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Effect of aluminium impurities on the oxidation behaviour of iron at room temperature

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The influence of aluminium, as an impurity, on the oxidation behaviour of iron films containing about 0.3 wt% of carbon at room temperature is described. In general, the presence of aluminium in the sample helps to form a protective oxide layer after a definite period, mainly decided by the percentage of aluminium in the sample. Furthermore, the number of breaks observed in the resistance–time oxidation curve of iron, probably due to the compressional stress introduced by the flow of oxygen ions into the sample, is reduced, with increasing aluminium content. Iron films, containing different percentages of aluminium, were etched after different oxidation times. It is found that the presence of aluminium in iron, although it gives corrosion resistance to iron in oxidizing environments, stimulates corrosion in reducing environments.

1. Introduction

The kinetics of oxide growth and the influence of an electric field on the oxidation rate of iron and aluminium have already been reported [1–3]. For iron, the oxidation reaction proceeds logarithmically as

$$x \propto \ln t \ , \qquad (1)$$

where x is the oxide thickness at a time t. However, for iron films of thickness greater than about 1 nm, several breaks have been found in the oxidation curve. From the study of the influence of an applied electric field on the oxidation behaviour of iron, conclusive evidence is obtained for the reaction being controlled by the inward diffusion of oxygen ions as suggested by Fehlner and Mott [4]. Due to the inward diffusion of oxygen ions, compressional stress is developed during the process of oxidation causing the film to break when a particular thickness of the oxide film is attained. After each break, the film thickens logarithmically with a different rate constant.

For aluminium thin films (< 50 nm), an enhancement in the rate of oxidation has been noted when the metal is at a negative potential with respect to the oxide [3]. The direction of the field is so as to assist the diffusion of the positively charged cation through the metal–metal-oxide interface. Also, the growth of oxide Al_2O_3 follows an asymptotic type of growth law [2],

$$x = x_1[1 - A \exp(Bt)], \qquad (2)$$

where x_1 is the constant value of thickness attained after a period determined by the constants A and B.

Thus, for iron and aluminium the oxidation is controlled by the diffusion of different types of ions; cations in the case of aluminium and anions in the case of iron. Also, they follow different kinetics. Hence, it is interesting to study the influence of one metal in the oxidation of the other, when introduced in small quantities. In this paper, the influence of aluminium on the oxidation of iron is investigated. This method of introducing an impurity in to the metal and studying its influence is one way of understanding the rate determining factors in oxidation. This kind of doping study in thin films of metals is not as common as doping in bulk samples. However, one cannot be sure that the impurity will be uniformly distributed in the evaporated film, as the evaporation rates of the two elements are in general totally dissimilar. Also, one cannot be sure, without experimental verification, that the oxide itself has been doped [5]. In spite of all these uncertainties, it has been possible to find a systematic variation in the oxidation kinetics of iron with increasing percentages of the doping element.

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2. Experimental procedure

Weighed samples of iron (commercial sample with 0.27% of carbon content) and aluminium (99.9% pure) are evaporated together from a single tungsten boat. The evaporated beam contains iron and aluminium vapour in proportion determined by the ratios of the samples taken. However, the boat temperature and vapour pressures of the two elements may affect this ratio so that in the evaporated film, the ratio of the two elements will be slightly different from the ratio of the weighed samples [6]. To get films of different proportions of impurity, different quantities of the impurity element (aluminium) are evaporated with the same amount of iron. The film is deposited on a clean glass slide. The aluminium content (wt % of Al) is determined by using the atomic absorption method.

After preparing the specimen it is transferred to a separate glass jar with a time delay of about two minutes, and the specimen is allowed to oxidize in a dust-free atmosphere. The oxidation characteristics of the film are noted, from the change in resistance of the film as a function of time [1]. The experiment is carried out with different percentages of aluminium in the range 0.5 to 10 wt%. Also for the same percentage of aluminium, the experiment was repeated for films of varying thicknesses (1 to 50 nm).

