6.1 General

The concluding remarks in the earlier chapter provided possible clues to the design and development of alloy(s) with improved performance. This led to the development of 22% Cr materials designated as B-series of alloys. Aluminium content was kept around 5.5% and different yttria contents were considered. The compositions of the alloys are already reported in table 3B.

The results reported in the following sections include:

i) High temperature oxidation behaviour,

ii) Initial characterization on the basis of hardness and final characterization based on high temperature mechanical properties,

iii) Electrical resistivity measurements,

iv) Metallographic studies,

v) Phase analysis by x-ray diffractometry and

(vi) assessment of homogeneity by EPMA.

In the final analysis, the performance of the alloys presently developed has been compared with that of some of the proprietary alloys already in use. This gave an overall assessment of the usefulness of the investigation undertaken.

6.2 RESULTS

6.2.1 High temperature oxidation behaviour

Thin samples, similar to those of the A-series of alloys, were subjected to isothermal oxidation at temperatures ranging
from 1050 to 1250°C for periods of upto 20 hours. The data so generated is presented in the form of plots (graphs) between weight change (gain) per unit area as a function of time at the reference temperatures of 1050, 1150, 1200 and 1250°C (Figs.6.1 - 6.3). High temperature oxidation behaviour of Kanthal A-1, as determined in the present study, is summarized in the Fig.6.4 where as Figs.6.5 to 6.8 represent the comparative oxidation behaviour of different alloys. Relevant data arising out of these figures is summarized in the tables GA and GB.

An analysis of the data summarized in the aforesaid figures and tables revealed that:

i) Barring some instances, the oxidation process comprises of two stages.

ii) The main effect of temperature was that the rate of oxidation and the time regimes over which the different stages existed were altered; in some instances even the number of stages were altered.

iii) The base alloy B1 showed strikingly improved oxidation resistance in comparison to the best alloy of the A-series (A4) in terms of time to attain the 'stabilized state', the weight gain corresponding to the 'stabilized state', the rate of oxidation and the overall weight gain over a period of 20hrs. The oxidation process occurred in two stages, except at 1250°C, when apparently three stages were observed. However, a more rationalized analysis suggests the existence of only two stages.
iv) Addition of 0.2% Y to the base alloy significantly improved the oxidation resistance (Fig. 6.2). Oxidation in the resultant alloy B2 occurred in two stages at all the reference temperatures.

v) Addition of 0.4% Y to the base alloy (Fig. 6.3), designated, as B3, resulted in a marked improvement in the oxidation resistance at all the reference temperatures. In fact, the alloy B3 is significantly superior to alloy B2 in terms of oxidation resistance (Figs. 6.2 and 6.3). The process of oxidation occurred in two stages up to 1200° and in three stages at 1250° C (Fig. 6.3).

vi) Fig. 6.3 also depicts a comparison between the oxidation resistance behaviour of alloys, one made from indigenous (I) and the other from Swedish (S) irons. The Swedish pre alloyed powder contained 17% Cr to which indigenous ferro-chrome was added in powered form to make up chromium to 22%. 0.4% yttria was added to this to get the desired composition. Its oxidation resistance at 1200° C was found to be superior to that of the alloy B3.

vii) The isothermal oxidation behaviour of Kanthal A-1, summarized in fig. 6.4, revealed that the basic features of the plots were similar to those observed in B-series of alloys.

viii) The results plotted in Figs. 6.5 - 6.8 gave a generalized picture about the relative superiority of the performance (oxidation resistance) of the B-series of alloys, as shown in the table given on page 119.
ix) On comparing the oxidation resistance of the B-series of alloys with that of Kanthal A-1 and alloy A4, within the temperature range 1050-1250°C it emerges that the behaviour of the B-series of alloys is significantly better till 1200°C, whereas at 1250°C Kanthal A-1 is at second preference after B3. This would be evident from the data summarized below:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Relative Superiority</th>
</tr>
</thead>
<tbody>
<tr>
<td>1050°C</td>
<td>B2 &gt; B1 &gt; B3 &gt; A4 &gt; Kanthal A-1</td>
</tr>
<tr>
<td>1150°C</td>
<td>B1 &gt; B2 &gt; B3 &gt; Kanthal A-1 &gt; A4</td>
</tr>
<tr>
<td></td>
<td>(Based on weight gain at level off state, however, 'level of conditions in B3 and B1 reached much earlier as compared to B2)</td>
</tr>
<tr>
<td>1200°C</td>
<td>B3 &gt; B1 &gt; B2 &gt; Kanthal A-1 &gt; A4</td>
</tr>
<tr>
<td>1250°C</td>
<td>B3 &gt; Kanthal A-1 &gt; B2 &gt; A4 &gt; B1</td>
</tr>
</tbody>
</table>
Table 6A: Effect of temperature on the rate of oxidation

