CHAPTER VIII
DECARBURIZATION AND OXIDATION OF SOME INDUSTRIAL STEELS

The experimental details containing material specifications, apparatus and procedures have already been given in Chapter II.

Specimens of 15 x 15 x 1 mm size or 12.5 mm diameter and 1.5 mm thickness were cut from steel sheets or steel rods. A 0.4 mm suspension hole was drilled near the middle of one end of the specimen. The specimens were sealed in a quartz tube and annealed at 900°C for 4 hrs.

The annealed alloys were subjected to oxidation (1 atm O₂) for 6-9 hrs, decarburization (H₂-H₂O) for 2-4 hrs. and decarburization-oxidation studies at 900°C for 9 hrs. on a laboratory fabricated thermal balance.

8.1 Results
8.1.1 Oxidation Kinetics

Figure 8.1 represents weight gain vs time plots for the oxidation of low alloy steels e.g. EN-24, EN-31, EN-36, EN-9 high speed steels (6 and 18 % W), silver steel and die-steel at 900°C in 1 atm. O₂. The plots in general are parabolic as indicated by the linear nature of weight gain² vs time plots (Fig. 8.2). The weight gain vs time plots for the oxidation of predecarburized alloy steels are shown in Figure 8.3. In general most of alloy steels are oxidized by
Fig. 8.1 Plots of weight gain Vs time for the oxidation of industrial steels.
Fig. 8.2 Plots of weight gain$^2$ vs time for oxidation of industrial steels.
Fig. 8.3 Plots of weight gain Vs time for the oxidation of predecarbonized industrial steels.
a parabolic rate law except a few as indicated by the breaks in the weight gain$^2$ vs time plots (Fig. 8.4).

Table 8.1 lists the values of the parabolic rate constants for the oxidation of alloy steels in as cast and decarburized condition. With a few exceptions, the oxidation rates of undecarburized alloy steels are slightly lower than the predecarburized-oxidized alloy steels. Amongst the undecarburized and predecarburized alloy steels, EN-9 has the highest oxidation rate followed by EN-31 alloy steel, high speed steel (18% W) and die-steels showing the lowest rates respectively.

**Table 8.1**

Values of parabolic rate constants, $K_p$ for the oxidation of alloys in Kg$^2$ m$^{-4}$ sec$^{-1}$ x 10$^{-7}$

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Plain oxidation 9 hrs. at 900°C</th>
<th>Decarburization and Oxidation 4 and 9 hrs. at 900°C respectively</th>
</tr>
</thead>
<tbody>
<tr>
<td>EN-9</td>
<td>51.3888</td>
<td>62.8333</td>
</tr>
<tr>
<td>EN-31</td>
<td>38.8888</td>
<td>55.555</td>
</tr>
<tr>
<td>Silver steel</td>
<td>33.3333</td>
<td>38.1944</td>
</tr>
<tr>
<td>EN-24</td>
<td>30.8333</td>
<td>13.8888</td>
</tr>
<tr>
<td>EN-36</td>
<td>17.3611</td>
<td>26.0416</td>
</tr>
<tr>
<td>HSS 6 % W</td>
<td>14.4472</td>
<td>8.68055</td>
</tr>
<tr>
<td>Die-steel</td>
<td>9.7777</td>
<td>4.6277</td>
</tr>
<tr>
<td>HSS 18 % W</td>
<td>5.1111</td>
<td>12.7305</td>
</tr>
</tbody>
</table>
Fig. 8.4 Plots of weight gain$^2$ VS time for oxidation of predecarburized industrial steels.
Table 8.2 contains weight loss data for different alloy steels after 4 hr. decarburization run in \( \text{H}_2-\text{H}_2\text{O} \) atmosphere at 900\(^\circ\)C. HSS steels show highest weight losses and EN-36 the lowest weight losses.