The effect of impurity is also studied by making use of etching techniques. Using suitable etchants, iron films containing different percentages of aluminium are etched at different times of oxidation. The two etchants used are an alcoholic solution of HNO_3, and an alcoholic solution of HCl and picric acids in the ratio 1 : 8 by volume. The results are compared with those obtained by etching pure aluminium and iron thin films. All these studies are conducted at room temperature (around 30° C) in the laboratory atmosphere.

3. Results and discussion

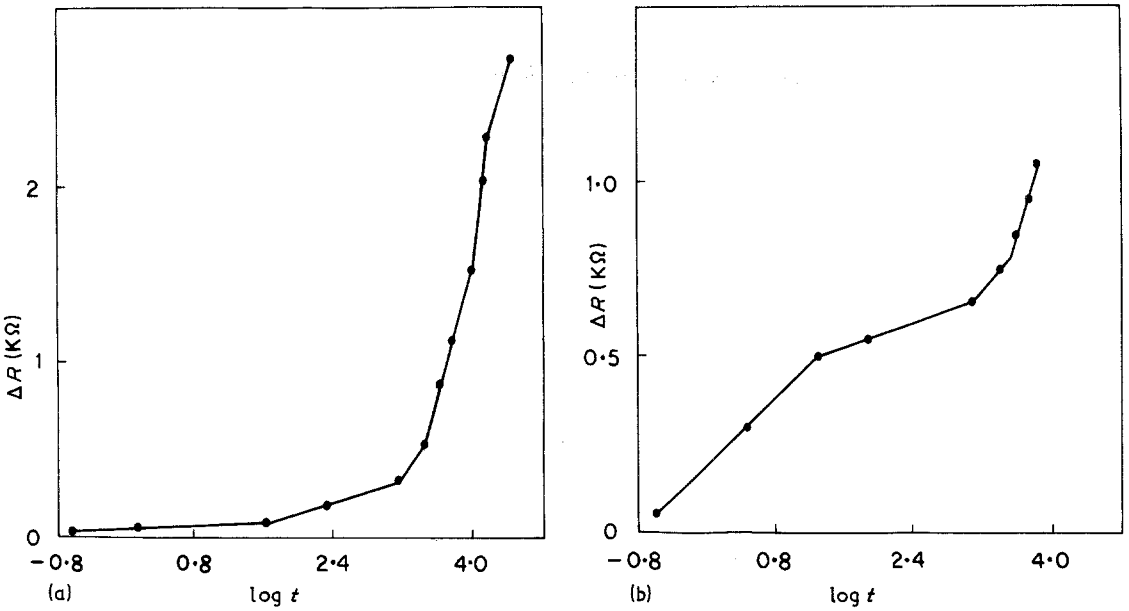
3.1. Kinetic studies

The presence of aluminium in iron does not change the logarithmic nature of the oxidation rate. However, an increase in the quantity of aluminium decreases the number of breaks observed in the oxidation curve. When the weight percentage of aluminium was less than 2%, the oxidation was very similar to that of pure iron. As in the case of iron, the oxidation curves exhibited distinct breaks at which sudden changes occurred in the oxidation rate. Also, the different stages of growth of the oxide structure observed under a low power microscope (of about × 325 magnification) were also similar to those as in the case of pure iron [1]. However, the different growth stages and also the number of breaks in the oxidation curve reduced as the percentage of aluminium was increased from 2; above 4 wt%, except for one break during the initial period, such sudden breaks in the oxidation did not occur. indicating the growth of a more protective oxide layer. Also, the structure of the oxide could not be observed under the same magnification, when the aluminium content was above 4 wt%. From a large number of observations taken for different samples, three typical oxidation curves are shown in Fig. 1 for three different weight percentages of aluminium. Except for the case when the aluminium content was less than 2 wt%, the oxidation stopped after a definite period of time, and this period decreased with the increase of aluminium content in the sample. Such observations are given in Table I, where the accuracy of the tabulated values are about 5% and 10%, respectively, for the aluminium content in the sample and the oxidation time.

