

Surface morphological investigation of iron films during oxidation

S VEENA KUMARI and V K VAIDYAN

Department of Physics, University of Kerala, Trivandrum 695 581, India

MS received 13 November 1987; revised 22 March 1988

Abstract. Different stages of iron films evaporated under a vacuum of about 10^{-5} torr were investigated with and without the addition of aluminium impurity at different percentages. Micrographs of such films heated at 623 K for 2 h show similar network spreading of oxide growth. Addition of aluminium significantly improves the oxidation resistance of iron films by the formation of Al_2O_3 layer.

Keywords. Morphology; oxidation; oxide growth; iron films; impurity.

1. Introduction

Several studies on the structure of metal oxide films formed during oxidation or corrosion have been carried out (Stott *et al* 1971; Bernabai *et al* 1980; Tomaszewicz and Wallwork 1984). The rate-determining factors of oxidation can be studied by addition of impurity elements. Al, Si, Cr, Ni, etc have been added to control the oxidation of iron resulting in chemically and structurally modified layers (Wood 1970; Pons *et al* 1982; Bhavani and Vaidyan 1982). Alloy components have different affinities for oxygen and do not oxidize at the same rate. For iron and aluminium, oxidation is controlled by the diffusion of anions and cations respectively. Also, they follow different oxidation kinetics. Hence, it is interesting to study the influence of one metal in the oxidation of the other, when added in small quantities. In this paper the influence of aluminium as an impurity on the surface structure of iron films at room temperature and at 623 K is described.

2. Experimental details

Thin iron films were prepared on clean glass substrates at room temperature by vacuum evaporation method from tungsten filament under a vacuum of about 10^{-5} torr. The study is confined to films of thickness 10 nm. The alloy films were prepared by evaporating weighed samples of iron and aluminium from a single tungsten filament. Thin films were then transferred to a glass jar and allowed to oxidize in a dust-free atmosphere. The oxide growths were photographed at different intervals. Thin films of iron were heated at 623 K for 2 h and different oxidation stages were photographed using a microscope (Zeiss Jenapol U).

3. Results and discussion

Oxidation of iron is a complex phenomenon. It can form different oxides depending on temperature and oxidizing atmosphere. The thickening of the oxide depends on the growth mechanism and the nature of oxide films. According to the Fehlner and Mott theory of oxidation the inward diffusion of anions at low temperatures is as

