CHAPTER - I

INTRODUCTION

The modern technology demands high strength durable materials. The study of the kinetics of precipitate growth will enable us to understand the stability and morphology of second phase which contributes to strengthening and hinders deterioration in service.

Available literatures[1-6] on cementite particle coarsening (Ostwald Ripening) during tempering show diverse views on rate controlling steps for the kinetics. These can be mainly divided into two groups (a) Interface controlled[1] (b) Diffusion controlled[2-6]. Various authors have designated diffusion of (i) Fe[2] (ii) Both Fe and C (coupled diffusion)[3-6] as the rate controlling step.

Plain carbon steels containing 0.68 %., 0.56 %. and 0.34 %. carbon have been isothermally tempered in the temperature range 973K to 861K for 1.5 hour to 209 hours and morphology has been studied by quantitative metallography. The effect of volume fraction on the kinetics of coarsening has been estimated and the value of the specific interfacial free energy has been calculated. A new time-temperature parameter has been developed to describe particle coarsening. Relationships among different stereological parameters have been established. Four master plots have been developed incorporating volume fraction in the relationships.

The mathematical relationship correlating parameters makes the effect of volume fraction on the parameters more vivid. Estimation of diffusivity and activation energy indicates that the process of cementite particle coarsening is a coupled diffusion controlled one. The parameters which have been estimated by fitting experimental data to the rate equation are in line with the same reported in the literature.

CHAPTER - II

LITERATURE SURVEY

2.1. Rate Equation :

The solubility of a spherical particle of radius r, noncoherent with the matrix is related to the size of the particle and is given by the Gibbs-Thomson[7] equation.

$$\ln \frac{C_\alpha(r)}{C_\alpha(\infty)} = \frac{2\sigma V_m}{RTr} \qquad \ldots\ldots (2.1)$$

where $C_\alpha(\infty)$ is the solubility of a particle of infinite radius

$C_\alpha(r)$ is the solubility of a particle of radius r

σ is the specific interfacial free energy between the particle and the matrix.

V_m is the molar volume of the particle and

RT has its usual meaning.

The principal assumptions are that the solution is ideal and that the specific interfacial free energy and the particle density are independent of particle size. There is a negligible change in the specific interfacial energy with radius of curvature where particle are greater than 1 μm in radius[8] and the dilute solution may be taken as an ideal one. The solute concentration around any particle can be derived from equation (2.1). The concentration around a smaller particle being more than that around a bigger one, there is

a concentration gradient from smaller particle to the larger one. This concentration gradient existing in a system containing particles of different sizes is the driving force for particle coarsening[9] in Ostwald ripening[9]. Solute transfer will take place from smaller to larger particles, which will cause the shrinkage of smaller particles and the growth of the larger one. Lifshitz and Slyozov[10] and Wagner[11] in their pioneering work have developed the theory of diffusion controlled particle coarsening. Martin and Doherty[12] following Greenwood[9] have developed an equivalent equation, a less rigorous solution of Ostwald ripening and then have referred to the more complete results of Lifshitz and Slyozov[10] and Wagner[11]. Assuming the instantaneous growth rate $\delta r/\delta t$ to be effectively constant, they have shown that

$$\frac{\delta r}{\delta t} = \frac{2D\sigma V_m C_\alpha(\infty)}{RTr}\left(\frac{1}{\bar{r}} - \frac{1}{r}\right) \qquad .....(2.2)$$

where $\bar{r}$ is the average radius of the precipitates. An approximate solution of equation (2.2) has been achieved by assuming that this is the same as the maximum value of $\frac{dr}{dt}$ at $r = 2\bar{r}$

$$\text{i.e. } \frac{d\bar{r}}{dt} = \left(\frac{dr}{dt}\right)_{max} = \frac{D\sigma V_m C_\alpha(\infty)}{2RT\ \bar{r}^2} \qquad .... (2.3)$$

which gives

$$\bar{r}^3 - \bar{r}_o^3 = \frac{3}{2}\ \frac{D\sigma V_m C_\alpha(\infty)\ t}{RT} = K_1 t \qquad .... (2.4)$$

where $K_1 = \frac{3}{2} \frac{D \sigma V_m C_\alpha(\infty)}{RT}$ and $\bar{r}_o$ is the average radius of the particles at the onset of coarsening. They have also shown that the rigorous analysis produces the very similar result except K_1, the numerical constant. Assuming a narrow Gaussian distribution the final rate equation for particle coarsening where steady state distribution has a sharp cut-off at $r = 1.5\ \bar{r}$, rather than 2, has been achieved, and is given as

$$\bar{r}^3 - \bar{r}_o^3 = \frac{8}{9} \frac{D \sigma V_m C_\alpha(\infty)\ t}{RT} = K(\phi)t \quad ....(2.5)$$

where $K(\phi) = \frac{8}{9} \frac{D \sigma V_m C_\alpha(\infty)}{RT}$ ....(2.6)

The equation (2.5) predicts that $\bar{r}^3$ follows a linear relationship with the time of coarsening, t, having $\bar{r}_o^3$ and $K(\phi)$ as intercept and slope respectively. It is also evident from the equation that σ and $C_\alpha(\infty)$ directly control the rate of coarsening and the diffusion coefficient D plays a very important role in Ostwald ripening.

From equation (2.2) several factors emerge :

(1) Particles having radius equal to the mean value of the system of particles ($r = \bar{r}$) are instantaneously neither growing nor dissolving.