CHAPTER-I

General Introduction
Part-A: Solidification of Eutectic Materials

1.1 Introduction

We have come a long way from our sylvan beginnings where the only concern of our ancestors was survival. After the stage of survival came the era of consolidation when man learnt to process some of the naturally occurring materials and change these into more useful forms. The origin of materials technology can be traced to 10th century B.C. when man converted lump of clay into a hardened pot by firing which resisted deformation even when heated. By the middle of 19th century it was realized that the empirical approach is not adequate in producing materials in sufficient amount and quality and perfection to meet the increasing exacting needs of the industry. This realization led to systematic scientific studies to understand the materials. These studies led to the emergence of the disciplines of solid state physics and structural chemistry which later on transformed into material science. Chemistry and chemical processes always had a major role to play in the development and use of materials. The different areas of materials chemistry have a common goal; the generation, study and application of a material. The definitions of materials connect substance with function and utility. In a sense, materials and their use underlie every aspect of human activity.

In the earliest ages of civilization the key materials were classified, according to use at that time, into stone, bronze and iron. However, in the present time solid materials are generally grouped into three broad categories based on both their chemical constitution and their typical physical properties (Fig.1.1).

1. Metals
2. Ceramics and
3. Polymers

Metallic materials are generally good conductors of both electricity and heat and are not transparent. Polymers are the materials which we commonly call plastics. Polymeric materials are currently in widespread use. Ceramics are typically insulative to the passage of electricity and heat and can resist to degradation at high temperatures.
Fig. 1.1: Classification of Materials

Metals and alloys
Steels, aluminum, gold, bronzes, mangin
Invar superalloys boron rare earth magnetic alloys

Organic Polymers
Plastics
Glass fiber-reinforced

Ceramics and Glasses
Silicon carbide boron carbide silicon nitride

Metal-reinforced plastics
Boride-reinforced steel
Si, Ge, GaAs

Elements and Compounds
Iron, copper, tin, lead, aluminum, magnesium, zinc, cadmium, nickel
Tungsten, molybdenum, niobium, tantalum, vanadium
Platinum, palladium, cobalt, manganese, chromium, nickel
Iron, copper, lead
Tungsten, molybdenum, niobium, tantalum, vanadium
Platinum, palladium, cobalt, manganese, chromium, nickel
In addition to above three, there are some other groups of important engineering materials as mentioned below:

*Composites*,

*Semiconductors*,

*Biomaterials*,

*Advanced materials which are utilized for high technology*,

*Future materials such as smart or intelligent materials, and Nanomaterials*.

### 1.1.1 Composites

Composites are multiphase materials formed from a combination of materials which differ in composition or form, remain bonded together, and retain their identities and properties. Composites maintain an interface between components and act in concert to provide improved specific or synergistic characteristics not obtainable by any of the original components acting alone. The individual materials in a composite are generally referred to as *constituent materials*. There are two categories of constituent materials: *matrix* and *reinforcement*. The matrix material surrounds and supports the reinforcement materials by maintaining their relative positions. The reinforcements impart their special mechanical and physical properties to enhance the matrix properties. Composites are of following types:

1. *Fibrous* (composed of fibers, and usually in a matrix),
2. *Laminar* (layers of materials),
3. *Particulate* (composed of particles or flakes, usually in a matrix) and
4. *Hybrid* (combinations of any of the above).

### 1.1.2 Eutectic Materials

Amongst the composite materials, *eutectic materials* and *alloys* are very important. An increased interest has been shown in eutectic composite materials, since they offer better properties especially for the development of advanced reinforced materials for the construction of supersonic aircraft, space vehicles, high pressures tanks, racing car bodies, boat and scull hulls, bicycle frames, fishing rods etc for which both strength and specific properties are required. These properties and strength cannot be provided by the existing homogenous materials [1]. The growth of number of metallic systems is equally important for several fields. For example, refractory metal disilicide

In recent years considerable interest has developed in the field of eutectic solidification to produce materials having controlled two-phase microstructures, forming in situ composites [12-16]. Eutectic materials are of potentially importance because of their unusual anisotropic properties that result due to their aligned composite microstructures. Presently low cost high strength materials with exceptionally superior tensile properties are in demand. Such high strength composite materials can be produced by unidirectional solidification method. The in situ composite materials have better properties than the pure components. Because of experimental convenience and wider choice, organic eutectic systems having low melting points have been investigated more extensively [17-28] than metallic and ceramic systems. But still there are a lot of organic compounds which form eutectics having various interesting properties that have not been investigated so far. Also the mechanism of formation of eutectics and their properties are not well understood.

