CHAPTER III
FORMULATION OF THE PROBLEM

3.1 CRITICAL REAPPRAISAL OF TECHNOLOGY OF SUPERALLOYS

A critical review of the literature on superalloys, their processing and high temperature oxidation behaviour leads to inferences of major technological relevance to alloy design and development. In essence they comprise information relating to the following:

3.1.1 Nature of the matrix

The choice is between three prominent matrices
(i) fcc (austenitic, Fe-based or Ni-based)
(ii) bcc (ferritic, Fe-based)
(iii) hcp (Co-based or Fe-Co based)

Generally, close packed crystal structures are preferred because they have less open space and hence would be more effective in resisting corrosion/oxidation as compared to a lesser closed packed crystal structure (bcc).

Having said this, it is equally true that alloys based on a bcc matrix can prove to be very effective up to 1100°C for general purpose applications and up to 1200°C for engineering applications (where load bearing capacity, both in terms of fatigue and impact are of paramount importance). Iron-based ferrite matrix is better suited in sulphur bearing atmospheres at high temperatures. Presence of a film forming element can adequately overcome the problem arising out of more voids in a bcc matrix. Other problems which are associated with bcc based microstructure such as poor formability, weldability and notch
ductility, have been suitably overcome to a large extent.

As against this, the superiority of a more closed packed structure namely fcc/hcp and more so the former, is well recognized. However, it is not necessary to use them as a matrix under all conditions and it is opined that they are better utilized when load bearing under high temperatures is an essential requirement. Their usefulness is undoubtedly further improved in the presence of scale/film forming elements.

From the point of view of creep resistance, low SFE (stacking fault energy) matrices are preferred and this is one of the major assets of Ni-bearing/Co-bearing matrices. However, this advantage is not carried over to the Ni-containing austenitic (matrices), since Ni increases the stacking fault energy of Fe-based austenites.

Grain size is yet another variable to be considered from creep resistance point of view. This is equally applicable to both the more close packed and less closed packed matrices. Grain size is controlled through a combination of heat-treatment and processing.

3.1.2 Nature of the second phase

Second phase is required for strengthening in general and for attaining the maximum in terms of high temperature strength/creep strength in particular. The second phase (to be present in the bulk) should:

(i) be in the form of an optimum dispersion with excellent high temperature stability,
(ii) exhibit optimum coherency with the matrix,
(iii) have a minimum surface area,
(iv) exhibit stability of shape and size over the temperature range of applications, and
(v) preferably be ordered

If second phase is also present along the grain boundaries, the latter will be additionally strengthened.

The strengthening mechanism would either comprise of precipitation or dispersion strengthening. Precipitates in decreasing order of preference are:
(a) inter-metallic compounds,
(b) high temperature carbides, and
(c) relatively lower temperature carbides.

Precipitation can be affected from bcc, fcc or hcp matrices
In so far as grain boundary strengtheners (Table 3.A) are concerned, the preference would either be for the carbides which form at grain boundaries (M_{23}C_6) and/or for elements which fill up grain boundary vacancies (Zr and B).

Additionally, although the solid solution strengthening effect may be employed in principle, its contribution is not as significant as that of the precipitation strengthening because at the temperatures normally encountered, the rate of migration of solute atoms and dislocations is nearly the same.

In dispersion strengthening, oxide dispersion is most extensively employed. The methodology adopted is to affect oxide dispersion either in the ferritic or in the austenitic matrices through mechanical alloying (involving high energy ball milling/attrition of oxides with a suitable base powder). This produces homogeneous composite powder particles which are
relatively coarse and free from contamination. The process involves recurrent cold welding of constituents to ball surfaces and flaking off until all are divided and uniformly distributed (Figs. 3.1, 3.2). This practice promotes particle welding in contrast to conventional ball milling where welding is inhibited by using liquid surfactants. Mechanical alloying is followed by consolidation processing.