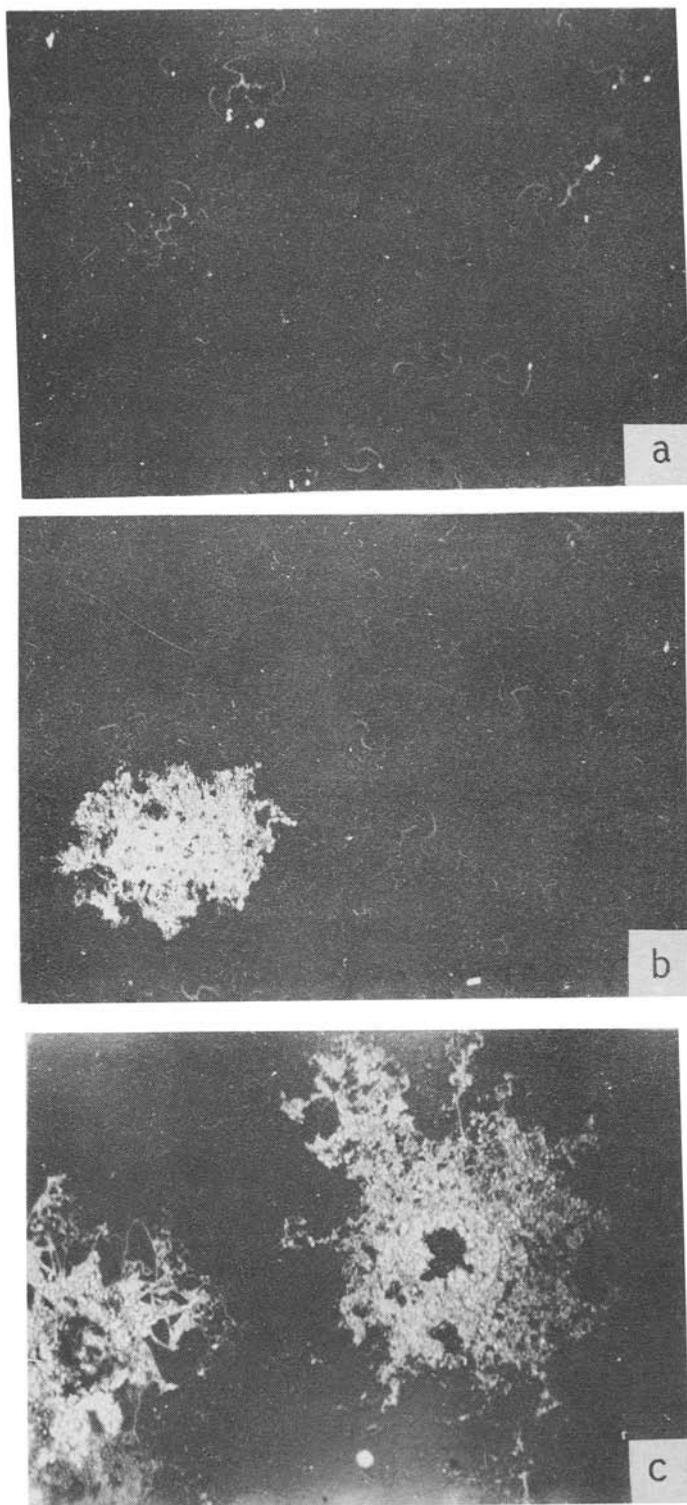


Figure 1. Different stages of oxidation of iron films at room temperature ($100\times$). **a.** after 2 days. **b.** after 14 days. **c.** after 30 days.