For a dopant with a fixed valency which is different from that of the matrix element, and whose oxide does not form subscales, Hauffe's valency rule [7–10] is of importance in determining the oxidation mechanism at relatively high temperature. Recent experiments on ion implantation show that electronegativity of additive ions may prove a more significant parameter than valency in determining oxidation rates [11]. Complex factors such as grain boundary diffusion and layered scale formation can also influence the oxidation. In other cases it is the ionic size and the way in which this governs the mechanical stress within the oxide, that determines the influence of the constituent. The

TABLE I Effect of aluminium impurity on the oxidation characteristics of iron

Aluminium impurity content (wt%)	Time taken for the oxidation to stop (h)
0.7	∞
2.6	241
4.1	167
4.4	132
5.5	115
8.1	80
10.0	4



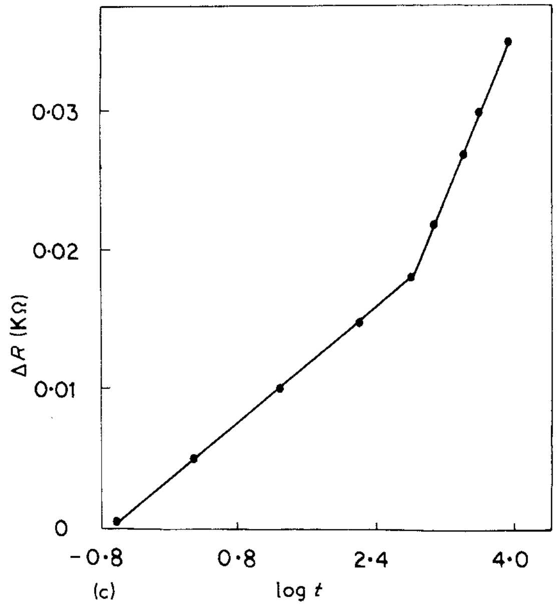


Figure 1 Oxidation curves of iron with aluminium impurities, showing change in resistance (ΔR) of film against logarithm of time in minutes for (a) 0.7 wt% and (b) 2.6 wt% of aluminium showing more than two breaks and (c) 4.4 wt% of aluminium with only one break.

miscibility of the oxides formed and the defect structure of the oxides can also influence the oxidation mechanism [12].

In the present cases, the dopant (aluminium), which is a minor constituent, forms a protective oxide layer very rapidly compared to the matrix element (iron). Though iron and aluminium form ordered alloys, their oxides are immiscible. Also, as already noted, the oxide formation of iron is by diffusion of oxygen ions [1] towards the metal–oxide interface, and that of aluminium by diffusion of interstitial cations [3, 13] towards the oxygen–oxide interface. Under these conditions, the mode of oxidation of the Fe–Al system can be schematically represented as in Fig. 2a. When the aluminium content is very low, the oxide particles of aluminium will only be dispersed in the iron oxide film as in Fig. 2b so that the oxidation characteristics correspond to that of pure iron. When the quantity of aluminium in the sample is increased, formation of a partial layer of Al_2O_3 takes place, and above a certain percentage of aluminium, a stage, depicted in Fig. 2a, is achieved.

Since the ionic diffusion in the formation of iron and aluminium oxide are different, the compressional stress produced due to the diffusion of oxygen ions for the formation of Fe_2O_3 is modified by the counter flow of aluminium ions for the formation of Al_2O_3. Since the breaks in the oxidation curves of iron are mainly due to rupture of the oxide film by the strain introduced by anion diffusion, the number of breaks can be limited by increasing the amount of aluminium. After a particular concentration of aluminium is avhieved, the flow of aluminium ions may be sufficient to eliminate the stress introduced by the diffusion of oxygen ions. Hereafter, for any higher