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Alloy</th>
<th>Slopes (tan θ values for each stage of oxidation)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Stage-I</td>
</tr>
<tr>
<td>1050</td>
<td>B1</td>
<td>0.3640</td>
</tr>
<tr>
<td></td>
<td>B2</td>
<td>0.0524</td>
</tr>
<tr>
<td></td>
<td>B3</td>
<td>0.4663</td>
</tr>
<tr>
<td></td>
<td>Kanthal A-1</td>
<td>0.3640</td>
</tr>
<tr>
<td>1150</td>
<td>B1</td>
<td>0.3640</td>
</tr>
<tr>
<td></td>
<td>B2</td>
<td>0.1228</td>
</tr>
<tr>
<td></td>
<td>B3</td>
<td>0.5543</td>
</tr>
<tr>
<td></td>
<td>Kanthal A-1</td>
<td>0.4663</td>
</tr>
<tr>
<td>1200</td>
<td>B1†</td>
<td>0.3640</td>
</tr>
<tr>
<td></td>
<td>B2</td>
<td>0.3249</td>
</tr>
<tr>
<td></td>
<td>B3(I)</td>
<td>0.7341</td>
</tr>
<tr>
<td></td>
<td>B3(S)</td>
<td>0.7265</td>
</tr>
<tr>
<td></td>
<td>Kanthal A-1</td>
<td>1.0</td>
</tr>
<tr>
<td>1250</td>
<td>B1†</td>
<td>0.8390</td>
</tr>
<tr>
<td></td>
<td>(1.0)*</td>
<td>(0.7002)</td>
</tr>
<tr>
<td></td>
<td>B2</td>
<td>1.3764</td>
</tr>
<tr>
<td></td>
<td>B3</td>
<td>2.7475</td>
</tr>
<tr>
<td></td>
<td>Kanthal A-1</td>
<td>0.6745</td>
</tr>
</tbody>
</table>

* Values based on four stages of oxidation
Table 6B: Effect of temperature on the duration of different stages of oxidation

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Alloy Designation</th>
<th>Duration of Each stage of oxidation (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Stage-I</td>
</tr>
<tr>
<td>1050</td>
<td>B1 up to 180</td>
<td>180-1200</td>
</tr>
<tr>
<td></td>
<td>B2 up to 600</td>
<td>600-1200</td>
</tr>
<tr>
<td></td>
<td>B3 up to 360</td>
<td>360-1200</td>
</tr>
<tr>
<td></td>
<td>Kanthal A-1 up to 780</td>
<td>780-1200</td>
</tr>
<tr>
<td>1150</td>
<td>B1 up to 240</td>
<td>240-1200</td>
</tr>
<tr>
<td></td>
<td>B2 up to 660</td>
<td>660-1200</td>
</tr>
<tr>
<td></td>
<td>B3 up to 360</td>
<td>360-1200</td>
</tr>
<tr>
<td></td>
<td>Kanthal A-1 up to 600</td>
<td>600-1200</td>
</tr>
<tr>
<td>1200</td>
<td>B1 up to 840</td>
<td>840-1200</td>
</tr>
<tr>
<td></td>
<td>B2 up to 1080</td>
<td>1080-1200</td>
</tr>
<tr>
<td></td>
<td>B3(I) up to 420</td>
<td>420-1200</td>
</tr>
<tr>
<td></td>
<td>B3(S) up to 300</td>
<td>300-1200</td>
</tr>
<tr>
<td></td>
<td>Kanthal A-1 up to 720</td>
<td>720-1200</td>
</tr>
<tr>
<td>1250</td>
<td>B1 up to 600</td>
<td>600-1080</td>
</tr>
<tr>
<td></td>
<td>up to 180</td>
<td>(180-540) (540-1080) (1080-1200)</td>
</tr>
<tr>
<td></td>
<td>B2 up to 540</td>
<td>540-1200</td>
</tr>
<tr>
<td></td>
<td>B3 up to 240</td>
<td>240-480</td>
</tr>
<tr>
<td></td>
<td>Kanthal A-1 up to 420</td>
<td>420-660</td>
</tr>
</tbody>
</table>
6.2.2 Rolling response and hardness

As has been already indicated, slabs were rolled into sheets by a combination of hot rolling and cold rolling interspersed with reheating cycles. The following observations are noteworthy:

i) The alloy B1 could be hot rolled up to a reduction of 50%. Any further attempt at rolling by employing reheating followed by oil/water quenching to soften the material did not prove useful. Moreover, extensive transverse edge cracking was observed. As such specimens could not be made out, this alloy for tensile testing. The alloy is extremely brittle.

ii) Addition of 0.2% Y₂O₃ to B1 (designated as B2) improved the rolling characteristics significantly. It was possible to roll down this alloy (B2) into sheets of reasonable thickness (1-1.5mm).

iii) A further increase in Y₂O₃ to 0.4% did not adversely affect the response of the resultant alloy B3. Infact, it could also be rolled down to the same thickness as B2. Surprisingly, the hardness of B3 was noted to have almost doubled that of alloy B2 (Table 6.1). As such the rolling response of alloy B3, in spite of its very high hardness, should be regarded as extremely favourable.

6.2.3 Electrical resistivity

The data summarized in Table 6.2 revealed that electrical resistivity decreased with an increase in the Y₂O₃ content. Further, on comparing the resistivity data with that of the
existing standard alloys it emerged that B3 compares favourably with MA 956 and B2 with Kanthal A-1.

6.2.4 Mechanical properties

The effect of temperature on tensile properties is summarized in tables 6.3 and 6.7 and in the figs. 6.9 to 6.14. It was observed that the tensile strength and proof strength of alloy B2 improved on heating from the ambient temperatures to 400°C. However, a further increase in temperature up to 1000°C resulted in a continuous decrease in both the UTS and proof strength (Figs. 6.9, 6.11 and Table 6.3).

The increase in UTS and PS, on raising the temperature to 400°C, was accompanied by a small increase in percentage elongation. It decreased on raising the temperature to 600°C. However, on increasing the temperature to 800°C there was an anomalous increase in ductility to about 18%. This anomalous increase persisted with reduced magnitude even on raising the temperature to 1000°C (Table 6.3, Figs. 6.9 and Fig. 6.12).

In the alloy B3, both the UTS and PS continuously decreased with an increase in temperature. Its effect on percentage elongation was similar to that observed in alloy B2, with the difference that the overall percentage elongation values were higher in B3 (Table 6.4, Figs. 6.10-6.12).

No comment is being made on the comparative tensile behaviour of the experimental and the proprietary alloys as this aspect has been critically analysed in the discussion (section 6.3). Of these, table 6.3 and 6.4 contain data on the experimental alloys B2 and B3 and tables 6.5-6.7 contain mechanical properties data on proprietary alloys Kanthal A-1, MA
956 and MA 754 respectively. Similarly, whereas the figs. 6.9 and 6.10 indicate the effect of temperature on the load-elongation plots of the experimental alloys B2 and B3, figs. 6.11 to 6.14 reveal a comparison between the high temperature tensile properties of B2 and B3 with that of the proprietary alloys Kanthal A-1, MA 956 and MA 754 respectively.

6.2.5 Optical metallographic observations

This was mainly confined to the alloys B2 and B3 so as to monitor the changes that occurred during different stages of product development. Representative micrographs are given in the fig. 6.15-6.19. Their perusal led to the following inferences:

B2 alloy

i) The product had been consolidated satisfactorily during hot forging. Grain structure was clearly revealed even in the as-forged condition (Fig. 6.15a). Undissolved bright particles were also observed (Fig. 6.15b). Porosity was in the form of large isolated pores. Dispersed micro-porosity was also observed (Fig. 6.15).

ii) On homogenizing for 5hrs at 1350°C (referred to as bulk homogenization), the area fraction of large isolated pores reduced and the porosity was now mostly in the form of dispersed microporosity (Fig. 6.15c). Higher magnification observation revealed the presence of some interconnected porosity along the grain boundaries and dispersed porosity within the matrix/grains (Fig. 6.15d). Undissolved bright particles were no longer present.

iii) Homogenizing for 7 hrs, led to an increase in porosity and
adversely affected the extent of consolidation (Fig.6.16 c-d).

iv) In fact similar studies had also been carried out by homogenising for 2, 3, 9, and 11 hrs at 1350°C. Since homogenization for 5 hrs at 1350°C yielded the best results, this combination of temperature and time was employed whenever required.

v) Another test run was made to cross check if homogenization at 1350°C for 5 hrs yielded optimum results. For this, small pieces cut from the as-forged stock were homogenized. On doing so it emerged that (a) the overall consolidation was even better and (b) the extent of porosity further reduced (Fig.6.16 a-b) than observed in bulk homogenised samples (Fig.6.15 c-d).

vi) The as-rolled specimens, (Fig.6.17) showed good consolidation with a fine graine size and a minimum of porosity.

vii) The same specimen when observed along the edge showed grains elongated in the direction of rolling (Fig.6.17 c-d).

B3 alloy

A similar situation as above existed even in the alloy B3 (with a higher yttria content) except that the overall state of consolidation was better, the extent of residual porosity was lower and the grain size finer at different stages of processing (Fig.6.18 and 6.19).

Fig.6.20 gives an idea of the length of the rolled sheets/strips that can be formed in the alloys B2 and B3.

Taking an overall view, the alloy B3 showed a higher degree
of consolidation, a finer grain-size and a lower level of porosity compared with alloy B2.

6.2.6 Electron probe micro analysis

EPM analysis was carried out on selected specimens of alloys B2 and B3 primarily to ascertain whether the homogenization cycle employed was indeed optimum, and to assess the element distribution in the as-forged and in the homogenized conditions. The data thus obtained is in the form of micrographs (Figs. 6.21 and 6.22) and line analysis (File numbers 74, 78, and 80 for alloy B2 and file numbers 62, 63, 65 and 67 for alloy B3). A perusal of these figures revealed that:

i) aluminium and yttria are more or less uniformly distributed right from the early stages of homogenization.

ii) This is not so for Cr distribution which became satisfactory only after homogenization was carried out for 5hrs at 1350°C.

iii) The effect of increasing the homogenization time from 5 to 7 hrs was that the overall elemental distribution became heterogeneous in both B2, B3 (profiles 65 and 67) and it had also been established that heterogeneity existed in B3 on homogenizing for a period / 5 hrs.

iv) On comparing the elemental distribution in B2 and B3 alloys in the 1350°C, 5hrs homogenized condition it emerged that all the elements and particularly Cr and iron were uniformly distributed in B3 and not in B2.

v) The undissolved bright particles observed in B2 (Fig. 6.21) represented Cr enriched regions (File numbers 74, 78 and
80). Such particles were not observed in B2 (File numbers 62, 63, 65 and 67).

vii) Results of the pie chart analysis carried out on alloy B3 (Fig.6.29) revealed that there was little difference between the analyses on which the alloy was designed and of the final product.

