SYNOPSIS

Most solids undergo phase transformations under elevated temperature \((T)\) and pressure \((p)\) conditions. This is due to the fact that under these conditions, an atomic arrangement, having a lower free energy than that at normal conditions, will result. The new phase develops at a finite rate only under nonequilibrium conditions because the driving force for the transformation is zero at the equilibrium conditions. A complete understanding of the properties, and behaviour of the new phase requires knowledge and information with regard to the mechanism involved in the transformation in addition to the equilibrium characterization. In principle, this information can be deduced from the studies of the kinetics of phase transformations.

At any point \((p_0, T_0)\) on the phase boundary separating the two phases, the free energies of both the phases are equal. A pressure induced transformation at \(T_0\) becomes observable at any applied pressure \(p > p_0\). The kinetics of the phase change at \(T_0\) will depend on the over-pressure \((p - p_0)\). The larger the over-pressure, the
faster is the kinetics. The effect of pressure on the
kinetics of the solid state transformations is discussed, on
the basis of classical theory of nucleation and growth, in
Chapter 1.

The present work aims at an experimental study of
the effect of pressure on the kinetics of first order phase
transformations in typical solids. Two types of phase
transformations are investigated in this study, and these
are the pressure-induced displacive type transformations,
and the crystallization of glass. The transformations
selected for the first type are the hcp(α) \rightarrow hexagonal(ω)
phase transformation in titanium, and the fcc \rightarrow bcc
transformation in ytterbium. Both these transformations
occur at room temperature under pressure, and are similar in
that the low pressure phase transforms to a more open
structure at high pressures. The transformation selected for
the second type is the crystallization, to trigonal phase,
of amorphous selenium. The studies of the kinetics of the
transformations in Ti and Yb form the major part of this
thesis and the kinetics of the crystallization of a-Se is
described in the remaining part.

The kinetics data in the present studies were
obtained under isobaric-isothermal conditions using the resistometric and the volumetric methods. For the resistometric method, it became necessary to set up a high pressure facility to obtain reproducible resistance-pressure data up to 10 GPa. An opposed anvil facility with pyrophyllite gasket and talc as the pressure transmitting medium was used to generate high pressures. A high pressure resistivity cell suitable for measuring the resistance of metallic samples by the dc four-probe method was employed.

In the opposed anvil apparatus, the specimen pressure has to be estimated by secondary methods. The maximum pressure attained, and the pressure distribution within the cell depend on the dimensions of the gasket and the talc discs. These dimensions were optimized with a view to obtaining a reasonable pressure amplification, and at the same time a uniform pressure distribution within the cell. These aspects are discussed in detail in Chapter 3.

The experiments under isobaric conditions require that the specimen pressure be raised to a desired value before the transformation can progress appreciably. Hence, a facility was developed for step-loading (sample pressurization rate 10 GPa s⁻¹) the opposed anvil set-up.
The study of the kinetics of phase transformations requires the determination of the transformed volume fraction $\zeta$, as a function of time $t$, under isobaric-isothermal conditions. The methods used to obtain the kinetics data from the measurement of the time dependence of the resistance and the volume change associated with the transformation are also described in detail in Chapter 3.

The features of the kinetics data of the $\alpha\rightarrow\omega$ transformation in Ti are described in Chapter 4. The increase in the electrical resistance of the specimen associated with the $\alpha\rightarrow\omega$ transformation has been used to obtain the fraction $\zeta$ of the $\omega$-phase as a function of time under isobaric-isothermal conditions in the pressure range 4-9 GPa at 300 K. An incubation time, decreasing exponentially with increase in over-pressure, is found to precede the transformation. In the entire pressure range, the $\zeta$-t data were found to fit the Johnson-Mehl-Avrami (JMA) equation which is used to describe the kinetics of transformations involving nucleation and growth. The rate of transformation is observed to increase with increasing pressure. The analysis of the kinetics data indicates that the activation free energy barrier of the total process
decreases rapidly with increasing pressure, and the activation volume is negative. The activation enthalpies obtained from the experiments above room temperature agree well with the activation energies obtained at 300 K. The extrapolation of the present kinetics data gives reasonable estimates of the thermodynamic equilibrium pressure, and also the transformation pressure under shock loading. The present data clearly indicate that the \( \alpha \rightarrow \omega \) transformation is nucleation controlled, and the nucleation process is strongly pressure dependent.

The features of the kinetics data of the fcc\( \rightarrow \)bcc transformation in Yb are described in Chapter 5. The decrease in the electrical resistance of the specimen associated with the transformation has been used to obtain the fraction \( \chi \) of the bcc phase as a function of time under isobaric-isothermal conditions in the pressure range 3.3 - 4.6 GPa at 300 K. The pressure dependence of the kinetics of the transformation in Yb exhibits all the features similar to those observed in the \( \alpha \rightarrow \omega \) transformation in Ti. In addition, it is seen that the kinetics data fit the JMA equation with a value of time exponent less than 1, not admissible in the JMA theory. The thermodynamic equilibrium
pressure of the fcc $\rightarrow$ bcc transformation is estimated using the pressure dependence of the kinetics of both the forward and the reverse transformations, and is found to be 2.9 GPa at 300 K.

The effect of pressure (0.28 - 0.89 GPa), on the kinetics of isothermal crystallization of amorphous selenium to trigonal form, over a temperature range 382 - 409 K is described in Chapter 6. The kinetics data, under isobaric-isothermal conditions, have been obtained by monitoring the time dependence of the volume change associated with the crystallization process. At a given pressure, the rate of crystallization is found to increase with increase in temperature. At a given temperature, it decreases with increase in pressure.

The temperature range of the present studies conforms to the region where the crystallization is governed by the activation energy ($\Delta G_d^*$) for viscous flow. The values of $\Delta G_d^*$ have been obtained from the temperature dependences of the incubation period ($t_i$) and the time ($t_{0.5}$) for the development of 50 per cent crystallized fraction, and exhibit an increasing trend with increase in pressure. The temperature dependence of the spherulitic growth rate ($g$),
at 0.28 and 0.69 GPa, has also been determined, and the values of $\Delta G^*$ obtained using these data agree reasonably well with those obtained from $t_1$ and $t_{0.5}$.

The kinetics data are found to satisfy the JMA equation with a value of the time exponent equal to 2, only up to crystallinites of 0.6. The $t_{0.5}$ and $g$ at different pressures and temperatures have been found to lie respectively on master curves with a reduced temperature (depending on the glass transition ($T_G$) and melting ($T_m$) temperatures) as a variable. This suggests that the effect of pressure on the isothermal crystallization rate correlates strongly with the increase, with pressure, of $T_G$ and $T_m$.

Appendix 1 describes a comparison of the transformed volume fractions ($\zeta$) obtained from the resistometric method using different models of electrical conductivity of a mixture of two phases. It is observed that the values of $\zeta$ differ appreciably when the magnitude of the resistance change at the transformation increases.

The effect of introducing the density change associated with a solid-solid phase transformation in the calculation of $\zeta$ by resistometry is discussed in Appendix 2.
It is observed that the neglect of the density change does not introduce large errors in $\zeta$ for most of the transformations encountered in practice.

Appendix 3 describes a time correction procedure used in the present studies to obtain the $\zeta$-t data when there is an appreciable transformation by the time the required isobaric-isothermal conditions are reached.