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The anodic dissolution of iron-chromium alloys

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Polarization curves were obtained for a range of Cr-Fe alloys, containing up to 29% chromium, in sodium chloride solutions with pH between 2 and 12. Selected surfaces were taken for examination on a scanning electron microscope. The results indicate a nearly linear relation between an 'apparent breakdown potential' and chromium content up to about 20% chromium whilst the same potential is independent of pH in the pH range 2–10. There is a sharp increase in this potential as the chromium content exceeds 20% and when pH is 12.

The results are discussed in terms of the pitting of the passive films and the transpassive phenomenon. Evidence is adduced that the films present under conditions of electropolishing are porous and that the pitting is not necessarily associated with features in the metal surface.

1. Introduction

The increasing use of complex alloys, particularly in the aerospace industry, has led, in the past twenty years or so, to new methods of forming and machining. One of the more important of these is electrochemical machining. The main advantages of ECM are, (i) the rate of metal removal is independent of the hardness of the work-piece, (ii) no work hardening can occur, and (iii) shapes can be made which are very difficult, or even impossible to make, by the conventional machining methods. Among the disadvantages are, (i) the high capital cost of equipment, (ii) the cost of the development of tools, and (iii) the corrosive nature of the electrolytes used.

The process of ECM involves the anodic dissolution of the work-piece and therefore it is essential that the anodic behaviour of the alloy to be machined is well-established. In particular, the machining conditions responsible for producing polished, etched or pitted surfaces must be demonstrated. The electrochemical problems have not decreased with the use of complex alloys, although it is generally accepted that, at the concentrations used, many of the alloying additions are not significant electrochemically and hence most ECM research has been restricted to the study of simplified systems. Stainless steels are being electrochemically machined industrially and because of the relation between stainless steel and the binary iron-chromium system, the latter was selected for a study of anodic properties in sodium chloride solution.

Iron and chromium differ greatly in their behaviour in chloride solutions, iron readily corroding and pitting in solutions containing very low chloride concentrations, whereas chromium is reported to be immune to local or general attack in hydrochloric acid over a wide range of potential [1, 2]. The addition of chromium to iron has been shown to increase the minimum concentration of chloride necessary for pitting up to about 28% chromium content; further increases in chromium content give no significant improvement [3]. The figure of 28% chromium content has also been found to be significant by Horvath and Uhlig [4] and Kolotyrkin *et al.* [5] who observed a rapid increase in the critical corrosion potential starting at about 28% chromium content, with

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a simultaneous transition from local to generalized corrosion. Horvath and Uhlig found that at these high chromium contents, the critical pitting potential overlaps the transpassive region, with CrO_4^{2-} and Fe^{3+} being produced as the anodic products which results in general dissolution as opposed to pitting. The alloy for which the passive film was found to be entirely amorphous [6] also contained 28% chromium.

In the application of ECM to commercial practice the electrolyte flow rate is an important variable, serving to prevent the electrolyte boiling and to sweep insoluble reaction products out of the inter-electrode gap. In a recent paper [7] the effects of flow rate on the concentration profiles at dissolving brass anodes have been discussed and it was shown that when the flow rate was 12 m s^{-1} the maximum pH changes were of the order of one unit. Similar changes were found for the copper and zinc systems. The overall mechanism of the anodic dissolution of copper in hydrochloric acid has also been investigated [8] in static and flowing solutions. It was shown that dissolution occurred to the monovalent state forming the two chlorocomplexes $CuCl_2^-$ and $CuCl_3^{2-}$ and that the initial dissolution mechanism is unchanged as the flow rate increased to 1·14 m s^{-1}.

Although the systems to be investigated in the present work are completely different to those reported above, it seems that the effect of electrolyte flow on the mechanisms is such that it can be ignored at this stage of the work.

2. Experimental

Iron of 4N purity (Koch-Light) was in the form of 5 mm diameter rods or 1·5 mm thick sheet, chromium of 3N5 purity (supplied by NPL) was also in rod form of ~ 10 mm diameter and the iron-chromium alloys were all high-purity, vacuum-melted ferritic alloys supplied as 1·5–2 mm thick cold-rolled sheet. The alloys of 4·7, 7·5, 12·1, 18·4 and 28·7% chromium were supplied by either NPL or BISRA with typical impurity contents of C 0·003–0·007%, N 0·005%, 0·003–0·05%, P 0·006%, Co, Si, Mn, Ni 0·01% and Al 0·002%. Electrolytes were made from AR grade sodium chloride, sodium hydroxide and hydrochloric acid (BDH AristaR) and deionized water. All solutions, used fresh for each polarization curve, were nitrogen-saturated by bubbling nitrogen through them for at least 1 h prior to and during each experiment and maintained within 0·05 of a pH unit and at 20 ± 0·2°C. Potentials were measured against an Ag/AgCl electrode in the electrolyte. All anodes were abraded down to 600 grade wet emery, degreased, washed and dried immediately before each polarization run. The specimens were then treated cathodically at $-1{\cdot}5$ V for 900 s and then for a further 1·350 ks at $-1{\cdot}0$ V, the potential at which the sweep started. All polarization curves were obtained by a slow sweep potentiodynamic method, using a sweep rate of 20·667 mV s^{-1}, and the reported curves are typical of several replicates.

