The passivity of ferritic (Fe-18% Cr) stainless steel in methanolic solutions

F. BELLUCCI[†], G. FAITA, C. A. FARINA, F. OLIVANI

Department of Corrosion and Electrochemistry, Istituto G. Donegani SpA, Novara, Italy

An experimental study to define the active–passive behaviour of a ferritic (Fe–18%Cr) stainless steel in methanol, as a function of the concentration of Cl⁻ ions and acidity level, is reported. The addition of water was considered to be an inhibitor capable of reinforcing the passive film of stainless steel. The effects of acidity and of the addition of water on the anodic and cathodic behaviour of Ni, Mo, Fe and The Fe–18%Cr alloy are reported.

1. Introduction

As part of a programme to study metal corrosion in non-aqueous media, ferritic stainless steel (Fe–18%Cr) with a low interstitial content was considered a suitable material for establishing the behaviour of chromium in the presence of anhydrous solvents, or solvents with low water contents. A comparison with data obtained for iron, nickel and molybdenum in methanol [1, 2] and with austenitic steels (types 304 and 316 [3]) produces quite a complete picture of the fundamental characteristics and possibilities for using iron-based alloys in methanol.

Interest in this field has been aroused by case histories of unexpected failures in stainless steel apparatus which held alcohol. A tank containing methyl alcohol at room temperature failed due to stress–corrosion cracking after only one month's use and a distillation column of isopropanol underwent intergranular stress–corrosion attack after one year's use. Cases like these show the need to investigate in detail the peculiarities of new materials intended for metal–non-aqueous environments in which localized corrosion phenomena are aggravated by low water content, which makes the reconstruction of the protective oxide difficult.

The research carried out on ferritic (Fe–18%Cr) stainless steel is intended to define the active–passive behaviour in methanol as a function of the chloride content and acidity level. The addition of water in solution is also considered, as water acts as an inhibitor capable of reinforcing or re-establishing the passive film.

2. Experimental

The material used for the experiments was taken from a sheet of ferritic stainless steel 1.5 mm thick, with the composition: C = 0.021%, Cr = 18.30%, Ni = 0.21%, Mo = 0.085%, Mn = 0.33%, Cu = 0.083%, Ti = 0.41%, Si = 0.33%, S = 0.024%, P = 0.023%. The specimens consisted of discs, 13.5 mm in diameter, mounted with a rubber gasket on to the end of a glass 'pipe'; the electric contact was made with an AISI-316 wire.

The base solution consisted of reagent-grade methanol with a water content equal to 500 ppm, to which was added 0.1 M $LiClO_4$ as the supporting electrolyte. The polarization curves were obtained following the standard ASTM procedures, using an ASTM G5 cell, counter-electrodes of smooth platinum, a saturated calomel electrode as the reference electrode and a scan rate of 40 mV min^{-1}. The solutions were de-aerated by nitrogen bubbling for 2 hours before each run and the specimens were polished with 600-grit emery paper and finished with alumina.