Phase equilibria, solidification behaviour and microstructures of organic eutectics have been studied with a view to understand how the properties of composite materials are better than the individual components. From the studies, it is also possible to have tailor made materials for specific purpose. In this section existing literature on phase equilibria, solidification process and microstructures of organic eutectics have been reviewed.
1.2 Phase Equilibria in Condensed Binary Systems

The understanding of the phase diagrams provide valuable informations about melting, casting, crystallization and other phenomenon. According to Gibbs phase rule [29] we have

\[ F = C - P + 2 \]

Where \( F \) is degree of freedom, \( C \) is numbers of components and \( P \) is number of phases. However, in the binary condensed system (solid-liquid equilibria) one degree of freedom i.e. pressure remains constant, so the Gibbs Phase rule becomes

\[ F = C - P + 1 \]

Different types of phase diagram showing the formation of eutectics including condensed systems have been discussed below.

1.2.1 Simple Binary Eutectic Phase Diagrams

A typical phase diagram showing the formation of simple eutectic is given in Fig. 1.2. \( T_A \) and \( T_B \) represent the melting points of pure component A and B respectively. Point E on the diagram represents the eutectic point and it has the minimum melting point than any other mixture in the series. Composition at point E is the eutectic composition and the temperature corresponding to E is the eutectic temperature. At point E, two solid phases and one liquid phase exist in equilibrium. For a condensed system, one of the variables pressure becomes constant, so the phase rule becomes \( F = C - P + 1 \).

According to phase rule (for condensed system), \( F = C - P + 1 = 2 - 3 + 1 = 0 \), the degree of freedom is zero and the system is invariant at the eutectic point E.

In Fig. 1.2, along the line \( T_A E \), solid A separates from the melt. The points on this line indicate the beginning of freezing and are the liquidus curve. Along this line solid-liquid equilibrium exists and according to the phase rule \( F = C - P + 1, F = 1 \) and hence the system is univariant. Similarly the line \( T_B E \) is the other liquidus curve and the points on this line indicate the beginning of freezing and the solid of B separates from the melt. The system has thus two liquidus curves, viz; \( T_A E \) and \( T_B E \). The end of freezing or the beginning of melting of different composition of the systems is given by the line PEQ. The temperature along line PEQ is also known as thaw-melting temperature. In recent years various systems showing the formation of eutectics have been studied in detail [1, 3, 28, 30-32].
1.2.2 Phase Diagram Showing Congruent Melting Point

A compound which melts sharply at a constant temperature into a liquid of the same composition as the solid is said to possess a congruent melting point. A typical phase diagram showing congruent melting point is shown in Fig. 1.3. A and B represent the melting points of pure components A and B respectively. The components of a binary system may react to form a solid compound which exists in equilibrium with liquid over a range of composition. The formation of compound usually leads to a maximum in the temperature composition diagram as indicated in Fig. 1.3. The melting point of the compound may be above, below or between those of the two components. The figure shows the eutectic point E₁ and E₂. At E₁, the solid A and solid AB separate, whereas at point E₂, the solid B and AB separate. At the eutectic points, the values of degree of freedoms are zero and the systems are invariant. The phase diagram can best be understood by considering it as a combination of two simple eutectic type phase diagrams placed side by side. At the congruent melting point C, the two component system has become one component system because both solid and liquid phases contain only the compound AB. According to phase rule since

\[ F = C - P + 1 = 1 - 2 + 1 = 0 \]

therefore, the system becomes invariant at the congruent melting point. These type of phase diagrams have also been studied extensively [21, 25, 27].

1.2.3 Phase Diagram Showing Incongruent Melting Point (Peritectic type)

Sometimes the compound formed between two components is so unstable that it decomposes completely at a temperature below its melting point. Thus the solid can not be in equilibrium with a liquid having the same composition as itself; in other words it does not have true melting point. The peritectic type phase diagram is shown in Fig. 1.4 in which it is supposed that 1: 2 compound AB₂ is formed. At a point P, which is incongruent (or peritectic) point below the hypothetical melting point, the compound AB₂ dissociates completely into its constituents. Along PE the solid AB₂ separates, but along PB, the solid B separates. The point E is the eutectic point. If the liquid, such as that represented by ɛ, is cooled, the first solid to separate will be B, and when the temperature reaches P, the compound AB₂ commences to form. Since at this point there are two solid phases and one liquid in equilibrium, the degree of freedom will be zero.
Fig. 1.2: Phase Diagram of a Simple Eutectic System.

Fig. 1.3: Phase Diagram of a Congruent Melting System.
and the system will be invariant. Kohler et al.[33] and Dobler et al.[34] have studied Cu-Sn system. Yasuda et al.[35] has studied acetamide – salicylic acid system. Fe-C, Fe-Ni, Cu-Zn, Ti-Al systems have also been reported in the category of peritectic type phase diagram [36, 37].

