Niobium carbide (NbC), tungsten carbide (WC) or chromium carbide (Cr₇C₃) (10 weight %) dispersed iron-base alloys containing 0.1 weight % carbon and 1.0 weight % rare earth oxide viz La₂O₃, Pr₂O₃ or Y₂O₃ were prepared by compaction and sintering techniques. The details of experimental procedure are given in Chapter II.

The annealed samples were changed to required size and were placed into reaction tube for oxidation, decarburization and decarburization-oxidation experiments. The oxidation kinetics of the alloys were measured on Sartorius Electronic Microbalance (Model 4410-MP8) in presence of pure oxygen under 1 atmospheric pressure at 900°C for 8 hrs. and decarburization in H₂-H₂O atmosphere at 900°C for 2 hrs.

The morphology of the oxidized/decarburized alloys was studied using optical and scanning electron microscopes. The identification of the various constituents present in the scales/substrate was made by using X-ray diffraction analysis. The details are given in Chapter II.

6.1 Results

6.1.1 Oxidation Kinetics

Weight gain Vs time plots for the oxidation of a series
of iron-base sintered alloys of the general composition

Fe-10MC-0.1C-1.0RE₂O₃ (MC is NbC, WC or Cr₇O₃-10 wt. %, C is 0.1 wt. % and RE₂O₃ is La₂O₃, Pr₂O₃ or Y₂O₃-1.0 wt. %) are shown in figures 6.1-6.3. All the alloys were oxidized under one atmospheric oxygen gas at 900°C for 8 hrs. Figures 6.4-6.6 show plots of weight gain² Vs time for the same alloys. In general, the weight gain Vs time plots are parabolic and weight gain² Vs time plots are linear, indicating the diffusion controlled growth of oxide scales. Table 6.1

**Table 6.1**

Values of parabolic rate constants Kp for the oxidation of undecarburized and predecarburized Fe-10MC-0.1C-1.0RE₂O₃ alloys at 900°C in Kg².m⁻⁴.Sec⁻¹ x 10⁻⁶.

<table>
<thead>
<tr>
<th>Alloy (wt. %)</th>
<th>undecarburized</th>
<th>predecarburized</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-10WC-0.1C-1.0La₂O₃</td>
<td>2.40</td>
<td>8.70</td>
</tr>
<tr>
<td>Fe-10WC-0.1C-1.0Pr₂O₃</td>
<td>0.36</td>
<td>2.77</td>
</tr>
<tr>
<td>Fe-10WC-0.1C-1.0Y₂O₃</td>
<td>0.26</td>
<td>0.35</td>
</tr>
<tr>
<td>Fe-10NbC-0.1C-1.0La₂O₃</td>
<td>25.69</td>
<td>31.60</td>
</tr>
<tr>
<td>Fe-10NbC-0.1C-1.0Pr₂O₃</td>
<td>27.78</td>
<td>31.81</td>
</tr>
<tr>
<td>Fe-10NbC-0.1C-1.0Y₂O₃</td>
<td>28.47</td>
<td>10.42</td>
</tr>
<tr>
<td>Fe-10Cr₇C₃-0.1C-1.0La₂O₃</td>
<td>10.01</td>
<td>6.81</td>
</tr>
<tr>
<td>Fe-10Cr₇C₃-0.1C-1.0Pr₂O₃</td>
<td>10.40</td>
<td>10.42</td>
</tr>
<tr>
<td>Fe-10Cr C-0.1C-1.0Y₂O₅</td>
<td>13.89</td>
<td>9.55</td>
</tr>
</tbody>
</table>
Fig. 6.1 Plots of weight gain Vs time for the oxidation of Fe-10NbC-0.1C-1.0RE₂O₃ alloys at 900°C.
Fig. 6.2 Plots of weight gain Vs time for the oxidation of Fe-10Cr$_7$C$_3$-0.1C-1.0RE$_2$O$_3$ alloys at 900°C.
Fig. 6.3 Plots of weight gain Vs time for the oxidation of Fe-10WC-0.1C-1.0RE$_2$O$_3$ alloys at 900°C.
Fig. 6.4 Plots of weight gain $^2$ Vs time for the oxidation of Fe-10NbC-0.1C-1.0RE$_2$O$_3$ alloys at 900°C.
Fig. 6.5 Plots of weight gain$^2$ vs time for the oxidation of Fe-10Cr$_7$C$_3$-0.1C-1.0RE$_2$O$_3$ alloys at 900°C.
Fig. 6.6 Plots of weight gain$^2$ Vs time for the oxidation of Fe-10WC-0.1C-1.0RE$_2$O$_3$ alloys at 900°C.
lists the values of parabolic rate constant, $K_p$ for the oxidation of Fe-10MC-0.1C-1.0RE$_2$O$_3$ at 900°C.