[†] Permanent address: Istituto di Principi di Ingegneria Chimica, Università di Napoli, P. le Tecchio, 80125, Napoli, Italy.
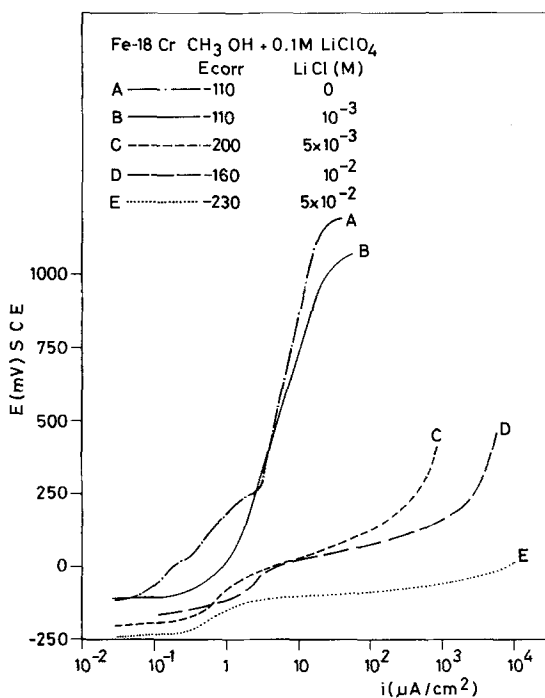
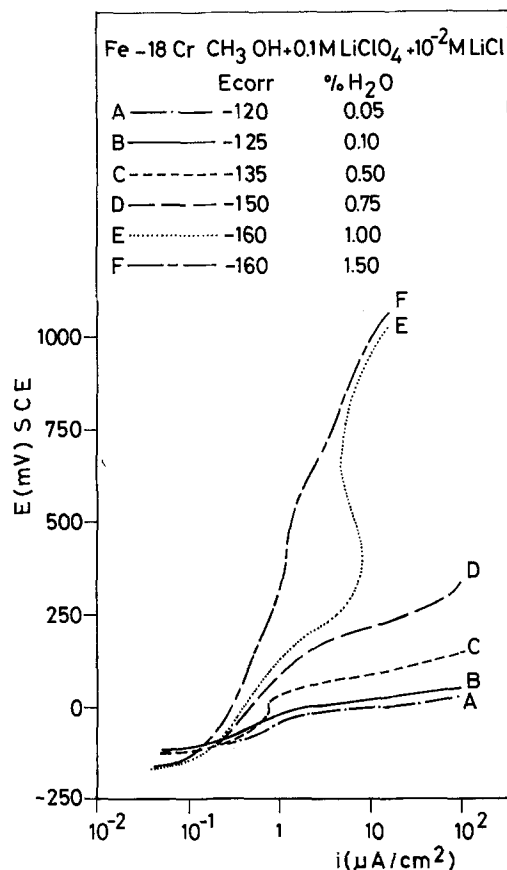Fig. 1. Anodic polarization curves of Fe—18%Cr in MeOH + 0.1 M LiClO$_4$ + Cl$^-$.

Fig. 2. Anodic behaviour of Fe—18%Cr in MeOH + 0.1 M LiClO$_4$ + 10^{-2} M LiCl as a function of water content.

3. Results and discussion

3.1. Effect of chlorides

In methanol solutions with 0.1 M LiClO$_4$ a clear transition from a stable passive state to breakdown of the film was observed at a chloride content equal to 5×10^{-3} M (Fig. 1). For curves C, D and E relating to high chloride contents, the anodic current reaches only a limiting value. For solutions which clearly produce a breakdown of the passive film, the water content capable of inhibiting chloride attack was investigated: this content seems to be equal to 1% for Cl$^-$ = 10^{-2} M and 5% for Cl$^-$ = 5×10^{-2} M (Figs. 2 and 3). Obviously, therefore, for a higher chloride content, the amount of water needed to inhibit the corrosion phenomena increases. It is also observed that the point which can be defined as a pitting potential E_c, increases as the water content increases, thus contributing by other means to a greater stability of the passive film.

3.2. Growth of pits under potentiostatic attack

In order to define the zones of potential where the pitting phenomenon occurs, a preliminary study was carried out of the growth morphologies of pits at different potentials. To obtain curve F of Fig. 3, the sample was first brought to + 250 mV where either growth of pits nucleated above the pitting potential (+ 50 mV in this hypothesis) or, less probably, corrosion in the active state can occur. The current–time response, shown in the insert in Fig. 3, indicates that it is a self-stimulating process which proceeds rapidly for the first few minutes and reaches a steady-state value after about 10 minutes. At the end of the test, the diffuse attack is seen to be of the pitting type. When maintaining the potential at + 800 mV for 24 hours, the current remains more or less constant with time (from 5 μA cm^{-2} to 11 μA cm^{-2})

