1. INTRODUCTION

The choice of ferritics in power industry, chemical and oil processing industries has necessitated the systematic development of the metallurgical data base of the creep resistant Cr-Mo steels, resulting in a spurt of activity in this field. Consequently, extensive literature has been made available in the last two decades and as a result, the metallurgy of this class of steels is almost completely understood [1,2]. However, most of the literature so far considers only the evaluation of properties of these steels, the changes in which are rationalised based on the corresponding microstructural variations. The limited controlled laboratory experiments to study all the physical metallurgical aspects are confined to only shorter ageing timings. Therefore, an extensive experimental programme was initiated to develop a systematic data base on the physical metallurgy of Cr-Mo steels.

The objective of the present thesis is to develop an extensive physical metallurgy basis for the 9Cr-1Mo class of steels, for which it was necessary to study the microstructural evolution using advanced techniques like Analytical Transmission Electron Microscopy (ATEM), Convergent Beam Electron Diffraction (CBED) and recent developments in thermodynamic modelling. A few highlights of the thesis are as follows:
A comprehensive mapping of the microstructure, microchemistry and variations in microscopic lattice strain of different microstructural constituents has been carried out. A flow chart has been developed to describe the synergistic effects of various factors which govern the precipitation behaviour in Cr-Mo steels. Critical analysis of local equilibrium and evolution of secondary phases has led to a new concept of Phase Evolution Diagram and its predictive abilities have been demonstrated. The role of PED in the existing life extension strategies is discussed.

2. SCOPE OF THE THESIS

The present thesis titled "STUDY OF MICROSTRUCTURE, MICROCHEMISTRY AND LATTICE STRAIN IN WROUGHT 9Cr-1Mo STEEL USING ANALYTICAL TRANSMISSION ELECTRON MICROSCOPY, CONVERGENT BEAM ELECTRON DIFFRACTION AND THERMODYNAMIC COMPUTATIONS" describes the results of an extensive experimental programme for developing the physical metallurgy basis for 9Cr-1Mo steel. The major themes (Figure 1) of the studies are as follows:

1) Dependence of decomposition modes of austenite (γ) on alloy chemistry and process parameters, and its rationalisation based on thermodynamic computations.

2) Development of flow chart to rationalise the role of fundamental parameters, which influence the local equilibrium and evolution of secondary phases.
Study of Microstructure, Microchemistry and Lattice Strain in Wrought 9Cr-1Mo Steel using Analytical Transmission Electron Microscopy, Convergent Beam Electron Diffraction and Thermodynamic Computations

Fig. 1. Flow Chart of the Major Themes of the Thesis
3) Development of predictive methods for evolution of secondary phases in 9Cr-1Mo steels.

4) Measurement of lattice strain across coexisting phases using CBED.

5) A unique characterisation of the local microstructural state of coexisting phases based on their structure, chemistry and strain and the one to one mapping of these parameters.

A brief description of the themes mentioned above is given below:

2.1 Decomposition modes of austenite

It has been observed that the austenite in 9Cr-1Mo steel, decomposes through various modes, depending on the alloy chemistry and process parameters like a) cooling rates (Q), b) solution treatment temperature (T_s) and c) carbon content [3-9].

Figure 2 shows the microstructural map generated for 9Cr-1Mo-0.07C for different rates of cooling. This map serves as a guideline to depict the type of transformation the austenite undergoes for various rates of cooling and the resultant microstructure [7-9].

In the studies carried out at different solution treatment temperatures, the high temperature limit of γ phase stability has been established. The dependence of the nature of the transformation products of austenite and the microstructural parameters, on the phase field at T_s has been established [7,8,10]. A new concept of "Microscopic Chromium Equivalent" (MCE) of the individual microstructural constituents has been introduced, based on the
estimation of solute repartitioning between the high temperature δ-ferrite and austenite phases (Fig.3). The comparison [7] of MCE with the expected Cr content from the Fe-Cr equilibrium diagram [11] and the influence of solute repartitioning on the subsequent transformation behaviour of γ, are discussed in the thesis.

Fig.2. Microstructural Map for 9Cr-1Mo-0.07C. The room temperature microstructures that form when the steel is cooled at different rates, is superimposed on the TTT diagram.
Based on similar studies in the same steel, with a different carbon content (0.1 wt%), the role of carbon in influencing the i) kinetics of transformation of γ → ferrite and ii) nature of phase fields during solution treatment has been established. The results are understood in terms of the tendency of carbon to stabilise the γ phase.

The influence of alloying elements like Cr and Mo was studied using thermodynamic computations. The free energy change for the martensitic transformation was evaluated to study the dependence of the driving force of the transformation on the substitutional alloy content. The mode of decomposition of austenite, expected based on computation compare favourably with the experimental results in few Cr-Mo steels [4,5].
2.2 Microstructural Modification During Exposure to Elevated Temperature

The microstructural characterisation of the commercially heat treated 9Cr-1Mo steel and the changes that take place when the steel is exposed to high temperatures (823-1023 K) for long durations form the second major theme. Exposure of the steel to high temperatures for prolonged durations results in a sequence of events - tempering of martensite, formation of subgrains of ferrite and evolution of secondary carbides. Study of tempering kinetics of martensite in normalised 9Cr-1Mo steel was carried out by evaluating the temperature dependence of recovery rate. The sequence, growth kinetics and microchemical nature of the secondary phases showed variations with temperature [12,13], which were useful in developing a flow chart.