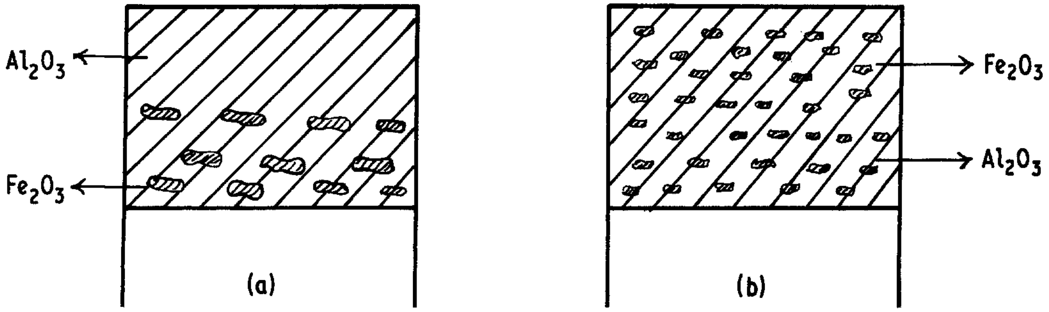


Figure 2 Schematic representation of two different modes of oxidation of iron with aluminium impurity with (a) above 2 wt% and (b) below 2 wt% of aluminium.

percentage of aluminium content, the oxidation curve yields only a single break (see Fig. 1c). This single break may be explained as follows.

During the initial stage of oxidation both iron and aluminium will be oxidized and the two oxides become separated. At this point the break occurs and hereafter the oxidation is mainly due to that of aluminium. The oxidation stops when the layer of aluminium oxide is sufficiently thick to resist the flow of further ions throught it. When the aluminium content increases, the separation of the two oxides and the thickening of the Al_2O_3 layer can take place quickly thus reducing the time required to stop oxidation. The gradual disappearance of the surface structure under an optical microscope with the increase of aluminium may be due to the enrichment of the surface layer with Al_2O_3.

3.2. Etching studies

For both the etchants, whether the film was of pure iron or iron containing aluminium impurity,