1.2.4 Monotectic Type Phase Diagrams

Monotectic is another important class of eutectic systems in which one liquid phase decomposes with decreasing temperature into a solid phase and a new liquid phase, i.e. it represents a three phase reaction:

\[ L_1 = S_1 + L_2 \]

Over a certain composition range, the two liquids are mutually immiscible and they constitute individual phases. A typical monotectic phase diagram is shown in Fig. 1.5, where \( T_A \) and \( T_B \) are the melting points of pure components A and B respectively and E is the eutectic point. The boundary of the \( (L_1 + L_2) \) field is the limit of liquid immiscibility. The point at the top of this area is known as critical point where the two phases are indistinguishable. The temperature corresponding to this point is known as consolute temperature \( (T_C) \) above which there exist only one liquid. At temperature \( T_M \) corresponding to the monotectic point M, the phases in equilibrium are \( L_1, L_2 \) and \( S_1 \). Rai et al. [38 - 43] have extensively studied the monotrectic type phase diagrams.

1.3 Thermodynamics of eutectics

Thermodynamics is an important tool to understand the solid-liquid equilibrium and eutectic solidification from the binary melt. As per thermodynamics consideration, eutectic may be defined as a heterogeneous system [44] made up of two or more solidus phases which are in equilibrium with a single liquidus phase. Eutectic is the lowest liquidus temperature in the binary solidus – liquidus phase. Activity coefficient of eutectic phases in their mixtures calculated from thermodynamic analysis of solidus – liquidus phase equilibrium data may be used in determining excess thermodynamic functions such as \( G^E, H^E, S^E \). With the help of these excess thermodynamics functions the molecular interactions and deviations from ideal behaviour of the eutectic mixtures can be explained.
Fig. 1.4: Phase Diagram of Peritectic Type System.

Fig. 1.5: Phase Diagram of Monotectic Type System.
The thermodynamics of phase diagram has been well discussed by Rastogi [45]. According to him the solidus - liquidus phase boundary can be predicted with the help of phase equilibrium relation [Eq. 1.1] as mentioned below

\[
-\ln x_i' \gamma_i' = \frac{\Delta_f h_i^0}{R} \left[ \frac{1}{T} - \frac{1}{T_i^0} \right] + \frac{\Delta_f C_p_i}{R} \left[ \ln \frac{T_i^0}{T} + \frac{1 - T_i^0}{T} \right] \quad \ldots (1.1)
\]

where \( x_i', \gamma_i' \) are the mole fraction and activity coefficient of the component \( i \) in the liquid phase; \( \Delta_f h_i^0 \), the heat of fusion of the component \( i \) at the melting point \( T_i^0 \), \( R \), the gas constant; \( T_i^0 \), the melting point of the mixture; and \( \Delta_f C_p_i \), the difference in the molar heat capacities at constant pressure of the component \( i \) between the liquid and the solid states. For ideal mixtures, the value of activity coefficient is taken as unity.

It is possible to predict the eutectic composition and temperature from Eq.(1.1) for the two components of the mixture, when it shows ideal behaviour (i.e. \( \gamma = 1 \)). If the subscript ‘\( e \)’ denotes the corresponding quantities at the eutectic point, the following relations could be written for ideal mixtures at the eutectic point for the two components;

\[
-\ln x_1'^e = \frac{\Delta_f h_1^0}{R} \left[ \frac{1}{T_e} - \frac{1}{T_1^0} \right] \quad \ldots (1.2)
\]

and

\[
-\ln x_2'^e = \frac{\Delta_f h_2^0}{R} \left[ \frac{1}{T_e} - \frac{1}{T_2^0} \right] \quad \ldots (1.3)
\]

Where \( T_1^0 \) and \( T_2^0 \) are the melting temperatures of the pure components 1 and 2 respectively.

The thermodynamics of the phase boundary (Fig. 1.3) representing the liquidus curve \( E_1CE_2 \), joining the two eutectic points \( E_1 \) and \( E_2 \) in the phase diagram of the system involving the formation of the congruent compound has also been explained by Rastogi [45]. The phase boundary could be predicted by Eq. 1.4.

\[
\frac{\Delta H_f}{R} \left[ \frac{1}{T_e} - \frac{1}{T_c} \right] = -\ln \left[ x_1'^e \right] \left[ x_1'^e \right] \ln \left[ x_1'^e \right] \left[ x_1'^e \right] \ldots (1.4)
\]

Where \( x_1'^e \) and \( x_2'^e \) are the mole fractions of the components 1 and 2 respectively. \( T_c \) is the congruent melting temperature and the quantities with the
subscript \( l \) denote the mole fractions corresponding to that which could exist in the molten addition compound, \( m \) and \( n \) are integers of the compound \( A_mB_n \).