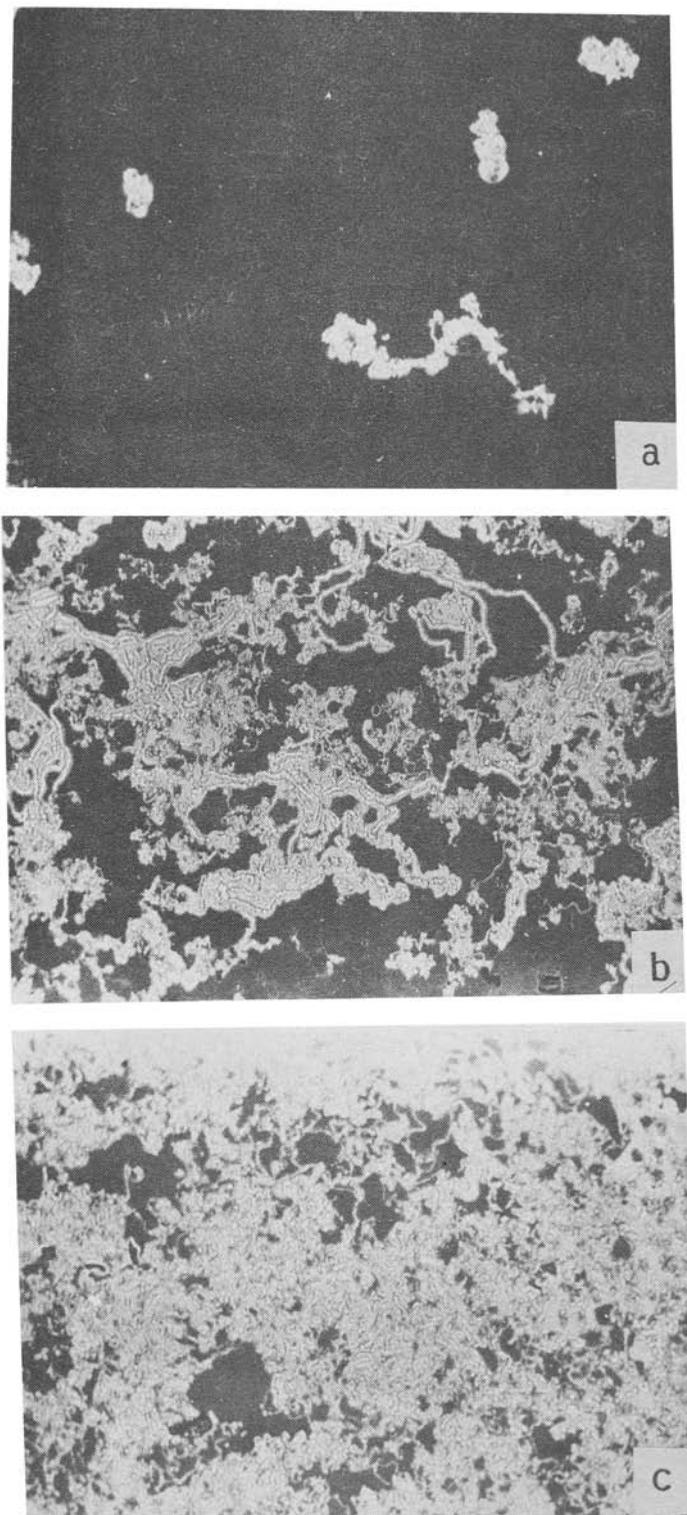


Figure 2. Oxide structures formed on iron films annealed at 623 K for 2 h (100 ×). **a.** after 1 day. **b.** after 2 days. **c.** after 10 days.

possible as the outward diffusion of cations. Predominance depends on the structure of the oxide. For Me_2O_3 -type oxides, anion migration dominates and forms a three-dimensional network (Fehlner and Mott 1970). Iron can form three oxides namely Fe_2O_3 , Fe_3O_4 and FeO depending on the oxidation temperature. The most stable among these three is Fe_2O_3 . At temperatures above 473 K the oxide film has been found to consist of magnetite, Fe_3O_4 and haematite Fe_2O_3 (Sewell and Cohen 1964).

The growth and development of the structure of iron films at room temperature is shown in figure 1. The thread-like pattern observed (figure 1a) shows that certain sites in the film surface are more favourable for oxidation. Specimen surfaces observed after 14 and 30 days (figure 1b, c) seem to spread over the entire surface by coalescence. On heating the sample, the oxide growth rate increases (figure 2) due to the rearrangement of surface atoms. This fast growth rate may be due to the formation of Fe_2O_3 and Fe_3O_4 at 623 K. With increasing time the mirror finish of the film surface changes to brownish colour indicating the formation of Fe_2O_3 . But the formation of Fe_3O_4 cannot be discarded.

In the case of alloy oxidation, either the component may be completely miscible producing oxide solid phase or may be completely or partly immiscible producing multiphase scales. Experiments carried out with the addition of aluminium impurity reveal that as the percentage of impurity is increased the oxide growth slows down. During the initial stages, an $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ layer is formed. For low aluminium percentages, either the impurity added is dispersed on the film or mixed oxide is formed. In the present case, if a spinel oxide is formed by chance, it will disappear on heating. As the percentage of impurity is increased a protective porous Al_2O_3 layer is formed by the outward diffusion of cations which covers the $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ layer. The schematic representation of the oxide growth on iron film on a glass substrate is shown in figure 3.

Thin films with 1 wt% Al show no surface structure for the first 48 h, when observed under a microscope with magnification 100 X. Photographs after 3, 8 and 30 days show that the oxide grows with centre and branches in an irregular manner (figure 4). Surface structures observed with 3 wt% Al (figure 5) after 8 and 30 days have no appreciable change indicating a stable oxide, i.e. as the percentage of the

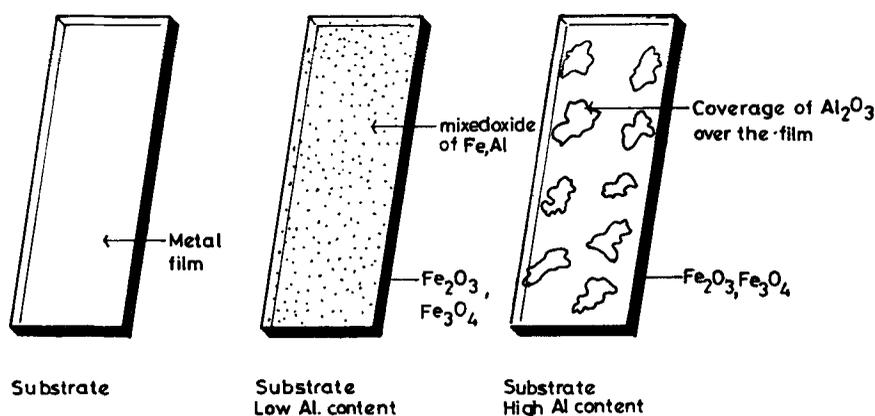


Figure 3. Schematic representation of oxide growth of iron films with different aluminium concentrations.