The alloys Fe-10MC-0.1C-1.0RE$_2$O$_3$ were decarburized in wet hydrogen ($H_2-H_2O$) for 2 hrs. at 900°C and were subsequently oxidized in $O_2(g)$ at the same temperature for 8 hrs. The weight gain Vs time and weight gain$^2$ Vs time plots are shown in Figures 6.7-6.9 and 6.10-6.12 respectively. The decarburized alloys are also seemed to follow a parabolic rate law during oxidation indicating the operation of a diffusion controlled mechanism during oxide growth. The values of rate constant are given in Table 6.1.

6.1.2 Metallographic Studies
6.1.2.1 Fe-1ONbC-0.1C-1.0RE$_2$O$_3$ Alloys

Figures 6.13-6.14 show photomicrographs of Pr$_2$O$_3$ and Y$_2$O$_3$ containing iron-base sintered alloys of the general composition: Fe-1ONbC-0.1C-1.0RE$_2$O$_3$ in as-cast condition. The photomicrographs show the presence of polygonal ferritic grains and the carbides at the grain boundaries. Rare earth oxide particles are also present as inclusions particularly in the ferrite phase. On decarburization in wet hydrogen ($H_2-H_2O$), there is much more segregation of carbides at the polygonal interstices (Figs. 6.15 and 6.16) otherwise the microstructures of decarburized and undecarburized alloys look the same.
Fig 6.7 Plots of weight gain Vs time for the oxidation of decarburized Fe-10NbC-0.1C-1.0RE₂O₃ alloys at 900°C.
Fig. 6.8 Plots of weight gain Vs time for the oxidation of decarburized Fe-10Cr$_7$C$_3$-0.1C-1.0RE$_2$O$_3$ alloys at 900°C.
Plots of weight gain vs. time for the oxidation of decarbured Fe-10WC-0.1C-1.0RE$_2$O$_3$ alloys at 900°C.
Fig. 6.10 Plots of weight gain² Vs time for the oxidation of decarburized Fe-10NbC-0.1C-1.0RE₂O₃ alloys at 900°C.
Fig. 6.11 Plots of weight gain$^2$ Vs time for the oxidation of decarburized Fe-10Cr$_7$C$_3$-0.1C-1.0RE$_2$O$_3$ alloys at 900°C.
Fig. 6.12 Plots of gain² Vs time for the oxidation of decarburized Fe-WC-0.1C-1.0RE₂O₃ alloys at 900°C.
Fig. 5.13 Photomicrograph of cross-section of Fe-1ONbC-0.1C-1.0Pr2O3 alloy, sintered. X 120

--- Ferrite
--- NbC dispersion
--- Pr2O3

--- Y2O3

--- NbC dispersion

Fig. 6.14 Photomicrograph of cross-section of Fe-1ONbC-0.1C-1.0Y2O3 alloy, sintered. X 120
Fig. 6.15 Photomicrograph of cross-section of Fe-10NbC-0.1C-1.0La$_2$O$_3$ alloys, decarburized at 900°C for 2 hrs. X 120

Fig. 6.16 Photomicrograph of cross-section of Fe-10NbC-0.1C-1.0Pr$_2$O$_3$ alloy, decarburized at 900°C for 2 hrs. X 120
Figure 6.17 shows a photomicrograph of Fe-10NbC-0.1C-1.0La₂O₃ oxidized at 900°C for 8 hr. The dark carbide particles consisting with the polygonal ferrite grains are remained almost unaffected but there is internal oxidation of iron at the ferrite/carbide interface and grey FeO particles are found at the ferrite grain boundaries. The scales are mainly consisted of iron oxides with Fe₂O₃ present in the outer scales. The rare earth oxide is incorporated with the internal oxides as well as with the inner scales. Figure 6.18 shows a scanning electron micrograph of the same alloy in the decarburized and oxidized condition. A net work of internal oxide particles surrounding the polygonal grains can be seen. The scales are uniform and adhered containing oxides of iron; the wustite is oxidized to Fe₂O₃ due to penetration of O₂ through porous scales and Fe₂O₃ is present at localized sites in the scale.