Table 8.2

Weight loss/area after a 4 hr. decarburization run in \( \text{H}_2-\text{H}_2\text{O} \) atmosphere at 900\(^\circ\)C.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Alloy</th>
<th>Kg/m(^2) ( \times 10^{-3} )</th>
<th>wt. loss Kg ( \times 10^{-6} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EN-9</td>
<td>15.9</td>
<td>3.0</td>
</tr>
<tr>
<td>2</td>
<td>EN-31</td>
<td>49.9</td>
<td>7.0</td>
</tr>
<tr>
<td>3</td>
<td>Silver steel</td>
<td>24.3</td>
<td>5.0</td>
</tr>
<tr>
<td>4</td>
<td>EN-24</td>
<td>32.5</td>
<td>5.0</td>
</tr>
<tr>
<td>5</td>
<td>EN-36</td>
<td>14.7</td>
<td>2.0</td>
</tr>
<tr>
<td>6</td>
<td>HSS 6% W</td>
<td>45.5</td>
<td>10.0</td>
</tr>
<tr>
<td>7</td>
<td>Die-steel</td>
<td>14.7</td>
<td>3.0</td>
</tr>
<tr>
<td>8</td>
<td>HSS 18% W</td>
<td>71.2</td>
<td>14.0</td>
</tr>
</tbody>
</table>

8.1.2 Metallographic studies

Figures 8.5 to 8.15 show typical optical photomicrographs and scanning electron photomicrograph of the cross-section of decarburized and undecarburized alloy steels. All alloy steels show a well defined decarburized layer and an increase in ferrite contents of the alloys. The thickness of
the decarburized layer increases with the increase in carbon contents as evident from the photomicrographs. However a deviation is found in some cases probably due to the varying percentage of carbide formers like Ni, Cr, Mo or W.

Figures 8.16 to 8.22 show the optical photomicrographs and scanning electron photomicrographs of the cross-section of undecarburized-oxidized alloy steels. There are three different phases in the scales. In all cases the oxide scales are adhered to the matrix except in silver steel, which is due to the polishing artifacts. Figures 8.23 to 8.27 represent the optical photomicrographs and scanning electron photomicrographs of the cross-section of predecarburized-oxidized alloy steels.

The oxides formed on the alloys under these conditions are similar to those obtained in undecarburized-oxidized alloys though more thicker, porous and fragile. The porosity and fragility of the scales are perhaps responsible for higher oxidation rates.

8.1.3 Microstructure of Alloy Steels

Figures 8.5 to 8.7 show some typical microstructures of the cross sections of alloy steels in as cast condition.

A photomicrograph of diecast steel (12 % Cr - 2 % C by weight) shows the presence of white flakes of graphite and Cr7C3 embedded in a pearlitic matrix Figure 8.5. Silver steel (1 % C - 1 % Cr) contains a structure in which carbides of Fe
Fig. 8.5 Photomicrograph of a cross section of undecarburized die steel. X 120

Fig. 8.6 Photomicrograph of a cross section of undecarburized EN-24 steel. X 120
and Cr are dispersed in a pearlitic matrix and EN-31 (1 % C - 1 % Cr) has Cr₇C₃ at grain boundaries in a pearlitic matrix. EN-24 (Ni-1.5, Cr-5, C-0.45) shows dispersion of spheroidal Cr₇C₃ and lamellar pearlite in a ferritic matrix (Fig. 8.6). EN-9 (0.45 % C) shows a pearlitic structure (Fig. 8.7). Mo-containing high speed tool steel (W-6, Cr-4) C-0.8, V-2 and Mo-5) in as cast condition shows a fine dispersion of the carbides of W, Mo and Cr in a ferritic matrix. 18:4:1 (W, Cr, V) high speed steel containing 0.75 % C shows a fine dispersion of carbides in a ferritic matrix. EN-36 containing 3 % Ni, 1 % Cr and 0.2 % C shows fine dispersion of Cr₇C₃ in a pearlitic matrix.

