CHAPTER-3
FORMULATION OF THE PROBLEM

High silicon irons, Ni-Resist (high nickel) irons, nickel-chromium (Ni-Hard) irons and high chromium irons are the most frequently used alloy cast irons. While the first two are alloyed gray cast irons, the last two belong to the family of alloyed white cast irons.

High silicon cast irons are the lowest cost irons. They resist both types of corrosions due to oxidizing and non-oxidizing acids. However, these irons have certain limitations such as low mechanical strength, poor impact strength and poor thermal shock resistance. Ni-Resist irons, even show heat resistance, good toughness and corrosion resistance though they suffer from graphitic corrosion.

Ni-Hard irons find major applications as wear resistant materials whereas high chromium irons with or without molybdenum, depending on chromium content, show excellent wear, heat and corrosion resistance.

Ni-Resist irons, Ni-Hard irons and high chromium-molybdenum irons are highly expensive due to elevated cost of the major alloying elements i.e. molybdenum and nickel. These scarce elements are not available in India. This fact has generated interest in developing low cost substitutes for these irons. Therefore other elements which are available in India are used here. These are manganese and copper; they can be used in place of nickel because of their similarity in features with nickel. Based on fundamental consideration, it is possible to substitute nickel partly by manganese and copper.

Manganese is an austenite stabilizer, it is a strong carbide stabilizer and a weak carbide former like nickel. Manganese is capable of refining pearlite. Desired steel matrix, such as martensite or austenite can be generated in the as-cast condition by controlling the manganese content [72]. Stefanescu and Basak confirmed that the carbide morphology of manganese alloyed chromium irons is similar to the one observed in high chromium irons i.e. $M_7C_3$ type because manganese and chromium have a similar carbide forming tendency [71, 73] Manganese can thus efficiently play duel role, one like of nickel and the other of like chromium.

Copper has limited solid solubility in iron and thus is not capable of stabilizing austenite completely [72]. It is for this reason that in order to stabilize austenite, copper is essentially always added in combination with some another austenite stabilizer. Henon
[74], based on a comparative study of a 4 Ni-2 Cr and a 1.5 Ni-2Cr-3Cu white iron, concluded that the nickel- chromium irons can be successfully substituted by the nickel chromium-copper irons for a number of applications. Encouraged by the positive results published by various workers, Patwardhan [75] initiated the work in the early seventies with a view to develop low cost substitutes for Ni-hard cast irons based on the utilization of indigenously available elements. Some of the early results based on the work of Srinivasan [68, 76] revealed that Fe-Cr-Mn-Cu alloy white irons could attain microstructures similar to those observed in Ni-Cr white irons. However, the carbides formed were massive and were rendered discontinuous only on heat treating from high temperature (> 850°C).

Sudan [69] and Sharma [77], under the supervision of Patwardhan and Mehta, tried to optimize copper and manganese content respectively. Sudan, Patwardhan and Mehta [78] while studying the effect of 0.5, 1, 2 and 3% Cu on the microstructure and hardness of a 7% Cr, 1.5% Si and 3.1% C cast iron, reported that hardness in excess of 650 VHN could be attained only on quenching. However, copper was extremely effective in rendering the carbide network discontinuous. Taking an overall view, the optimum copper content appeared to be = 1%.

Reported work of Patwardhan, Mehta and Sharma [79] related to the effect of 2, 4 and 6% Mn on the transformation behavior of 7% Cr-1.5% Si- 3.1C cast iron, concluded that high hardness (> 600 VHN) values can be attained in air-cooled alloys thereby eliminating the necessity of quenching like that with copper. However, manganese in comparison to copper was found relatively less effective in making the carbide network discontinuous. The optimum manganese content was = 4 percent.

