CHAPTER III

DECARBURIZATION AND OXIDATION OF Fe-C ALLOYS

The experimental details have already been referred in Chapter II.

3.1 RESULTS

3.1.1 Oxidation Kinetics

The oxidation kinetic measurements were carried out at four different temperatures i.e. 700, 800, 900, 1000°C in 1 atm. O₂ for 24 hrs.

The weight gain vs time plots for the oxidation of plain carbon steels at 700, 800, 900 and 1000°C in O₂ (1 atm.) are shown in Figure 3.1. The steels oxidized at a much slower rate than pure iron. The weight gain² vs time plots are shown in figure 3.2. The weight gain vs time plots are parabolic and weight gain² vs time plots are linear indicating the growth of oxide scales by a diffusion controlled mechanism. The values of parabolic rate constant Kp for the oxidation of Fe-C alloys at different temperatures are given in table 3.1.

3.1.2 Oxidation Kinetics of Decarburized Alloys

The decarburization studies of Fe-C alloys was carried out in H₂(g) saturated with water flowing at a rate of 100 ml/min. through a mixture of oxalic acid/oxalic acid dehydrate for 2-3 hrs. in the same apparatus used for oxidation studies.
Fig. 3.1 Plots of weight gain Vs time for the oxidation of Fe-C alloys
Fig. 3.2 Plots of weight gain$^2$ Vs time for the oxidation of Fe-C alloys.
### Table 3.1

Parabolic rate constants for the oxidation of Fe-C alloys at 900°C in Kg^2.m^-4.Sec^-1 x 10^-6.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>700°C</th>
<th>800°C</th>
<th>900°C</th>
<th>1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-0.1C</td>
<td>0.22</td>
<td>4.44</td>
<td>9.95</td>
<td>30.38</td>
</tr>
<tr>
<td>Fe-0.8C</td>
<td>0.27</td>
<td>2.43</td>
<td>3.47</td>
<td>18.92</td>
</tr>
<tr>
<td>Fe-1.2C</td>
<td>0.23</td>
<td>2.08</td>
<td>5.56</td>
<td>20.66</td>
</tr>
</tbody>
</table>

### Table 3.2

Parabolic rate constants for the oxidation of predecarburized Fe-C alloys at 900°C in Kg^2.m^-4.Sec^-1 x 10^-6.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Undecarburized</th>
<th>Predecarburized</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-0.1C</td>
<td>9.95</td>
<td>53.47</td>
</tr>
<tr>
<td>Fe-0.8C</td>
<td>3.47</td>
<td>5.69</td>
</tr>
<tr>
<td>Fe-1.2C</td>
<td>5.56</td>
<td>1.56</td>
</tr>
</tbody>
</table>
The oxidation kinetic of decarburized alloys was carried out at 900°C in O₂ (1 atm.) for 6 hrs using the same apparatus as that used for previous oxidation/decarburization studies. In most cases, the decarburized alloys are oxidized by a diffusion controlled mechanism as indicated by the parabolic nature of weight gain vs time plots (Fig. 3.3-3.5) and linear nature of weight gain² vs time plot (Fig. 3.6). The values of parabolic rate constant, Kₚ for the oxidation of decarburized alloys at 900°C in 1 atm. O₂ are given in table 3.2.

3.1.3 Metallographic Studies

The oxidized, decarburized and decarburized-oxidized specimens were mounted, using Araldite as a cold setting resin. The mounted specimens were hand abraded on 186-, 380- and 600 grade silicon carbide papers and were polished sequentially with 40 μ, 8 μ, 6 μ and 1 μ grade diamond pastes using refined mobile oil as a lapping liquid. Metallographic examination of polished cross-section of the specimens were carried out using a Lietz Metallux-2 photometallurgical microscope. Figures 3.7-3.12 present some typical optical and scanning electron photomicrographs of Fe-C alloys oxidized in O₂ (1 atm.) at 4 different temperatures. The morphological features of the scales on plain carbon steels are similar irrespective of the carbon content. The scales are separated from the alloys substrate due to decarburization during oxida-
Fig. 3.3 Plots of weight gain Vs time for the oxidation of predecarburized Fe-0.1C alloy at 900°C.
Fig. 3.4 Plots of weight gain Vs time for the oxidation of predecarburized Fe-0.8C alloy at 900°C.
Fig. 3.5 Plot of weight gain Vs time for the oxidation of predecarburized Fe-1.2C alloy at 900°C.
Fig. 3.6 Plots of weight gain$^2$ vs time for the oxidation of predecarburized Fe-C alloys at 900°C.
Fig. 3.7 Photomicrograph of cross-section of Fe-0.1C alloy, oxidized at 800°C for 24 hrs. X 100
Fig. 3.8 Photomicrograph of cross-section of Fe-0.8C alloy, oxidized at 800°C for 24 hrs. X 100
Fig. 3.9 SEM picture of Fe-0.1C alloy, oxidized at 900°C for 24 hrs. X 60

Fig. 3.10 SEM picture of Fe-0.8C alloy, oxidized at 900°C for 24 hrs. X 75
Fig. 3.11 Photomicrograph of cross-section of Fe-1.2C alloy, oxidized at 700°C for 24 hrs. X 100

Fig. 3.12 SEM picture of Fe-1.2C alloy, oxidized at 900°C for 24 hrs.
A relatively thin irregular layer of wustite is invariably present in the inner scales. Due to separation and or/disruption of the outer scales, the wustite (FeO) scale come into contact with $O_2$ and oxidized to higher oxides of iron e.g. $Fe_3O_4$ and $Fe_2O_3$. The outer scales of oxidized alloys became porous as a result of the penetration of CO/CO$_2$(g) produced during oxidation.

