Chapter V

OXIDATION OF IRON AT ROOM TEMPERATURE

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OXIDATION OF IRON AT ROOM TEMPERATURE

5-3 Introduction

The study of the oxidation of iron is of particular importance because of its widespread use. On the purely scientific side, the study helps to understand the exact oxidation mechanism, which may involve charge transfer, adsorption, nucleation, solidstate diffusion or any surface reactions. Since metals are required to operate at high temperatures in industrial plants and because the adverse effects of oxidation are felt largely at high temperatures, most of the studies are limited to high-temperature regions. Iron alloyed with chromium, aluminium or silicon are used extensively for high temperature applications. Also, the oxidation behaviour of iron alloyed with these elements are being investigated, in the high-temperature
region. The aim of the present work is to understand the mechanism of the oxidation of iron at low temperature (\( \sim 30^\circ \text{C} \)) with help of kinetic data and field experiments. Ways of improving the oxidation by the introduction of aluminium and tin as impurities are also investigated with the help of kinetic study, etching and surface morphology.

5-2  Oxidation kinetics

5-2.1  Experimental

All experiments were carried out on thin films of iron prepared by the method of evaporation in vacuum. The rate of oxidation was measured by noting change in resistance, \( R \) along the length of film. The oxide growth law was deduced by plotting \( 1/R \) against the appropriate function of time as described in section 3-7.1. The experiment was conducted for metal films of different thicknesses below 500 Å. In each case the thickness was estimated from its electrical resistance. To understand the influence of humidity, the experiment was conducted at different times of the year when the humidity varied from 70 to 90\%.
5-2.2 Results

For iron films of thickness greater than 10 Å exposed to air, the oxidation-time curves exhibited distinct breaks at which sudden increase occurred in the oxidation rate. After four or five such breaks the rate rapidly increased, and the film attained nearly infinite resistance. Before this rapid increase, between two successive breaks, the oxidation was found to follow a direct logarithmic relation. A plot of log t (where t is time in min) against 1/R (where R is resistance of film in ohm) of the film gave straight lines. However, an inverse logarithmic plot did not represent the experimental values satisfactorily. From a large number of observations six typical oxidation time graphs are presented in figure 5-1.

For a few cases, where the iron film thickness was less than 10 Å, such spurts in oxidation did not occur. Instead, the oxide grew according to a logarithmic rate and the oxidation ceased practically within two or three days, sometimes within a period of a few hours. (Figures 5-2). In both the cases the results could be reproduced during different periods of year. However,
FIG 5-1A OXIDATION CURVES OF IRON FILMS (THICKNESS > 10Å) SHOWING SEVERAL BREAKS. INITIAL RESISTANCE OF THE FILM: (a) 170Ω (b) 160Ω
FIG 5-IB OXIDATION CURVES OF IRON FILMS (THICKNESS > 10Å) SHOWING SEVERAL BREAKS. INITIAL RESISTANCE OF THE FILM: (a) 135 Ω  (b) 120 Ω
FIG 5-IC OXIDATION CURVES OF IRON FILMS (THICKNESS $10^A$) SHOWING SEVERAL BREAKS. INITIAL RESISTANCE OF THE FILM: (a) 350 $\Omega$ (b) 290 $\Omega$
FIG 5-2 OXIDATION CURVES OF IRON FILMS OF THICKNESS LESS THAN 10Å. INITIAL RESISTANCE OF THE FILM: (a) 790Ω (b) 680Ω (c) 637Ω
for films of same resistance prepared at different times the rate of oxide growth was different.

From the surface study of the specimen under an optical microscope, we could trace a series of the growth stages of oxide as illustrated by figure 5-3. For films having sudden breaks in the oxidation curve, all these four stages were present, but for films having no breaks in the oxidation curve, only the first stage (figure 5-3a) could be obtained.

