Synopsis
1. **Introduction**

Reduced Activation Ferritic / Martensitic (RAFM) steels, are potential structural material for test blanket module (TBM) and first wall of the International Thermonuclear Experimental Reactor (ITER) due to their excellent resistance to radiation-induced swelling, He embrittlement and acceptable high temperature mechanical properties [1,2]. Though the general metallurgical characteristics of the steel is similar to P91 steel, the replacement of Mo by W and Nb by Ta exerts significant influence on the phase transformation characteristics of the steel [1]. An extensive data base exists for the 9Cr class of steels w.r.t the metallurgical characteristics of the steel [3]. However, there is limited literature on the physical metallurgy aspects like phase transformation and microstructural evolution of W and Ta added RAFM steels during thermal exposures and existing reports mainly deal with property evaluation [4, 5]. Further, for the Indian TBM, RAFM steels have been developed indigenously based on an extensive Research and Development effort involving optimisation of composition and processing window, developmental and industrial scale production of the steels, characterisation and structure–property correlations. Therefore, efforts have been made to evaluate the phase transformation characteristics and microstructural evolution of RAFM steels with varying W and Ta content and different thermal treatments.

The main aim of the present 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 $\alpha \rightarrow \gamma$ transformation characteristics using differential scanning calorimetry (DSC), microstructural investigation through Analytical Transmission Electron Microscopy. Also, Orientation Imaging Microscopy (OIM) in TEM, a newly emerging technique has been used to study the martensite characteristics. The thesis highlights the role of
alloy content and process parameters on the mechanism and kinetics of phase transformation by a systematic experimental investigation and simulation using JMatPro and Thermocalc software.

2. **Scope of the Thesis**

This thesis titled “STUDY OF TRANSFORMATION CHARACTERISTICS AND MICROSTRUCTURAL EVOLUTION IN 9Cr REDUCED ACTIVATION FERRITIC / MARTENSITIC STEEL USING ELECTRON MICROSCOPY, CALORIMETRY AND COMPUTATIONAL METHODS” 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. This study on microstructural aspects of 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 given below–

- Phase transformation in RAFM steels
- Decomposition modes of high temperature austenite and characteristics of martensite
- Microstructural evolution - Effect of alloy content, temperature and stress

A brief description of the above themes is discussed below.

2.1. **Phase transformation in RAFM steels**

2.1.1 Phase transformation characteristics using Differential Scanning Calorimetry

Based on DSC results, the following transformation sequence has been established on heating the normalised and tempered RAFM steels.

\[
\alpha\text{-Ferrite (ferromagnetic)} + M_{23}C_6 + MX \rightarrow \alpha\text{-ferrite (paramagnetic)} + M_{23}C_6 + MX \rightarrow \gamma\text{-austenite} + M_{23}C_6 + MX \rightarrow \gamma + MX \rightarrow \gamma + \delta \rightarrow \gamma + \delta + L \rightarrow \delta + L \rightarrow \text{Liquid}.
\]

The \(\text{Ac}_1\), \(\text{Ac}_3\), \(M_s\), and \(M_f\) temperatures have been evaluated for the four steels.
• An increase in $A_c_1$, $A_c_3$ was observed with heating rate in 1.4W–0.06Ta steel.
• The critical cooling rate for $\gamma \rightarrow \alpha'$ transformation was found to be close to 40 K min$^{-1}$ for the 1.4W–0.06Ta steel. The decrease in $M_f$ with increase in cooling rate was more significant than $M_s$, suggesting that, though martensite nucleation takes place at same temperature, completion of martensite transformation requires higher undercooling.
• With increase in W content of the steel, $A_c_1$ and $A_c_3$ showed a small increase, while $M_s$ and $M_f$ showed a significant decrease.
• Sluggish dissolution of carbides in 1.4W–0.06Ta and 2W–0.06Ta steels was found to influence the kinetics of $\alpha \leftrightarrow \gamma$ transformation.

2.1.2 Phase transformation and precipitation behaviour - JMatPro® & Thermocalc® simulations

Phase equilibria simulations for all the steels were performed using JMatPro® and Thermocalc®. Figure 1 shows the phase fraction and transformation temperatures of different phases for the steel containing 1.4 wt. % W. The equilibrium phases predicted and the computed values of $A_c_1$ and $A_c_3$ agreed with the experimental results. However, there is a mismatch between equilibrium simulation and experimental studies regarding the prediction of formation of secondary phases.