6.2.7 X-ray diffractometric analysis

X-ray diffractometric analysis was carried out on three experimental alloys namely, B1, B2, B3 after they were subjected to isothermal oxidation at 1200°C for a period of 20 hrs. Kanthal A-1 was also studied along with above mentioned alloys under identical conditions of time and temperature, from a comparison point of view. The data thus generated is summarised in the tables 6.8 to 6.16.

A critical perusal/review of above mentioned tables revealed that;

(i) Fe$_3$O$_4$ was the main constituent in all the specimens,
(ii) Al$_2$O$_3$ was indexed with certainty,
(iii) Cr$_2$O$_3$ was also indicated,
(iv) Y$_2$O$_3$ was practically not found, may be because of too small a percentage and
(v) There was an indication that mixed oxides including were present.

6.2.8 Cyclic oxidation behaviour

Limited studies were carried out to assess the aforesaid behaviour of B-series of alloys and to compare them with cyclic oxidation behaviour of some of the proprietary alloys—Kanthal A-1 and MA 956. The data summarized in the figures 6.24 and 6.25...
revealed that: (i) amongst the B-series of alloys the behaviour was proportional to the amount of yttria present i.e. the performance was in the order B3 > B2 > B1, (ii) however the overall behaviour of the B3 alloy was inferior to both Kanthal A-1 and MA 956.

6.3 DISCUSSION

Discussion has been organized in two ways (a) relating to the data reported in this chapter and (b) through which an overall view could emerge of the work in totality with special emphasis on the features of the technology/product that has been developed. To begin with, stress will be laid on the former.

6.3.1 Oxidation resistance

The B-series of alloys were designed from two sets of powders namely, the Fe-17 Cr alloyed powder imported from Sweden and elemental iron-powder available indigenously. It is noteworthy that the alloys designed from both the sets of powders exhibited similar oxidation behaviour. The B-series of alloys contained 22% Cr and 5.5% Al. This enabled a comparison to be made between these alloys and some of the proprietary alloys namely Kanthal A-1 (Table 2.8) and MA 956 alloy (84). As isothermal oxidation behaviour data on MA 956 alloy is not available, comparison in this regard was limited to Kanthal A-1 alloy. However, vis-a-vis the mechanical properties, the B-series of alloys have been compared both with Kanthal A-1 and MA 956. This aspect would be taken up later.

Commenting now on the high temperature oxidation behaviour, as summarized in Figures 6.1 to 6.8, tables 6A and 6B...
the one given below, the superiority of B1 over B2 and B3 up to 1150°C and over B2 up to 1200°C is evident. However, the higher yttria alloy B3 is decidedly superior to others at the reference temperature of 1250°C. Discounting a possible comparison with Kanthal A-1 for the time being, the remainder of the data on B-series of alloys is similar to the one observed in the A-series of alloys except that the B-series of alloys are vastly superior and can, therefore, be explained on similar lines as in the A-series of alloys. While saying so, it should not be overlooked that whereas the yttria content of the A-series of alloys was 0.3%, in the B-series of alloys there are two yttria levels namely, 0.2 and 0.4%. Since the effect of 6% aluminium has been found to be decidedly better than 0.3% yttria in A-series of alloys even up to 1200°C (Fig. 5.8) the relative performance of the B-series of alloys stands readily explained. Just as combined additions of aluminium and yttria have proved useful in A-series of alloys, a similar situation has also been observed in the B-series of alloys with the addendum that the higher of the two yttria contents is evidently proving to be more effective (Figs. 6.7 & 6.8).

<table>
<thead>
<tr>
<th>Alloy Designation</th>
<th>Stabilized Weight Gain, gm/m² (at various temperatures)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1050°C</td>
</tr>
<tr>
<td>B1</td>
<td>5.745</td>
</tr>
<tr>
<td>B2</td>
<td>1.878*</td>
</tr>
<tr>
<td>B3</td>
<td>7.314</td>
</tr>
<tr>
<td>Kanthal A-1</td>
<td>16.467</td>
</tr>
<tr>
<td>A4</td>
<td>16.073</td>
</tr>
</tbody>
</table>

* Not consistent with other data.
Considering the relative performance of B-series of alloys with Kanthal A-1 and alloy A4 (Fig.6.5 to 6.8), it is to be expected that the former (B series) would exhibit better high temperature oxidation resistance than A4 in view of their higher Cr and/or yttria contents. This is what has been observed. A similarity in performance between A4 alloy (containing a much lower alloy content) and Kanthal (A-1) upto 1150°C clearly (Figs.6.5 and 6.6) reflects on the superiority of the processing technology developed in the present investigation. Had this not been so, Kanthal A-1 was expected to exhibit better oxidation resistance in view of its higher Cr content and because of the presence of 0.5% Co and after duly remembering that the yttria present in A4 alloy would manifest its beneficial effect only at higher temperatures.