**1.3.1 Excess Thermodynamic Functions**

For having a quantitative idea about the molecular interactions in the eutectic melts, the excess thermodynamic functions such as excess Gibbs free energy \( (G^E) \), excess enthalpy of mixing \( (H^E) \) and excess entropy of mixing \( (S^E) \) of the eutectic could be calculated with the help of Eqs. (1.5), (1.6) and (1.7).

\[
G^E = RT \left( X_1 \ln \gamma_1 + X_2 \ln \gamma_2 \right) \quad \ldots \quad (1.5)
\]

\[
S^E = - R \left[ X_1 \ln \gamma_1 + X_2 \ln \gamma_2 + X_1 T \frac{\partial \ln \gamma_1}{\partial T} + X_2 T \frac{\partial \ln \gamma_2}{\partial T} \right] \quad \ldots \quad (1.6)
\]

\[
H^E = - RT^2 \left[ X_1 \frac{\partial \ln \gamma_1}{\partial T} + X_2 \frac{\partial \ln \gamma_2}{\partial T} \right] \quad \ldots \quad (1.7)
\]

Where \( T \) is the melting temperature, \( \gamma_1 \) and \( \gamma_2 \) are the activity coefficients of components 1 and 2 respectively.

The activity coefficient, \( \gamma_i \) of the component \( i \) is given by Eq. (1.8)

\[
- \ln \gamma_i X_i = \frac{- \Delta_f H_i}{R} \left[ \frac{1}{T^e} - \frac{1}{T^0_i} \right] \quad \ldots \quad (1.8)
\]

where \( X_i, \Delta_f H_i, T^e \) and \( T^0_i \) are the mole fraction, heat of fusion, eutectic temperature and melting temperature of the component \( i \) (\( i = 1, 2 \)) respectively. Further, on differentiating Eq. (1.8) one obtains

\[
\frac{1}{X_i} \frac{\partial X_i}{\partial T} - \frac{\partial \ln \gamma_i}{\partial T} = - \frac{(\Delta_f H_i)}{RT^2}
\]

which on rearranging may be written as

\[
X_i \frac{\partial \ln \gamma_i}{\partial T} = X_i \frac{(\Delta_f H_i)}{RT^2} - \frac{\partial X_i}{\partial T} \quad \ldots \quad (1.9)
\]

Since the liquidus curves in the phase diagrams are reasonably straight in the region of eutectic composition, the value of \( \frac{\partial X_i}{\partial T} \) appearing in Eq.(1.9) can be calculated accurately by using Eq.(1.10).

\[
X_i = \alpha + \beta T \quad \ldots \quad (1.10)
\]
Where $\alpha$ and $\beta$ are constants and the value of $\beta$ is equal to \(\frac{\partial X_i}{\partial T}\). Thus, by knowing the value of \(\frac{\partial X_i}{\partial T}\), the values of \(\frac{\partial \ln \gamma_i}{\partial T}\) \((i = 1, 2)\) can be determined with the help of Eq.(1.9).

The activity coefficient values of the two components in different eutectic systems have been calculated by various researchers [25, 30]. These values are given in Table 1.1. The calculated values of excess thermodynamic functions viz; excess Gibbs free energy \((G^E)\), excess enthalpy of mixing \((H^E)\) and excess entropy of mixing \((S^E)\) of various eutectic systems [25,30, 43] are also given in Table 1.2.

1.4 Thermochemistry of Eutectics

Useful information about the microstructures of eutectics may be obtained from the heat of fusion values of the eutectics. They are also important in describing the nature of interaction between the two components in the eutectics. If \(H'_e\) and \(H'_s\) are the heat contents of the eutectic mixture in the liquid and solid phases respectively, then the heat of fusion of the eutectic, \((\Delta_f H)_e\) is given[13] by

\[
(\Delta_f H)_e = H'_e - H'_s
\]

where

\[
H'_e = (X_1)_e H'_1 + (X_2)_e H'_2 + H'_m
\]

and

\[
H'_s = (X_1)_e H'_1 + (X_2)_e H'_2 + H'_m
\]

\((X_1)_e\) and \((X_2)_e\) are the mole fractions of the two components of the eutectic, \(H'_1\) and \(H'_2\), the heat contents of the pure components in the liquid phase while \(H'_s\) and \(H'_s\) are their heat contents in the solid phase respectively. \(H'_m\) and \(H'_m\) are the heats of mixing in the liquid and solid phases respectively. The value of \(H'_m\) is nearly equal to zero. Further, If the eutectic is assumed to be simply a mechanical mixture of the two pure components then the heat of fusion value of the eutectic is given by

\[
(\Delta_f H)_e = (X_1)_e[H'_1 - H'_s] + (X_2)_e[H'_2 - H'_s] + H'_m
\]

or simply as

9
Table 1.1: Activity coefficient values of various binary eutectic systems

<table>
<thead>
<tr>
<th>Systems</th>
<th>Iny₁</th>
<th>Iny₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanillin – p-Anisidine [25]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E₁ (eutectic)</td>
<td>0.1934</td>
<td>-0.7523</td>
</tr>
<tr>
<td>E₂ (eutectic)</td>
<td>-1.1086</td>
<td>0.1142</td>
</tr>
<tr>
<td>Benzil – Azobenzene [30]</td>
<td>1.0090</td>
<td>-0.6560</td>
</tr>
<tr>
<td>Acenaphthene – Benzil [30]</td>
<td>0.2436</td>
<td>-0.9542</td>
</tr>
<tr>
<td>Naphthalene – Phenanthrene [30]</td>
<td>-0.8942</td>
<td>-0.0005</td>
</tr>
<tr>
<td>Naphthalene – Acenaphthene [30]</td>
<td>-0.0367</td>
<td>-0.5127</td>
</tr>
<tr>
<td>Benzoic acid – Benzil [30]</td>
<td>-0.0156</td>
<td>0.1204</td>
</tr>
</tbody>
</table>