Figure 1. Calculated (a) phase diagram for 1.4W–0.06Ta steel showing different transformation regimes (b) calculated minor phases showing different phases ($M_2X$ phase not considered).
like M\(_2\)X, M\(_3\)C and Z phase due to the influence of kinetic factors. Computations showed no significant change in transformation/dissolution temperature of phases with increase in W content of the steel, while the dissolution temperature of MX increased with Ta content.

### 2.2. Decomposition modes of high temperature austenite and characteristics of martensite

All the steels showed a martensitic microstructure after normalising from 1253 K and 1323 K, while furnace cooling resulted in a mixture of ferrite and martensite. A mixture of \(\delta\) – ferrite and martensite formed after solutionising at 1553 K.

#### 2.2.1 Effect of alloy content and solution treatment conditions

Normalising 1.4W steel at 1253 K showed predominantly martensite with an average lath size 200-300 nm, while fine needles of Fe rich precipitates were observed in a few wide laths measuring 1-2 \(\mu\)m (Fig. 2). Such precipitates are not expected in air hardenable 9Cr steels. The carbides identified as a function of solution treatment temperature and cooling rate for the three steels with varying W content are summarised in Table 1.

![Thin foil micrograph of normalised 1.4W steel showing needle like precipitates](image)

**Figure 2.** Thin foil micrograph of normalised 1.4W steel showing needle like precipitates
The present study has established that formation of Fe rich carbides is not due to para-equilibrium precipitation or by auto-tempering of martensite. Due to compositional inhomogeneity of austenite caused by the undissolved carbides, the solute lean austenite in the vicinity of undissolved carbides transform to ferrite + carbides above the $M_s$ temperature, while solute rich austenite away from the undissolved carbides transforms to martensite. This has been confirmed by analysis of DSC profile during cooling of 1.4W–0.06Ta steel and detailed microstructural analysis.

2.2.2 Martensite Characteristics and optimisation of tempering parameters

Orientation imaging of normalised 1.4W-0.06Ta steel revealed random orientation of the martensite laths (Fig.3(a)) suggesting no variant selection due to a relatively high cooling rate. A low amount of retained austenite (~2%) was also found to be present as shown in fig. 3(b).

<table>
<thead>
<tr>
<th>Steel</th>
<th>1253 K / AC</th>
<th>1253 K / WQ</th>
<th>1323 K / AC</th>
<th>1323 K / WQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1W – 0.06Ta</td>
<td>$\alpha'$ + UC</td>
<td>$\alpha'$ + UC</td>
<td>$\alpha'$ + UC</td>
<td>$\alpha'$ + UC</td>
</tr>
<tr>
<td>1.4W – 0.06Ta</td>
<td>$\alpha'$ + UC + M$_{13}$C$^*$</td>
<td>$\alpha'$ + UC</td>
<td>$\alpha'$ + UC + M$_{23}$C$_6^*$</td>
<td>$\alpha'$ + UC</td>
</tr>
<tr>
<td>2W – 0.06Ta</td>
<td>$\alpha'$ + UC + M$_{23}$C$_6^*$</td>
<td>$\alpha'$ + UC + M$_3$C$^*$</td>
<td>$\alpha'$ + UC + M$_{23}$C$_6^*$</td>
<td>$\alpha'$ + UC</td>
</tr>
<tr>
<td>1W – 0.14Ta</td>
<td>$\alpha'$ + UC</td>
<td>$\alpha'$ + UC</td>
<td>$\alpha'$ + UC</td>
<td>$\alpha'$ + UC</td>
</tr>
</tbody>
</table>

UC – undissolved carbides; *acicular intralath Fe rich carbides

**Table 1 Summary of microstructure of the austenitised steels**

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![Figure 3](image)
The mechanism and kinetics of tempering with W and Ta content has been studied. The activation energy (Q) was calculated by Arrhenius type of analysis using hardness and strain variation from XRD studies. The values of Q varied from 0.5 to 1 eV, corresponding to interstitial diffusion of C in α-ferrite.