Preliminary results showed that annealing the iron and 18% chromium-iron alloys had no significant effect on the polarization curves when these were compared with curves from specimens in the cold-rolled condition. Therefore all the reported results refer to measurements on the materials in the cold-rolled condition.

For microscope examination of the surfaces the potential was taken directly to the selected value after the cathodic treatment and maintained for periods of between 0·6 and 3·6 ks.

3. Results and discussion

The effects of pH on the polarization of the alloys in 4 M chloride solutions may be characterized by a parameter, E_{APP}, which will be referred to as the 'apparent breakdown potential'. It is defined here as 'the potential at which there is the maximum increase of current with potential on that part of the curve immediately preceding a high potential-current plateau'. This definition takes account of all phenomena manifested by a rapid increase in current when the potential is increased and includes the usual definition which refers to pitting breakdown. Fig. 1 shows the variation of E_{APP} for each composition as a function of pH. E_{APP} is nearly independent of pH over the range 2–10 for all the materials investigated, but a marked increase occurs over the pH range 10–12. This increase becomes smaller as the chromium content increases so that there is no increase for

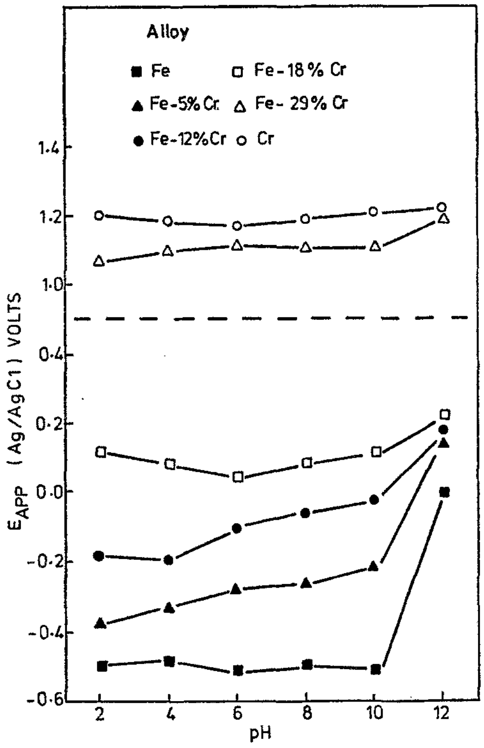

Fig. 1. Effect of pH on E_{APP}.

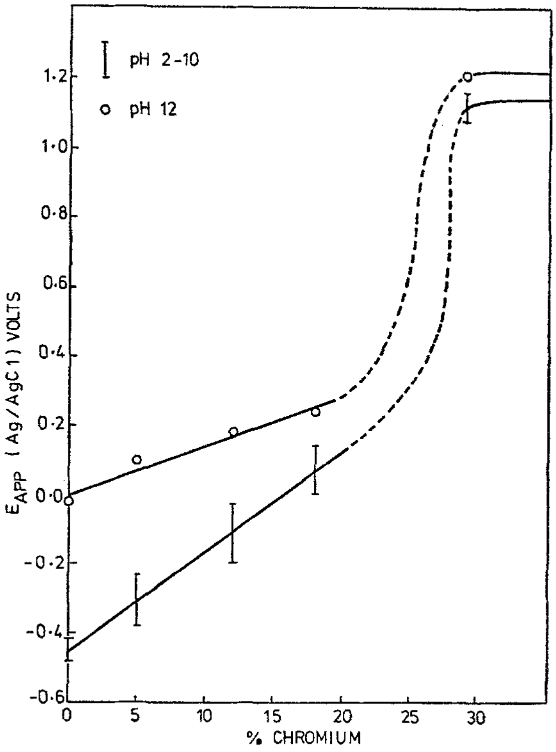

Fig. 2. Effect of Cr content on E_{APP}.

pure chromium.