Table 1.2: Excess thermodynamic functions of different binary eutectic systems

<table>
<thead>
<tr>
<th>Systems</th>
<th>G² (J.mol⁻¹)</th>
<th>H² (kJ.mol⁻¹)</th>
<th>S² (J.mol⁻¹K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanillin – p-Anisidine [25]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E₁ (eutectic)</td>
<td>-2.56</td>
<td>-10.30</td>
<td>-29.04</td>
</tr>
<tr>
<td>E₂ (eutectic)</td>
<td>-3.61</td>
<td>-9.94</td>
<td>-29.50</td>
</tr>
<tr>
<td>Carbotetralbromide – Succinonitrile [43]</td>
<td>376.8</td>
<td>3.9</td>
<td>11.0</td>
</tr>
<tr>
<td>Acenaphthene – Benzil [30]</td>
<td>-21.05</td>
<td>-</td>
<td>6.25</td>
</tr>
<tr>
<td>Naphthalene – Acenaphthene [30]</td>
<td>-6.12</td>
<td>-</td>
<td>1.88</td>
</tr>
<tr>
<td>Benzoic acid – Benzil [30]</td>
<td>-4.44</td>
<td>-</td>
<td>1.28</td>
</tr>
<tr>
<td>Benzoic acid – Phenylacetic acid [30]</td>
<td>-14.4</td>
<td>3.26</td>
<td>4.43</td>
</tr>
</tbody>
</table>
\[
\left( \Delta_f H \right)_e = (X_1)_e \Delta_f H_1 + (X_2)_e \Delta_f H_2 + H'_m + H_{ii} \quad \ldots (1.15)
\]

Where \( \Delta_f H_1 \) and \( \Delta_f H_2 \) are the heats of fusion of the two components 1 and 2 respectively. Approximately \([46]\), the value of heat of fusion, at any temperature, may be represented by Eq. (1.16).

\[
(\Delta_f H)_T = (\Delta_f H)_{T_m} - (C_p^L - C_p^S) T_m - T \quad \ldots (1.16)
\]

Where \((\Delta_f H)_T\) and \((\Delta_f H)_{T_m}\) are the heats of fusion at temperature \(T\) and melting point \(T_m\) respectively, \(C_p^L\) and \(C_p^S\) are the specific heats in the liquid and solid phases respectively. During the melting of eutectics \([46]\), beside heat of mixing, the solid-liquid interfacial tension \(\sigma_{LS}\) and some other parameters \(\varepsilon\) may also contribute to the heat of fusion. If this is so, the heat of fusion may be represented as

\[
(\Delta_f H)_e = (X_1)_e \Delta_f H_1 + (X_2)_e \Delta_f H_2 + H'_m + \sigma_{LS} A + \varepsilon \quad \ldots (1.17)
\]

where \(H'_m + \sigma_{LS} A + \varepsilon\) is the total interaction energy which arises due to non ideal nature of the eutectic mixture and \(A\) is the surface area.

If eutectics are considered as a simple mixture of the two components and there exists neither heat of mixing, nor any type of association in the melt, the heat of fusion value of the eutectic is then given by the following Eq. (1.18).

\[
(\Delta_f H)_e = (X_1)_e \Delta_f H_1 + (X_2)_e \Delta_f H_2 \quad \ldots (1.18)
\]

But as a eutectic melts, the possibility of generation of heat of mixing and association may result in the violation of the mixture law Eq. (1.18). The heat of fusion values determined experimentally then do not tally with the calculated values obtained from the mixture law. This suggests that the eutectics are not simply a mechanical mixture of the two components but there exists some type of weak interaction. The heats of fusion values of some systems \([21,27]\) are given in Table 1.3.