Table 3 A Important strengtheners for different matrices

<table>
<thead>
<tr>
<th></th>
<th>hcp</th>
<th>bcc</th>
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<tbody>
<tr>
<td>Ni-based or</td>
<td>Co-based or</td>
<td>Ferrite</td>
</tr>
<tr>
<td>Ni-Fe base</td>
<td>Fe-Co based</td>
<td>Fe based</td>
</tr>
<tr>
<td>τ'(Ni₃(Al,Ti))</td>
<td>τ&quot;</td>
<td></td>
</tr>
<tr>
<td>τ&quot; (Ni₃Nb)</td>
<td>Carbides</td>
<td></td>
</tr>
<tr>
<td>MC type carbides</td>
<td>M₂₃C₆</td>
<td></td>
</tr>
<tr>
<td>M₆C</td>
<td></td>
<td>&quot;(Ni₃Ti)</td>
</tr>
<tr>
<td>M₂₃C₆</td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ(Ni₃C)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is opined that in view of its distinctly superior high temperature stability, oxide(s) should be regarded as the most favourable dispersoid(s). The observation that τ' as a strengthening precipitate can not be used above 1050-1100°C supports the contention. In fact looking to their versatility, oxides are expected to replace other strengthening precipitates in the future alloys.

Formation of topologically close packed phases (TCP) e.g, δ and Laves phases is not expected to improve mechanical properties as they are generally brittle. They have been found to
be present along the grain-boundaries, and their presence may be utilized to advantage to reduce grain-boundary sliding by suitably altering their morphology.

3.1.3 Role of protective scale forming elements

The development of high temperature alloys has considerably depended on the formation a protective, adherent, and self-healing film even during thermal cycling. A considerable attention has been paid to obtain a film of this type. Although the state-of-the-art technology, starting from the very simple Cr2O3 film attained in austenitic stainless steels to its present status involving the use of 'rare earth' elements or their oxides in amounts not exceeding 2%, now stands perfected, ambiguity still persists for reasons for their effectiveness. In essence, all that is required is to ensure that the outward migration of cations and inward migration of anions has to be so impeded that 'status-quo' is maintained, duly remembering that the rate of cation migration is faster. Of the two normally employed scale forming elements namely Cr and Al, the latter is preferred because of lesser cationic mobilities (through its oxide scale) that provide a larger 'barrier effect'.

3.1.4 Processing techniques

Of the various techniques whose salient features are summarized in a tabular form (Table 3.1), the P/M hot forging technique offers major technological advantages over the conventional and other modified versions in view of the following:
(i) absence of segregation thereby ensuring a greater homogeneity; markedly lower inclusion content,
(ii) elimination of cumbersome melting/refining and casting procedure,
(iii) elimination of machining and other operations generating large volume of high value scrap,
(iv) possibility of attaining a combination of incompatible constituents in any proportion not possible with other techniques,
(v) freedom from infrastructural complexities associated with techniques such as PMR, VADER, EBCUR, single crystal growth and eutectic grain growth,
(vi) possible freedom from directionality in properties,
(vii) possibility of attaining a reasonable uniformity in the composition of the alloy, and
(viii) side stepping sintering.

3.2 Definition of the problem

Based on the above mentioned analysis it emerged that a considerable scope existed to explore the design and development of oxidation/heat-resistant materials. Of the various alloys mentioned, the metallic heating element materials held immense potential because of their technological importance and also because many of the alloys currently in use are not manufactured within the country through the P/M route. An equally important aspect to emerge was that of two types of alloys, namely, austenitic-based and ferritic-based, the latter showed promise for reasons already highlighted.

The present problem was undertaken in response to the
aforesaid analysis and comprised an effort aimed at developing ferritic based heating element alloys, starting from the indigenous raw materials. It was decided to focus attention on improving the isothermal oxidation behaviour of the alloys being developed and to evaluate mechanical properties at high temperatures for possible comparison with MA 956 alloy. The P/M processing technique was selected due to the major technological advantages foreseen. It was decided to employ mechanical alloying in view of its technical superiority. Raw materials employed in the present study were either in the form of imported atomized iron-chromium alloys or indigenously available commercial purity elemental powders/ferro-alloys; use of latter would enable assessment of the quality of the product being developed in the 'rock bottom' condition. Evidently, the quality of the product being developed by using better quality raw materials was expected to be superior to the quality of the product likely to be currently attained. Commercially, if it were to emerge that good quality products could be attained by using inferior quality raw materials then a technological breakthrough would be achieved.

