CHAPTER V

DECARBURIZATION AND OXIDATION OF Fe-10MC-0.1C-20Cr ALLOYS

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

Chromium- and iron-containing transition metal carbide dispersed iron based alloys: Fe-10MC-0.1C-20Cr (where C is 0.1 wt. %; MC is TiC, WC, Cr$_7$C$_3$ or NbC 10 wt. %, and Cr is 20 wt. %) were prepared by sintering. Tablets of 1.4 cm diameter were prepared by mixing carbon (0.1 wt. %), metal carbide (10 wt. %), chromium (20 wt. %) and iron (balance) powders in an agate mortar. The total amount of material used for each tablet was about 2.0 g. The mixture was put in a steel mould and was compacted at 15 tons/cm$^2$ using a hydraulic press. The green tablets were sintered in a quartz tube placed in a glober tubular furnace under dried hydrogen atmosphere at 1200°C for 2 hrs. and subsequently annealed under nitrogen atmosphere at 1000°C. Each sintered alloy was examined under a photometallurgical microscope and invariably shows a homogeneous 2-phase microstructure.

The sintered alloys were subjected to oxidation (1 atm. O$_2$), decarburization (H$_2$-H$_2$O) and decarburization-oxidation studies at 900°C on a laboratory fabricated helical thermal balance.
5.1 **Results**

5.1.1 **Oxidation kinetics**

Weight gain Vs time and weight gain² Vs time plots for the oxidation of undecarburized Fe-10MC-0.1C-20Cr alloys at 900°C in 1 atm. O₂ have been shown in figures 5.1 and 5.2, respectively. Furthermore, the alloys have been decarburized in wet hydrogen (H₂-H₂O) at 900°C for 2 hrs. followed by oxidation at the same temperature in 1 atm. O₂, the weight gain Vs time and weight gain² Vs time plots for the oxidation of decarburized-oxidized alloys are given in figures 5.3 and 5.4 respectively. In both the conditions, the weight gain Vs time plots are parabolic and weight gain² Vs time plots are linear. Therefore, the oxidation of undecarburized as well as decarburized alloys seem to proceed by a diffusion-controlled mechanism. The values of parabolic rate constant, Kp are listed in Table 5.1. A glance on the values of rate constant of different alloys indicates that Fe-10WC-0.1C-20Cr has the lowest oxidation rates in undecarburized and decarburized states. However, in an undecarburized state, Fe-10Cr₇C₃-0.1C-20Cr has the highest oxidation rate whereas in the decarburized state, the corresponding NbC-containing alloy has the highest oxidation rates although the oxidation rates of the alloys in both the states differ only marginally.
Fig. 5.1 Plots of weight gain Vs time for the oxidation of Fe-10NiC-0.1C-20Cr alloys at 900°C for 8 hrs.
Fig. 5.2 Plots of weight gain$^2$ Vs time for the oxidation of Fe-10MC-0.1C-20Cr alloys at 900°C for 8 hrs.
Pre-decarburization - Oxidation

10TiC + 0.1C + 20Cr
10NbC + 0.1C + 20Cr
10Cr7C3 + 0.1C + 20Cr
10WC + 0.1C + 20Cr

Fig. 5.3 Plots of weight gain Vs time for the oxidation of decarburized Fe-10M-0.1C-20Cr alloys at 900°C for 8 hrs.
Fig. 5.4 Plots of weight gain^2 Vs time for the oxidation of decarburized Fe-10M-0.1C-20Cr alloys at 900°C for 8 hrs.
Table 3.1
Values of parabolic rate constants $K_p$ for the oxidation of undecarburized and predescarburized Fe-10MC-0.1C-20Cr alloys at 900°C in $kg^{2}m^{-4}Sec^{-1}x10^{-7}$

<table>
<thead>
<tr>
<th>Alloy (wt.%)</th>
<th>undecarburized</th>
<th>predescarburized</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-10TiC-0.1C-20Cr</td>
<td>23.43</td>
<td>30.65</td>
</tr>
<tr>
<td>Fe-10NbC-0.1C-20Cr</td>
<td>25.93</td>
<td>33.34</td>
</tr>
<tr>
<td>Fe-10Cr7C3-0.1C-20Cr</td>
<td>50.93</td>
<td>19.26</td>
</tr>
<tr>
<td>Fe-10WC-0.1C-20Cr</td>
<td>4.81</td>
<td>8.80</td>
</tr>
</tbody>
</table>