The consistently superior performance of the B-series of alloys over Kanthal A-1 (Figs.6.5 to 6.7), barring at 1250°C (Fig.6.8), wherein Kanthal A-1 was found to be better than B1 and B2 but inferior to B3, can once again be attributed to the superiority of the processing technology and to the presence of aluminium and a higher yttria content in B3 (with specific reference to the data at 1250°C). It is worth noting that 0.4% yttria additions are 1.4-1.5 times more effective than 0.5% cobalt addition (present in Kanthal A-1 deduced on the basis of weight gain) in enhancing oxidation resistance. It would therefore, be desirable to investigate the effect of yttria in a greater detail by using both lower as well as higher yttria contents to affirm the present finding.
6.3.2 Hardness

Considering now the hardness values (Table 6.1), the hardness of the alloys B1 and B2 is similar to that expected from Cr based ferritic alloys (19,24) and compares favourably with that of Kanthal A-1 (supplier's specification). It may be mentioned here that the actual hardness of Kanthal A-1 was found to be 100 VPN higher than what is stipulated. In the light of this observation the exceptionally high hardness exhibited by alloy B3 may not be regarded as totally unexpected. The reasons for this observation are, however, not clear. It may however, be stated that the higher hardness of B3 is duly reflected in the higher UTS of this alloy which is about 100 MPa higher than attained in alloy B2 but not enough to justify a difference of about 240 VPN in hardness (Tables 6.1 and 6.3 and 6.4). It is likely that the alloy B3 shows a high rate of work hardening and this may account for the exceptionally higher hardness it attains. However, the proposed mechanism needs to be confirmed.

6.3.3 Formability

As a prelude to a discussion on the mechanical properties and electrical resistivity values, it may be appropriate to comment upon the formability of the B-series of alloys although this would be in purely qualitative terms. As in the A-series of alloys, the alloy B1 (Fe-22Cr-5.5Al), showed poor formability. The reasons for this observation are (a) the large solid solution hardening effect introduced due to aluminium additions and (b) the presence of a high Cr content. It may be mentioned here that for a similar reason the alloy A2 although
containing relatively lower Cr content, exhibited poor formability. Since the magnitude of solid solution hardening due to Cr additions is relatively smaller (85), it is the presence of aluminium which is primarily responsible for poor formability. The mechanism(s) through which formability is lowered in the presence of aluminium addition may comprise (i) a large solid solution hardening effect and (ii) embrittlement due to the formation of aluminium bearing precipitates/intermetallics.

An effective method of overcoming the problem (as already inferred from the findings of the earlier chapter) is to add yttria. This is an important element of 'alloy design' adopted in the present study. It is for this reason that two different yttria levels were considered. Whereas Allam et al (62) have anticipated problems during hot working in the presence of yttria, Francis and Whitlow (52) have commented favourably but none of these authors have made detailed observations. The present investigation has shown that yttria additions markedly improved formability. This is amply borne out by the observation that whereas 'yttria free' alloys are very difficult to form, the yttria containing alloys can be very easily rolled and formed into sheets even in the presence of 5.5-6% aluminium whose presence is primarily responsible for poor formability. In fact, a higher yttria content (=0.4%) is even more promising and can promote good formability even at a higher level of hardness as has been observed in alloy B3 (Table 6.1). The probable mechanism through which the beneficial effect of yttria additions could be explained is that its presence in the form of a uniform distribution of very fine particles promotes
deformation to be homogeneously distributed (i.e. the presence of a uniformly distributed fine particulate mass promotes deformation to be distributed homogeneously/uniformly). This leads to an improvement in formability without the possibility of any 'premature' cracking. The inference is based on the observation that a uniform distribution of spherical 'aplastic' inclusions, promotes (i) deformation to be distributed homogeneously/uniformly and (ii) also, reduces anisotropy normally observed in wrought products (86). However, if the inclusions are coarse and not uniformly distributed then the said observation is no more valid (87). Another possible reason is that yttria is useful in suppressing the precipitation of Fe-Al intermetallics (which may otherwise induce embrittlement) (29). Whether the beneficial effect of yttria in suppressing the oxidation of aluminium inside the existing porosities contributes to an improvement in formability is not clear. The experimental observation in the present study that an increase in yttria content improves workability needs a more careful examination before the precise mechanism(s) through which yttria additions improve formability is/are established. However, what clearly emerges is that by promoting deformation to be distributed uniformly, the presence of yttria would certainly promote improved densification. Whether this alone accounts for an improvement in formability or whether some additional factors are also operating, e.g. reduced embrittling effect due to the supression of a precipitation process and grain refining, needs further examination.
6.3.4 Electrical resistivity

On the basis of the aforesaid discussion it may now be possible to comment upon the electrical resistivity values of the experimental alloys (Table 6.2).