Recovery of martensite and coarsening of precipitates was sluggish at 923 K. Fe rich intralath M$_{23}$C$_6$ carbides formed in the initial stages of tempering at 923 K were unstable, while Cr rich interlath M$_{23}$C$_6$ carbides formed at later stages. Tempering at 973 and 1033 K showed faster recovery than at 923 K. However subgrain formation and coarsening of precipitates was fastest at 1033 K. Microchemical variation of M$_{23}$C$_6$ showed a systematic change as a function of W content of the steel. Although M$_{23}$C$_6$ was Cr rich, it showed a large solubility for W. This also explains the sluggish dissolution of carbides with increase in W content discussed in section 2.1.

2.3. Microstructural evolution - Effect of alloy content, temperature and stress

2.3.1 Effect of temperature and stress exposure

1W – 0.06Ta steel aged at 773 K upto 5000h showed an insignificant hardness variation with time, whereas a significant decrease was observed at 823 K, which was correlated to the softening of matrix, due to the depletion of solute elements through the coarsening of M$_{23}$C$_6$ carbides. However, aging at 873 K showed a secondary hardening behaviour after 2 h of thermal exposure, due to fresh nucleation of fine MX precipitates. V and Ta rich MX precipitates were in the size range of 20 – 40 nm and did not coarsen with long term aging at any temperature. Microchemical variation of M$_{23}$C$_6$ precipitates showed an increase in Cr / Fe and W / Fe ratios beyond 823 K after long term thermal exposure.
Significant change in subgrain size was not evident with thermal exposure, due to effective pinning by the fine MX precipitates. However, the combination of thermal and stress exposure showed considerable coarsening of sub-structure and $M_{23}C_6$ precipitates [6].

2.3.2 Role of W and Ta on evolution of secondary phase

Replacement / addition of W in RAFM steel retards the coarsening of $M_{23}C_6$ precipitates as compared to P91/ T91 steel [7]. The present study showed the increase in amount of Laves phase with W and Ta content of the steel. Detailed TEM analysis revealed the formation of Laves phase around $M_{23}C_6$, suggesting that $M_{23}C_6$ acts as nucleation centre. X-ray mapping showed that the Laves phase is richer in Fe and W, with little solubility for Cr and Ta. The coarsening of Laves phase is accompanied by the exchange of Cr and W at the Laves phase / $M_{23}C_6$ interface. Influence of Ta on formation of Laves phase was also evident from the microstructural characterisation of 0.14 Ta steel after long term thermal exposure. The above result was also supported by JMatPro® calculations.

3. 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 specific issues related to the physical metallurgy aspects of RAFM steels that need to be addressed.

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 OIM in TEM. 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.

The topics addressed in this thesis are summarised in Figure 4.
STUDY OF TRANSFORMATION CHARACTERISTICS AND MICROSTRUCTURAL EVOLUTION IN 9 Cr REDUCED ACTIVATION FERRITIC / MARTENSITIC STEEL USING ELECTRON MICROSCOPY, CALORIMETRY AND COMPUTATIONAL METHODS

RAFM steel composition (wt. %)
- W – 1 to 2
- Ta – 0.06 to 0.14
- C – 0.08 to 0.12

Phase transformations
- Decomposition modes of \( \gamma \)
- Characteristics of \( \alpha' \)

Thermophysical properties
- Transformation characteristics - \( F(X) \)
- Kinetics of phase transformations
  - Heating / cooling rate
- Transformation Enthalpy

Phase equilibria calculations
- Transformation temperature - \( F(X) \)
- Phase fields

Microstructural evolution – \( F(X, T, t, \sigma) \)
- Alloy content
- Solution treatment
- Cooling rate
- Microtexture analysis
- OR between \( \alpha' \) and \( \gamma \)
- Kinetics of Tempering - \( F(T, t) \)
  - Activation energy
  - Strain evaluation
- Microstructural evolution – \( F(X) \)
  - Substructure
  - Precipitation
  - Optimisation of parameters

\( X, T, t \) and \( \sigma \) are composition, Temperature, time and stress respectively

Figure 4. Flow chart of the major themes of the thesis
References:


