Chapter 1
An Introduction to
Physical Metallurgy of
Reduced Activation Ferritic-Martensitic
Steels
1.1 Development of 9Cr ferritic martensitic steels for nuclear applications

The worldwide growing demand for energy and the limited fuel resources have thrown open a challenge, which can be met partly by enhancing the efficiency of conventional energy sources and by alternate energy sources, with high priority on the environmental aspects associated with the option. Although renewable energy sources such as solar, wind etc. can provide clean energy, their technology as a viable commercial option is still evolving. Nuclear energy is one of the environmentally safe and viable options among other alternate energy sources, with worldwide established technologies. The increasing number of operating reactors in the world stands testimony to this. Today the water moderated/ cooled thermal reactors and sodium cooled fast reactors have established the safety, reliability, economics and robustness of the technology for power production. The experience gained by different countries to build and operate the fission reactors has led to an international collaboration to build the first fusion reactor called the International Thermonuclear Experimental Reactor (ITER), and efforts towards this are in progress in various directions [1,2].

The selection of structural materials for critical components is of utmost importance to achieve both performance and the designed life of the plant. Selection of structural material for the plasma facing components in a fusion reactor namely the first wall and blanket is a bigger challenge and stems from the difference in the fission and fusion environments. A much higher energy and higher neutron flux in addition to the high rate of production of hydrogen and helium in a fusion reactor demand materials which can withstand such aggressive environments [1-4]. Austenitic stainless steels were the first to be considered as structural materials for both fast fission and fusion reactors. In order to achieve high operating temperatures exceeding 973K, superalloy and refractory alloys of Mo, Nb and V were also considered for fusion applications. The inhibition in
employing ferritic steels was primarily due to a possible interaction of the ferromagnetic alloy with the high magnetic fields in a fusion reactor [1]. The refractory alloys of Mo or Nb are not considered due to their inadequate mechanical properties. Austenitic steels also have a limitation with respect to high rates of void swelling, low thermal conductivity and high thermal expansion coefficient. Intensive research over the last several decades have narrowed down the choice of materials to vanadium alloys, SiC/SiC composites and ferritic-martensitic (F-M) steels. Among these, the F-M steels possess an advantage over the other classes of materials for the present due to their well known metallurgical behaviour and industrial experience on fabrication and joining of components. Since the 1970s the ferritic steels became candidate materials for both the fission and fusion applications in view of their enhanced void swelling resistance [5,6] besides other attractive properties like good thermal conductivity, moderate high temperature creep strength and microstructural stability [1,7-9]. Ferritic-martensitic steels with 9-12%Cr containing about 0.1% carbon and about 1%Mo along with small amounts of V, Nb, W have been known to possess adequate elevated temperature strength including creep strength upto ~823K and good thermal properties with high resistance to thermal stresses along and have been employed in power plants, chemical and petrochemical industries. [1,9]. Figure 1.1 illustrates the dependence of Cr content on creep strength and ductile to brittle transition temperature (DBTT) of ferritic martensitic steels. It is observed that the steel with 9% Cr possess the optimum combination of high creep strength, high toughness and low DBTT among all the other steels considered. Again, a decrease in creep strength, ductility and increase in DBTT is observed with increases in Cr concentration beyond 10% due to the formation of coarse δ- ferrite grains [2,3]. It is evident that 9Cr steels have an edge over other ferritic or F-M steels. It is also of interest to note that steels of the type of modified 9Cr-1Mo (9Cr-
1MoVNb steel) have been approved for design by code bodies in countries such as USA, Japan and Europe for applications in conventional power plants and steam generator circuitry in liquid metal cooled fast reactors.

![Figure 1.1. Variation of DBTT and creep strength with variation in Cr content (unirradiated)](image)

**Figure 1.1. Variation of DBTT and creep strength with variation in Cr content (unirradiated)**[3]

### 1.2 Development of Low and Reduced Activation F-M steels

As already discussed, 9Cr ferritic / martensitic steels with good mechanical properties [1-4] are proven structural material for steam generator circuits [10,11], due to the good thermal conductivity and low thermal expansion coefficient [12,13]. Modified 9Cr–1Mo with addition of V and Nb, showed superior mechanical properties, due to the formation of very fine particles of MX, which are stable [14-16] in the service temperature of 773–873 K [1,17] as compared to their unmodified counterparts [18]. 9Cr–1Mo steel variants are also selected as core structural material for the fast breeder reactors due to their excellent radiation swelling resistance and compatibility with liquid sodium [19,20].
However, in a nuclear plant in addition to the general performance criteria discussed above, it is important to have a ‘low activation’ material, which means that the structural material would not become radioactive or alternately would decay rapidly into nearly non-radioactive levels of activity [21,22]. Such a low activation material would provide the necessary protection from radioactive debris in the extreme case of an accidental situation. Under normal conditions maintenance of the plant and disposal of radioactive waste also call for “low activation” steel. It is well known that the elements like Mo and Nb in modified 9Cr–1Mo transmute on neutron irradiation to produce long lived isotopes [23-25] and do not satisfy the criterion of low activation. Environmental effects associated with disposal of fusion reactor components after replacement during operation or after decommissioning of the plant need to be borne in mind while selecting the material. Based on the constituent elements in the alloy the time for decay of induced radioactivity can be a few thousand years and requires deep geological storages.

No structural material has been developed so far which meets the criterion of ‘low activation’ i.e material does not activate or activates to very low levels. In view of this requirement, efforts were initiated internationally in the 1980s to produce a ‘reduced activation’ F-M steel, which can be disposed by shallow land burial or by suitable recycling methods after adequate cooling period of about hundred years [26]. Although guidelines exist for disposal of nuclear waste from fission reactors it remains yet to be seen as to how they can be applied to wastes from fusion reactors. It is imperative that the composition of the steel should be tailored to consist of only those elements whose radioactive products will decay relatively faster probably within hundreds of years rather than thousands of years. Based on calculations elements that need to be minimized or eliminated in Cr-Mo steel for a rapid decay of induced radioactivity after
irradiation in a fast reactor have been determined. It is understood that elements such as Mo, Nb, Cu, Ni and N should be either eliminated or kept to very minimum levels [27]. Reduced Activation Ferritic / Martensitic (RAFM) steels without the addition of any of the above restricted elements have been developed for evaluation of the physical and mechanical properties and to demonstrate that their properties are comparable or superior to the Cr-Mo steels [28]. Besides these elements, it is also essential to restrict the level of other elements such as Co, Bi, Cd, Ag etc., that could appear as tramp impurities and pose difficulties to achieve reduced activation. It is also of importance to restrict the level of metalloids or residuals such as S, P, As, Sb which are embrittlement promoting elements. 9Cr RAFM steels have been developed where Mo and Nb are replaced by W and Ta in modified 9Cr–1Mo [23,25]. RAFM steels are considered for the first wall and test blanket module, which are plasma facing components in the International Thermonuclear Experimental Reactor (ITER). These steels are reported to show good thermophysical and mechanical properties in addition to the excellent resistance to void swelling [29-32] and He embrittlement [32-34]. The operative temperature of RAFM steel is 773 – 823 K, while oxide dispersoid strengthened (ODS) variants of the steel is expected to enhance the operating temperature to 923 K [35]. Worldwide efforts more notably from the European Union, USA, Japan, China and India have been made towards optimising the chemical composition of RAFM steels [36-47] and processing parameters. Many countries have developed RAFM steels based on the chemical composition of EUROFER 97, which has been taken as a reference for the development. The developments have aimed towards meeting the specifications of Eurofer 97 for the operating conditions of ITER, and intense research on materials for the future DEMO and PROTO reactors, having high operating temperature and neutron
flux is in progress [21]. Chemical composition of the RAFM steels used worldwide is compared in Table 1.1.

Use of clean raw materials and melting practice has been adopted to minimise the impurities like Nb, Ni, Cu and Co [44,48]; with special emphasis on the Nb content. Chemical composition and heat treatment has been optimised for the desired mechanical properties and to obtain a stable microstructure during service exposure. Mechanical properties of the developed steels have shown to meet the requirement of ITER-TBM, with some data also generated on mechanical properties after irradiation [44,49,50].