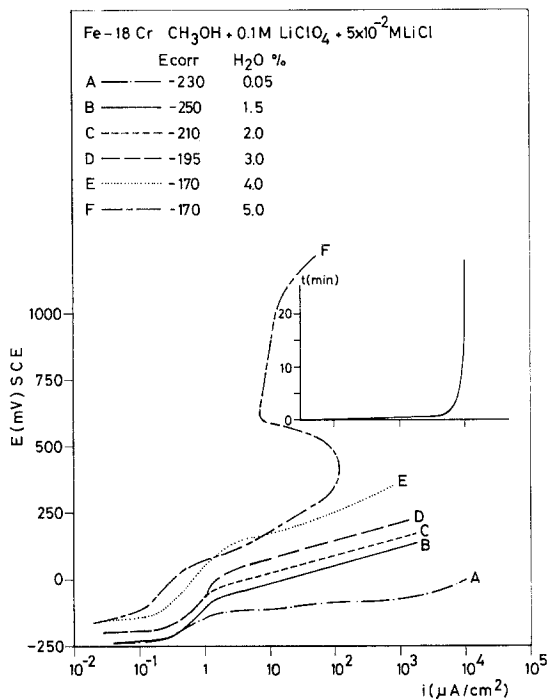Fig. 3. Anodic behaviour of Fe–18%Cr in MeOH + 0.1 M LiClO$_4$ + 5 × 10^{-2} M LiCl as a function of water content.
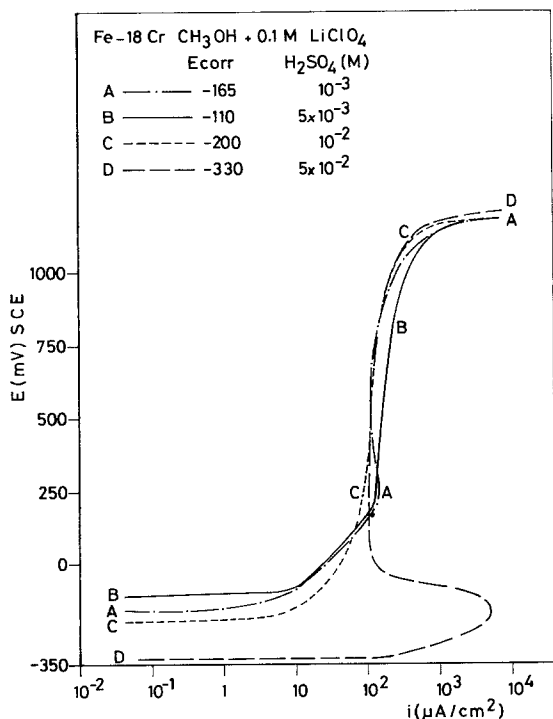

Fig. 4. Anodic polarization curves of Fe–18%Cr in MeOH + 0.1 M LiClO$_4$ as a function of H$_2$SO$_4$ additions.

and the specimen shows only a few isolated points of attack.

Starting from comparable initial current values, there is therefore in one case rapid increase of the current, which changes in a few minutes from 30 μA cm^{-2} to 10 000 μA cm^{-2}, whilst in the second case, the current remains practically constant. When the specimen is kept in the transpassive zone (1200 mV/SCE) there is a pitting-type attack with characteristics similar to those revealed at the potential of + 250 mV.

3.3. Effect of acidity

In methanol solutions, a concentration of H$_2$SO$_4$ = 5 × 10^{-2} M is necessary to observe the active–passive behaviour which is typical of aqueous solutions acidified with sulphuric acid (Fig. 4). The passive current ($\sim$ 150 μA cm^{-2}) and the transpassive potential ($\sim$ 1200 mV) remain unchanged in the range 10^{-3} M to 5 × 10^{-2} M H$_2$SO$_4$.