8.1.4 Morphology of Oxide Scales

8.1.4.1 Oxidized alloys

Figure 8.8 shows a cross section of silver steel decarburized in H₂-H₂O atmosphere at 900°C for 2 hrs. A well defined decarburized zone is present at the metal interface. The decarburized layer is ferritic in nature. The undecarburized matrix, contains dispersion of Cr₇C₃ in a ferritic matrix, the Fe₃C contents are considerably lowered on decarburization. A cross section of decarburized EN-31 steel shows the presence of a thin decarburized layer at the metal interface followed by a carbide rich layer. In the middle of the specimen, polygonal grains of carbides are gulfed in a ferritic matrix (Fig. not shown). Decarburized alloy steel
Fig. 8.7 Photomicrograph of a cross-section of undecarburized EN-9 steel. X 120

Fig. 8.8 Photomicrograph of a cross-section of silver steel, decarburized at 900°C for 2 hrs. X 120
EN-24 shows a well defined decarburized layer, the photomicrograph (Fig. 8.9) indicates extensive decarburization, the undecarburized zone contains dispersion of carbide in a ferritic matrix. Figure 8.10 shows the SEM picture of the matrix of decarburized alloy. The presence of carbide particles is clearly shown. Decarburized alloy steel EN-9 shows uniform decarburized layer at the alloy interface (Fig. 8.11). The undecarburized zone shows dispersion of cementite in a ferritic matrix. Figure 8.12 shows a photomicrograph of a cross section of decarburized high speed steel containing Mo and V. Although no well defined decarburized layer is present but there is depletion of carbide in the vicinity of alloy interface. Beyond this zone, there is a dispersion of carbides in the ferritic matrix. The microstructure of decarburized 18:4:1 (W:Cr:V) high speed steel is very similar to the low tungsten high speed steel mentioned above (Fig. 8.13).

Figure 8.14 shows a cross section of decarburized EN-36 steel. On comparison with the microstructure of undecarburized alloy, it appears that some decarburization has occurred although a decarburized layer is missing. The decarburized alloy shows the dispersion of carbide in a ferritic matrix (Fig. 8.15). The decarburized die-steel shows a thin carbide depleted zone at the alloy interface. The area beyond this zone contains a dispersion of carbides in a pearlitic matrix.

Figure 8.16 shows a photomicrograph of a cross-section
Fig. 8.9 Photomicrograph of a cross-section of EN-24 steel, decarburized at 900°C for 2 hrs. X 120

Fig. 8.10 SEM picture of EN-24 steel, decarburized at 900°C for 2 hrs. X 1000
Fig. 8.11 Photomicrograph of a cross-section of EN-9 steel, decarburized at 900°C for 2 hrs. X 120

Fig. 8.12 Photomicrograph of a cross-section of HSS (6-W), decarburized at 900°C for 2 hrs. X 120
Fig. 8.13 Photomicrograph of a cross-section of HSS (18-W), decarburized at 900°C for 2 hrs. X 120

Fig. 8.14 Photomicrograph of a cross-section of EN-36 steel, decarburized at 900°C for 2 hrs. X 120
Fig. 8.15 SEM picture of EN-36 steel, decarburized at 900°C for 2 hrs. X 2000

Carbides

FeO.Cr2O3
Cr2O3 (dark grey)
Cr7C3 (grey)
Fe3C (light)