The salient features of these studies are as follows:

- Study of the tempering kinetics of $\alpha'$ in 9Cr-1Mo steel showed that the activation energy for the process is about 0.6 eV. This values compares with the activation energy for migration of C in $\alpha$-ferrite [14].

- Commercial heat treatment conditions have been rationalised based on observed microstructures and their impact on relevant properties [9,12].

- Effect of prolonged exposure of (normalised and tempered) 9Cr-1Mo steel at different temperatures is characterised by the reaction

$$\alpha + M_2X + M_{23}C_6 \rightarrow \alpha + M_{23}C_6$$
Microchemistry of $M_{23}C_6$ is found to depend crucially on temperature and ageing time. The variation in microchemistry of $M_{23}C_6$ has been understood in terms of basic thermodynamic and kinetic factors, like the free energy of formation of $Cr_{23}C_6$ and relative diffusivities of the solutes at different temperatures.

The factors which govern the sequence of precipitation in ferrite have been understood in terms of a number of synergistic effects like difference in the relative affinities of elements towards carbon, initial concentration of alloying elements, efficiency of various carbides in scavenging the matrix of its carbon, relative differences in the carbon level in depleted $\alpha$ and the consequent shift in local phase equilibrium.

Based on the observed trends in precipitation behaviour in several Cr-Mo steels with respect to ageing parameters, a comprehensive flow chart has been developed [15]. This flow chart shown in figure 4 explains the observed variations in the type and chemistry of carbides from one steel to another.

2.3 Phase Evolution Diagrams for Prediction of Microstructural Evolution

The next theme describes an attempt to develop procedures to predict the evolution of secondary phases in 9Cr-1Mo steels. Such an attempt involves identification of a single parameter with which the complete sequence of evolution of secondary phases can be rationalised. Based on the variation of such a parameter with time a new concept of "Phase Evolution Diagram" (PED) is introduced and its predictive ability is demonstrated [15-17].
Supersaturated ferrite (SS\textsubscript{a})

\begin{itemize}
  \item \textbf{Cr/Mo ratio vs Mo-C affinity}
  \item \textbf{Depletion of C in SS\textsubscript{a}}

\end{itemize}

\begin{itemize}
  \item Shift of phase equilibria towards Cr\textsubscript{23}C\textsubscript{6}
  \item Cr\textsubscript{23}C\textsubscript{6} precipitates
  \item Solubility of C in \(\alpha\) in pseudoequilibrium with Cr\textsubscript{23}C\textsubscript{6} is less than that in pseudoequilibrium with M\textsubscript{7}X
  \item C concentration gradient sets

\end{itemize}

\begin{itemize}
  \item In low Cr steel, phase equilibrium shifts away from M\textsubscript{23}C\textsubscript{6} due to increase in [C] and is offset by stronger Mo-C interaction
  \item Mo\textsubscript{2}C forms

\end{itemize}

\begin{itemize}
  \item In high Cr steel, shift in phase equilibria away from M\textsubscript{23}C\textsubscript{6} due to increase in [C] is offset by increase in [Cr]
  \item Cr\textsubscript{23}C\textsubscript{6} continues to precipitate
  \item Eventually [Cr]/[Mo] decreases
  \item Lower order carbides and Mo carbides form
  \item [C]\textsubscript{\alpha} attains equilibrium value of 0.02

\end{itemize}

Fig. 4. Flow Chart for the evolution of secondary carbides from the supersaturated ferrite.
The salient features of the study are as follows:

* PED depicts the variation of C content of the parent ferrite matrix with time.

* The choice of carbon content of ferrite as the fundamental parameter has been explained using a simple binary model system.

* Phase evolution diagrams for 9Cr-1Mo steels at three different temperatures have been generated. The different phase fields which evolve at the three temperatures have been identified and superimposed on the phase evolution diagram. Figure 5 shows the PED for 9Cr-1Mo steel at 1023 K.

![Phase evolution diagram for 9Cr-1Mo steel at 1023 K.](image)
* The usefulness of PED in the determination of the past thermal history and prediction of future microstructural evolution in the steel of a component in a commercial application is discussed.

* The role of PED in the presently available life extension strategies is discussed in detail in the thesis.

2.4 Lattice Strain Measurements Using CBED

The conventional diffraction techniques for evaluation of lattice strain can be employed for estimation of lattice strain only from macroscopic regions. The measurement of lattice strain from microscopic phases requires a measuring probe whose size is as small as the region of interest. The newly emerging technique called "Convergent Beam Electron Diffraction" (CBED) offers the possibility of measurement of lattice strain from microscopic regions.