On the basis of above reported works, Patwardhan was of the opinion that probably a white cast iron composition having about 4% manganese, 1% copper, 7% chromium and about 1.5% silicon can generate hardness values in as-cast and in heat treated condition comparable with Ni-Hard 4 cast irons and hence can prove to be a useful alternative to Ni-Hard 4 cast iron. Jha [80] worked on this composition and could attain microstructural features and hardness values similar to those attained in Ni-hard irons. It proved the utility of the Fe-Mn-Cr-Cu alloys.
Encouraged by the results, Patwardhan and co-workers worked in two different directions. The one was related to the development of low cost wear resistant compositions while the other was concerned with the development of low cost corrosion resistant compositions. This first line of approach was pursued by Singh [81]. He investigated a series of Fe-Mn-Cr-Cu alloy white irons to arrive at optimum alloy compositions which could serve as low cost substitute for Hi-Hard and/or Cr-Mo wear resistance cast irons.

The second direction i.e. development of low cost corrosion resistant white cast iron composition is of much significance. Corrosion resistant alloy cast irons, namely, ferritic high silicon gray cast irons, austenitic high nickel gray cast irons and high chromium white cast irons with or without molybdenum, though are being used extensively have certain limitation. High silicon gray cast irons provide best result under oxidizing conditions [82-85]. However, less mechanical strength and shock resistance associated with these irons limit their general engineering applications [82]. Although Ni-resist gray cast irons offer excellent corrosion resistance against a large number, these lack sufficient mechanical strength and cannot be used at service temperatures higher than 800°C [84-87]. High nickel gray cast irons and high silicon gray cast irons suffer from a severe form of corrosion i.e. graphitic corrosion which hinders their wide applicability. High chromium white cast irons, by careful control of chromium content, can be used as wear and corrosion resistant irons. These can be employed at higher temperatures. Mechanical properties specifically toughness can also be improve up to desirable levels by controlling the carbon contents [22]. Dodd [60-61] reported that chromium irons containing 0.5-2.0% carbon and 20-28% chromium exhibit an optimum combination of corrosion and abrasion resistance.

It is a fact that the difference in electrochemical potentials between austenite and graphite is higher than that of austenite and carbide; hence it provide a solution of the problem of graphitic corrosion by the use of white cast iron compositions, because it has properties similar to corrosion resistant gray cast iron compositions. Additionally, such an alloy development possibility by utilizing low cost indigenously available alloying elements will lower the cost. Patwardhan and Kumar [75, 87] worked on some Fe-Mn-Cr-Cu white cast iron compositions and found that such an alloy system resists well against corrosion,
wear and corrosive wear, Different matrix structures i.e. pearlitic, bainitic, martensitic and austenitic can be generated in this system. Shingh [81] and Basak et al [88] confirmed the above stated results.

Jain [86] studied a number of alloys belonging to Fe-Mn-Cr-Cu system (essentially white cast irons) for their microstructural features, corrosion resistance and deformation response. Published work of Jain [89-92] has been summarized in the Table 3.1.

### TABLE - 3.1

**SUMMARY OF THE STRUCTURE PROPERTY RELATIONS IN SOME Fe-Mn-Cr-Cu-Mo CORROSION RESISTANT CAST IRONS**

<table>
<thead>
<tr>
<th>1. Alloy studied</th>
<th>3%C, 5% Cr, 6.8% Mn, 1.5-3% Cu cast irons</th>
</tr>
</thead>
<tbody>
<tr>
<td>2. Heat treatments</td>
<td>Held at 800, 850, 900, 950, 1000 and 1050°C for 2, 4, 6, 8 and 10 hours followed by OQ (62) and AC (83).</td>
</tr>
</tbody>
</table>
| 3. Microstructure | (a) As-cast : P/B + M+ MC+ some RA  
(b) Up to 900°C : M + τ + MC + DC  
(c) Up to 1000°C : τ + DC + MC or τ +MC  
(d) At 1050°C + MC (M₇C₃ in eutectic form) |
| 4. Effect of cooling | OQ : larger τ, lesser DC  
AC : more DC, lesser τ, "M" up to higher heat treating temperatures |
| 5. Various carbids formed | M₃C, M₅C₂, and M₂₃C₆  
M₃C : up to 950°C prolonged soaking  
M₂₃C₆: boundary carbide up to 900 °C, 10 hrs.  
M₅C₂ & M₇C₃ : up to 1050°C |