3.2.1 Design of alloys

(i) The present investigation concentrates upon exploring the Fe-Cr-Al system. This alloy system was selected so that it would cover two major proprietary products namely wrought Kanthal A-1 and MA 956 (of course without Ti and Co).

(ii) Cr content was selected to be around 16-17% and 22% to
ensure that a large amount of Cr is available in solution without the possibility of attaining sigma-phase during heat-treatment/processing. Further, this level of Cr was considered as optimum since a Cr level higher than this was likely to adversely affect formability as according to Felton (50), 25%Cr is the maximum that can be alloyed with iron without sacrificing mechanical properties. Similarly, the Cr content of Kanthal A-1 is also around 22%. By keeping the Cr level, a comparison between the standard alloy (made through the conventional melting and casting route) with that of the experimental alloys was possible.

(iii) The addition of Al to Fe-Cr base alloys provides an oxide film that prevents inter-granular oxidation at high temperatures. As such the Al content was adjusted to be around 5.5% i.e., at a level lower than maximum solubility of Al in iron which is about 9%.

(iv) Y was selected as the ‘reactive element’ to be added and two levels namely, 0.2%Y and 0.4%Y were chosen. It was decided to introduce yttrium in the form of yttrium-oxalate and

(v) Alloys with and without yttrium were also investigated to assess the role of yttrium.

Thus in all a total of seven alloys were planned whose compositions are given in Table 3 B.
### Table 3 B Composition of the alloys designed and developed in the present investigation

<table>
<thead>
<tr>
<th>Alloy Designation</th>
<th>Composition (wt. %)</th>
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<tbody>
<tr>
<td></td>
<td>Cr</td>
<td>Al</td>
</tr>
<tr>
<td>A1 *</td>
<td>17</td>
<td>-</td>
</tr>
<tr>
<td>A2 *</td>
<td>17</td>
<td>6</td>
</tr>
<tr>
<td>A3 *</td>
<td>17</td>
<td>-</td>
</tr>
<tr>
<td>A4 *</td>
<td>17</td>
<td>6</td>
</tr>
<tr>
<td>B1 =</td>
<td>22</td>
<td>5.5</td>
</tr>
<tr>
<td>B2 =</td>
<td>22</td>
<td>5.5</td>
</tr>
<tr>
<td>B3 =</td>
<td>22</td>
<td>5.5</td>
</tr>
</tbody>
</table>

* with imported prealloyed powder
# with both imported and indigenous raw materials

### 3.2.2 The approach

Based on aforesaid analysis it clearly emerges that the P'M technique would prove to be the most effective route for developing the proposed alloys. However, there is a general lack of information on manufacturing of these steels through hot encapsulated powder forging. The technology developed employs low cost indigenously available materials rather than conventional and costly imported powders viz; Fe, Ni and Co. Slabs obtained through encapsulated forging were subsequently hot rolled into strips which were characterized for their high temperature response and electrical resistivity. Other properties of interest namely, workability, strength, elongation and high temperature oxidation resistance were also evaluated.

### 3.2.3 Planning of experiments/Work schedule

The experiments were planned as follows:
Phase 1
(a) Preparation/making of alloys as per design criteria given above by hot forging of encapsulated powder.
(b) Homogenization and
(c) Thermo-mechanical working.

Phase 2
Characterization of alloys so developed through metallography and mechanical testing.

Phase 3
(a) Establishing the high temperature isothermal oxidation behaviour of the alloys by weight gain method using a cathetometer rig and further structural examination of the oxide film by x-ray diffraction.
(b) Electrical resistivity measurement by two-probe method.
(c) EPMA studies to assess the distribution of ingredient elements and extent of homogenization.