5.1.2 Metallographic Studies
5.1.2.1 Fe-10TiC-0.1C-20Cr Alloy

Figure 5.5 shows an optical micrograph of sintered Fe-10TiC-0.1C-20Cr alloy. The micrograph shows the presence of polygonal ferrite in a Cr-rich iron matrix porous in nature. The alloy on oxidation forms an internal $Cr_2O_3$ surrounding the ferrite polygonals, TiC is segregated at the grain boundaries (Fig. 5.6). The oxides are the result of preferential oxidation of Cr in the matrix. The thick inner oxide scales largely contain $FeO.Cr_2O_3$ and $Cr_2O_3$. Due to the presence of carbon, some decarburization occurred during oxidation resulting in the evolution of $CO/CO_2$ and consequently in the formation of porous scales.
Fig. 5.5 Photomicrograph of a cross-section of Fe-10TiC-0.1C-20Cr alloy undecarburized.

X 120

Fig. 5.6 Photomicrograph of a cross-section of Fe-10TiC-0.1C-20Cr, oxidized at 900°C for 8 hrs.

X 120
Figure 5.7 shows a photomicrograph of TiC-containing sintered alloy decarburized in wet hydrogen (H₂-H₂O) for 2 hrs. at 900°C. There is quite a bit similarity between undecarburized and decarburized alloys, the only significant difference is the greater porosity of the decarburized alloy. The microstructure of decarburized-oxidized Fe-10TiC-0.1C-20Cr alloy is very similar to that of the corresponding undecarburized-oxidized alloy albeit the scales are less thicker and relatively less porous (Fig. 5.8). The scanning electron photomicrograph of decarburized-oxidized alloy shows the dispersion of TiC in the matrix in conjunction with internal Cr₂O₃ (Fig. 5.9). The incorporation of TiC in the innermost layers of the chromia scales is also apparent. The inner layers of the oxide scales are mainly comprised of FeO·Cr₂O₃ and the outer layers contain Fe₂O₃, the middle layers of the scale show a sort of dendrite growth of iron oxide, Fe₃O₄ in which Cr₂O₃ and TiO₂ are also incorporated.

5.1.2.2 Fe-10NbC-0.1C-20Cr Alloy

Figure 5.10 shows a photomicrograph of Fe-10NbC-0.1C-20Cr sintered alloy. The microstructure contains coarsened polygonal grains of ferrite. In oxidized condition at 900°C, the photomicrograph (Fig. 5.11) exhibits internal Cr₂O₃ particles which are segregated at the grain boundaries of ferrite matrix. The NbC grains are dispersed in a ferrite matrix. A relatively thick layer of Cr₂O₃ is present in the inner scale
Fig. 5.7 Photomicrograph of a cross-section of Fe-10TiC-0.1C-20Cr alloy, decarburized at 900°C for 2 hrs. X 120

Fig. 5.8 Photomicrograph of a cross-section of predecarburized (2 hrs) Fe-10TiC-0.1C-20Cr alloy, oxidized at 900°C for 8 hrs. X 120
Fig. 5.9 SEM picture of predecarburized (2 hrs) Fe-10TiC-0.1C-20Cr alloy, oxidized at 900°C for 8 hrs. X 120

Fig. 5.10 Photomicrograph of a cross-section of Fe-10NbC-0.1C-20Cr alloy, undecarburized X 120
Fig. 5.11 Photomicrograph of a cross-section of Fe-10NbC-0.1C-20Cr alloys, oxidized at 900°C for 8 hrs. X 120

Fig. 5.12 Photomicrograph of a cross-section of Fe-10NbC-0.1C-20Cr alloys decarburized at 900°C for 2 hrs. X 120
in which some NbC is also incorporated. The outer scales are mainly comprised of iron oxides containing Cr$_2$O$_3$ and Nb$_2$O$_5$ inclusions.

The optical micrograph (Fig. 5.12) of sintered Fe-10NbC-0.1C-20Cr alloy decarburized in wet hydrogen (H$_2$-H$_2$O) shows the presence of polygonal grains of ferrite in which NbC is present as a dispersed phase. The structure is porous and internal Cr$_2$O$_3$ formed during decarburization is present at the grain boundaries. Figure 5.13 shows a photomicrograph of the decarburized-oxidized sintered alloy. The oxide scales are almost entirely consisted of Cr$_2$O$_3$ in which NbC is incorporated and like undecarburized-oxidized alloy, presence of internal Cr$_2$O$_3$ grains can be seen at the ferrite interstices.

