steel. However, the I_{pas} values obtained from polarization curves were higher than from chronoamperometry and showed a greater dispersion. The reason for this can be traced to the fact that under potentiostatic conditions the passive currents reached steady-state conditions before measurements were made. This, in turn, excludes the possibility that the heat treatment of HSS results in higher values of I_{pas}, as suggested by the polarization curves only.

The addition of 10 mM chloride did not change the passive film stability of chromium steel and HSS, while it led to metastable pitting corrosion of passive carbon steel, contrary to what was suggested from the decrease in the I_{pas} values in the polarization curves. However, chloride delays the passivation of these steels, shifting the primary passivation and open circuit potentials in the positive direction.

The pitting potentials of chromium steel and HSS determined in the presence of 0.1 M chloride were found to be more positive than those of carbon steel, corroborating the improved protective properties of the passive film. Again, as in the absence of chloride, this is probably the result of the presence of the alloying elements in the passive film composition, and the same considerations apply as given above.

4. Conclusions

The studies undertaken regarding the passive films formed on carbon steel, chromium steel and HSS, in 0.5 M $NaHCO_3$ solution lead to the following conclusions:

- The films have primary passivation potentials, E_{pp}, as well as open circuit potentials, E_{ocp}, for chromium steel and HSS $\sim$250 mV less negative than carbon steel, demonstrating their greater ability to passivate. This parallels their smaller critical anodic current densities, I_{crit}.
- Values of passive current density, I_{pas} were systematically higher for HSS and were associated with the presence of Mo and W in the passive film composition, or to the greater thickness of the HSS passive film.
- The I_{pas} values obtained potentiodynamically were systematically higher than those obtained at fixed potential, probably as a consequence of the steady state attained in the latter case.
- The presence of 10 mM of chloride in 0.5 M $NaHCO_3$ shifts E_{ocp} to more positive values in the case of chromium steel and HSS, evidencing its ability to delay passive film formation. This is corroborated by the same behaviour of E_{pp}, and higher I_{crit} values.

- For chromium steel and HSS the I_{pas} values were lower in presence of chloride (from the polarization curves). However, these values did not change systematically in the presence or absence of chloride at fixed potential, signifying that this anion is not able to alter film stability.
- For carbon steel, the I_{pas} values were lower in the presence of chloride, suggesting thinning of the passive film. Additionally, the appearance of current transients pointed to the occurrence of metastable pits.
- The heat treatment of chromium steel and HSS does not alter the passive film properties, such as E_{pp}, I_{crit}, I_{pas} and E_{ocp} values, compared to the respective steels as-received.

Acknowledgements

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