The value of E_{APP} is shifted to more noble values with increasing chromium content, Fig. 2. The lower curve shows the variation of E_{APP} in the range pH 2–10, while the upper curve, displaced to more noble potentials, is applicable to pH 12. The effects of chromium concentration on E_{APP} are linear up to 18% Cr and can be represented by

$$E_{APP} = -450+29(\mathrm{Cr}\%)\ \mathrm{mV}\ \text{in the pH range 2–10}$$

and

$$E_{APP} = 0+15(\mathrm{Cr}\%)\ \mathrm{mV}\ \text{at pH 12.}$$

The 29% alloy has an E_{APP} near to that of pure chromium and 800 mV more noble than that predicted by extrapolation of the linear relation presented above. The data also showed that the pre-breakdown current increases with increasing chromium content and with increasing pH. Thus at pH 2 the 29% alloy passed a current exceeding 0·1 mA cm^{-2} at potentials higher than −590 mV, whereas the current passed by the 18% alloy did not exceed this value until −400 mV. At pH 12 all the iron-chromium alloys passed higher currents than pure iron below E_{APP} for pure iron, even though the E_{APP} potential for the alloys is more noble than that of pure iron.

Thus the main effect of increasing chromium content on the polarization behaviour is an increase in E_{APP} with the greatest increase occurring between 18 and 29% chromium.

A reduction in the concentration of the chloride ions in solution produced a corresponding reduction in the limiting current density, a similar effect being reported for the anodic behaviour of a range of copper-zinc alloys in chloride by Flatt and Brook [9]. In contrast to this earlier work, the concentration changes had little effect on the form of the polarization curves in the present work.

During the polarization experiments visual examination of the pure iron surfaces revealed the presence of a black film of apparent thickness up to 1 mm, over certain potential ranges for solutions in the pH range 2–10. As the potential increased to −570 mV, where a current maximum was observed, black particles could be seen falling from the surface and at the subsequent current minimum occurring at a potential of −480 mV the surface was covered with a dense coherent film which broke away from the surface at E_{APP}. In solutions of pH 12 iron anodes revealed no film until E_{APP} had been exceeded, but at this point surface coverage occurs quickly and the film does not subsequently detach from the surface but is covered by, or transformed into, a grey translucent film. The 4·7% Cr alloy behaved in a similar manner. The 12·1% Cr alloy only grew films at pH 10 and 12 and the higher alloys only at pH 12.

The scanning electron microscope examination of the surfaces revealed that the appearance of the surface of pure chromium was unaltered by a change in solution pH while the surfaces of pure iron and the iron-chromium alloys only showed significant changes at pH 12.

The surface of pure iron after polarization at a potential of −500 mV in 4M chloride at pH 2 (Fig. 3), taken as representative of all pH between 2 and 10, is rough with non-metallic particles visible on the surface, possibly of the black material observed during the polarization run. At −400 mV, just on the noble side of the current minima, a very similar surface is observed. However, on the current plateau, at 400 mV, the surface is covered with debris and at higher magnifications a porous film can be observed (Fig. 4). At pH 12 there is a film on the surfaces, easily seen by the unaided eye, which is only loosely attached to the surface and can be removed during the washing process. The surface beneath these loose films is shown in Fig. 5. The surface appearance of the anodically dissolved 5% alloy is similar to that of pure iron except that on the current plateau the superficial porous film is much coarser in the case of the alloy.

The 12% alloy when polarized at the 'apparent breakdown potential', −300 mV, shows, for the first time, the appearance of crystallographic etching (Fig. 6) but as the potential is increased this is lost. The two higher alloys, 18% and 29%, pit at potentials below E_{APP} and at all pH. Just above E_{APP} the surfaces show two areas, one of which is smoother and is seen at higher magnifications to be covered by a porous film. The second is more heavily attacked. As the potential increases, and hence also the current, the heavily attacked areas increase in extent. A detailed examination shows that the surface is covered with an agglomeration of pits which appear to be areas of penetration of the surface films (Fig. 7).

The arrangement of the pits shows clearly that pitting of a surface film is not a single event under these experimental conditions. The growth of the numerous sub-pits indicates that whatever event (or sequence of events) was responsible for the original penetration of the film it is capable of frequent occurrence within the original pit producing the highly complex arrangements visible. This would seem to be evidence that pitting need not be associated with features in the underlying metal surface.

Anodically polarized chromium is featureless at potentials below the onset of transpassivity and at potentials above this the surface becomes etched with a number of pits present. There is some evidence that some of the pits are associated with inclusions (Fig. 8).