CBED experiments have been carried out in wrought 9Cr-1Mo-0.07C steel with three different thermal histories, consisting of ferrite with different degrees of lattice strain. The angular position of high order Laue zone (HOLZ) lines in the (000) disc of CBED patterns, an index of lattice strain is found to depend on two factors, namely excitation strength of FOLZ lines and the lattice strain. The appropriate selection of experimental conditions enabled the measurement of lattice strain from the shift in the angular position of HOLZ lines by maintaining the excitation strength constant. The details of the above study are discussed in the thesis.
2.5 Mapping of local microstructural states

Very often the identification of a phase based on morphology and microchemistry is inadequate. The unique description of a phase is complete only if three parameters namely structure, chemistry and strain can be defined. In the case of coexisting phases the unique representation of variation in local microstructural state involves a one to one mapping of all the three parameters mentioned above. Such an attempt has been made to map the microchemistry, lattice parameter and lattice strain of a δ-ferrite phase in a martensitic - α' matrix in 9Cr-1Mo-0.07C steel.

A comprehensive three dimensional mapping of the three fundamental parameters has been carried out, which has provided a means for a unique description of local microstructural state of δ-ferrite phase in a α' matrix. It is expected that such a diagram would be useful to distinguish phases which vary only in one parameter with the other two parameters remaining the same.

To sum up, the thesis introduces a number of comprehensive maps, flow charts and new concepts like microscopic chromium equivalent and phase evolution diagrams which help in the detailed understanding of the Physical Metallurgy of wrought 9Cr-1Mo Steel. The major highlights of the thesis are as follows:

- Development of predictive methods for evolution of secondary phases in 9Cr-1Mo steels using the new concept of "Phase Evolution Diagrams".
• Comprehensive representation of variation in structure, chemistry and strain in microscopic regions.

• Development of a flow chart to rationalise the precipitation behaviour in Cr-Mo steels.

• Microstructural maps to depict the decomposition modes of high temperature austenite and room temperature microstructures.

• New concept of microscopic chromium equivalent to rationalise the solute repartitioning among co-existing microstructural constituents.

3. ORGANISATION OF THE THESIS

The thesis titled "STUDY OF MICROSTRUCTURE, MICROCHEMISTRY AND LATTICE STRAIN IN WROUGHT 9Cr-1Mo STEEL, USING ANALYTICAL TRANSMISSION ELECTRON MICROSCOPY, CONVERGENT BEAM ELECTRON DIFFRACTION AND THERMODYNAMIC COMPUTATIONS." has six chapters and is organised as follows:

The first introductory chapter reviews the role of ferritics for various industrial applications. This chapter provides a detailed review of the present state of understanding of the behaviour of ferritic steels and the specific problems which need further attention.

The second chapter "EXPERIMENTAL DETAILS" describes the details of various experimental procedures adopted during this study.
The third chapter titled "TRANSFORMATIONS IN 9Cr-1Mo STEEL WITH DIFFERENT CARBON CONTENTS - ROLE OF PROCESS PARAMETERS" describes the dependence of the decomposition mode of γ on the i) rate of cooling and ii) solutionising temperature. Based on these studies, comprehensive microstructural maps depicting the various products of γ have been generated for the two steels with different C contents. The variation of a number of microstructural parameters has been understood in terms of the various decomposition modes of γ. The dependence of decomposition modes of γ on substitutional alloy content has been computed using thermodynamic models and found to be in agreement with the observed experimental results.

The fourth chapter titled "MICROSTRUCTURAL EVOLUTION IN 9Cr-1Mo STEEL DURING HIGH TEMPERATURE EXPOSURES" discusses the modification of the initial microstructure during high temperature exposures (823-1023 K) for various durations (2-5000h). The dependence of precipitation behaviour on the local chemistry has been rationalised based on fundamental parameters which has been depicted as a flow chart. A new concept of "phase evolution diagram" has been proposed and PED's have been generated for 9Cr-1Mo steel at three different temperatures. The use of PED in the determination of the past thermal history and prediction of future microstructural evolution in the steel of a component in a commercial application is discussed.

The fifth chapter on "MAPPING OF MICROSTRUCTURAL STATES OF COEXISTING PHASES" discusses two aspects namely:
i) the identification of the presence of lattice strain using Convergent Beam Electron Diffraction and

ii) the one to one mapping of the parameters which uniquely describes the local microstructural states of the coexisting phases, namely δ-ferrite in a martensitic matrix.

The variation in lattice strain of α in 9Cr-1Mo steel, introduced during different thermal treatments, has been studied using CBED technique. Three parameters namely structure, chemistry and lattice strain have been identified to uniquely describe the local microstructural state of a phase. A one to one mapping of the above parameters in a martensitic matrix containing δ-ferrite has been carried out followed by a comprehensive mapping of the local microstructural state.

The sixth chapter summarises the results of the present study. Scope for future work in these areas have been identified.