5-2.3 Discussion

The oxidation of iron is a complex phenomenon. Depending upon the temperature, it forms more than one oxide, viz., FeO, Fe$_3$O$_4$ and Fe$_2$O$_3$, above 570°C all these oxides will be present and the composition of each layer changes continuously on passing from one surface to the other, the metal content being highest at the interface closest to the metallic base$^1$. However, from the results of recent investigations the most stable phase at room temperature is Fe$_2$O$_3$, although we cannot completely neglect the formation of magnetite$^2-4$. 
Fehlner and Mott\textsuperscript{5} have suggested a direct logarithmic kinetic for oxidation of metals in the low-temperature region, when the reaction is controlled by the inward diffusion of oxygen ions. In fact, the stable form of iron oxide at room temperature, viz., Fe$_2$O$_3$ is an \textit{n} type conductor having an ion deficiency or metal excess. This type of lattice defect is ideal to promote oxygen ion diffusion. This fact along with the observed direct logarithmic kinetics supports Fehlner and Mott's mechanism of oxidation in this case. With further experiments we could also get convincing evidence to favour the diffusion of oxygen ions.

Oxidation curves exhibiting sudden breaks have been observed in the case of both metals and alloys\textsuperscript{6–12} and have been attributed to the development of stresses and the absence of oxide plasticity\textsuperscript{13}. The stresses are developed mainly by the diffusion of cations and anions. When these stresses are sufficiently high, relief may occur by plastic deformation of either the film itself or of the metal substrate. In the absence of such plastic deformation the oxide film may fracture and provide direct access of the
oxidant to the metal film. Thus, oxidation becomes more rapid. The process may get repeated giving rise to several breaks in the oxidation-time graph.

If the diffusing species is cations, the outward diffusion of cations may result in the production of vacancies at the metal-oxide interface. If these vacancies are not eliminated either by some diffusional creep processes or by inward transfer of oxidant as gas molecules or oxide anions, the vacancies may collect and form cavities. As long as the roof of the cavity remains in tact, oxidation proceeds slowly. When the roof of the cavity breaks, this causes the oxidation to increase abruptly.

If the oxide growth takes place by the inward diffusion of anions, this can result in the development of compressional stresses within the oxide and can lead to eventual rupture of the oxide film. In such cases the magnitude of stress is determined by the Pilling-Bedworth rule. The stress is proportional to both the Pilling-Bedworth ratio and also to the thickness of film.

Since we have enough reasons to believe the oxidation of iron is controlled by the inward diffusion of oxygen ions, the breaks in the oxidation curve
may be due to the rupture of the oxide film by the development of stresses as described in the later case. The oxide to metal volume ratio for Fe₂O₃-Fe is greater than unity. This volume increase of oxide and inward diffusion of oxygen ions can develop compressional stresses parallel to the surface making the oxide more protective than if it were without strain. This strain cannot cause a collapse of very thin oxide films since the work needed for the detachment of film may exceed the decrease in strain energy which occurs when the film is able to assume a shape of minimum constrain.  But, when the oxide film thickness exceeds a certain limit, the strain energy which can be released is sufficient to supply the energy needed for the detachment of the film. At this stage, the film breaks down spontaneously and the rate of oxidation increases. This would explain the breaks in the oxidation curve of figure 5-1.

If any stress relieving mechanism other than the rupture of the oxide film can happen, then the film should grow logarithmically without any breaks and give rise to a protective film (figure 5-2). This is what happens in the case of iron films having
thickness less than 10 Å. Such thin films are not continuous, the effective surface area being much greater than the actual surface area of the film. This can compensate for the volume ratio of oxide to metal. Hence the compressional stress produced will also be correspondingly reduced. The oxide can grow for a much greater thickness before the logarithmic nature of film growth at low temperature causes the rate of oxide growth to practically cease. Thus the oxide film acts as a protective one.

In the surface structure of the films, which show continuous oxidation with several breaks, we have observed well defined patterns as in figure 5-3. However, for specimens having a protective nature, the pattern is as in figure 5-3a, where we observe only very small particles of oxide scattered uniformly over the surface. In the latter case, when only a few monolayers of oxygen are adsorbed, the diffusion of further ions is resisted and the oxide nuclei formed under this condition do not have the opportunity to grow laterally and inwards to form a three dimensional oxide structure. In the former case when a few monolayers of oxygen have been adsorbed there is
a sudden breakdown and rapid adsorption of further oxygen ions takes place. At this stage, i.e., after the first break in the oxidation (see figure 5-1), the oxide particles begin to grow laterally to form a network like structure as in figure 5-3b. The breakdown of the film and increase of oxidation rate complete this growth, and before the final breakdown the whole surface is uniformly covered by the network structure. After the final breakdown there is a difference in the structure as shown by figures 5-3c and 5-3d. This may be due to the fact that the oxide grows inward as well. After the final break, the three dimensional structure develops, and the resistance of the iron film rapidly approaches a very large value.

5-3. **Effect of the electric field on the oxidation kinetics**

5-3.1 **Experimental details**

To understand the most mobile species during the oxide growth of iron, experiments were conducted by applying an electric field, across the growing oxide layer as detailed in section 4-3 in the case of aluminium. The film was kept either at a positive
or negative potential by connecting a variable voltage source through a high resistance so that the potential drop between the two ends of the metal film was a few millivolts. For a potential of 200 V the potential drop corresponded to about 600 mV. The effect due to this potential gradient along the length of the film was not sufficient to produce any effect on the oxidation properties of the iron film. When the metal was kept at a positive or negative potential with respect to the ground, a capacitive field was developed across the oxide film and the magnitude of the field depended on the applied potential. In our set up, for a potential of 100 V, the drop across the metal oxide was found to be \(0.7 \pm 0.1\) V.

In a particular experiment, a constant positive or negative voltage was applied. The field was applied to the specimen alternately in an increasing order, starting from 2 min during the initial period of oxidation to about 20 min at the final stage. Thus a comparison of the rate of oxidation with and without the field is possible for the same specimen. The experiment was carried out at
different voltages in the range 100 to 200 for positive and negative fields. To confirm that the influence on the rate of oxidation is due to the presence of the electric field alone (and not due to the flow of current through the specimen) the experiment was repeated for different values of current (from 3 mA to 75 μA). The effect of the current flow on the oxidation rate was also investigated by keeping the metal film at zero potential and applying current at regular intervals. The experiment was repeated for metal films of different thicknesses below 500 Å. In each case the thickness of the metal film was estimated from its electrical resistance.

5-3.2 Results

The rate of oxidation was greater when the film was at a positive potential than when it was at a zero potential (figure 5-4). The reverse effect of lower oxidation rate while the film was at a negative potential was also observed (figure 5-5). The flow of current did not seem to have any effect on the oxidation rate. When current through the film was reduced keeping it at the same potential the influence of electric field on the oxidation rate was observed (figures 5-6 and 5-7). But, when the experiment was
FIG 5-4A COMPARISON OF OXIDATION RATE WITH AND WITHOUT APPLYING POSITIVE POTENTIALS OF (a) 100V, (b) 140V, (c) 120V. PLUS SIGN INDICATES THE PERIOD OF APPLICATION OF POSITIVE POTENTIAL.
FIG 5-4B COMPARISON OF OXIDATION RATE WITH AND WITHOUT APPLYING POSITIVE POTENTIALS OF (a) 200V, (b) 160V, (c) 180V. PLUS SIGN INDICATES THE PERIOD OF APPLICATION OF POSITIVE POTENTIAL
FIG 5-5A COMPARISON OF OXIDATION RATE WITH AND WITHOUT APPLYING NEGATIVE POTENTIALS OF (a) 160V, (b) 140V, (c) 120V. MINUS SIGN INDICATES THE PERIOD OF APPLICATION OF NEGATIVE POTENTIAL
FIG 5-5B COMPARISON OF OXIDATION RATE WITH AND WITHOUT APPLYING NEGATIVE POTENTIALS OF (a) 200V, (b) 100V, (c) 180V. MINUS SIGN INDICATES THE PERIOD OF APPLICATION OF NEGATIVE POTENTIAL
FIG 5-6 EFFECT OF ELECTRIC FIELD ON THE OXIDATION CURVES OF IRON AT LOW CURRENT VALUES (≈ 75µA). PLUS SIGN INDICATES THE PERIOD OF APPLICATION OF AN APPLIED POSITIVE POTENTIAL: (a) 175V (b) 150V.
FIG 5-7 EFFECT OF ELECTRIC FIELD ON THE OXIDATION CURVES OF IRON AT LOW CURRENT VALUES (~75μA). MINUS SIGN INDICATES THE PERIOD OF APPLICATION OF AN APPLIED NEGATIVE POTENTIAL: (a) 150V (b) 175V
repeated for the same current at zero potential.

no change in oxidation was observed during the
interval when the current was allowed to flow through
the specimen. The oxidation proceeded quite smoothly
(figure 5-3).