Figures 3.13-3.18 show some photomicrographs of plain (undecarburized) carbon steels and decarburized steels in wet hydrogen ($H_2-H_2O$) at 900°C. The decarburized steels show well defined ferrite decarburized layers, the thickness of decarburized layer increases with increase in alloys carbon content, exposure time or temperature.

Figures 3.19-3.21 show some typical optical and scanning electron photomicrographs of decarburized-oxidized Fe-C alloys. The morphology of the oxide scales found on decarburized-oxidized alloys is quite similar to that of the scales formed on undecarburized-oxidized alloys. However, the scales formed on decarburized-oxidized alloys are relatively thicker, porous and more fragile.

3.2 DISCUSSION

The presence of carbon greatly lowers the oxidation rates of the alloy, however, the dependence on carbon content is somewhat complex. Considering the oxidation of plain
Fig. 3.13 Photomicrograph of cross-section of Fe-0.1C alloy. X 120

Fig. 3.14 Photomicrograph of cross-section of Fe-0.1C alloy, decarburized at 900°C for 2 hrs. X 120
Fig. 3.15 Photomicrograph of cross-section of Fe-0.8C alloy. X 120

Fig. 3.16 Photomicrograph of cross-section of Fe-0.8C alloy, decarburized at 900°C for 1 hr. X 120
Fig. 3.17 Photomicrograph of cross-section of Fe-1.2C alloy. X 120

Fig. 3.18 Photomicrograph of cross-section of Fe-1.2C alloy, decarburized at 900°C for 1 hr. X 120
Fig. 3.19 Photomicrograph of cross-section of predecarburized Fe-0.1C alloy, oxidized at 900°C for 6 hrs. X 120
Fig. 3.20 Photomicrograph of cross-section of predecarburized Fe-0.8C alloy, oxidized at 900°C for 6 hrs. X 120

Fig. 3.21 SEM picture of predecarburized Fe-1.2C alloy, oxidized at 900°C for 6 hrs. X 80
carbon steels, at $700^\circ C$, Fe-1.2C alloy has the highest oxidation rate and 0.1 % C alloy has the lowest oxidation rate. However, at higher temperatures, the situation is reversed and 0.1 % C steel has the highest oxidation rates. Although at a definite temperature, the oxidation rates are similar at varying carbon contents, but even then the behaviour can be satisfactorily explained on the basis of phase structure and morphology of the scales. At $700^\circ C$ the alloy structure consists of $\alpha$-ferrite in case of 0.1 % C and $\alpha + Fe_3C$ at higher carbon content. At temperatures in the range of 800-1000$^\circ C$, the structures are $\alpha + \gamma$ (0.1 % C), $\gamma$ (0.4 and 0.8 % C) and $\gamma + Fe_3C$ (1.2 % C). At low temperature ($700^\circ C$) there is a sufficient carbon available for decarburization in case of 1.2 % C and therefore, the oxidation rate is highest. However, at higher temperatures the presence of $Fe_3C$ is perhaps responsible for lower oxidation rates of high carbon alloys.

The morphological features of the scales on plain carbon steels are similar. The scales are separated from the alloy due to decarburization. A relatively thin layer of wustite is invariably present. Due to separation and/or disruption of the scales, the wustite (FeO) scales would come into contact with $O_2$ and oxidized to higher oxides of iron: $Fe_3O_4$ and $Fe_2O_3$. The copious oxide scales containing $Fe_3O_4$ and $Fe_2O_3$ are found. Due to disruption or cracking of the
scales, fresh alloy surface comes into contact with O\textsubscript{2} and oxide growth on alloy is rate controlling factor. After sufficient exposure time, the healing of the disrupted scales is not ruled out. The outer scales are porous due to evolution of carbonaceous gases. The substrate shows dispersion of cementite (Fe\textsubscript{3}C) in a ferrite matrix.

Considering the oxidation of decarburized plain carbon steels at 900°C; the oxidation rate of the decarburized alloy increases with increasing carbon content of the alloy. Furthermore, the oxidation rates of the decarburized Fe-1.2C is much lower than the undecarburized alloys. The metallographic studies show the oxidation of ferrite layer of decarburized alloy. The scales are separated from the alloy matrix partially due to decarburization and partially due to polishing artifacts. The matrix of the oxidized-decarburized alloy show the dispersion of coarse polygonal shaped carbide particles. Due to diffusion of iron and simultaneous decarburization, the matrix is depleted in dissolved carbon (or ferrite) and cementite seems to be the dominant and discrete phase. Since the cementite dispersion acts as an obstacle for the transport of iron during oxidation, the oxidation rates of decarburized steels are lower than undecarburized steels.