**Table 1.1. Composition of RAFM steels developed in different countries**

<table>
<thead>
<tr>
<th>Program</th>
<th>Designation</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>V</th>
<th>W</th>
<th>N</th>
<th>Ta</th>
<th>Ref</th>
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<tbody>
<tr>
<td><strong>USA</strong></td>
<td>9Cr2WVTa</td>
<td>0.11</td>
<td>0.03</td>
<td>0.39</td>
<td>8.84</td>
<td>0.18</td>
<td>1.97</td>
<td>0.022</td>
<td>0.065</td>
<td>[38]</td>
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<td>9Cr1WVTa</td>
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<td> </td>
<td> </td>
<td>9.24</td>
<td>0.18</td>
<td>1.06</td>
<td>0.003</td>
<td>0.1</td>
<td>[39]</td>
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<td> </td>
<td>9Cr3WVTa</td>
<td>0.17</td>
<td> </td>
<td> </td>
<td>9.16</td>
<td>0.16</td>
<td>3.08</td>
<td>0.003</td>
<td>0.10</td>
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</tr>
<tr>
<td> </td>
<td>JLF1</td>
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<td>0.05</td>
<td>0.52</td>
<td>8.70</td>
<td>0.18</td>
<td>1.91</td>
<td>0.028</td>
<td>0.08</td>
<td>[40]</td>
</tr>
<tr>
<td> </td>
<td>F82H</td>
<td>0.09</td>
<td>0.1</td>
<td>0.21</td>
<td>7.46</td>
<td>0.15</td>
<td>1.96</td>
<td>0.006</td>
<td>0.023</td>
<td>[40]</td>
</tr>
<tr>
<td><strong>Japan</strong></td>
<td>LA4Ta</td>
<td>0.14</td>
<td>0.03</td>
<td>0.78</td>
<td>11.0</td>
<td>0.23</td>
<td>0.72</td>
<td>0.041</td>
<td>0.07</td>
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<tr>
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<td>LA12Ta</td>
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<td>0.03</td>
<td>0.88</td>
<td>9.86</td>
<td>0.28</td>
<td>0.84</td>
<td>0.043</td>
<td>0.1</td>
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<tr>
<td> </td>
<td>LA13Ta</td>
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<td>0.04</td>
<td>0.79</td>
<td>8.39</td>
<td>0.24</td>
<td>2.79</td>
<td>0.048</td>
<td>0.09</td>
<td>[40]</td>
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<td>Eurofer 97</td>
<td>0.12</td>
<td>0.03</td>
<td>0.48</td>
<td>8.96</td>
<td>0.18</td>
<td>1.04</td>
<td>0.022</td>
<td>0.15</td>
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<td>Asturfer(AF1)</td>
<td>0.12</td>
<td>0.05</td>
<td>0.39</td>
<td>8.9</td>
<td>0.19</td>
<td>1.4</td>
<td>0.01</td>
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<tr>
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<td>Asturfer(AF2)</td>
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<td>0.44</td>
<td>8.8</td>
<td>0.19</td>
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<td>0.007</td>
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<tr>
<td> </td>
<td>OPTIFER (Ia)</td>
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<td>0.5</td>
<td>9.3</td>
<td>0.26</td>
<td>0.96</td>
<td>0.015</td>
<td>0.066</td>
<td>[43]</td>
<td></td>
</tr>
<tr>
<td> </td>
<td>OPTIFER (Ib)</td>
<td>0.12</td>
<td>0.49</td>
<td>9.5</td>
<td>0.23</td>
<td>0.98</td>
<td>0.006</td>
<td>0.163</td>
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<td> </td>
<td>OPTIFER (II)</td>
<td>0.12</td>
<td>0.49</td>
<td>9.5</td>
<td>0.28</td>
<td>0.006</td>
<td>0.015</td>
<td>0.018</td>
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</tr>
<tr>
<td> </td>
<td>OPTIFER (III)</td>
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<td>0.49</td>
<td>9.32</td>
<td>0.24</td>
<td>0.023</td>
<td>0.017</td>
<td>1.60</td>
<td>[43]</td>
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</tr>
<tr>
<td> </td>
<td>OPTIFER (IV)</td>
<td>0.11</td>
<td>0.57</td>
<td>8.5</td>
<td>0.23</td>
<td>1.16</td>
<td>0.06</td>
<td>0.15</td>
<td>[43]</td>
<td></td>
</tr>
<tr>
<td><strong>Europe</strong></td>
<td>CLF1</td>
<td>0.1</td>
<td>0.5</td>
<td>8.5</td>
<td>0.25</td>
<td>1.5</td>
<td>0.025</td>
<td>0.1</td>
<td>[44]</td>
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<tr>
<td> </td>
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<td>0.49</td>
<td>0.20</td>
<td>1.44</td>
<td> </td>
<td>0.15</td>
<td>[45]</td>
<td></td>
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<td> </td>
<td>CNS-1</td>
<td>0.1</td>
<td>0.4</td>
<td>0.4</td>
<td>9.3</td>
<td>0.05</td>
<td>2.2</td>
<td>0.043</td>
<td>0.05</td>
<td>[13]</td>
</tr>
</tbody>
</table>
Based on the data obtained the composition of RAFM steels considered by different countries varied within the narrow range of 1 – 2 wt. % W and 0.05 – 0.15 wt. % Ta. In India, a three stage alloy development program is in place for the indigenous development of RAFM steel to meet the international specifications and a unique composition has been identified, which is discussed subsequently.