3.4. Concomitant effect of the H$^+$ and Cl$^-$ ions

Examination of Figs. 1 and 4 shows that concentrations of H$^+$ = 5 × 10^{-3} M and Cl$^-$ = 10^{-3} M are not sufficient to damage the passive layer of the Fe–18%Cr alloy. In Fig. 5 some experimental data obtained in H$_2$SO$_4$ (curve A), LiCl (curve B). LiCl + H$_2$SO$_4$ (curve C), LiCl + H$_2$SO$_4$ + 0.5% and 1% of H$_2$O (curves D and E) are given. The synergistic effect of Cl$^-$ and H$^+$ ions in the dissolution of the oxide film can be seen.

The alloy goes into active dissolution without a pitting potential or critical repassivation current: the limit of 13 mA cm^{-2} is caused by a limiting diffusion process of the dissolution products. The presence of traces of water (0.5% curve D) is sufficient to bring the material back to a passive state, practically equivalent to that in the presence of only acid. A further addition of water (1%) does not change the anodic characteristic of the alloy (curve E).

3.5. Effect of alloy components

The anodic behaviour of Ni, Mo, Fe and the Fe–Cr alloy is given in Fig. 6 in relation to the effect of acidity and the addition of water. The effect
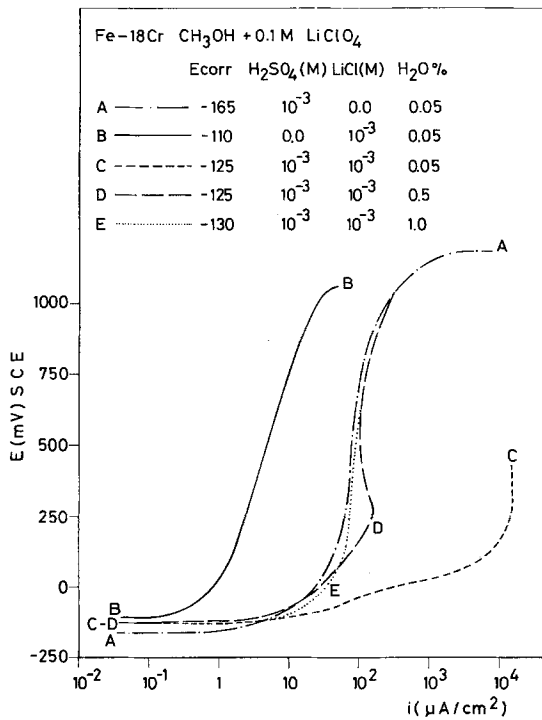
Fig. 5. Concomitant effect of the H^+ and Cl^- ions in the anodic behaviour of Fe–18%Cr.

of the Cl^- ion has been discussed in a previous paper [2]. Molybdenum alone presents a well-defined active behaviour, whilst iron and nickel show a clear active–passive behaviour.

3.6. Cathodic reduction of hydrogen ions

The cathodic polarization curves relating to Fe, Ni, Mo and Fe–18%Cr are given in Fig. 7 for the solution 0.1 M $LiClO_4$ in $CH_3OH + 10^{-2}$ M $H_2SO_4 + 1\%\ H_2O$. For Ni and Fe–18%Cr a typical Tafel relationship with a slope of about 130 mV/decade is recorded; for iron different behaviour is observed because of a mixed potential and high corrosion rate.