Figures 6.19 and 6.20 show scanning electron and optical photomicrographs of Fe-10NbC-0.1C-1.0Pr₂O₃ alloy in decarburized-oxidized and oxidized condition. Almost similar morphologies are observed as those found in La₂O₃-containing alloys. The Y₂O₃-containing alloy in the decarburized and oxidized conditions (Fig. 6.21) show a denser net work of carbide grains in which internal oxide particles are incorporated otherwise the features are similar to those observed in corresponding Pr₂O₃-and La₂O₃-containing alloys.
Fig. 6.17 Photomicrograph of cross-section of Fe-10NbC-0.1C-1.0La$_2$O$_3$ alloy, oxidized at 900°C for 8 hrs. X 120
Fig. 6.18 SEM picture of Fe-10NbC-0.1C-1.0La₂O₃ alloy, oxidized at 900°C for 8 hrs.
X 80

Fig. 6.19 SEM picture of predecarburized Fe-10NbC-0.1C-1.0Pr₂O₃ alloy, oxidized at 900°C for 8 hrs.
X 100
Fig. 6.20 Photomicrograph of cross-section of Fe-10NbC-0.1C-1.0Pr₂O₃ alloy, oxidized at 900°C for 8 hrs. X 120
Fe₂O₃

Fe₃O₄ + Y₂O₃

FeO + Y₂O₃

NbC + FeO
(internal oxide)

Fig. 6.21 Photomicrograph of a cross-section of predecarburized Fe-10NbC-0.1C-1.0Y₂O₃ alloy, oxidized at 900°C for 8 hrs. X 120
6.1.2.2 Fe-10Cr$_7$C$_3$-0.1C-1.0RE$_2$O$_3$ Alloys

Figures 6.22-6.24 show photomicrographs of La$_2$O$_3$-, Pr$_2$O$_3$- and Y$_2$O$_3$- containing iron-base sintered alloys in as-cast condition. The photomicrographs show a dispersion of Cr$_7$C$_3$ particles in a ferrite matrix, the RE$_2$O$_3$ are also present as dispersed phase but it is difficult to identify these particles in the photomicrograph. In the decarburized state, the amount of ferrite is enhanced and segregation of carbide along the grainboundary is more clearly observed (Figs. 6.25).

Figure 6.26 shows a scanning electron photomicrograph of the Y$_2$O$_3$-containing alloy oxidized at 900°C. At the ferrite grain boundaries some of the Cr$_7$C$_3$ is oxidized to Cr$_2$O$_3$ and appears as a network along with Cr$_7$C$_3$. The iron oxide scales contain inclusions of Cr$_2$O$_3$. The decarburized-oxidized alloy shows (Fig. 6.27) similar features although the scales are more thicker and porous. The Pr$_2$O$_3$-containing alloy in oxidized condition shows oxide network in the matrix formed due to selective oxidation of Cr$_7$C$_3$ into Cr$_2$O$_3$ (Fig. 6.28). The inner scales contain Cr$_2$O$_3$ and FeO.Cr$_2$O$_3$ and outer scales contain a relatively thick layer of Fe$_2$O$_3$, the middle layers have inclusions of Cr$_2$O$_3$ in Fe$_2$O$_3$/Fe$_3$O$_4$ scales. Figure 6.29 shows a scanning electron photomicrograph of La$_2$O$_3$-containing alloy decarburized and oxidized at 900°C. The interesting features of the oxide scale is that FeO and Cr$_2$O$_3$ are present
Fig. 6.22 Photomicrograph of cross-section of Fe-10Cr_7C_3-0.1C-1.0La_2O_3 alloy, sintered x 120.

Cr_7C_3 dispersion
Fig. 6.23 Photomicrograph of cross section of Fe-10Cr$_7$C$_3$-0.1C-1.0Pr$_2$O$_3$ alloy, sintered. X 120

Fig. 6.24 Photomicrograph of cross-section of Fe-10Cr$_7$C$_3$-0.1C-1.0Y$_2$O$_3$ alloy, sintered. X 120
Fig. 6.25 Photomicrograph of cross-section of Fe-10Cr<sub>7</sub>C<sub>3</sub>-0.1C-1.0La<sub>2</sub>O<sub>3</sub> alloy, decarburized at 900°C for 2 hrs. X 120

Fig. 6.26 SEM picture of Fe-10Cr<sub>7</sub>C<sub>3</sub>-0.1C-1.0Y<sub>2</sub>O<sub>3</sub> alloy, oxidized at 900°C for 8 hrs. X 100
Fig. 6.27 Photomicrograph of cross-section of predecarburized Fe-10Cr7C3-0.1C-1.0Y2O3 alloy, oxidized at 900°C for 8 hrs. X 120

Fig. 6.28 SEM picture of Fe-10Cr7C3-0.1C-1.0Pr2O3 alloy, oxidized at 900°C for 8 hrs. X 100
Fig. 6.29 SEM picture of predecarburized Fe-10Cr7C3-0.1C-1.0La2O3 alloy, oxidized at 900°C for 8 hrs.
X 100

Fig. 6.30 Photomicrograph of cross section of Fe-10WC-0.1C-1.0La2O3 alloy, sintered.
X 120
in the outer and inner layers and the inner scale is largely consisted of FeO in which Cr$_7$C$_3$ is also incorporated.