Structure property interrelations

<table>
<thead>
<tr>
<th>(a) Marten site</th>
<th>Resist corrosion, but embrittles</th>
</tr>
</thead>
<tbody>
<tr>
<td>(b) Austenite</td>
<td>Most desirable matrix to resist corrosion &amp; to give good strength and ductility Increase in the amount and stability enhance properties.</td>
</tr>
<tr>
<td>(c) Dispersed</td>
<td>* They precipitate as M₃C/M₅C₂ from matrix during heat</td>
</tr>
</tbody>
</table>
| Carbides | Treatment (represented as number of particles or by distribution factor).  
* Overall adverse effect on properties; attains a maximum at 950 °C, 10 hours treatment. |
|----------|------------------------------------------------------------------|
| (d)      | Massive carbides  
* Represented as area fraction  
* Plate morphology in as-cast/low temperature heat treatment  
* Rounding off at ≥ 950 °C  
* Platy morphology detrimental to properties (corrosion & mechanical)  
* Near rounded/hexagonal forms preferred. |
| (e)      | Grain boundary carbide M\textsubscript{23}C\textsubscript{6}  
* Adversely affects corrosion resistance and deformation behavior |
| (f)      | M\textsubscript{7}C\textsubscript{3} & M\textsubscript{5}C\textsubscript{2}  
* M\textsubscript{7}C\textsubscript{3} present in the form of MC and also as eutectic carbide (eutectic form not preferred).  
* M\textsubscript{5}C\textsubscript{2} present as MC and part of DC |

**Structure property correlations (Models)**

(a) Heat treating temperature, time and hardness.  
(b) Weight gain as a function of temperature.  
(c) A correlation between corrosion rate and microstructure denoting the effect of MC & DC  
(d) Interrelating corrosion & deformation behavior.

Rao [93] while working on near eutectic alloy compositions of Fe-Mn-Cr-Cu system reported results matching with the finding of Jain. Much attention has been paid to the stability of austenitic matrix as it is major requirement for obtaining good corrosion resistance. Its importance can be realized on the basis of finding Rao [93], where it was shown that stress relieving adversely affected the corrosion behavior of Fe-Mn-Cr-Cum cast irons. One of the prime reasons put forward to explain the anomalous behavior is
that stress relieving (at 650°C) lead to the decomposition of the austenitic matrix thereby implying that the matrix was not stable enough.

Bansal [92] and Mayank [92] worked on the same system but with different compositions also confirmed that this system can be effectively employed for the development of corrosion resistant alloys. Due to high hardness values that can be generated in these compositions have the additional advantage of imparting good resistance against wear and as such these alloys can also be successfully used as corrosive-wear resistant alloys. The present investigation was accordingly conducted to study the parameters of the various microstructures found in low cost white iron compositions including Mn, Cr and Cu Mo as the major alloying elements and to refer the impact of matrix / micro-agents with the hardness, deformation behavior and resistance to corrosion. The ingredients were taken so as to get desired microstructures with reduced alloying as in the as-cast condition or as in simple heat treatments. Microstructure of austenite and carbide is developed because single phase austenite was adjudged to be most effective in resisting corrosion. Though austenite based microstructures is favorable for hardening purpose, and useful in generate high resistance to wear.

Compositions based on the Fe-Mn-Cr system with copper Mo were chosen for the present study by keeping in mind the above stated facts. The element carbon was kept around 3.2% Carbon, besides increasing fluidity, stabilizes austenite and enhances solubility of copper in cast irons. Silicon was controlled around 1.8%. Chromium was selected around 6%, a manganese content of about 10% was considered suitable to ensure the formation of a completely or nearly complete austenitic matrix.