5-3.3 Discussion

As soon as a thin continuous oxide film is
formed on a metal surface, the metal and gaseous
reactants are separated by a barrier and the reaction
can proceed only if cations, anions or both and elec-
trons diffuse through the oxide layer. The rate
determining step in the oxidation reaction is either
mass transport (diffusion of cations or anions) or
charge transport (diffusion of electrons). When
the oxide film thickness is very small electrons can
diffuse very easily by tunnel effect and cannot
form as the controlling factor. Also, the existing
results on the oxidation of iron at room temperature
show that the oxide thickness cannot exceed 35A° for
an exposure of 100 hours to the oxidizing atmosphere.

Thus, in the present case, when the experiment was
conducted for one or two hours of exposure to the
oxidizing atmosphere at room temperature, the possi-
bility of electrons controlling the oxidation reaction
FIG 5-8 COMPARISON OF OXIDATION RATE WITH AND WITHOUT PASSING A CURRENT OF 3 mA THROUGH THE FILM KEPT AT ZERO POTENTIAL. 'i' INDICATES THE PERIOD OF PASSAGE OF CURRENT.
can almost be neglected. Hence, the oxidation can only be controlled either by the diffusion of cations or anions or by any other phase-boundary reactions. From field experiments, it is found that an enhancement in the rate of oxidation occurs when the film is at a positive potential. Now the direction of the field is favourable to assist the movement of anions inward through the metal-oxide barrier. Thus, if the anions are the most mobile species, an increase in the rate of oxidation is possible, while the film is at a positive potential. For the same reason, a decrease in the rate of oxidation happens when the film is at a negative potential, as observed experimentally. Also, at room temperature the most stable form of oxide is Fe₂O₃, an n-type conductor having metal excess or anion deficiency which is an ideal case to promote anion diffusion.

According to the Fehlner and Mott’s theory of oxidation at low temperature, the inward diffusion of anions is as probable as the outward diffusion of cations. The predominance of the diffusion of anions or cations is determined by the structure of the oxide, whether it is a network former or a modifier. For a
net work modifier, cation diffusion predominates, while for a network former, anion migration dominates. Oxides of the type $\text{Me}_2\text{O}_3$ can be network formers if oxygen forms triangles around each metal atom$^{20, 21}$. This forms a three dimensional random network, having five or six membered rings and producing channels extending through the network. A large anion can move more easily than a small cation in such an open structure because it is bonded less tightly to the network. Thus, network formers allow anion diffusion. In this case the film grows under a constant field giving rise to logarithmic kinetics of form $^{22}$

$$x = A \ln (1 + Bt) \quad (5-1)$$

where $x$ is the oxide thickness at time $t$, and $A$ and $B$ are constants characteristic of the film.

Thus, the observed results of the electric field experiments and the logarithmic kinetics (section 5-2) along with the above theory seems to suggest the formation of $\text{Fe}_2\text{O}_3$ controlled by the diffusion of anions.
5-4 Effect of impurities on the oxidation of iron

5-4.1 Experimental details

Alloying of an element affects the oxidation behaviour of the matrix element in a number of ways\(^{23}\). During the oxidation of an alloy the phase composition of the oxide formed is determined by rates of diffusion of the different elements, and also by the oxygen activity gradient within the scale. The stability of a particular oxide phase depends upon the free energy of reaction in the prevailing conditions. If the impurity introduced can produce a stable oxide film, the resistance to the oxidation of the matrix element can be increased. In some cases when the two elements (impurity and the matrix element) oxidize at different rates a heterogeneously stressed region may be formed. This gives rise to the cracking of the film\(^{13}\). In certain other cases the impurity element can increase the plasticity of the matrix element\(^{13,24}\).

Aluminium and tin are two fairly oxidation resistant elements. As such it is of interest to study whether the formation of their oxides in iron
can prevent oxidation and the breakage of iron oxide film during its oxidation. Also for both aluminium and tin the oxide growth is controlled by the outward diffusion of cations. Hence another aim is to understand whether during the oxidation of iron by the inward diffusion of oxygen ions, the formation of $\text{Al}_2\text{O}_3$ or $\text{SnO}_2$ by a counter flow of cations, can contribute towards the stress relieving mechanism and development of a protective oxide layer without any eventual breakdown.