Rastogi and coworkers \([47]\) have derived an empirical equation (Eq. 1.19) to calculate the heat of fusion values of various organic eutectics

\[
(\Delta_f H)_e = \frac{K (T_e)^2}{X_e T_e + (1-X_e) T_{B_1}} \quad \ldots (1.19)
\]

where \(K\) is the constant whose value is equal to 0.0175 ,\(T_e\) is the eutectic temperature, \(X_e\) , the eutectic composition with respect to the first component ; and
Table 1.3: Heat of fusion values of various binary eutectic systems

<table>
<thead>
<tr>
<th>Systems</th>
<th>Heat of fusion</th>
<th>Heat of fusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta fH$</td>
<td>$\Delta fH$</td>
</tr>
<tr>
<td></td>
<td>(Experimental)</td>
<td>(Calculated)</td>
</tr>
<tr>
<td></td>
<td>kJ mol$^{-1}$</td>
<td>kJ mol$^{-1}$</td>
</tr>
<tr>
<td>Pyrene – $p$-Benzoquinone [21]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_1$ (eutectic)</td>
<td>10.1</td>
<td>18.1</td>
</tr>
<tr>
<td>$E_2$ (eutectic)</td>
<td>18.1</td>
<td>19.1</td>
</tr>
<tr>
<td>1:1 CTC</td>
<td>18.5</td>
<td>18.5</td>
</tr>
<tr>
<td>Pyrene – $m$-Dinitrobenzene [21]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_1$ (eutectic)</td>
<td>10.6</td>
<td>19.5</td>
</tr>
<tr>
<td>$E_2$ (eutectic)</td>
<td>15.0</td>
<td>25.2</td>
</tr>
<tr>
<td>1:1 CTC</td>
<td>14.6</td>
<td>20.9</td>
</tr>
<tr>
<td>Pyrene – $m$-Nitrobenzoic acid [21]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_1$ (eutectic)</td>
<td>15.3</td>
<td>16.9</td>
</tr>
<tr>
<td>$E_2$ (eutectic)</td>
<td>14.2</td>
<td>16.0</td>
</tr>
<tr>
<td>1:1 CTC</td>
<td>15.7</td>
<td>16.4</td>
</tr>
<tr>
<td>Phenothiazine – $m$-Nitrobenzoic acid [27]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_1$ (eutectic)</td>
<td>13.4</td>
<td>16.1</td>
</tr>
<tr>
<td>$E_2$ (eutectic)</td>
<td>15.2</td>
<td>18.4</td>
</tr>
<tr>
<td>1:1 CTC</td>
<td>14.3</td>
<td>19.5</td>
</tr>
<tr>
<td>Phenothiazine – $m$-Dinitrobenzene [27]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_1$ (eutectic)</td>
<td>15.3</td>
<td>27.1</td>
</tr>
<tr>
<td>$E_2$ (eutectic)</td>
<td>16.1</td>
<td>25.5</td>
</tr>
<tr>
<td>1:1 CTC</td>
<td>19.4</td>
<td>26.3</td>
</tr>
</tbody>
</table>
11

1.4.1 Entropy of Fusion ($\Delta_f S$) of Eutectics

The entropies of fusion of eutectics and pure components can be calculated from their enthalpies of fusion by using the following relationship:

$$\left(\Delta_f S\right) = \frac{\left(\Delta_f H\right)}{T} \quad \ldots (1.20)$$

where $T$ is the melting temperature. Jackson [48], on the basis of entropy of fusion of the two components, predicted that the growth of the eutectic melt depends upon the roughness parameter factor $\alpha$, which is defined by Eq.(1.21).

$$\alpha = \xi \frac{\left(\Delta_f S\right)}{R} = \xi \frac{\left(\Delta_f H\right)}{RT} \quad \ldots (1.21)$$

where $\xi$ is a geometrical coefficient often called as crystallographic factor depending upon the geometry of the molecules. The value of $\xi$ lies between 0.5 and 1.0. $\Delta_f H$ is heat of fusion and $R$ is gas constant.

Singh et al. [13] reported that the entropy of fusion $(\Delta S)_i^e$ of any component $i$, at the eutectic temperature can be expressed by

$$\left(\Delta S\right)_i^e = \left(\Delta S\right)_i^e + \left(\Delta S\right)_i^m \quad \ldots (1.22)$$

where $(\Delta S)_i^e$ and $(\Delta S)_i^m$ are the entropy of fusion at the eutectic temperature and the melting point respectively of the pure component $i$, and $(\Delta S)_i^m$ is the contribution to the entropy change on mixing the component $i$ ($= 1, 2$). Since $(\Delta S)_i^m$ is positive so one can write

$$(\Delta S)_i^e > (\Delta S)_i^m \quad \ldots (1.23)$$

Further, since the heat of fusion of the component $i$ remains unchanged

$$T_e < T_i^0$$

and therefore, the melting point of a particular component is lowered when the second component is added. The lowering of melting point depends on the randomness. In a binary eutectic, the components are miscible in the liquid phase, but immiscible in the
solid phase, and hence the entropy of mixing is positive. At the eutectic point, one can write [13]

\[(AS)_e^m = (AS)_1^m + (X_1)_e \cdot (AS)_1^m + (X_2)_e \cdot (AS)_2^m \] 3.14

where the superscript \(m\) denotes the eutectic mixture, \((X_1)_e\) and \((X_2)_e\) are the mole fractions of components 1 and 2 at the eutectic point and \(\Delta S_0^m\) is given by

\[\Delta S_0^m = (AS)_1^o + (AS)_2^o \] 3.15

1.5 Nature of Interaction in Eutectic Mixtures

Therefore studies of some physical parameters such as viscosity, computational simulation and flexural strength measurements of the eutectic mixtures could also give an idea about the non-ideal behaviour of the eutectics. Since eutectic materials are widely used in various technologies, their physical studies are very important [18, 49]. The detailed mechanism of eutectic nucleation and solidification can be considerably judged by providing a physical insight in the experimental results in both solid and liquid state.

1.5.1 Viscosity Measurements

When the eutectics are in molten state, their viscosities when compared to those of components, give some informations regarding the nature of interactions between the components in the eutectic mixtures. Many workers [18, 49, 50] have studied the viscosities of Pb-Sn, Sb-Pb and Pb-Fe eutectic alloys in the molten state. Viscosities of a large number of organic eutectic mixtures in molten state have also been studied [1, 51, 52] and the energy of activation for viscous flow were calculated for some systems [52] (Table 1.4). The values indicate the existence of some sort of association between the components in the molten eutectic mixtures. The viscosity data of all these systems obey the following relationship

\[\eta = \eta_0 e^{(-E_{vis}/RT)} \] 3.16

where \(\eta_0\) is a constant and \(E_{vis}\) is activation energy for the viscous flow.

1.5.2 Computational Studies

By using different computer programs, one can compute the energy of a particular molecular structure, perform geometry optimizations and also compute the vibrational frequencies of molecules resulting from interatomic motion within the molecules. The nature of interaction between the components in the eutectic mixture of
Vanillin - p- Anisidine system [25,53] have been obtained by computational studies with the help of *ab initio* (GAMESS) program [54]. The ground state geometry of the product (shown in Fig. 1.6) was optimized by density functional theory method using B3LYP function. The mechanism of the reaction has been studied with the help of a potential energy profile (Fig. 1.7).

### 1.5.3 Flexural Strength Measurements

A physical understanding of mechanical properties of composites materials is important for the improvement of the properties of the final products by controlling the growth rates from the melt. Composites materials exhibit unique strength properties that cannot be provided by the existing homogenous materials [1, 17, 55-59]. The mechanical properties of the material can be estimated with the help of following strength relationship.

\[
\sigma = \frac{F_f}{\pi R^2} \cdot \frac{L}{3} 
\]

where \(F_f\) is load at fracture, \(L\) is length of the cylindrical sample and \(R\) is radius of the sample.

The mechanical properties of various eutectic systems viz. benzoic acid- benzil, benzoic acid – phenyl acetic acid, vanillin-naphthalene, naphthalene- phenyl acetic acid, Pb-Sn has been studied various researchers [1,52]. The modulus of rupture values of these systems are given in Table 1.5.

### 1.6 Solidification

Solidification is the transformation of solid phase from its melt. It is important to understand the mechanism of solidification to control the various properties of materials that can be used in single crystal growth for semiconductors and directionally solidified composite materials [60]. Solidification is a two step process:

1. **Nucleation**
2. **Crystal growth**

#### 1.6.1 Nucleation

Nucleation involves formation of small solid particles surrounded by liquid and separated from the liquid by a definite boundary. At the temperature at which a pure solid exists in equilibrium with a pure liquid, a cluster of atoms or molecules come together to form an embryo or potential nucleus in liquid and consequently a surface is
Table 1.4: Activation energy values for the viscous flow of various binary eutectic systems

<table>
<thead>
<tr>
<th>Systems [52]</th>
<th>Activation energy $E_{vis} \times 10^2$ (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene- Phenylacetic acid eutectic</td>
<td>2.40</td>
</tr>
<tr>
<td>Naphthalene- Vanillin eutectic</td>
<td>2.39</td>
</tr>
<tr>
<td>Benzoic acid- Benzil eutectic</td>
<td>2.95</td>
</tr>
<tr>
<td>Benzoic acid – Phenylacetic acid eutectic</td>
<td>2.70</td>
</tr>
</tbody>
</table>

Table 1.5: Values of modulus of rupture for various binary eutectic systems

<table>
<thead>
<tr>
<th>Systems [52]</th>
<th>Modulus of Rupture (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anisotropic Growth (MPa)</td>
</tr>
<tr>
<td>---------------------------------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>Naphthalene- Phenylacetic acid eutectic</td>
<td>5.47</td>
</tr>
<tr>
<td>Benzoic acid- Benzil eutectic</td>
<td>6.55</td>
</tr>
<tr>
<td>Benzoic acid – Phenylacetic acid eutectic</td>
<td>5.90</td>
</tr>
</tbody>
</table>
Fig. 1.6: Optimized geometry of product NHM obtained by the DFT method.

Fig. 1.7: Potential energy profile of the product NHM with change in the C=H bond length.
formed. As soon as the embryo attains the critical size [61, 62] or the total free energy is decreased, they constitute nuclei to start the crystallization.