Fig. 8.16 Photomicrograph of a cross-section of die-steel, oxidized at 900°C for 6 hrs. X 60
of die-steel oxidized at 900°C for 6 hrs. The oxidized alloy contains 2-layered scales which are adhered and relatively uniform. The inner porous scales and outer scales contain Cr₂O₃ (dark grey) and FeO.Cr₂O₃ (light) respectively. Inclusions of FeO in the inner scales and that of Cr₂O₃ in the outer scales are also noted. The carbide dispersion remain unaffected during oxidation. Figure 8.17 shows a cross section of the silver steel oxidized in oxygen at 900°C. The alloy seems to oxidize at a rapid rate and extensive disruption of the scales occur due to decarburization. The fragmentation of the alloys is also observed. A ferritic zone containing dispersion of carbide particles is present at the alloy/scale interface. Like silver steel, EN-31 oxidizes at rapid rate and scales have similar morphologies although the substrate has a pearlitic structure (Fig. 8.18). Figure 8.19 shows a photomicrograph of oxidized EN-24. Relatively thick scales are appeared in the form of stratified layers, the inner layer contain FeO.Cr₂O₃ and the outer layers contain mainly iron oxides. Due to decarburization during oxidation the layers are separated providing extensive gaps in between the layers. The carbides have higher concentration at the scale/alloy interface than the middle portion of the oxidized specimen. EN-9 steel seems to oxidize by a considerably high oxidation rate and shows the inner scales are rich in chromium (Fig. 8.20). The oxidized (6W-5Mo) high speed steel forms multilayered porous scales (Fig. 8.21). The inner scales
Fig. 8.17 Photomicrograph of a cross-section of silver steel, oxidized at 900°C for 8 hrs. X 60

Fig. 8.18 SEM picture of EN-31 steel, oxidized at 900°C for 8 hrs. X 200
Fig. 8.21 Photomicrograph of a cross-section of HSS (6-W), oxidized at 900°C for 17 hrs. X 60

Fig. 8.22 Photomicrograph of a cross-section of HSS (18-W), oxidized at 900°C for 24 hrs. X 60
contains oxides of W, Mo, V and Cr followed by iron oxide layers containing inclusions of \( \text{Cr}_2\text{O}_3 \). The carbide density in the alloy matrix is considerably reduced on oxidation. The substrate has dispersion of spheroidal carbides in a ferritic matrix. The oxidized 18:4:1 (W, Cr, V) high speed steel shows interesting scale morphology (Fig. 8.22). The outer scales appear in the form of an uniform semi-porous oxide scale adhered to a relatively thick scale band of \( \text{W}_2\text{O}_3 \) in which \( \text{Cr}_2\text{O}_3 \) is also incorporated. This inner oxide band seems to act as barrier against oxidation. The outer scales contain FeO in which \( \text{Cr}_2\text{O}_3 \) is present as inclusions. The substrate show fine dispersion of carbides in a ferritic matrix. In EN-36 steel, decarburization during oxidation results in the fragmentation of the alloy scale moreover due to the separation of the scales the fresh alloy exposed to oxygen and oxidized at a faster rate, protrusion of alloy is observed. The matrix is ferritic with dispersion of carbides. The small voids in the substrate are perhaps inherent in the alloy during casting. The inner oxide scales are rich in \( \text{Cr}_2\text{O}_3 \) but are incorporated with \( \text{Fe}_3\text{O}_4/\text{Fe} \), the outermost scales contain \( \text{Fe}_2\text{O}_3 \).

8.1.4.2 Predecarburized-Oxidized Alloys

Figure 8.23 shows a cross section of predecarburized oxidized die-steel. The predecarburized steel seems to oxidize at a much lower oxidation rates than the undecarburized alloy.
Fig. 8.23 Photomicrograph of across-section of predecarburized die steel, oxidized at 900°C for 9 hrs. X 120

Decarburized zone

Fe$_3$C

Fig. 8.24 SEM picture of predecarburized silver steel, oxidized at 900°C for 9 hrs. X 150

Fe$_2$O$_3$

FeO·Cr$_2$O$_3$

light matrix
The scales of the predecarburized-oxidized steel are thinner and much more fragile and lost contact from the substrate during polishing. In the variety of alloy/scale interface, the substrate structure is ferritic and perhaps represent decarburized layer. This is followed by a zone which is pearlitic in nature. Both the zone contains dispersion of Cr$_7$C$_3$ and Fe$_3$C. Figure 8.24 represents scanning electron micrograph of a cross section of a decarburized oxidized silver steel. The substrate structure is largely pearlitic containing grey cementite in considerable portion. Due to decarburization the FeO-Cr$_2$O$_3$ porous scales are detached from the matrix, this gives rise to higher oxidation rates. EN-31 forms multilayered copious scales in which inner scales are richer in chromium and outer scales contain oxides of iron Fe$_3$O$_4$/Fe$_2$O$_3$. While comparing with undecarburized oxidized alloy, the concentration of pearlite is much lower and it has almost a ferritic structure.