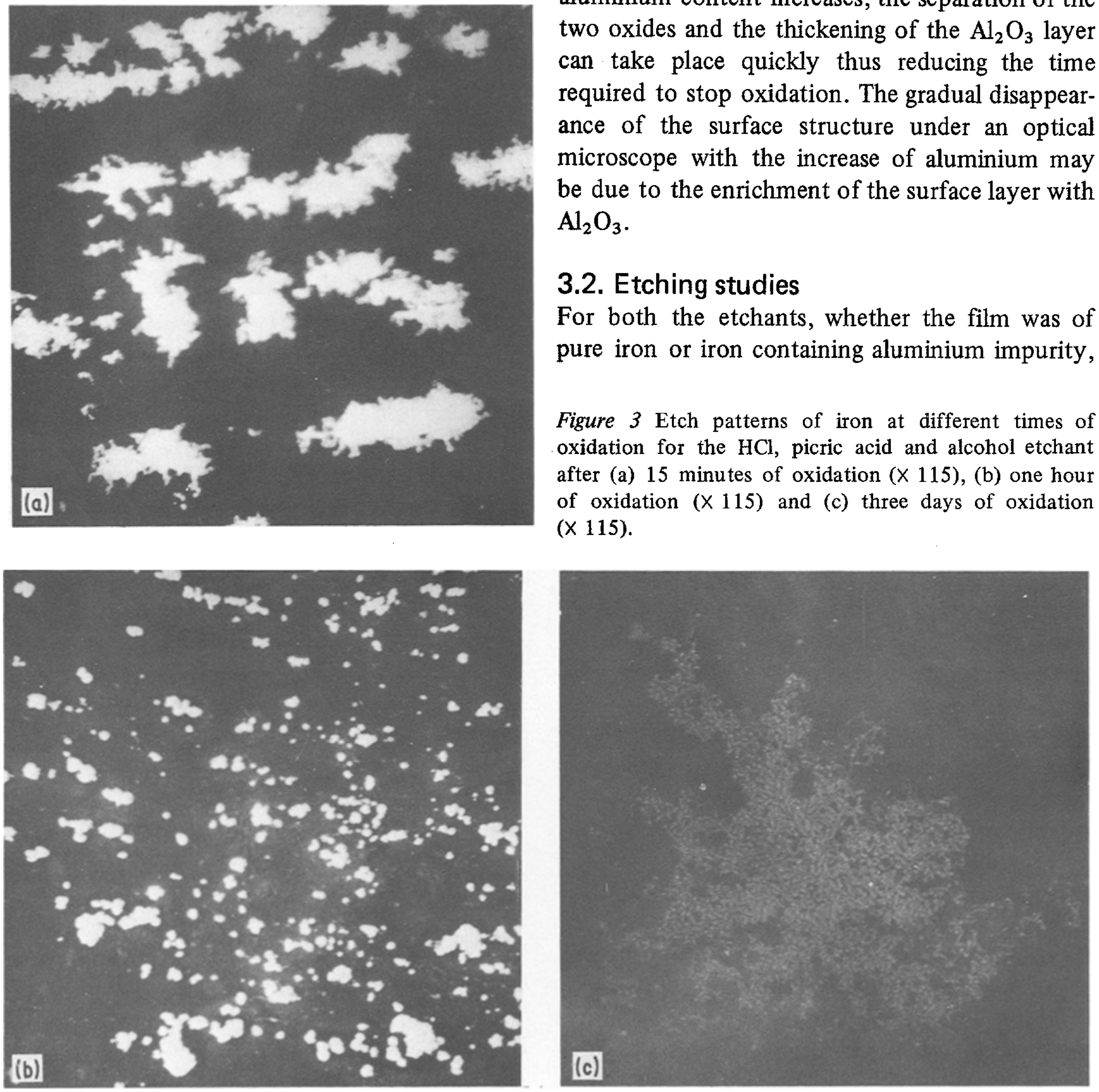


Figure 3 Etch patterns of iron at different times of oxidation for the HCl, picric acid and alcohol etchant after (a) 15 minutes of oxidation (X 115), (b) one hour of oxidation (X 115) and (c) three days of oxidation (X 115).