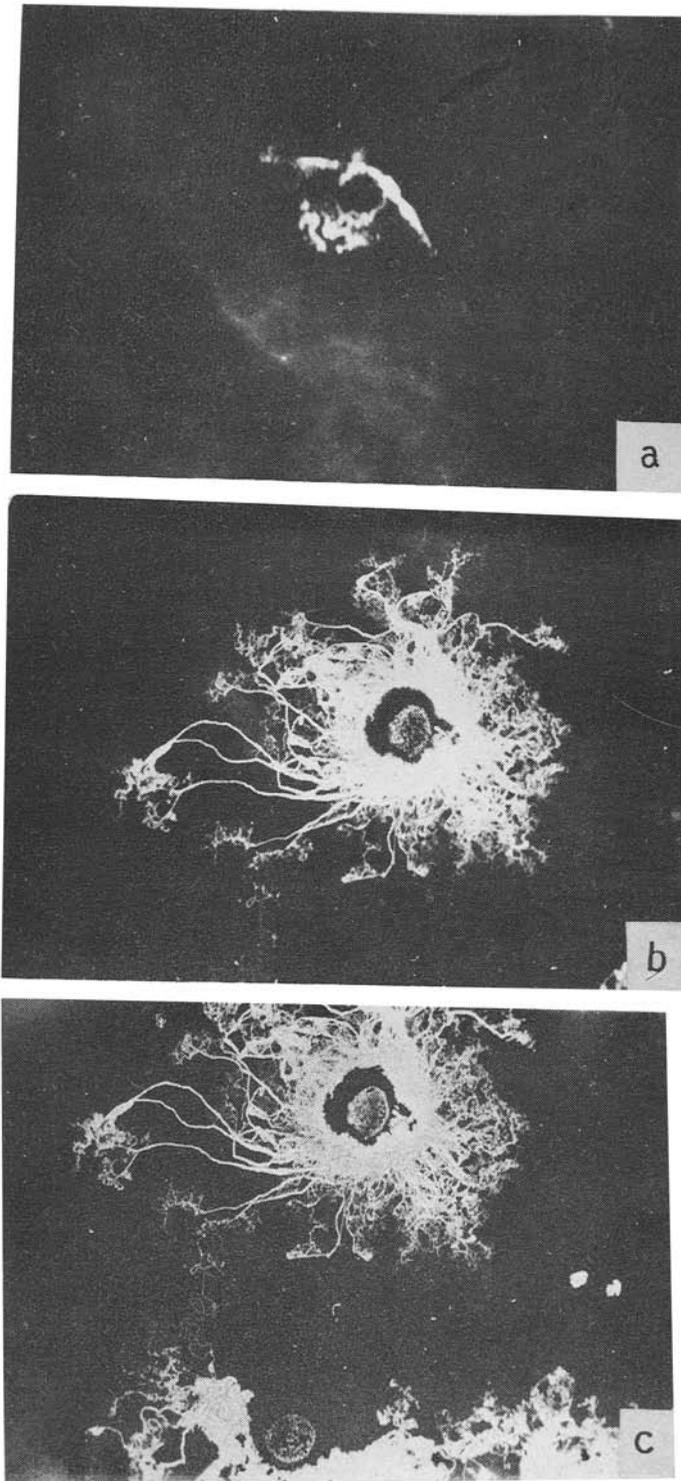


Figure 4. Growth and development of iron films with 1 wt% aluminium at room temperature ($100\times$). **a.** after 3 days. **b.** after 8 days. **c.** after 30 days.