Weighed samples of iron and the impurity element were evaporated together from a single tungsten basket. The evaporated beam contains iron and the impurity element in the proportion determined by the ratios of the samples taken. The exact ratio of the weight of two elements are evaluated by the atomic absorption method. The specimen so prepared was transferred to a separate glass jar with a time delay of 1 to 5 minutes, and was allowed to oxidise in a dust free atmosphere. The oxidation rate was followed from the rate of the change of resistance. The experiment was carried out with different weight percentages of impurity, 0–10% in the case of aluminium and 0–20%
for tin. For the same percentage of impurity the experiment was repeated for different thicknesses (10 to 500 Å) of the film.

The effect of the impurity was also studied by making use of etching studies. Using suitable etchants iron films containing different percentages of either aluminium or tin were studied and the results were compared with the results obtained by etching the pure elements.

5-4.2 **Effect of aluminium**

(a) **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 during oxidation. When the weight percentage of aluminium was less than 2% oxidation was very similar to that of pure iron. As in the case of iron, here also the oxidation time curves exhibited distinct breaks at which sudden increases occurred in the oxidation rate (figure 5-9). After four or five such breaks the rate rapidly increased and the film attained infinite
FIG 5-9A OXIDATION CURVES OF IRON THIN FILMS (THICKNESS > 10Å) WITH LOW wt.% OF ALUMINIUM:
(a) 0.5 wt.%  (b) 0.7 wt%
FIG 5-9B OXIDATION CURVES OF IRON THIN FILMS (THICKNESS $\approx 10\AA^*$) WITH LOW wt.% OF ALUMINIUM:
(a) 2.6 wt.%  (b) 3.6 wt.%  (c) 4.2 wt.%
resistance. Also, different stages of oxide growth were observed when examined under a low power microscope (figure 5-3). However, these different patterns of oxide growth and the number of breaks in the oxidation curve gradually reduced as the percentage of aluminium increased from 2%. For approximately above 4 wt.% of aluminium such sudden breaks did not occur, except one break during the initial period, indicating the growth of a more protective layer. This gradual reduction in the number of breaks in the oxidation time graph is shown in figure 5-9 and 5-10. Also the structure of oxide (figure 5-3) was not observed under the same magnification when the aluminium content was above 4%. Except for the case when the aluminium was less than 2%, the oxidation practically stopped after a period of time, and this period decreased with increase of aluminium content. Such an observation is reported in table 5-1, where the accuracy of the tabulated values are about 5% and 10% in the determination of aluminium impurity and oxidation time, respectively.

For a dopant with a fixed valency other than the matrix element and whose oxide does not form subscales, Mauff's valency rule 25, 26 is of importance
FIG 5-10A OXIDATION CURVES OF IRON FILMS (THICKNESS 10Å) SHOWING A SINGLE BREAK FOR HIGHER wt.% OF ALUMINIUM: (a) 4.4 wt.% (b) 8.1 wt.%
FIG 5-10B OXIDATION CURVES OF IRON FILMS (THICKNESS > 10 A) SHOWING A SINGLE BREAK FOR HIGHER wt.% OF ALUMINIUM: (a) 10 wt.% (b) 9 wt.% (c) 5.5 wt. %
Table 5-1  Effect of aluminium impurity on the oxidation characteristics of iron.

<table>
<thead>
<tr>
<th>Weight percentage of aluminium impurity in the sample.</th>
<th>Time taken for the oxidation to stop (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>∞</td>
</tr>
<tr>
<td>0.7</td>
<td>∞</td>
</tr>
<tr>
<td>2.6</td>
<td>241</td>
</tr>
<tr>
<td>3.6</td>
<td>222</td>
</tr>
<tr>
<td>4.1</td>
<td>167</td>
</tr>
<tr>
<td>4.4</td>
<td>132</td>
</tr>
<tr>
<td>5.5</td>
<td>115</td>
</tr>
<tr>
<td>8.1</td>
<td>80</td>
</tr>
<tr>
<td>9</td>
<td>13.5</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
</tr>
</tbody>
</table>
in determining the oxidation mechanism at relatively high temperature. Recent experiments on ion implantation shows that electro-negativity of additive ions may prove a more significant parameter than valency, in determining oxidation rate\textsuperscript{27}. Complex facts 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 element. The solubility of the oxides formed and the defect structure of the oxides can also influence the oxidation mechanism.