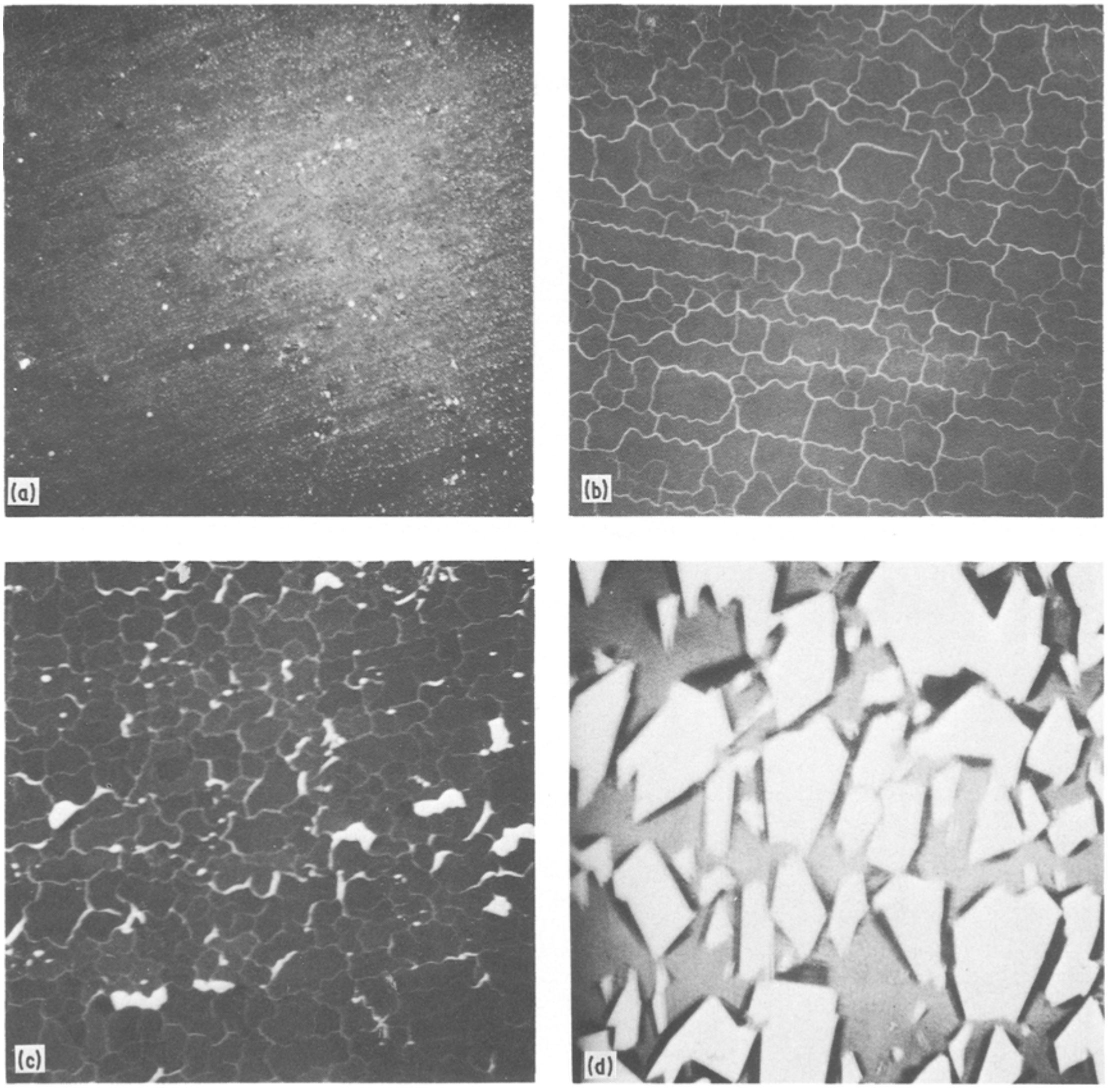
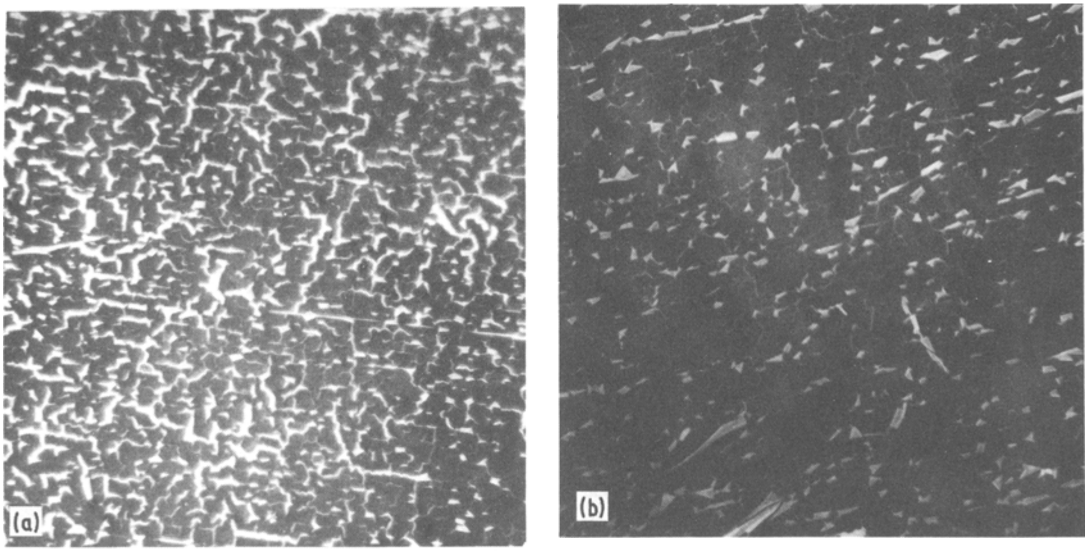


Figure 4 Etch patterns of iron with 5.5 wt% aluminium at different times of oxidation for the HCl + picric acid + alcohol etchant, after (a) one hour of oxidation (X 115), (b) four hours of oxidation (X 115), (c) eight hours of oxidation (X 115) and (d) two days of oxidation (X 115).

the action of the etchant was very intense during the initial stage of oxidation. For pure iron the action of both the etchants (an alcoholic solution of HNO_3 and an alcoholic solution of HCl and picric acid) become less and less intense with oxidation. Fig. 3 illustrates this etching action at different times of oxidation using the etchant HCl + picric acid + alcohol. Observations similar to those illustrated in Fig. 3 were obtained for the other etchant. In the figure the shaded regions are the unetched regions on the film. When oxidation structure begins to appear, the etchant produced no additional patterns other than those observed in Fig. 3c.

