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The Influence of Alloying on the Passive Behaviour of Steels in Bicarbonate Medium Studied by Electrochemistry and XPS

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Abstract. Passive films formed in 0.5 M $NaHCO_3$ and 0.5 M $NaHCO_3$ + 0.01 M KCl aqueous solution on carbon steel, chromium steel and high speed steel have been characterized by electrochemistry and XPS. The influence of heat treatment on the passive film properties of chromium steel and HSS was also studied. Polarisation curves show that the steel composition influences the onset of passive film formation. Chromium and high speed steels show a higher ability to passivate as a result of the higher alloying content, corroborated by open circuit potential measurements. Passive current density values, obtained from potentiodynamic curves and by chronoamperometry, were higher for HSS than for carbon and chromium steels, and are associated with the presence of Mo and W oxides in the passive film, as confirmed by XPS analysis. The presence of 0.01 M chloride ion in solution shifts the passivation of chromium steel and HSS to more positive potentials but does not interfere with passive film stability. For carbon steel, chloride ion does not influence the initiation of passive film formation, but diminishes film stability. Tempered chromium steel and HSS show passive film behaviour with similar characteristics to the respective as-received steels.

Introduction

The passivation of steels is a subject of much interest due to its influence on the rate of corrosion, since it can protect the metallic surface underneath from aggressive agents present in the local environment, such as Cl^-. The microstructure, composition and thickness of the passive films are crucial parameters in determining the extent of protection. By promoting the formation of passive films on different low-alloyed steels, the influence of content and/or type of alloying elements on the electrochemical behaviour can be more deeply probed as can the relation to their different pitting susceptibilities. It has been shown [1] that certain elements such as Cr, Mo and W are able to affect the composition of the passive films formed on steels, and therefore their electrochemical properties and corrosion.

Bicarbonate solution at pH ~8.5 was chosen as passivating medium, since it has been used recently with success by Simard *et al.* [2] and Cheng *et al.* [3] in the study of pitting of passivated steels. Passive films were formed on three different types of mild steel which were, in order of alloying element complexity: carbon steel, chromium steel and high speed steel, HSS. The influence of the presence of 10 mM chloride ion on passive film stability and properties, as well as changes in the surface microstructure of chromium steel and HSS caused by heat treatment, were also studied.

Passivation of mild steel as the potential becomes sufficiently positive has been ascribed to formation of a $\gamma\text{-}Fe_2O_3/Fe_3O_4$ film [4]. Simard *et al.* [2] showed that this film is not affected by the presence of HCO_3^-/CO_3^{2-} in solution so 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.

Experimental

The chemical compositions of the three types of steels studied – 1015 carbon steel, Calmax chromium steel and M2 high speed steel - are given elsewhere [5]. Carbon steel was used as received; chromium steel and high speed steel were used both as-received and after heat treatment, the details of which are in [5]. Chromium steel was tempered at 450°C and HSS at 550°C and 650°C.

The samples were polished with SiC papers of 600 and 1000 grit sizes and were then rinsed with water and ethanol. Non-deaerated solutions of 0.5 M $NaHCO_3$ (pH 8.6) and of 0.5 M $NaHCO_3$ + 0.01 M KCl (pH 8.5) were used; they were prepared using analytical grade reagent and Millipore Milli-Q water. A three-electrode cell containing a Pt foil auxiliary electrode and a saturated calomel electrode (SCE) as reference was employed, controlled by an EG&G PAR273A potentiostat with M352 Corrosion Analysis Software. XPS analysis of steels passivated in 0.5 M $NaHCO_3$ or 0.5 M $NaHCO_3$ + 0.01 M KCl at the open circuit potential, OCP, during 24 h was done with a MICROLAB 310 F VG Scientific spectrometer using 1253.7 eV Mg-Kα radiation and a sample chamber pressure of ~5×10^{-9} mbar.

Results and Discussion

Electrochemical techniques - polarisation curves, measurements of OCP, current-time behaviour at fixed applied potential in the passive region – and XPS analysis were used to characterise the passive films formed on the different steels.

Polarisation curves. *Influence of alloying.* The onset of the passive region of chromium steels and high speed steels, HSS, occurs at more negative potentials (~-0.3 V vs. SCE) than for carbon steel (~0.0 V vs. SCE), Fig. 1a, reflecting the greater ability of these steels to passivate. Higher values of passive current density, I_{pas}, were observed for HSS samples, Fig. 1b, associated with the different HSS passive film composition which contains the more highly conducting Mo and W oxides as shown by XPS (see below). The appearance of one peak for chromium steel and 2 or 3 peaks for HSS in the polarisation curves is probably related to electrochemical reactions in the solid state involving a transition to higher oxidation states of Cr in the case of chromium steel, and Cr, Mo and W for HSS.