The case of the reduction of hydrogen ions on molybdenum is more complex. In Fig. 7, it can be seen that, starting from a free corrosion potential of + 320 mV, there is a cathodic current in the range + 320 to − 400 mV. Comparing these results with the data given in the Pourbaix diagram relative to the aqueous environment, the first plateau of the cathodic current corresponds to the reduction of pre-existing oxides. At the potential of − 550 mV/SCE the hydrogen cathodic reduction
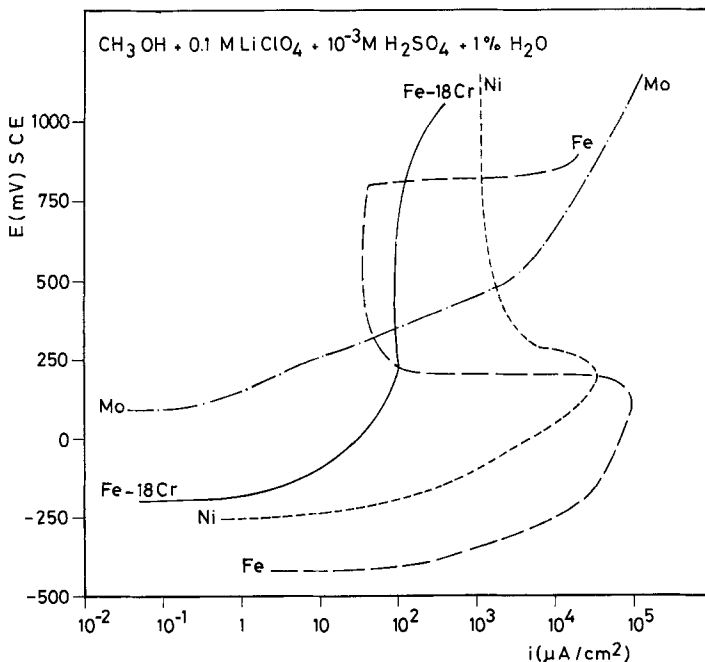

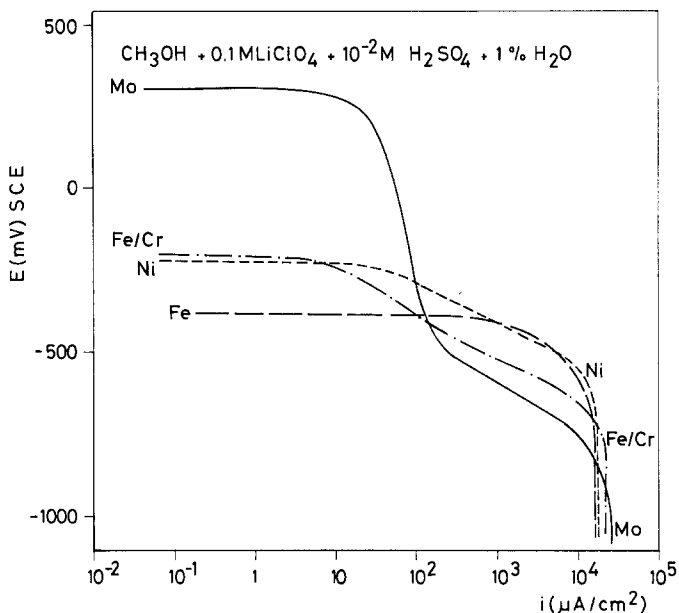Fig. 6. Anodic behaviour of Ni, Mo, Fe and the Fe–Cr alloy in MeOH + 0.1 M $LiClO_4 + 10^{-3}$ M $H_2SO_4 + 1\%H_2O$.

Fig. 7. Cathodic polarization curves in MeOH + 0.1 M LiClO$_4$ + 10^{-2} M H$_2$SO$_4$ + 1%H$_2$O.

process begins, with a slope of about 150 mV/decade. The limiting reduction current in comparable conditions of agitation (nitrogen bubbling) is independent of the type of metal or alloy tested.

References

[1]   C. A. Farina, G. Faita, F. Olivani, *Corr. Sci.* **18** (1979) 465.

[2]   F. Bellucci, C. A. Farina, G. Faita, *Mater. Chem.* 5 (1980) 185.

[3]   *Idem, 20th Corrosion Science Sympsium, 19–21 September* (1979), University of Bath.