Optimisation of heat treatment conditions showed that the steels in the normalised and tempered condition exhibits a good combination of strength, ductility and toughness [51,52]. It is well known that the alloy content plays an important role in the phase transformations, microstructural and mechanical properties of the steel. The effect of W and Ta on the mechanical properties of the steel is rather well studied [47,53,54]. However, the influence of microstructural changes on the mechanical properties stems from the various phase transformations, which in turn are dictated by the alloying elements. Hence a systematic study on the phase transformation characteristics with alloying elements is essential to understand the microstructural evolution in the steel. The general physical metallurgy aspects of the steel are discussed in section 1.2, addressing the phase transformation in RAFM steel and the microstructural characteristics on thermal exposure.

1.3. Physical metallurgy of RAFM steel

Figure 1.2 presents the pseudo binary diagram of Fe–Cr–C system with 0.1 % C. It is seen that the γ loop for the equilibrium diagram closes if the Cr content exceeds 12 %. Therefore the high Cr (9-12%) steels are austenitic or duplex in the temperature range of 1120 to 1470 K. Hence the normalising temperature for steel with 9% Cr is chosen to be below 1120 K to confine to single γ phase field. However, the actual phase diagram for the steel is also sensitive to other alloying elements which can be ferrite stabilisers like Cr, W, V, Ta etc or austenite stabilisers like C, N, Mn, etc., [1]. The constitution of the
steels with both ferrite and austenite stabilisers at room temperature on cooling from the γ phase field is predicted from the Schaeffler-Schneider diagram using the Cr and Ni equivalent of the steel [1]. To suppress the formation of δ-ferrite, the Cr equivalent element content should be ≤ 9 wt.%. The equation for Cr equivalent of such steels is written as-

\[
Cr_{eq} = Cr + 6*Si + 4*Mo + 11*V + 5*Nb+1.5*W + 8*Ti + 12*Al - 4*Ni - 2*Co - 2*Mn - Cu - 40*C - 30*N
\]  

(1.1)

where all the compositions are expressed in wt. % [1].

Cr equivalent for the RAFM steel developed world wide is in the range of 9-10 wt. %, which is well within the γ loop at the austenitisation temperature. Therefore, phase transformations in RAFM steel, is reported to be similar to that of other 9Cr steels [55].
However, replacement of Mo and Nb by W and Ta is expected to change the kinetics of phase transformation [56,57] which will have a significant impact on the microstructures and mechanical properties of the steel. As mentioned earlier, the steels are used in normalised and tempered condition [51,52], which has a lath martensitic microstructure with precipitates decorating the lath and grain boundaries and fine intra granular precipitates [4]. The steel derives its strength from the martensitic substructure and precipitation in this matrix [4,1,47]. Based on an extensive survey of literature, a brief description on the phase transformation and microstructural aspects is discussed in the following section.

1.3.1. Role of alloying elements on phase transformation in RAFM steel

Literature reports on phase transformations in a variety of steels studied showed the sensitivity of alloy content on phase transformation temperatures namely $Ac_1$ and $Ac_3$ [55-57,58-61] as an interplay between the ferrite and austenite stabilisers. It is known that the phase transformation characteristics of the 9Cr RAFM steel particularly, the $Ac_1$ and $Ac_3$ temperatures are sensitive to the W and Ta content [41,58-61]. The increase in $Ac_1$ and $Ac_3$ with ferrite stabilisers W and Ta content of the steel is reported [58]. Reports also show the variation of phase transformation temperatures ($Ac_1$, $Ac_3$, $M_s$ and $M_f$) for the different steels [41,60].