Influence of addition of 10 mM chloride ion to 0.5 M $NaHCO_3$. Chloride ion destroys the passivity only of carbon steel, delaying the anodic passive film formation of HSS and chromium steels. As seen in Fig. 1b, it does not affect the I_{pas} values.

Influence of heat treatment. From analysis of the polarisation curves, the passive film properties

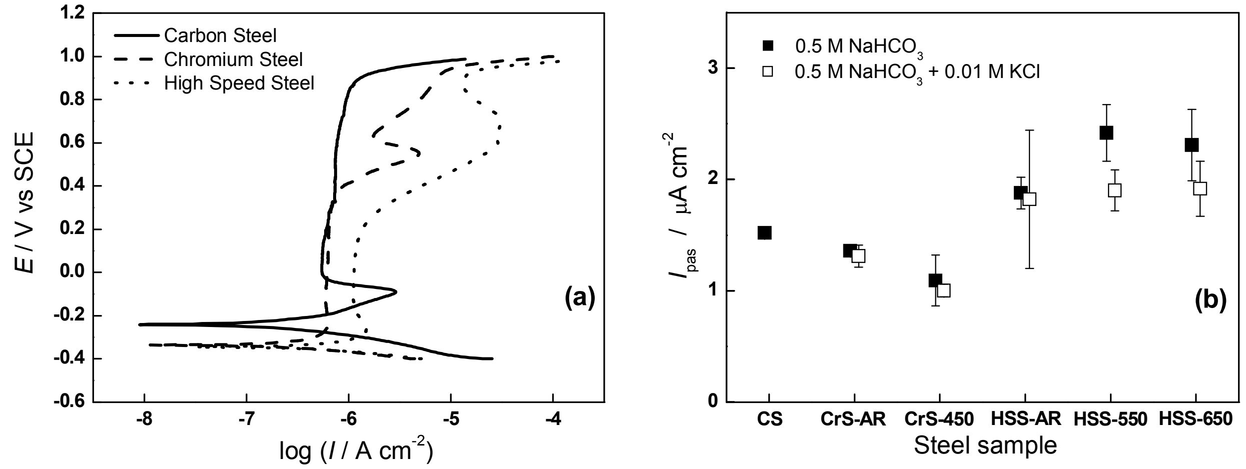

Figure 1. (a) Polarisation curves of steel samples in 0.5 M $NaHCO_3$; scan rate: 0.2 mV s^{-1}. (b) I_{pas} values obtained from the anodic passive region of the polarisation curves of **CS**: Carbon steel (E = 0.7 V); **CrS-AR**: chromium steel as-received (E = 0.3 V); **CrS-450**: chromium steel tempered at 450°C (E = 0.3 V); **HSS-AR**: HSS as received (E = 0.0 V); **HSS-550**: HSS tempered at 550°C (E = 0.0 V); **HSS-650**: HSS tempered at 650°C (E = 0.0 V).

appear not to be affected by heat treatment.

OCP measurements. *Effect of addition of 10 mM chloride ion to 0.5 M* $NaHCO_3$. Except for carbon steel, all curves are shifted in the positive direction, confirming the influence of chloride on shifting the passivity region in a positive direction, as already seen through the polarisation curves.
Effect of alloying. HSS and chromium steel showed more negative OCP values, i.e. a greater ability to form the passive film.
Effect of heat treatment. Unlike polarisation curve data, OCP measurements suggest that heat-treated HSS is more easily passivated.

Current-time measurements at applied potential. *Influence of addition of 10 mM chloride ion to 0.5 M* $NaHCO_3$. Current transients related to metastable pitting appeared for carbon steel (see Fig. 2a), which were not observed for HSS or chromium steel, demonstrating that the passive films formed on these higher-alloyed steels have a higher resistance towards metastable pitting. This concentration of chloride causes a lowering of the carbon steel I_{pas}, Fig. 2b, related to the formation of iron (III) hydroxychloro complexes.
Influence of alloying. HSS again shows higher I_{pas} values (see Fig. 2b), as also observed from the I_{pas} values obtained through the polarisation curves.
Influence of heat treatment. I_{pas} values did not change in the case of either HSS or chromium steel.