Increasing the yttria content shows decrease resistivity and this can be attributed to the beneficial effect of yttria in lowering porosity. The aforesaid effect would be directly proportional to the yttria content. Expectedly, therefore, the alloy B3 exhibits the least resistivity even lower than Kanthal A-1. This reflects favourably on the processing technology. The alloy B2 exhibits resistivity comparable to Kanthal A-1, whereas the best alloy emerging from the present investigation B3 has an electrical resistivity similar to MA 956 (Table 6.2). This a very favourable observation from the point of view of commercial applications. In so far using the presently developed material(s) as resistance heating elements are concerned, even B2 can be used as a possible substitute for Kanthal A-1 for temperatures up to 1200°C. However, if the excellent high temperature oxidation resistance of the alloy B3 is proposed to be utilized then steps would have to be initiated to increase its resistivity. A possible method to achieve that would be employing 'controlled' cold deformation.

6.3.5 Mechanical properties

The Fe-Cr alloys, with or without yttria additions, have primarily been characterised on the basis of high temperature oxidation behaviour. Since the initial aim of the present investigation was to design and develop an alloy for electrical resistance heating applications through the P/M route, oxidation
resistance data on Kanthal A-1 was also generated to effect such a comparison. This aspect has been discussed in detail earlier. It was soon to emerge that characterization of the alloys could not be restricted to oxidation resistance alone. Therefore, high temperature mechanical properties of B-series of alloys (Table 6.3-6.4 and Figs.6.9-6.10) and that of Kanthal A-1 (Table 6.5) were also determined. On comparing the properties listed in tables 6.3-6.5, the marked superiority of the alloys B2 and B3 over Kanthal A-1, based on UTS and elongation data, is evident. The difference is even more marked at temperatures higher than 600°C. The marked superiority of B2 and B3 over Kanthal A-1 is due to the presence of yttria in the former and due to the superior processing technology developed in the present study.

A more detailed analysis of the currently available literature revealed that a considerable interest was being shown in the alloy MA 956 which is extensively in use in aeroengine and land based turbine applications. Since the final compositions developed in the present study (B1 to B3) bore resemblance to the composition of MA 956, it was felt appropriate to compare the performance data of B-series of alloys with that of MA 956. Although this alloy has been extensively characterized on the basis of high temperature tensile properties, stress-rupture properties, cyclic oxidation and hot corrosion behaviour, the experimentally investigated alloys have, at best, been characterized on the basis of high temperature mechanical properties alone. None the less, as a beginning,
comparision on the basis of this data alone was considered as reasonable. The mechanical properties data for MA 956 and MA 754 is summarized in the tables 6.6-6.7. On a perusal of the data summarized in Tables 6.3-6.7 and figs. 6.11-6.14 it emerges that UTS and proof strength values of B2 and B3 are higher than MA 956 upto 600°C. This implies that the nearly fully dense microstructure of the experimental alloy is behaving better than the microstructure of MA 956 (mechanically alloyed and thermo-mechanically processed) inspite of its (i) higher yttria content and (ii) the additional presence of 0.50 Ti. Between 600°C-800°C the general level of UTS and proof strength (in MA 956, B2 and B3) are similar which again augers well for the experimental alloys. However, beyond 800°C MA 956 is decidedly superior in terms of strength because of (i) a higher yttria content and (ii) the additional presence of Ti.

Elongation values attained in MA 956 (Tables 6.3, 6.4, 6.6 and 6.7 and figs. 6.11 to 6.14) are in general inferior to those attained in B2 and B3 particularly beyond 600°C primarily due the presence of Ti in solution. Amongst B2 and B3 elongation values in B3 in general are higher perhaps due to higher yttria content and a finer grain size (section 6.3.5).

Taking an over all view, the data summarized in Tables 6.3-6.7 reveals that if UTS values were to be be considered along with percentage elongations at all temperatures (from room temperature to 1000°C), then it would emerge that the alloys B2 and B3 may have an edge over MA 956 provided the UTS could be increased. This inference is of major interest to alloy designers. In fact there is a definite scope to improve the
tensile properties of B2 and B3 because they are deficient with respect to yttria/alloy content vis-a-vis MA 956. That the alloys B2 and B3 even then exhibit superior high temperature tensile properties, prima facie establishes the superiority of the processing technology.

A comparison of the data summarized in tables 6.3 to 6.7 also leads to the inference that if Fe-based ferritic super alloys with improved alloy design are optimally processed then they may respond as favourably as some of the Ni-based superalloys such as MA 754.

It is noteworthy that in the experimental alloys both UTS and percentage elongation values increased with yttria content. The observation, although contrary to the normal expectation that elongation decreases on increasing the amount of refractory dispersoids, is however, duly supported by the deductive inference that yttria additions improve formability. It is suggested this aspect, related with workability/deformability, needs a more detailed investigation/analysis.

6.3.6 Microstructural studies

Metallographic studies were confined to B2 and B3 because they emerged as the most promising alloys arising out of the present study. The specific aim of carrying out these studies was to obtain information on (a) the extent of consolidation/densification in the as-forged condition, (b) the effect of homogenizing period on the degree of consolidation, (c) the possible effect of processing on the nature and magnitude of porosity and, (d) the effect of rolling on the state
of the final product.