5.1.2.3 Fe-10WC-0.1C-20Cr Alloy

The photomicrograph of sintered Fe-10WC-0.1C-20Cr alloy (Fig. 5.14) shows the presence of polygonal ferrites in a Cr-enriched matrix, the WC particles are present rather ununiformly at the grain boundaries. Figure 5.15 shows the photomicrograph of the same alloy oxidized at 900°C for 8 hrs. in 1 atm. O$_2$. Chromium is internally oxidized to Cr$_2$O$_3$ and is present with WC at the grain boundaries. A layer of FeO.Cr$_2$O$_3$ is present in the inner scales in which some WC particles are also incorporated, the outer layers of the scales contain Fe$_2$O$_3$ in which some Cr$_2$O$_3$ is also present. The scales are comparatively less
Fig. 5.13 Photomicrograph of a cross-section of predecarburized (2 hrs.) Fe-10NbC-0.1C-20Cr alloys, oxidized at 900°C for 8 hrs. X 120

Fig. 5.14 Photomicrograph of a cross-section of Fe-10WC-0.1C-20Cr alloy, undecarburized X 120
porous than the scales of TiC- and NbC-containing iron-base alloys. The scanning electron photomicrograph of oxidized alloy shows the presence of a relatively nonporous and more adherent scales (Fig. 5.16). The innermost layer of the scales are comprised of \( \text{Cr}_2\text{O}_3 \) and outermost contains \( \text{Fe}_2\text{O}_3 \) incorporating some \( \text{Cr}_2\text{O}_3 \). The middle portion of the scales show denderite of iron oxide(s) in which \( \text{WO}_3 \) and \( \text{Cr}_2\text{O}_3 \) particles are also participated. Figure 5.17 shows a photomicrograph of Fe-10WC-0.1C-20Cr sintered alloy decarburized in wet hydrogen at 900°C for 2 hrs. By and large WC does not seem to be much affected but some Cr present in the matrix got oxidized internally at the grain boundaries. In the decarburized-oxidized condition (Fig. 5.18), the inner scales are largely consisted of \( \text{Cr}_2\text{O}_3 \) followed by thicker but porous layers of wustite containing \( \text{Cr}_2\text{O}_3 \) and \( \text{WO}_3 \). The porosity is perhaps developed due to evolution of CO/CO\(_2\) during oxidation.

5.1.2.4 Fe-10Cr\(_7\)C\(_3\)-0.1C-20Cr Alloy

Figure 5.19 represents a photomicrograph of sintered Fe-10Cr\(_7\)C\(_3\)-0.1C-20Cr alloy in as cast condition, the microstructure indicates the presence of 2 phases: a polygonal ferritic phase (light) and a Cr\(_7\)C\(_3\)-rich iron solution phase (dark) separated by well defined boundaries. When this alloy is oxidized at 900°C for 8 hrs. (Fig.5.20), the innermost layers of the porous oxide scales are consisted of \( \text{Cr}_2\text{O}_3 \) whereas the
Fig. 5.15 Photomicrograph of a cross-section of Fe-10WC-0.1C-20Cr alloy oxidized at 900°C for 8 hrs. X 120

Fig. 5.16 SEM picture of Fe-10WC-0.1C-20Cr alloy, oxidized at 900°C for 8 hrs. X 100
Fig. 5.17 Photomicrograph of a cross-section of Fe-10WC-0.1C-20Cr alloy, decarburized at 900°C for 2 hrs. X 120

Fig. 5.18 Photomicrograph of a cross-section of predecarburized (2 hrs.) Fe-10WC-0.1C-20Cr alloy, oxidized at 900°C for 8 hrs. X 120
Fig. 5.19 Photomicrograph of a cross-section of Fe-10Cr₇C₃-0.1C-20Cr alloy, undecarburized. X 120

Fig. 5.20 Photomicrograph of a cross-section of Fe-10Cr₇C₃-0.1C-20Cr alloy, oxidized at 900°C for 8 hrs. X 400
outer scale contains Fe$_2$O$_3$. The middle layers of the scales are nonporous and contain mainly the spinel FeO.Cr$_2$O$_3$. The inner chromia scales have incorporated some Cr$_7$C$_3$. The scanning electron photomicrograph of the oxidized alloy (Fig. 5.21) shows the presence of a dark phase which entirely consists of internal oxide, Cr$_2$O$_3$ with dispersion of Cr$_7$C$_3$ particles. This phase co-exists with a light ferritic phase, the Cr$_7$C$_3$ particles are concentrated at the grain boundaries of this phase.