During oxidation of predecarburized EN-24 alloy, the entire decarburized layer is consumed and the substrate has a ferritic matrix in which carbides are embedded. The scales are detached from the alloy as a result of decarburization during oxidation. Cr$_2$O$_3$ forms the main constituent of thick but porous inner scales, the outer layers of the external scales contain Fe$_2$O$_3$ in which NiO is incorporated (Fig. not shown). The scales on decarburized-oxidized EN-9 contain
inner layer of FeO and the outer layers contain Fe$_2$O$_3$ the middle layers which comprises the bulk of the scale contain Fe$_3$O$_4$. The alloy is oxidized profusely due to decarburization during oxidation. FeO scales formed initially are disrupted and fresh alloy is exposed to oxygen. The substrate structure is pearlitic, the decarburized layer of the decarburized alloy is totally consumed during oxidation. A uniform decarburized layer is present in the oxidized predecarburized 6W-5Mo high speed steel and this followed by a carbide dispersed ferritic matrix (Fig. 8.25). This goes to show that during oxidation, the decarburized layer present in the predecarburized alloy remains intact. Figure 8.26 shows a scanning electron photomicrograph of a cross section of the predecarburized-oxidized 18:0.75:1 (W,C,V) high speed steel. Multilayered scales in the form of band structure are formed. The inner scales shows crystals of WO$_3$ admixed with FeO and Cr$_2$O$_3$ this is followed by Cr$_2$O$_3$ scales the outer layers contain oxides of iron. The adhered scales are seemed to be responsible for relatively lower oxidation rates of the alloy. The matrix shows fine dispersion of carbides. The predecarburized-oxidized EN-36 forms relatively thick scales which are porous and separated from the alloy. The inner scales are richer in Cr$_2$O$_3$ and the outer scales contain Fe$_2$O$_3$ in which Cr$_2$O$_3$ is incorporated. The alloy matrix shows dispersion of carbides in a coarsened ferritic matrix. During oxidation, the decar-
Fig. 8.25 Photomicrograph of a cross-section of predecarburized HSS (6-W), oxidized at 900°C for 9 hrs. X 120

Fig. 8.26 SEM picture of predecarburized HSS (18-W), oxidized at 900°C for 9 hrs. X 400
burized layer of the decarburized alloy seems to be completely consumed.

8.2 Discussion

The oxidation of low alloy steels e.g. EN-9, EN-24, EN-31, EN-36 and silver steel, high speed tool steels (low and high tungsten) and cold die-steel in one atmospheric oxygen at 900°C proceeds by a diffusion controlled mechanism as indicated by the linear nature of weight gain vs time plots. The increasing oxidation rate sequence for the different alloys is as follows:

EN-9 > EN-31 > Silver Steel > EN-24 > EN-36 > 6W-4Cr-5Mo-2V-0.8C high speed steel > cold die steel > 18W-4Cr-1V-0.75C high speed steel

18:4:1 high speed steel and cold die steel have the lowest oxidation rates and EN-9 and EN-31 have the highest oxidation rates. The alloy phase structure and the morphology of the oxide scales seem to influence the oxidation rates of the alloys. The alloy forming chromia scales and containing dispersion of carbides in the matrix have relatively lower oxidation rates. These alloys do not either undergo decarburization or to a very little extent. It has been established that the presence of carbide dispersions could restrict the mobility of carbon. Thus the high speed steels and die steel have nearly homogeneous and dense dispersion of transition metal
carbides which restricts the transport of carbon during oxidation, the Cr₂O₃ which forms the inner layer of the scale are not disrupted and largely remain adhered to the alloy surface. These two factors contribute mainly toward in declining the oxidation rates of the alloy steels. The plain carbon steel (EN-9) or low chromium steels (EN-24,-31 and-36) form copious oxide scales mainly containing oxides of iron.