6.1.2.3 Fe-10WC-0.1C-1.0RE$_2$O$_3$ Alloys

Figures 6.30-6.32 show photomicrographs of RE$_2$O$_3$-containing WC-dispersed iron-base sintered alloys. The photomicrographs indicate the presence of polygonal ferrite particles along with WC particles. On decarburization the amount of ferrite phase is enhanced significantly and the carbide particles are segregated along the grain boundaries, presence of RE$_2$O$_3$ inclusions is also indicated. In the decarburized Y$_2$O$_3$-containing alloy (Fig. 6.33), some internal oxidation at the grain boundaries is also indicated. Figures 6.34 and 6.35 show scanning electron photomicrograph of Fe-10WC-0.1C-1.0La$_2$O$_3$ and Fe-10WC-0.1C-1.0Pr$_2$O$_3$ oxidized at 900°C for 8 hrs. Both the alloys show separation of the scale at the alloy interface and separation of the outer and inner scales. The inner scales are largely consisted of FeO.WO$_3$ and the outer scales contain oxides of iron. The microstructure of matrix shows segregation of WC along the grain boundaries and presence of internal FeO or FeO.WO$_3$ along with the carbides.

The scanning electron photomicrograph (Fig. 6.36) of Fe-10WC-0.1C-1.0Y$_2$O$_3$ represents typical morphology for the decarburized (H$_2$-H$_2$O) and oxidized (O$_2$) alloy at 900°C. The
Fig. 6.31 Photomicrograph of cross-section of Fe-10WC-0.1C-1.0Pr2O3 alloy, sintered. X 120

Fig. 6.32 Photomicrograph of cross-section of Fe-10WC-0.1C-1.0Y2O3 alloy, sintered. X 120
Fig. 5.33 Photomicrograph of cross-section of Fe-10WC-0.1C-1.0Y₂O₃ alloy, decarburized at 900°C for 2 hrs. X 120

Fig. 6.34 SEM picture of Fe-1OWC-0.1C-1.0La₂O₃ alloy, oxidized at 900°C for 8 hrs. X 390
Fe$_2$O$_3$

FeO+Fe$_3$O$_4$+WO$_3$

FeO+WO$_3$+WC

WC+FeO+Pr$_2$O$_3$

Fig. 6.35 SEM picture of Fe-10WC-0.1C-1.0Pr$_2$O$_3$ alloy, oxidized at 900°C for 8 hrs. X 390

WO$_3$+FeO

Fe$_2$O$_3$

WO$_3$+FeO

FeO+WC+Y$_2$O$_3$

Fig. 6.36 SEM picture of predecarburized Fe-10WC-0.1C-1.0Y$_2$O$_3$ alloy, oxidized at 900°C for 8 hrs. X 300
The microstructure of the matrix shows segregation of WC particles at the grain boundaries which remain undisturbed during oxidation of the decarburized alloy. The inner scales contain $WO_3$ or $WO_3$.FeO and the outer scales contain $Fe_2O_3$. The scales are more compact and adhered than those obtained during the oxidation of undecarburized alloys.

6.2 Discussion

Fe-10MC-0.1C-1.0RE$_2$O$_3$ sintered alloys have agglomeration of carbides at the grain boundaries. During decarburization this agglomeration remains undisturbed. On oxidation, internal oxidation of the carbide-depleted phase occurs and the oxidation product FeO is present either admixed with carbide or as a separate phase near the grain boundaries. Oxidation rates of Fe-10MC-0.1C-RE$_2$O$_3$ sintered alloys are largely dependent on the extent of internal oxidation. Thus the WC-containing alloys have relatively very little internal oxidation and have usually lowest oxidation rates. The pattern of oxidation rates of these alloys are very similar to Fe-10MC alloys, NbC-containing alloys have the highest oxidation and WC-containing lowest rate. The addition of RE$_2$O$_3$ provide more adherent and uniform oxide scales. The oxidation rates of Fe-10MC-0.1C-RE$_2$O$_3$ in undecarburized and decarburized states are much lower (about one order of magnitude) than the corresponding Fe-10MC alloys. This goes to show that the presence of RE$_2$O$_3$ play some role in restricting the oxidation
rates of the alloy. However, the oxidation rates of RE$_2$O$_3$-containing alloys are higher than 20% Cr-containing alloys (Chapter V). It is obvious from these observations that the presence of internal Cr$_2$O$_3$ net work at the grain boundaries restricts the transportation of Fe or any alloying element and therefore, restrict the oxidation rates. In WC-containing alloys, the higher thermodynamic stability of WC towards oxidation itself plays an important role.

The influence of RE$_2$O$_3$ on the oxidation of the alloys is not fully understood, but they do play some role in reducing the oxidation rates either affecting the mobility of carbon or providing more adherent nonporous oxide scales.