The information summarized in figures 6.15-6.19 categorically reveals that the alloy B3 has responded more favourably to processing than alloy B2 on the basis of the following:

(i) B3 showed well defined grain structure and a finer grain size (Figs.6.18) compared to B2 (Fig.6.15) in the as-forged condition, which also exhibited a fairly uniform grain structure. This was discernible even in the final as-rolled condition (Figs.6.17 and 6.19).

(ii) B3 attained a lower level of porosity as compared to B2 in the as-forged condition (Figs.6.15 and 6.18).

(iii) B2 showed presence of undissolved particles (Fig.6.15) in the as-forged condition where as B3 did not (Fig.6.18) and,

(iv) B3 responded more favourably to the homogenizing treatment (Fig.6.18 c-d) than B2 (Fig.6.16).

The first, second and fourth observations can be explained on the basis of better ease of forming associated with the alloy B3. In fact it would be appropriate to observe that the metallographic observations duly confirm the hypothesis that the presence of yttria in general and a higher yttria content in particular, improves formability thereby promoting/enhancing densification/consolidation for a given temperature-time cycle.

Figures 6.15 c-d, 6.16 a-b and 6.18 c-d further reveal that the 5 hrs. homogenizing period is optimum for both the alloys. At a period lower than 5 hrs, the porosity is not fully eliminated because of insufficient time available for diffusion to occur. The porosity will be at a minimum corresponding to the
optimum period (which is 5 hrs. in the present study). However, on increasing the homogenizing time beyond the optimum, the level of fine microporosity within the matrix increased (Fig.6.16 c-d) on account of Kirkendall effect involving inter-diffusion of iron and chromium atoms.

The observation that small specimens showed better consolidation and reduced porosity (Fig.6.16 a-b) compared with the bulk homogenized specimens (Fig.6.15 c-d), can be explained by stating that specimen thickness was smaller thereby leading to enhanced consolidation/densification for a given temperature-time cycle.

Studies on the as-rolled specimens merely affirm the observations discussed earlier, namely that the alloy B3 showed improved consolidation than the B2 alloy (Figs.6.17 and 6.19). The presence of directionality in the edge rolled condition (Figs.6.17 c-d and 6.19 c-d) indicates the presence of a rolling texture inspite of employing interspersed reheating cycles during rolling. It may be mentioned that in the processing of MA 956, conscious efforts are made to introduce texture through thermo-mechanical controlled processing so as to obtain 'pancake' shaped grain structure. This apparently contributes to strength and toughness in all directions. In the present study, however, no specific effort was made to introduce such a texture nor did the capacity of the rolling mill facilitate this to be easily achieved. None the less some texture is still observed (Figs.6.17 & 6.19 c-d). It would be worth investigating whether a situation similar to that in MA 956, exists in the
The finer grain size attained in the alloy B3, compared to that in B2, is primarily responsible for its exhibiting better overall ductility (Tables 6.3-6.7 and Figs. 6.9-6.14). This is explained on the basis of the well known Hall-Petch relations. The mechanism through which grain refinement is being affected in the system under study needs to be understood before any further comment could be made.

The photographs of the rolled strips of alloy B2 and B3 (Fig.6.20), are included to indicate that the material could be successfully worked to large lengths.

Detailed metallographic examination in respect of mechanically alloyed super alloys is not readily available in the literature so as enable a comparison to be made between the results of the present investigation with those of the others. However, metallographic observations as given above not only confirm the inferences arrived at the present study and mentioned earlier but put forth the various assessments, concerning mechanical properties, electrical resistivity and high temperature oxidation behaviour, on a firm footing. The uniqueness of the observations is that it is extremely difficult to carry out optical metallography of P/M based products - a contention which is duly supported by a paucity of such an information in the literature.

6.3.7 Electron probe micro analysis

Optical metallography was not helpful in identifying the undissolved bright particles observed in the B2 alloy in the as-forged condition. Similarly, it was necessary to arrive at
information on the distribution of elements in the as-forged and homogenized conditions so as to make a final assessment of the processing technology developed. The information summarized in the line profiles 62, 63, 65, 67, 74, 78 and 80, which represents elemental analysis along the lines indicated on the micrographs (Figs. 6.21 and 6.22), reveals that,

i) the undissolved particles in the B2-alloy represent Cr, (File number 74, 78, 80).

ii) B3 alloy showed negligible heterogeneity especially in terms of the Cr content on being homogenized under optimized conditions (File numbers 62, 63, 65, 67).

iii) under similar conditions the B2 alloy showed more heterogeneity especially with regard to Cr distribution.

iv) the pores showed a high concentration of aluminium and yttrium and were depleted in Cr and Fe.

The first three observations favourably reflect on the beneficial effect of a higher concentration of yttrium in promoting enhanced consolidation/densification. This would lead to reduced heterogeneity. Similarly, the observation that porosities contain a large concentration of aluminium and yttrium and are deficient in Cr affirms the reasoning put forward to explain the possible role of porosity in influencing the high temperature oxidation behaviour of the A-series of alloys (section 5.3.)