Literature reports from Zheng et al., in 2011 [61] and Alamo et al., in 1998, [58] explained the development of Continuous Cooling Transformation (CCT) curve for CLAM (9Cr–2W–TaV) and F82H (7.5Cr-2WTaV) steel through dilatometric experiments. The CCT diagram for CLAM steel is presented in Figure 1.3 [61]. It is evident from the diagram that the microstructure of the steel is either martensite or ferrite depending on the cooling rate. The critical cooling rate for the complete formation of martensite is 50-60 K min$^{-1}$ (Figure 1.3). The Time-Temperature-
Transformation (TTT) diagrams for different reduced activation steels have also been generated to show the dependence of $\gamma \leftrightarrow \alpha$ transformation, and the dependence of $M_s$ as a function of C+N content [58]. Raju et al., reported that the transformation temperatures and $\gamma \leftrightarrow \alpha$ transformation kinetics [56,57] for RAFM steel, was sensitive to the heating and cooling rate. Although the precipitation behaviour in F-M steels is well studied in literature with respect to their type and microchemistry, only few have addressed the formation and dissolution temperatures of $M_{23}C_6$ and MX precipitates in 9Cr class of steels, which is useful in knowing the stability regime of these precipitates, since the steels derive strength from these precipitates [51,52].

![CCT diagram for CLAM steel showing the transformations for different cooling rates [61]](image)

**Figure 1.3.** CCT diagram for CLAM steel showing the transformations for different cooling rates [61]

Simulation of phase transformations using Thermocalc® [62] and JmatPro® [63] software supported the experimental findings in RAFM steels. Simulations provided the necessary information on the formation / stability regime of different phases in the steels [64-68], which was in close agreement with the experimental data presented by Alamo et al. [58].
1.3.2. Evolution of secondary phases in 9Cr F-M steels and the role of alloy content

The role of alloy content on the mechanism and kinetics of phase transformation is very significant. It is also well known that the microstructural parameters of the steel primarily depend on the phase transformation characteristics, a one to one correspondence between them is apparent. Several researchers have reported a myriad of microstructures in 9Cr class of steel after different thermo-mechanical treatments [65,69]. The steels are generally air-hardenable resulting in a martensitic structure for a range of cooling rates when cooled from the austenite phase field [69-71] with high hardness ranging from 360 – 470 VHN [58]. The steels are employed after tempering, which brings down the hardness and improves the toughness [72-75]. Tempering of martensite is also reported to bring down the internal energy [76] in low C martensite steel, thereby stabilising the microstructure. It is also reported that the presence of fine carbides after tempering stabilises the microstructure against recovery and recrystallisation [3,77]. In addition, prolonged thermal / creep exposure at 773 to 923 K is known to form Z phase and intermetallics like Laves phase [78,79], which are beneficial when they nucleate with a fine size, a fast growth of these phases degrades the mechanical properties [4,1]. Hence it can be inferred that the nature and kinetics of precipitation exert a significant influence on the microstructural stability of the steel, which in turn controls the mechanical properties. Therefore, it is necessary to possess a detailed knowledge of the different phases that can form in 9Cr F-M of steels and the effect of alloying elements, specially those related to the chemical composition of RAFM steels, which is discussed below-

\[ M_3C \]

\[ M_3C \] carbides are Fe rich with a complex orthorhombic structure. Formation of \[ M_3C \] carbides are familiar in low chromium steel [80], while these carbides are not expected
to form in 9Cr class of steels [81]. However, precipitation of Fe rich M$_3$C carbides has been reported in normalised steel [82]. However, according to thermodynamic calculations, M$_3$C is not a stable phase in 9Cr steels [48].

$M_7C_3$ and $M_6C$

Formation of $M_7C_3$ or $M_6C$ during tempering of steel is reported [48, 77, 83] in low Cr steels. However Danon et al., [48] predicted the formation of $M_7C_3$ or $M_6C$ in 9Cr RAFM steel also. Tamura et al., [77] experimentally showed the presence of Fe$_7$C$_3$ precipitate during tempering at 1023 K in 9Cr-1Mo steel. Recent literature on CS25 steel with 8.5% Cr also reported [83] the formation of $M_7C_3$ in few grains at 873 K, as a consequence of repartitioning of W. Though such a precipitation can add to the high temperature strength, dissolution of these precipitates after prolonged thermal exposure suggested their metastable nature in high Cr steels [77].