In the present case 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 (or insoluble). Also as already noted, the oxide formation of iron is by the diffusion of oxygen ions towards the metal oxide interface, and that of aluminium by diffusion of interstitial cations towards the oxygen oxide interface. Under these conditions the mode of
oxidation of Fe(Al) system can be schematically represented as in figure 5-11a. When the aluminium content is very low the oxide particles of aluminium will only be dispersed in the iron oxide film as in figure 5-11b, so that the oxidation characteristics corresponds to that of pure iron. When we increase the quantity of aluminium in the sample, partial layer of \( \text{Al}_2\text{O}_3 \) formation takes place and after a certain percentage of aluminium, a stage depicted in figure 5-11a is achieved.

Since the ionic diffusion in the oxide formation of iron and aluminium are different, the compressional stress produced due to the diffusion of oxygen ions for the formation of \( \text{Fe}_2\text{O}_3 \) is modified by the counter flow of aluminium ions for the formation of \( \text{Al}_2\text{O}_3 \). Since the breaks in the oxidation curves of iron are mainly due to the 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 achieved, the flow of aluminium ions may be sufficient to eliminate the stress introduced by the diffusion of oxygen ions. However, for any higher percentage of aluminium
FIG 5-11 SCHEMATIC REPRESENTATION OF MODES OF OXIDATION OF IRON WITH ALUMINIUM IMPURITY
content, the oxidation curve yields only a single break (figure 5-10). This single break may be explained as follows. During the initial stage of oxidation both iron and aluminium will get oxidized and the two oxides get separated. At this point a break occurs and hereafter oxidation of aluminium predominates. The oxidation stops when the oxide layer of aluminium is sufficiently thick to resist the flow of further ions, through it. When the aluminium content increases, the separation of the two oxides and the thickening of the \( \text{Al}_2\text{O}_3 \) layer can take place quickly, thus reducing the time required to stop the oxidation. The gradual disappearance of the oxide pattern of iron under an optical microscope may also be due to the enrichment of the surface layer with \( \text{Al}_2\text{O}_3 \) the structure of which could not be observed under the same magnification.

(b) Etching studies

The etchants used were alcoholic solution of nitric acid and alcoholic solution of hydrochloric acid and picric acid in the ratio 1:8. Both pure iron films and iron films containing different weight percentages of aluminium were etched at different
times of oxidation. For both the etchants, whether the film was of pure iron or iron containing aluminium, the action of the etchant was very intense as soon as the film was taken from the vacuum chamber. For pure iron the action of both the etchants (alcoholic solution of nitric acid, and alcoholic solution of hydrochloric acid and picric acid) decreases with oxidation. Figure 5-12 illustrate this etching action of the two etchants at different times of oxidation. In the figure, shaded portion is the unetched region on the film. When oxidation structure began to appear, the etchant produced no additional etch pattern other than the oxide structure (figure 5-12). But for films with aluminium impurity the results were different for the two etchants. For the etchant (hydrochloric acid + picric acid + alcohol) the etching action was found to increase with oxidation time, and when the film was fully oxidized whole surface of the film etched away. The result was reproducible for different weight percentages of aluminium from 2 to 12%. Among these observations photographs illustrating the etching action for three percentages are presented in figure 5-13.
When alcoholic solution of HNO\textsubscript{3} acid was used the intensity of etching action was decreased with oxidation time (figure 5-14). The same results were obtained for all films containing aluminium above 2%.

The difference in the actions of the two etchants at different times of oxidation of iron containing aluminium impurity gives additional evidence for the diffusion of aluminium ions to the surface, and for the formation of galvanic cells. For iron thin films, at the early stages of oxidation, the surface may not be completely covered by ferric oxide. But as oxidation proceeds and a more active area is covered by the oxide, the etching action decreases with oxidation, for both the etchants. 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 reducing environments the oxide film on iron is easily disrupted, and at the same time the oxide film on aluminium is more protective so that iron may form an efficient cathode for the attack to proceed. 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 hydrochloric acid and picric acid increases. For bulk samples of iron reductive dissolution of ferric oxide film in contact with aluminium and particularly the pH value has been investigated by Pryor and Keir$^{28}$.