However, for films with an aluminium impurity the results are different for the two etchants. For the HCl, picric acid and alcohol etchant, the etching action was found to increase with oxidation time (see Fig. 4) and when the film was fully oxidized the whole surface of the film was etched away. When an alcoholic solution of HNO_3 was used, the intensity of etching action decreased with oxidation time (see Fig. 5). The same results were obtained for all films containing above 2 wt% aluminium.

The different actions of the two etchants at different times of oxidation on iron containing an aluminium impurity gives additional evidence



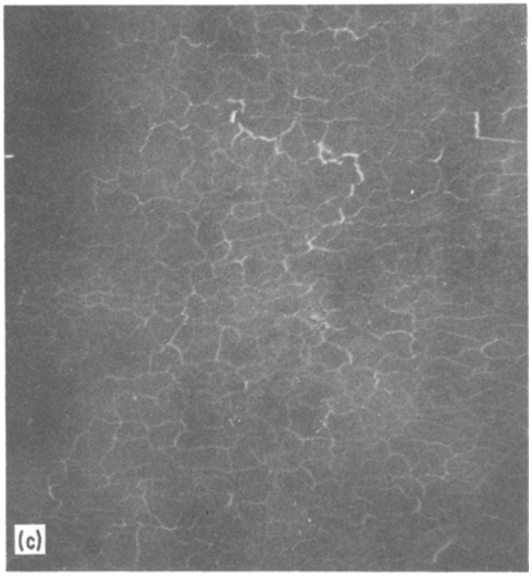


Figure 5 Etch patterns of iron with 7 wt% of aluminium at different times of oxidation using the etchant HNO_3 + alcohol after (a) 20 minutes of oxidation (X 120), (b) 2.5 hours of oxidation (X 120) and (c) 24 hours of oxidation (X 120).

for the diffusion of aluminium ions to the surface, and for the formation of galvanic cells. For iron thin films, at early stages of oxidation, the surface may not be completely covered by ferric oxide. But, as oxidation progresses, more of the active area of the film is covered by the oxide and hence the addition of the etchants decreases with oxidation. When aluminium is introduced as an impurity, the surface may contain a few aluminium atoms also. These aluminium atoms in contact with iron can form numerous galvanic cells in the presence of the etchant. In a reducing environment the oxide film on iron is easily disrupted, and at the same time, the oxide film on aluminium is more protective so that iron forms an efficient cathode so that the attack proceeds. As time passes more and more aluminium ions diffuse towards the surface, increasing the number of galvanic cells. Hence, with oxidation time, the action of the etchant like alcoholic solution of HCl and picric acid increases (see Fig. 4). For bulk samples, the reductive dissolution of ferric oxide film by contact with aluminium and particularly the influence of pH value has been investigated by Pryor and Keir [14].

It is also possible to envisage conditions where iron will not function as a metallic cathode even in the presence of aluminium [15, 16]. In oxidizing environments, as in the presence of nitric acid, the oxide films on both iron and aluminium are highly protective, so that the adverse effects of galvanic cell formation are not observed. Hence, increase of aluminium ions cannot intensify the etching action with oxidation time, but the oxide formed can only make the reaction less intense. This is what happens in the etching action of alcoholic solution of nitric acid (Fig. 5).

4. Conclusions

The addition of aluminium as an impurity in iron films gives a protective oxide layer to the sample at room temperature and in the laboratory atmosphere. When the impurity is more than about

2 wt%, oxide growth of the sample stops after a definite period. The presence of aluminium gives high corrosion resistance to iron in oxidizing environments, but in reducing environments its presence becomes more dangerous.

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