$M_{23}C_6$

Formation of the faced cantered cubic $M_{23}C_6$ carbides is favoured in high Cr steels, which also remains stable phase during long term service [4,84] in the temperature range of 773 to 1033 K. However, considerable coarsening of the carbide phase is reported to soften the ferrite matrix [84]. The carbide mainly consists of Cr$_{23}$C$_6$; however solubility of other elements is also reported [85]. In RAFM steels $M_{23}C_6$ contains Cr, W and Fe as major elements [69,44,86], a small amount of V also is reported [2]. Enrichment of Cr is reported in 9 Cr class of steels as it grows [87,73]. Addition of W in RAFM steel is reported to control the coarsening of $M_{23}C_6$ [4]. Fine precipitates of $M_{23}C_6$ are beneficial in increasing the strength [88] by pinning the boundaries. However the coarsening of the carbides leads to the recovery of dislocations...
and coarsening of lath during creep, which results in a decrease in resistance to creep deformation [89].

\textit{MX}

In many of V, Nb and Ta added creep resistant steels, a stable fine intralath NaCl type fcc monocarbides / carbonitrides are evident [1,4, 14,83,73]. Thermocalc calculations showed that these precipitates nucleate in the range of temperatures from 770 to 1300 K [65]. It is reported [90-92] that these carbides do not coarsen significantly during prolonged thermal exposure and even under creep exposure [93]. Hence, these carbides are responsible for the high temperature strength during prolonged service [90-92]. Two types of MX precipitates, namely V rich and Ta rich are possible in V and Ta added steels [90]. These carbonitrides are reported to be stable up to 1681 K [94].

\textit{M}_2\textit{X}

It is reported that tempering the high nitrogen steel at relatively lower temperature for longer time can favour the formation of a nitrogen rich \textit{M}_2\textit{X} phase [95,96]. Recent study on high Cr steel also showed the formation of Cr\textsubscript{2}N; while it is unstable during longer durations of thermal exposure. Haribabu et al., [97] also showed the formation of \textit{M}_2\textit{X} phase in Eurofer 97 steel. However stability of \textit{M}_2\textit{X} in 9Cr steel tempered at 1033 K is less probable, which dissolves during further aging.

\textit{Z-phase}

\textit{Z}-phase, is known to be a complex tetragonal nitride with the general formula Cr(X)N, where X= Nb, Ta, V which forms simultaneously with the dissolution of the cubic MX-phase, precipitates and coarsens much faster than the MX phase. Hence, formation of \textit{Z}-phase is reported to lead to a steep reduction in the creep strength of the 9–12% Cr ferritic steels [98], since the increased creep resistance is attributed to the presence of
carbonitrides in the matrix [99]. The Z-phase was observed in the ternary CrNbN and CrTaN systems, but no Z-phase was found in the CrVN system [100], though Cr(V,Nb)N has been observed. However, in multicomponent steels containing Ta, the effect of Ta on Z-phase formation has not been experimentally reported [48].

*Laves Phase*

Other than carbides or nitrides Laves phase precipitation is reported in 9Cr creep resistant steels containing Mo or W, during low temperature thermal exposure, [101]. Tamura et al., [102], report that the presence of stress accelerates its formation and coarsening [103], based on the TTP diagram for Laves phase in RAFM steels developed by them. Fine precipitation of Laves phase is beneficial to increase the strength [4,104], while its rapid coarsening has shown a detrimental effect on mechanical properties of the steel, especially on the toughness [4,103]. In Mo added steels it is reported that, a Mo / C ratio greater than 5, can promotes the formation of Laves phase [105]. However, in RAFM steels the formation of Laves phase depends on the W content of the steel [48]. Increase in W content increases the formation of Laves phase [48]. Role of Ta on the formation of Laves phase is speculated based on the Fe-W-Ta ternary diagram [106], while no experimental evidences to this effect exist so far.