It is also possible to envisage conditions where iron will not function as a metallic cathode even in the presence of aluminium. In the oxidising 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, the 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. Thus, the presence of aluminium gives high corrosion resistance to iron in oxidizing environments, and in reducing environments its presence becomes more dangerous.
5-4.3 **Effect of tin**

(a) **Kinetic studies**

With the presence of tin the rate of oxidation of iron changed from a direct logarithmic relation to a power law of form

$$x = kt^n$$  \hspace{1cm} (5-2)

where \(x\) is the oxide thickness at time \(t\) and \(k\) and \(n\) are constants characteristic of the film formed. Hence, a plot of log \(1/R\) against log \(t\) gave straight lines, since the oxide thickness at any instant is proportional to the reciprocal of resistance \(R\) of the film. Except for one break during the initial period of oxide growth, the reaction followed smoothly obeying the above relation.

The same results were obtained when different weight percentages of tin ranging from 0 to 20 were introduced. From a large number of observations a few typical oxidation time curves are presented in figure 5-15.

During oxidation, the different growth stages of the oxide pattern were very similar to those obtained in the case of pure iron (figure 5-3).
FIG 5-15A LOG ΔR vs LOG t PLOT FOR IRON FILMS WITH DIFFERENT wt.% OF TIN: (a) 20 wt.% (b) 15 wt.% (c) 7 wt.%
FIG 5-15B LOG ΔR vs LOG t PLOT FOR IRON FILMS WITH DIFFERENT wt.% OF TIN: (a) 14 wt.% (b) 18.5 wt.%
FIG 5.15C LOG $\Delta R$ vs LOG$t$ PLOT FOR IRON FILMS WITH DIFFERENT wt% OF TIN: (a) 5 wt% (b) 3.2 wt% (c) 11 wt%
Even with 20 weight percent of tin no change in the surface oxide pattern could be observed.

The oxidation of tin at room temperature follows a logarithmic relation\textsuperscript{29, 30} and the reaction is mainly controlled by the outward diffusion of cations. Thus, the rate law is the same as that of iron, but the controlling factor is cation diffusion, instead of the anion diffusion of iron. Perhaps, as in the case of aluminium, this diffusion of cations during the oxidation of tin against the flow of oxygen ions for oxidation of iron may be responsible in eliminating the compressional stress produced in the oxide film of iron by oxygen ion diffusion, since the oxidation was found to proceed without any breaks. However, since the rate changes from a logarithmic to a power law, the rate of oxidation is greater with tin. That is the presence of tin aids the oxidation process. Since the surface layer of oxide is very similar to that of pure iron, we may assume that the oxide of tin formed does not come to the surface layer. It may be either dispersed in the matrix element or be forming a layer beneath the iron oxide.
(b) Etching studies

The etchants used were alcoholic solution of nitric acid and alcoholic solution of hydrochloric acid and picric acid. Unlike in the case of aluminium, here with both the etchants the intensity of the etching action decreased with oxidation time (figures 5-16, 5-17). This effect is very similar to that obtained for pure iron. It indicates that the surface oxide layer does not contain tin or tin oxide.

5-5 Conclusion

In agreement with Fehlner-Mott theory of low temperature oxidation, the present investigation of the kinetics of oxidation of iron and the effect of electric field on it demonstrates that the growth of ferric oxide occurs by inward diffusion of oxygen ions for the oxidation of iron at room temperature in a laboratory atmosphere. However, the method is not sufficient to understand the role of phase-boundary reactions and surface reaction during the oxidation process. During oxidation compressional stresses are found to develop leading to the eventual break down of oxide.
film and a sudden rise in the oxidation rate. The thickness and hence the structure of the iron film formed can contribute much towards the development and relief of stress during the course of oxidation. The addition of certain impurities whose oxides grow by cation diffusion also seems to relieve the compressional stress due to flow of anions. The presence of more than 4 wt.% of aluminium in iron totally prevents the rupture of oxide film. When the aluminium content increased above 2% the oxidation even stopped after a definite period which decreased with increase of aluminium content. The etching studies clearly indicates that the presence of aluminium gives high corrosion resistance to iron in oxidizing environments, but in reducing environments, its presence becomes more dangerous. The presence of tin also prevents the periodical breakage of the oxide film. But it changes the rate law of the oxide growth.