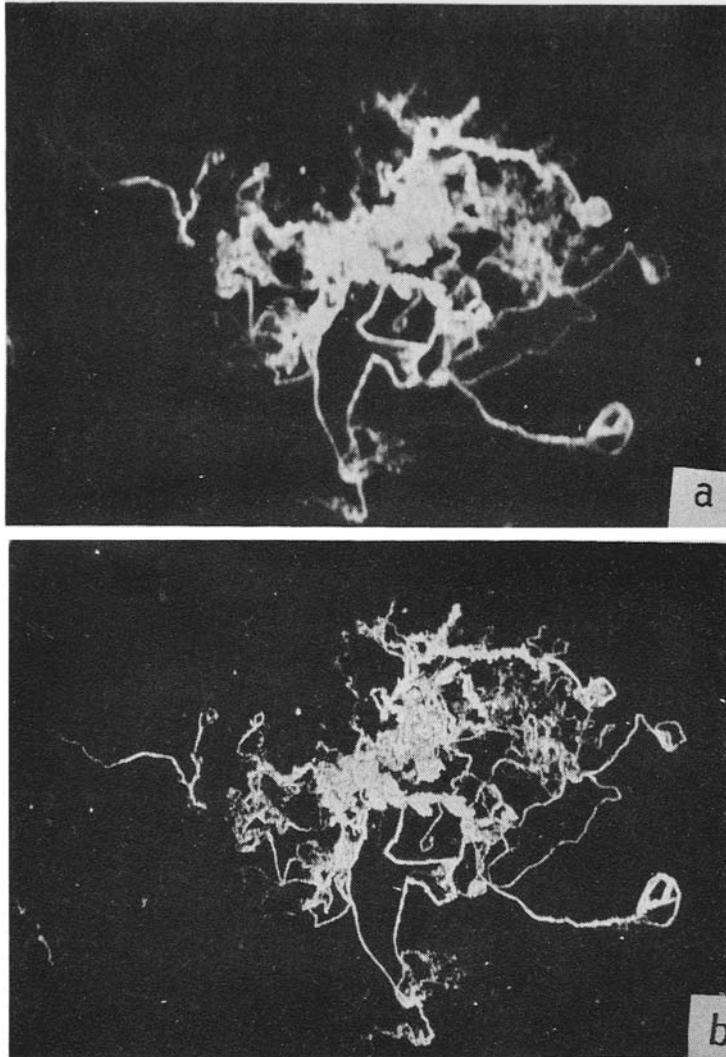


Figure 5. Stable structure of iron films with 3 wt% aluminium at room temperature. a. after 8 days b. after 30 days.

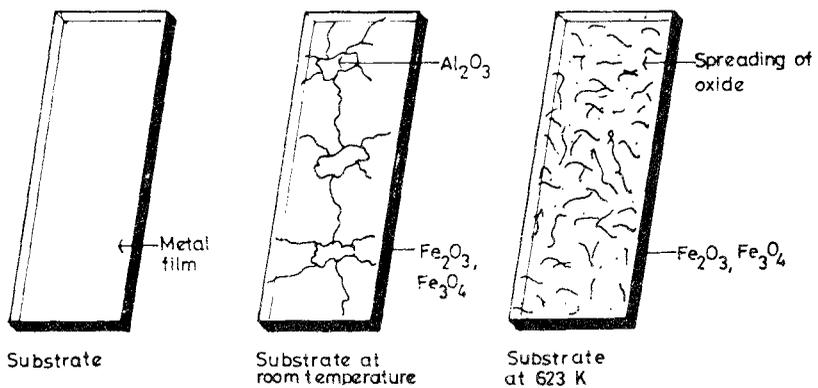


Figure 6. Mode of oxidation in iron films.