From the above description of the various phases, it is understood that phases like \(M_2X\), \(M_7C_3\), \(M_6C\) are metastable carbides that form at low temperatures at shorter durations of tempering. Typical tempered martensitic structure in high Cr steels consists of \(M_{23}C_6\) precipitates decorated along the lath / grain boundaries with size varying from 100 to 300 nm [72,74] and fine intra lath MX precipitates with size 10 to 40 nm [74-75]. The formation of Z and Laves phase are important to be considered during long term thermal exposure more so under stress, due to their detrimental effect on mechanical properties.
1.4 Role of Microstructure on Mechanical properties

It is well known that the maximum service temperature of a structural material is decided by its stability in the operating environment and degradation of mechanical properties [1,35], specially creep properties. At a given temperature, the mechanical properties of the steel largely depend on the alloy content [47,107] and microstructural properties of the steel [35]. 9Cr steels as already discussed, derive their strength from the fine substructure and precipitates which pin the grain / lath boundaries [35,3]. However, during long term thermal or creep exposure, these precipitates coarsen, weakening the boundaries [104]. Furthermore, the appearance of intermetallics like Laves phase, on the grain boundaries offers a beneficial strengthening effect during initial stages of its nucleation [4,104]. However, the accelerated coarsening of Laves phase particles compared to the M_{23}C_{6} [4,103,104] carbides decreases the grain boundary strength and hence the toughness of the steel [7].

As already discussed in the previous section, increase in W content retards the coarsening of M_{23}C_{6}, which in turn helps to retard the substructural recovery due to the pinning effect of carbides. This increases the long term stability of microstructure and hence the long term mechanical properties [103,108,109]. Also, addition of W from 1 to 3%, in 9Cr RAFM steel is reported to increase the creep strength of the steel considerably. However, further addition of W, above 4 % is reported [2] to form δ – ferrite, which decreases the creep strength. The tensile strength of the steel is reported to show an insignificant change with W content of the steel [35]. Figure 1.4(a) shows the dependence of the Ductile to Brittle Transition Temperature (DBTT) on W content of the steel. For the normalised and tempered steel a decrease in DBTT with addition of W is seen compared to a steel without W. However, large addition of W increases the
DBTT. A similar trend is observed in a steel aged at 873 K. This result shows that 1 – 2% W is optimum for the RAFM steel to achieve better mechanical properties.

![Graph showing variation of DBTT as a function of W content and aging temperature.](image)

**Figure 1.4.** (a) Variation of DBTT as a function of W content (b) Variation of DBTT with aging temperature showing drastic increase in the presence of Laves Phase [2].

However, addition of W in the range 1 – 3 wt% is reported to increase the δ – ferrite content in the weld and heat affected zone, which deteriorates the impact properties of
the steel [110, 111]. Formation of delta ferrite is also reported to reduce the creep ductility of the steel [112]. The formation of delta ferrite and Laves phase due to the addition of W is also reported to influence DBTT [3,35]. Addition of W also favours the formation of coarse Laves phase in the steel during creep exposure [2]. Figure 1.4(b) shows the effect of M$_{23}$C$_{6}$ and Laves phase on DBTT in the W added 9 Cr steels. It is seen that coarsening of both M$_{23}$C$_{6}$ and Laves phase increase the DBTT, however, the increase is high in steel containing 3% W in the presence of brittle Laves phase compared to that in 1% W.

Addition of small amount of Ta was reported to be beneficial to reduce the grain size and improve the mechanical properties of the steel [54]. Addition of Ta from 0.05 to 0.08% is also reported to decrease the DBTT [54]. However, further increase in Ta up to 0.16% is reported to increase the DBTT [113]. A decrease in tensile and creep rupture strength of the steel is reported with increase in Ta content from 0.06 to 0.14 wt.% [47].