These alloys do not form protective chromia scales due to the presence of insufficient amount of chromium and are subjected to decarburization. The evolution of carboneous gases during oxidation results in the disruption, cracking and fragmentation of the oxide scales which eventually led to the separation of alloy and oxide scales. When the ruptured scales are separated the fresh alloy is again exposed to O₂(g) and it oxidizes at a faster rate. The morphology of the oxide scales supports this viewpoint.

Figure 8.27 shows a plot of parabolic rate constant, Kₚ vs (Cr+C) % for different alloys. With some exception the oxidation rate decreases with increasing (Cr+C) content, this indirectly indexed the influence of chromium carbides and other transition metal carbides on the oxidation rate of alloys. In general, plain carbon low alloy steels, high speed steels and die-steel decarburize in H₂-H₂O atmosphere at 900°C. Except high speed steels and die steel all the steels exhibit a well defined decarburized layer. The carbon losses noted during a 4 hr. decarburization run in H₂-H₂O atmosphere (Table 8.2)
Fig. 8.27 Plot of parabolic rate constant, $K_p$ VS (Cr+C) % for different industrial steels.
follow the sequence:

High speed steel (18% W) $< \text{EN-31} < $ High speed steel (6% W) $< \text{EN-24} < $ silver steel $< \text{EN-9} < \text{EN-36} -$ die steel

Interestingly, although high speed steels show high carbon losses during decarburization, no well defined decarburized layer is found. During decarburization in $\text{H}_2-\text{H}_2\text{O}$ atmospheres, the carbide dispersion net work remain unaffected but the free carbon present in solid solution or as graphite is removed as $\text{CH}_4$; alloys containing no or low carbide dispersion-containing matrix show well defined decarburized layer. The decarburized layer is usually ferrite containing dispersion of carbides. It means that absence of a decarburized layer is not necessarily related to the decarburization rate or carbon losses during decarburization.

Predecarburized steels follow a parabolic rate law during oxidation, however, in some cases breaks are observed in weight gain vs time plots. The breaks in the oxidation kinetic curves are observed in case of EN-24, EN-36 and silver steels. The breaks in the oxidation curves can be explained on the basis of oxide scales morphology. Due to low Cr-contents and higher carbon contents, decarburization during oxidation occurs which results in the rupture of otherwise protective scales. The scales are not only separated from the alloy but also intra-separated into different layers as revealed by the
scale morphology. An interesting observation revealed during oxidation study was the presence of a well defined ferritic layer/band at the alloy/scale interface of predecarburized-oxidized high speed and die-steel which was otherwise absent from the corresponding decarburized steel. The presence of such a layer is perhaps the result of rapid diffusion of Cr and other alloying elements, which undergo oxidation and forming protective oxides. This would create a depletion in Cr concentration at the alloy/interface resulting in the formation of a ferritic zone. With some exceptions, the predecarburized alloys on oxidation follow the same oxidation sequence as that observed during the oxidation of undecarburized alloys. The oxidation rates of the decarburized alloys are slightly higher than the undecarburized alloys. This could be explained on the basis of the oxidation of decarburized layer which is ferritic in nature, the layer oxidizes at a much higher rate than carbide dispersed ferrite layer present in the undecarburized alloys. Such a behaviour has also been reported in decarburized carbide dispersed Fe-5 % M-C alloys (where M is a transition metal) which oxidize at a much higher rate than the corresponding undecarburized alloys. However, a reverse behaviour has been observed in case of carbide-dispersed iron base sintered alloys where decarburized alloys have lower oxidation rates. In sintered alloys (Chapter IV), decarburization behaviour contributes three factors responsible for lowering the
oxidation rates namely,

(i) the marked decrease in the porosity of the alloy;
(ii) production of a homogeneous and refined matrix structure; and
(iii) formation of a thin metal oxide film during decarburation which act as a barrier layer.