A review of the pie-charts (Fig. 6.23) indicating that the average analysis of the final product namely Fe-21.53Cr-5.18Al-0.36Y was only marginally lower than the
designed composition (Fe-5.5Al-0.4Y) once again affirms the usefulness of the processing technology developed.

6.3.8 X-ray diffraction

The x-ray diffractometric studies, restricted to specimens isothermally oxidized, were carried out to assess the possible oxides that are present in the surface film. Cr$_2$O$_3$ in the experimental alloys is a desirable feature since it has been reported in the literature that vaporization of Cr$_2$O$_3$ to CrO$_3$ starts at 1150°C and above leading to a decrease in the oxidation resistance. Presence of CrO$_3$ has not been detected either in the experimental alloys or in Kanthal A-1.

The presence of mixed oxides in most instances augurs well for the experimental alloys since it would mean that the beneficial effects of the individual oxides are working in collaboration in resisting oxidation. Similarly the presence of Fe$_3$O$_4$ is as per expectation since the stable oxide to form under the prevailing conditions should be Fe$_3$O$_4$.

It is recommended that a further detailed analysis should be carried out to identify the constitutions of the oxide film at 1250°C to be supplemented by data obtained from other sophisticated tools such as EDAX, EPMA and/or ESCA.

6.3.9 High temperature cyclic oxidation behaviour

From the point of view, the cyclic oxidation behaviour of the alloys currently developed cannot be regarded as satisfactory when compared with the performance of the proprietary alloys. However, it may be mentioned that the superiority of the proprietary alloys is due to their higher alloy content, reduced porosity, their having been processed by
the wrought product route (valid for Kanthal A-1) and also because high quality raw materials have been used to develop them. Bearing this in mind, there is a considerable scope to improve upon the cyclic oxidation behaviour of the alloys being developed in the present programme of study.

6.4 Overview/critical appraisal

The present investigation is a critique on the design and development of high temperature alloys containing Cr and aluminium (in some measures, further strengthened with dispersion of yttrium oxide) from indigenously available low cost raw materials. Although the initial aim of the investigation was to assess whether useful products could be developed with possible applications as electrical resistance heating element material, it soon emerged that the scope of the investigation could be made broad based. This has been duly reflected in the extensive amount of data generated and analysed.

It was felt appropriate to select the modified P/M route for developing the alloys/products. In view of this the use of mechanical alloying through attrition and that of encapsulated hot powder forging and subsequently rolling is apt and timely. The attrition time was restricted to about 2 hrs. Although a review of the literature had indicated that attrition for longer periods was considered as a prerequisite to attain dense products, our results are to the contrary.

The major advantage in selecting a combination of powder forging followed by rolling was to do away with the batch nature of the conventional P/M technology and to convert it into a more
less continuous product development based technology in conformity with what in generally followed in the 'wrought product' route. In so far as this aspect is concerned the investigation has proved to be extremely successful especially looking to the quality of the raw material that has been used to develop products.

The design and development of the lower Cr alloys belonging to the A-series was essential to assess the usefulness of the processing technology by comparing the performance of the alloys with some of the standard lower Cr alloys already in use. This was also likely to provide clues to the design of subsequent alloy compositions. These alloys were primarily characterized on the basis of isothermal high temperature oxidation behaviour using a simple quartz spring balance whose vertical traverse was recorded through a cathetometer and converted into weight gain. The accuracy of measurements was ±0.0002 gm/mm and accordingly the high temperature oxidation data has to be viewed in this context. The effect of aluminium and yttrium additions in influencing the high temperature oxidation behaviour are already lucidly brought out and need no repeating. First indications were available at this stage that yttria is not only beneficial in improving oxidation resistance but also in improving formability. Since such indications were also available at the preliminary stages of experimentation, special efforts were made to ensure that yttria was added in as fine a state as is possible. Hence the use of the oxalate route to disperse yttria.

An important observation to emerge from the present study is that aluminium additions (5-6%) are very useful in resisting
oxidation up to 1200°C. Their effect being even better than 0.4% Y when added singly. In fact at 1200°C, Y addition proved at best marginally in resisting oxidation. However, aluminium addition adversely affected formability.

The design, development and characterization of the D-series of alloys further bring out the usefulness of yttria additions in improving oxidation resistance, formability, densification, and homogeneity of the product developed especially when added in combination with 5-6% aluminium. This is duly corroborated by high temperature tensile testing, optical metallography, electron probe micro analysis and electrical resistivity measurements. Comparing the performance of the D-series of alloys with some of the proprietary products such as Kanthal A-1 as well as MA 956 and MA 754 amply indicates the favourable direction in which the programme is proceeding. The usefulness of the alloys developed leads us to believe that the enthusiasm in developing robust products from ordinary quality raw materials such as ferro-alloys is laudable. Alloys with markedly improved performance could be developed for which necessary design guidelines have been evolved.

The high point of the investigation has been the usefulness of the processing methodology/technology developed and the major role played by yttria in making it extremely successful even in the presence of embrittling aluminium. Bearing this in mind it is felt appropriate to designate the processing technology as DISPERSOID AIDED CONSOLIDATION PROCESSING.