Even though pitting was observed in the 29% alloy at potentials as much as 700 mV below E_{APP}, the variation of E_{APP} with chromium content has the same form as that of the E_{CRIT} with chromium content [4, 5], where E_{CRIT} is the potential above which pitting is observed.

Horvath and Uhlig [4], and Kolytyrkin *et al.* [5] showed that breakdown changed from pitting to a more general attack, such as transpassive dissolution, at chromium contents above 50%.

It is clear from these results that the presence on the anodes of massive films up to 1 mm thick need not hinder the electrochemical reactions associated with dissolution. Hoar *et al.* [11] have indicated that the highly conducting films present on electropolished surfaces are contaminated by the presence of foreign anions and this concept has been expanded [12] to suggest that when a mild steel is electrochemically machined in nitrate/chlorate electrolytes the films have a 'matrix-type honeycomb' with the foreign anions and water molecules adsorbed in the interstices. The matrix of Fe_3O_4 is an electronic conductor and hence is protective but the presence of the anions allows dissolution followed by outwards

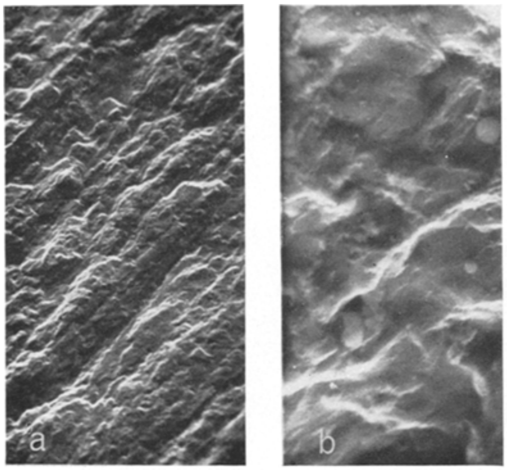

Fig. 3. Pure iron polarized at -500 mV and 30 mA cm^{-2} in 4 M chloride at pH 2. (a) ×430, (b) ×4·3 K.

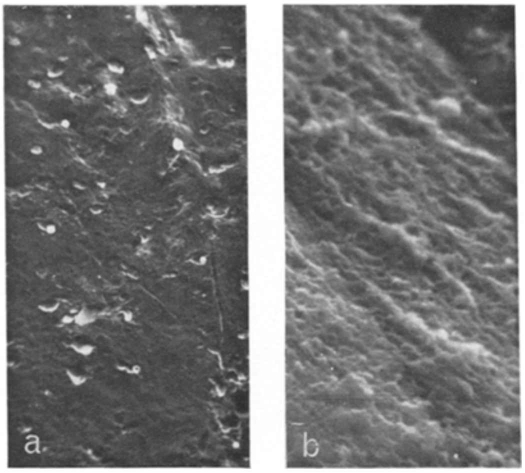

Fig. 4. Pure iron polarized at $+400$ mV and 710 mA cm^{-2} in 4 M chloride at pH 2. (a) ×430, (b) ×8·25 K.

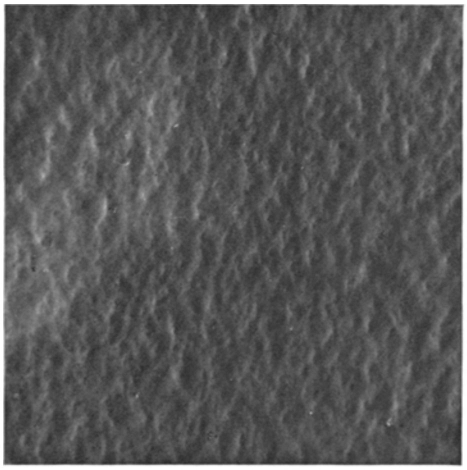

Fig. 5. Pure iron polarized at -400 mV and 300 mA cm^{-2} in 4 M chloride at pH 12, ×1·5 K.

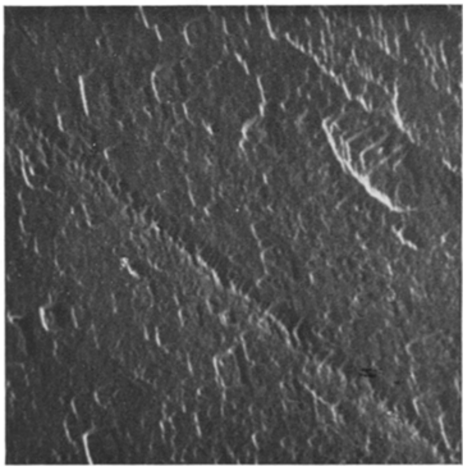

Fig. 6. Fe–12% Cr, polarized at -200 mV and 48 mA cm^{-2} in 4 M chloride at pH 2, ×625.