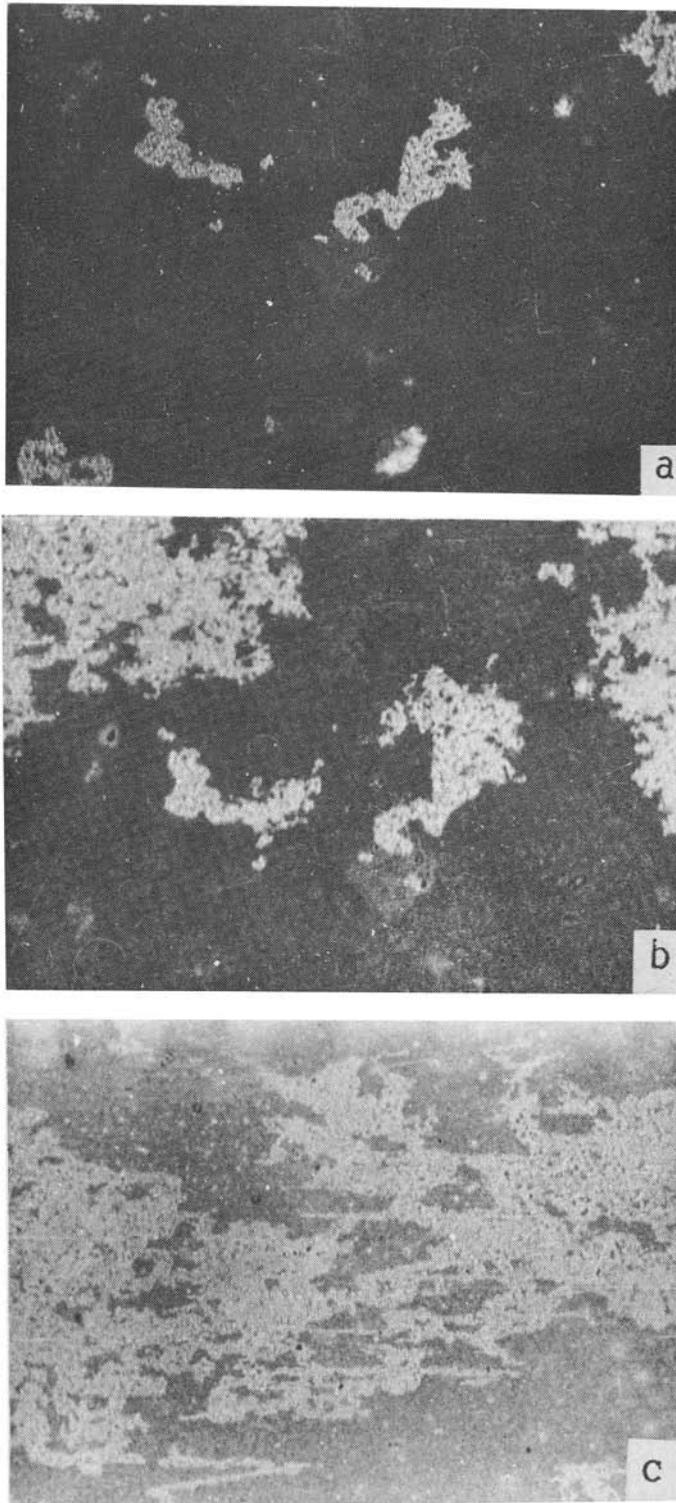


Figure 7. Different stages of oxidation of iron films with 1 wt% Al heated at 623 K for 2 h (100 ×). **a.** after 1 day. **b.** after 2 days. **c.** after 10 days.