The decarburized Fe-10Cr$_7$C$_3$-0.1C-20Cr in its microstructure (Fig. 5.22) shows the presence of 2 phases: the light phase representing ferrite and a dark phase representing Cr-rich iron solid solution, the Cr$_7$C$_3$ particles are dispersed in both the phases. Some Cr is oxidized to Cr$_2$C$_3$ in the Cr-rich phase. The Cr-rich phase is much more porous than the ferritic phase. Figures 5.23 and 5.24 show optical and scanning electron photomicrographs, respectively of Fe-10Cr$_7$C$_3$-0.1C-20Cr decarburized in H$_2$-H$_2$O atmosphere for 2 hrs. followed by oxidation in 1 atm. O$_2$ for 8 hrs. The alloy matrix of decarburized-oxidized alloy shows the presence of internal Cr$_2$O$_3$ phase along with light ferritic phase. Cr$_7$C$_3$ grains are segregated at the ferritic grain boundaries. The thicker inner scale is largely consisted of Cr$_2$O$_3$/Cr$_2$O$_3$.FeO. Due to decarburization and subsequent exposure of FeO to oxygen, some Fe$_2$O$_3$ is formed in the inner
Fig. 5.21 SEM picture of Fe-10Cr$_7$C$_3$-0.1C-20Cr alloys, oxidized at 900°C for 8 hrs. X 200

Fig. 5.22 Photomicrograph of a cross-section of Fe-10Cr$_7$C$_3$-0.1C-20Cr alloy, decarburized at 900°C for 2 hrs. X 120
Fig. 5.23 Photomicrograph of a cross-section of predecarburized (2 hrs.) Fe-10Cr$_7$C$_3$-0.1C-20Cr alloy, oxidized at 900°C for 8 hrs. X 120

Fig. 5.24 SEM picture of predecarburized (2 hrs.) Fe-10Cr$_7$C$_3$-0.1C-20Cr alloy, oxidized at 900°C for 8 hrs. X 100
scales. The outer scales contain $\text{Fe}_2\text{O}_3$ in which some $\text{Cr}_2\text{O}_3$ is also included.

5.2 **Discussion**

The oxidation behaviour of iron-based sintered alloys of the composition: Fe-10MC-0.1C-20Cr was studied in the normal (undecarburized) state in 1 atm. $\text{O}_2$ at 900°C. The alloys oxidized following a parabolic rate law indicating a diffusion controlled mechanism operated during oxidation. The WC-containing alloy oxidized at the slowest rate and Cr$_7$C$_3$-containing alloy at the fastest rate. There are three important morphological features of the oxidized alloys. An internal Cr$_2$O$_3$ is formed as a separate phase along with a ferritic phase, Cr$_7$C$_3$ is present as a dispersion but mainly concentrated at the ferritic polygonal grain boundaries, Cr$_2$O$_3$/FeO.Cr$_2$O$_3$ layer is present invariably at the alloy/scale interface. These three factors seem to be responsible for relatively low oxidation rates of Fe-10MC-0.1C-20Cr alloys. This contention is further evident from the fact that Fe-10MC alloys (Chapter IV) have oxidation rates at least one order of magnitude higher than the latter. During oxidation of Fe-10MC-0.1C-20Cr, the carbide is largely remained unaffected which is shown by the incorporation of the carbides in the scales. Due to presence of carbon, some decarburization occurs during oxidation, resulting in the disruption of the protective film.
Fe-10MC-0.1C-20Cr alloys are decarburized in low oxygen potential atmosphere ($\sim 10^{-19}$) of $O_2$ at $900^\circ$C, although there is no well defined decarburized layer but there is evidence of decarburization from microstructures. The decarburized alloys were further oxidized at $900^\circ$C in 1 atm. $O_2$. With the exception of NbC-containing alloys, the decarburized alloys oxidize at a slightly higher rate than the undecarburized alloy. This could be attributed to the highly porous structure of the decarburized alloys. But it is to be noted that there is only marginal difference in the oxidation rates of decarburized and undecarburized Fe-10MC-0.1C-20Cr alloys. In Fe-10MC system (Chapter IV), an opposite behaviour is observed, the oxidation rates of undecarburized alloys are at least one order of magnitude higher than the decarburized alloys. The oxidation behaviour of decarburized Fe-10MC alloy has been explained firstly on the basis of the formation of a thin protective film during decarburization in $H_2$-$H_2O$ atmosphere which retards the mobility of carbon atoms and secondly, the presence of a fine carbide dispersion in an austenitic matrix which considerably reduces the level of decarburization during oxidation and in consequence assists in retaining the integrity of oxide scales. In Fe-10MC-0.1C-20Cr system, these factors are valid but unlike Fe-10MC, the undecarburized alloys in addition also have a protective chromium oxide layer which drastically restricts the oxidation rates. This is
reflected by the values of oxidation rates of undecarburized and decarburized Fe-10MC-0.1C-20Cr alloys which are very similar.