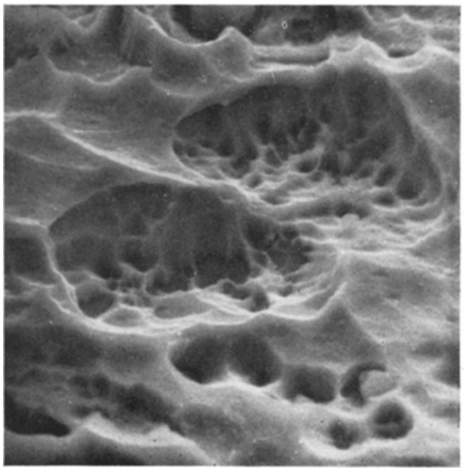

Fig. 7. Fe–29% Cr, polarized at +2000 mV and 450 mA cm^{-2} in 4 M chloride at pH 2, ×4 K.

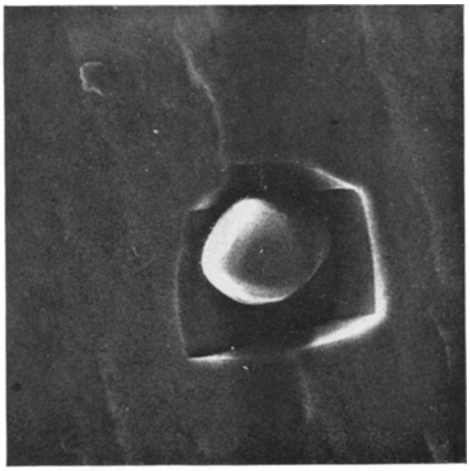

Fig. 8. Fe–29% Cr, polarized as in Fig. 7 to show a pit associated with an inclusion, ×2 K.

diffusion of the metal ion to occur via the interstices. Although there is no mention of size of the interstices, if the porous films shown in Fig. 4 are of a similar type then the pore size must be of the order of 1 μm or less. The selective nature of the dissolution occurring at the bottom of the pores could be responsible for the uneven appearance of the iron surface in Fig. 5.

It has been suggested [4] that transpassivity and pitting are two separate phenomena and that pitting may occur at some potential within the transpassive region, so that for pitting to occur in the transpassive region the potential must exceed E_{CRIT} as well as E_{APP}. This independence is in agreement with the present observations. On the other hand Horvath and Uhlig [4] did not observe pitting on alloys or on chromium on which transpassive dissolution occurred before pitting. In the present work pits were observed on transpassive chromium but not on the 18% and 29% alloys in the same regime. However the situation in these alloys is complicated by the presence of a thick film.

The large increases in E_{APP} and E_{CRIT} [4, 5] in the range 18 to 29% are in agreement with the observations of McBee and Kruger [6] who found that films on the alloys became amorphous at 25% chromium. They concluded that these amorphous films would be more protective.

The effects of pH on the anodic processes was found not to be significant in the pH range 2–10 although a large change in E_{APP} was observed when the pH changed from 10 to 12, particularly in the lower chromium alloys. It is thought that at the higher concentration of OH^- ions, the OH^- ions are preferentially adsorbed on the surfaces, this inhibiting the dissolution process. At pH 10 and below the concentration of OH^- ions is insufficient for this effect to be important but at higher pH the mechanism becomes significant. The pH effect is shown to a lesser extent in the more concentrated chromium alloys because of the passivating effects of chromium itself.

The relation between chromium content and pitting potential has been well-established [4, 5], and these earlier papers both suggest that the onset of some type of transpassive behaviour is similarly linked to the composition of the alloy. The present work clearly establishes this relationship, showing that there is a simple relation between composition and potential, E_{APP} up to a chromium content of $\sim 29\%$. The additive effect of alloying additions has been discussed previously from a theoretical viewpoint [10]. It was suggested that a consideration of the electrochemical properties of the films present and the mode of breakdown of the pure metals which are constituents of the alloy would enable a prediction of the electrochemical properties of the alloys to be made. In part this has been confirmed by the present results except that the need for the boundary conditions to be specified is paramount. Thus it is not yet possible to predict on electrochemical grounds that the 29% alloy will behave as pure chromium.

This conclusion suggests that the selection of conditions for electrochemical machining alloys can be predicted from a knowledge of the alloy's composition and the electrochemical behaviour of its major constituents. The presence of minor alloying constituents could be important but there are virtually no data concerning this available at the present time.

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