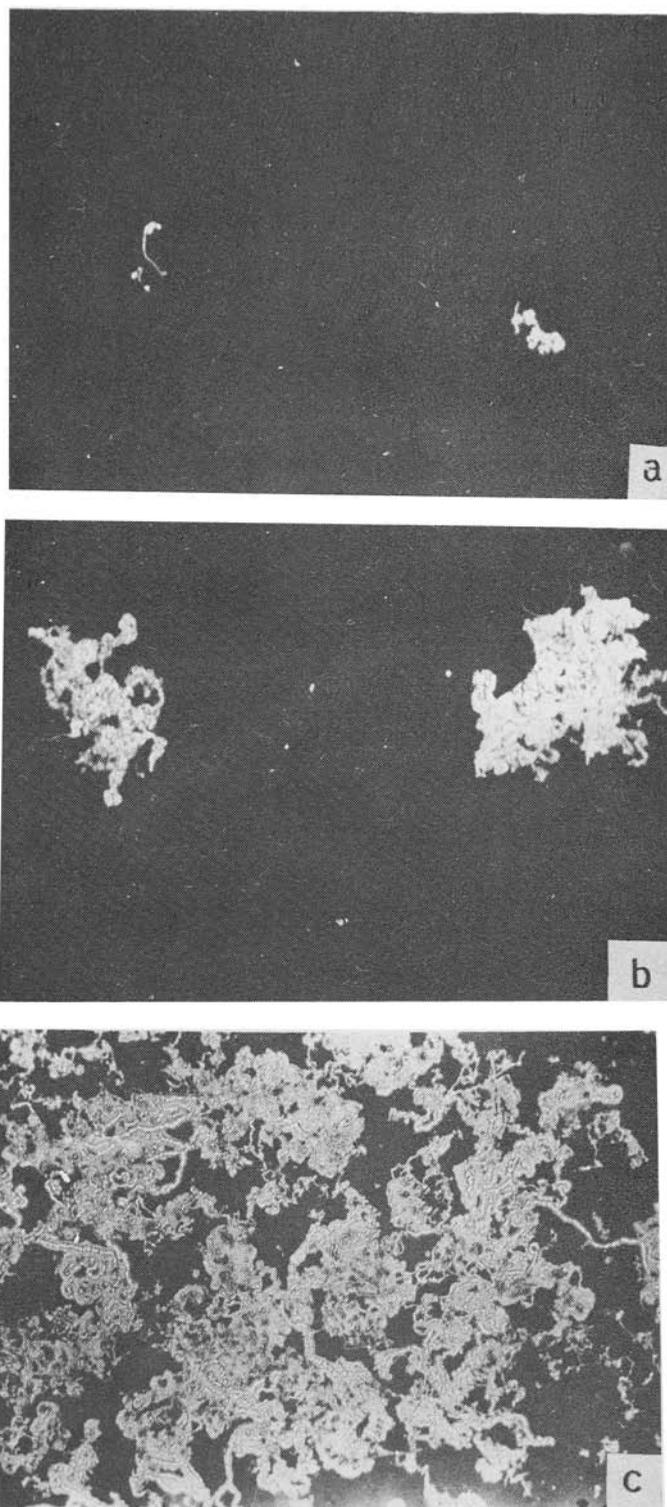


Figure 8. Different stages of oxidation of iron films with 3 wt% Al heated at 623 K for 2 h ($100\times$). **a.** after 1 day. **b.** after 2 days. **c.** after 10 days.

dopant increases the protective Al_2O_3 layer is covered over the $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$. The effect of aluminium is to gather oxygen forming Al_2O_3 . This indicates that 3 wt% Al impurity is sufficient to slow down the corrosion of iron films.

The mode of oxide growth on heated samples is schematically represented in figure 6. Lateral spreading of the oxide and net-work pattern are observed for samples heated with aluminium impurity (figures 7 and 8). As temperature increases the spinel phase, if formed, disappears and the formation of Al_2O_3 layer is favourable which protects the surface. With further increase in aluminium concentration the oxide growth decreases under the experimental conditions used. These specimens show no further change in the surface structure even after 3, 6 and 9 months.

4. Conclusion

Surface morphological investigations of iron films with and without addition of aluminium impurity reveal that the presence of aluminium gives high corrosion resistance to iron in oxidizing environments. With increasing aluminium content, Al_2O_3 layer protects the film surface and hence slows down the oxide growth. Annealing treatment quickens the formation of surface oxides.

Acknowledgements

The authors are grateful to Dr V Prasannakumar for help and to the Science, Technology and Environmental Committee, Kerala State for financial assistance. One of the authors (SVK) thanks the University of Kerala for the award of a fellowship.

References

- Bhavani K and Vaidyan V K 1982 *J. Mater. Sci.* **17** 1059
- Bernabai U, Cavalline M, Bombari G and Dearneley G 1980 *Corros. Sci.* **20** 19
- Fehlner F P and Mott N F 1970 *Oxid. Met.* **21** 59
- Pons M, Caillet M and Galcrie A 1982 *Corros. Sci.* **22** 239
- Sewell P B and Cohen M 1964 *J. Electrochem. Soc.* **111** 508
- Stott I H, Wood G C and Hobby M G 1971 *Oxid. Met.* **3** 103
- Tomaszewicz P and Wallwork R 1984 *Corrosion* **20** 152
- Wood G C 1970 *Oxid. Met.* **21** 11