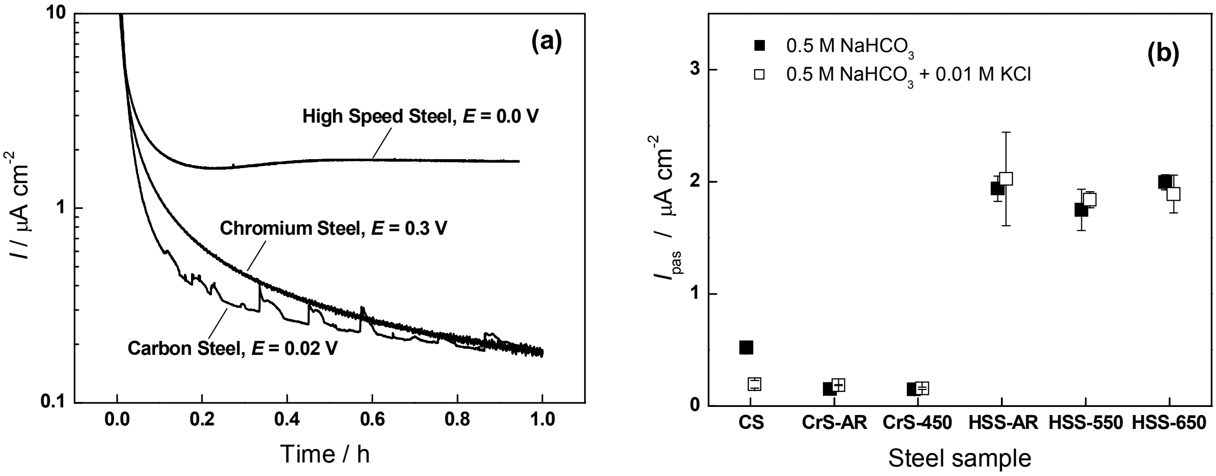

Figure 2. (a) Current-time behaviour of steels in 0.5 M $NaHCO_3$ + 0.01 M KCl at applied potentials within the passive region. (b) Values of I_{pas} for the steels obtained at the end of the I vs time curves exemplified in (a). **CS**: Carbon steel; **CrS-AR**: chromium steel as-received; **CrS-450**: 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.

XPS analysis of passivated steels. XPS analysis was performed after passivation of the steel samples by immersion during 24 h at the OCP in 0.5 M $NaHCO_3$ and in 0.5 M $NaHCO_3$ + 0.01 M KCl. The main peaks in the XPS spectra were those of Fe, O and C (for all three types of steels), Cr (for chromium steel and HSS) and Mo, W (only for HSS). Independent of the type of steel, the deconvolution of the O1s spectra showed three values of binding energies, corresponding to three oxygen species present in the passive films: oxide (strongest signal), hydroxide, and water. This confirms the formation of an oxide film on the surface of the steels. Quantification of the chemical species in the film, after deconvolution of the respective peaks, indicated that the film is mainly composed of iron oxides and hydroxides (see Fig. 3). The other types of oxides and hydroxides present in the passive film composition of chromium steel (such as Cr) and HSS (such as Cr, Mo, W) explain the differences in their I_{pas} values and stability towards pitting corrosion in the presence of chloride.

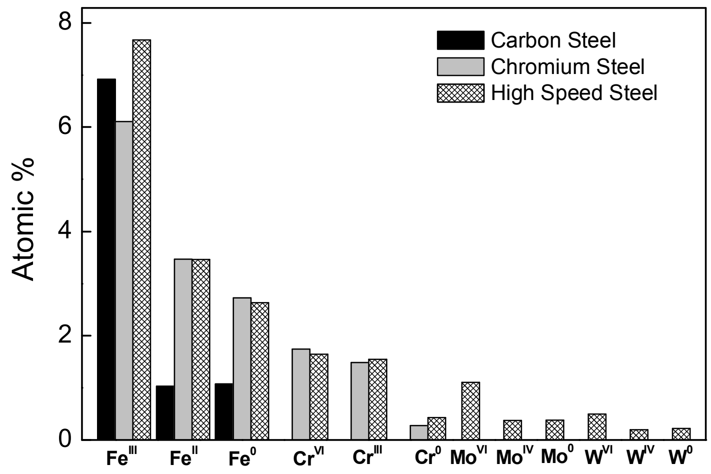

Figure 3. Atomic percentage of metallic components, obtained through quantification of the XPS spectra of the respective elements, present in the composition of the passive film formed on the studied steels in presence of 0.5 M $NaHCO_3$ during 24 h at OCP.

Conclusions

Conclusions which can be taken from this study of passive films on steels are:

- Chromium steel and HSS demonstrate a greater ability to passivate than carbon steel in bicarbonate medium, due to the presence of alloying elements (Cr, Mo, W).
- I_{pas} values were highest for HSS, associated with Mo and W oxides in the passive film composition, as shown by XPS.
- Addition of 10 mM Cl^- to 0.5 M $NaHCO_3$ shifts the open circuit potential of chromium steel and HSS to more positive values, showing its ability to inhibit passive film formation, corroborated by the polarisation curves.
- For carbon steel, I_{pas} values were lower in the presence of Cl^-, suggesting thinning of the passive film. Additionally, the appearance of current transients pointed to the existence of metastable pits.
- Heat treatment of chromium steel and HSS does not measurably alter the passive film properties.

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