1.5 Development of India specific RAFM steel

In India, considerable R&D efforts have been made on various aspects of material development and establishment of fabrication technologies as a part of ITER-TBM program [114,115]. A three-phase alloy development program on the 9Cr RAFM steel is in progress [47,114], The three stage program includes, (a) demonstration of India’s capability to produce RAFM steel, with physical and mechanical properties comparable to the internationally produced RAFM steels, (b) optimisation of chemical composition of the steel through mechanical property evaluation and (c) development of RAFM steel in commercial scale. Efforts to indigenously develop an RAFM steel with a specific composition for the Indian Test Blanket Module, as a part of second phase of the program, has been successful [47]. This has been possible by a systematic alloy
development program as a collaborative venture between several organisations like Institute of Plasma Research, Gandhinagar, MIDHANI, Hyderabad, and Indira Gandhi Centre for Atomic Research, Kalpakkam, India[47,116-128]. Four heats of 9Cr-W-Ta RAFM steel having different tungsten (1, 1.4 and 2 wt. %) and tantalum (0.06 and 0.14 wt. %) contents were produced. By a detailed characterization of physical and mechanical properties, the chemical composition with optimum combination of impact, tensile, low cycle fatigue and creep properties has been arrived at [47,116-119,122-128]. India-specific RAFM steel designated as Indian Reduced Activation Ferritic Martensitic (INRAFM) steel conforms to a composition of 1.4 wt. % of W and 0.06 wt. % of Ta which meets the property requirements of ITER. The third stage of the development, namely production of the INRAFM steel at a commercial scale and into various product forms is in progress. Establishment of fabrication technologies for the TBM by different welding methods HIPing is also in progress [129-132].

1.6 Objective of the thesis

The objective of this thesis is to obtain an in-depth understanding on thermodynamic and physical metallurgy aspects of indigenously developed 9Cr RAFM steels with different W and Ta content, which involves the study of $\alpha\leftrightarrow\gamma$ transformation characteristics using differential scanning calorimetry (DSC) and microstructural investigation through Analytical Transmission Electron Microscopy and related techniques. The thesis highlights the role of alloy content and process parameters on microstructure by a systematic experimental investigation and simulation using JMatPro and Thermocalc software.

1.7 Scope of the thesis

This thesis presents the results of an extensive physical metallurgy study on 9Cr RAFM steels with W and Ta varying from 1–2 wt. % and 0.06 – 0.14 wt. % respectively.
These microstructural aspects studied in four compositions of the RAFM steels forms a part of a large Research and Development program on indigenous development of RAFM steel as a structural material for ITER. The thesis addresses three major themes, namely

- $\alpha \leftrightarrow \gamma$ phase transformation in RAFM steels
- Decomposition modes of high temperature austenite and characteristics of martensite
- Microstructural evolution - Effect of alloy content, temperature and stress

1.8 Organisation of the thesis

This thesis consists of six chapters and is organised as follows-

**Chapter 1, Introduction**, briefly presents a review of the existing literature on the RAFM steel, with emphasis on basis of alloy development, physical and mechanical properties of the steel. Chapter 1 also highlights the physical metallurgy aspects of RAFM steels and defines the objective and scope of the thesis.

**Chapter 2** deals with the **Experimental Methodology** adopted in this study. Details of processing parameters, heat treatments and specimen preparation are given. Details of different experimental techniques, operating conditions, analysis procedures and sources of error are described. A brief description the computational methods namely JMatPro® and Thermocalc® are also presented.

**Chapter 3** titled **“Phase transformation in RAFM steels”** discusses the thermodynamic studies carried out to establish the temperatures and enthalpy of the transformation. Simulation of thermodynamic data using JMatPro® and Thermocalc® software have been correlated with the experimental data. The kinetics of martensite transformation in the W added RAFM steels with variation in cooling rate has been discussed.
Chapter 4 titled “Decomposition modes of high temperature austenite and characteristics of martensite” describes the microstructures that evolve during the decomposition of austenite as a function of temperature and cooling rate. The role of alloy content in controlling the kinetics of martensitic transformation has been understood in terms of the heterogeneity of austenite at solution treatment temperatures, which is a consequence of the incomplete dissolution of the pre-existing carbides. The transformation products have been characterised using Mossbauer Spectroscopy and Orientation Imaging Microscopy in TEM, a newly emerging technique. This chapter also discusses about the kinetics of tempering of martensite. The phase evolution and microchemistry of the phases, which varies with W content has been discussed extensively.

Chapter 5 titled “Microstructural evolution - Effect of alloy content, temperature and stress” provides a detailed description on the effect of prolonged exposure to high temperature and stress on recovery and recrystallisation of substructure and evolution of secondary phases. Extensive studies on the effect of W and Ta on evolution of secondary phases and the mechanism of formation of Laves phase are dealt with in this chapter.

Chapter 6 presents the summary of important findings of this study and also identifies the future directions for further studies.