Nucleation is a thermally activated process. This means that nucleation threshold energy must be overcome to build critical and post critical nuclei. The activation energy arises from the solid-liquid interfacial energy. Therefore, the interfacial energy between a solid and a liquid is an important parameter for the description of nucleation kinetics.

In general, nucleation depends on the physical conditions of the system such as undercooling, temperature and presence of impurities etc. Nucleation process can be classified into two categories [63]

(i) homogeneous nucleation
(ii) heterogeneous nucleation

Homogeneous nucleation occurs within a structurally pure phase [64] while heterogeneous nucleation is the nucleation on structural impurities. [64]

1.6.1.1 Homogeneous Nucleation

When nucleation in melt occurs without the influence of foreign materials or factors, the process is known as homogeneous nucleation. This type of nucleation requires a large driving force [63] because of the greater contribution of surface energy to the total free energy of very small particles. This is the reason for the rare occurrence of homogeneous nucleation.

The critical size concept is the basis of almost all theories explaining the homogeneous nucleation. It is observed that due to statistical accident a number of atoms can come together to form a rudimentary nucleus. If the size of this nucleus remains below the critical size, then the particles redissolve but if the size exceeds the critical size, the particles grow into nucleus which is accompanied with reduction in free energy making the process thermodynamically feasible.

1.6.1.1.1 Thermodynamics of Homogeneous Nucleation

An undercooled liquid is considered to contain a distribution of crystal-like clusters which are constantly changing in size by monoatomic addition or dissolution. By minimizing the net free energy change due to cluster formation, the equilibrium number of clusters n containing i atoms is found to be

\[ n_i = n \exp \left( -\Delta G_i / k_B T \right) \] 

... (1.28)
where $\Delta G_i$ is the minimum standard free energy of formation of a cluster. Assuming that Gibbs theory of surfaces applies to the spherical clusters and that the interface tension $\sigma_{SL}$ on cluster formation is independent of cluster radius $r$, the Gibbs free energy $\Delta G_i$ is given by

$$
\Delta G_i = 4\pi r^2 \sigma_{SL} + \frac{4\pi r^3}{3} \Delta G_v \quad \ldots (1.29)
$$

where $\Delta G_v$ corresponds to Gibbs free energy difference between liquid and crystal per unit volume. Thus for a cluster containing $i$ atoms $\Delta G_i$ as a function of crystal size goes through a maximum. The coordinates of the maximum ($\Delta G_i = \Delta G_i^*$ and $i = i^*$) are found by the condition $d(\Delta G_i) / di = 0$ to be

$$
\Delta G_i^* = \frac{16\pi}{3} \frac{\sigma_{SL}^3}{\Delta G_v^2} \quad \ldots (1.30)
$$

and

$$
i^* = -\frac{32\pi}{3\nu} \left( \frac{\sigma_{SL}}{\Delta G_v} \right)^3 \quad \ldots (1.31)
$$

with $\nu$ corresponding to the atomic volume. A cluster containing just $i^*$ atoms is called a nucleus with "critical" radius

$$
r^* = -2\frac{\sigma_{SL}}{\Delta G_v} \quad \ldots (1.32)
$$

A cluster smaller than the critical nucleus will, on the average, completely dissolve, whereas a cluster larger than $r^*$ will grow, and will become a domain of the new phase. Thus when the largest size fraction of the cluster size distribution develops a size equal to the critical size $n^* = n \exp (-\Delta G_i^* / k_B T)$, the nucleation occurs.

### 1.6.1.1.2 Nucleation Rate

The homogeneous nucleation rate per unit volume, $J_v$ is simply the collision frequency of single atoms with clusters of critical size resulting in a nucleation rate.

$$
J_v = n_v u_0 \exp \left( -\frac{\Delta G_v}{k_B T} \right) \exp \left( -\frac{16\pi \sigma_{SL}^3}{3 \Delta G_v^2 k_B T} \right) \quad \ldots (1.33)
$$

or

$$
J_v = \frac{\Omega_n}{\eta} \exp \left( -\frac{16\pi \sigma_{SL}^3}{3 \Delta G_v^2 k_B T} \right) \quad \ldots (1.34)
$$

where $n_v$ is the number of atoms per unit volume, $u_0$ a frequency factor of the order of $10^{13}$ Hz and $\Delta G_A$ the activation energy for atom addition to a cluster.
\[ \Omega_v, \text{ the prefactor term, is given as} \]
\[ \Omega_v = n_v \nu_b \exp \left( - \frac{\Delta G_A}{k_B T} \right) \]  \hspace{1cm} \ldots (1.35)

### 1.6.1.2 Heterogeneous Nucleation

The nucleation process which takes place on foreign surfaces or cavities is called *heterogeneous* nucleation. Heterogeneous nucleation involves the formation of a nucleus on an energetically favourable catalytic surface. During the process [13], a smaller amount of surface energy is needed since the nucleus formation occurs on the surface of the nucleating agent. The heterogeneous nucleation, during solidification from the liquid, proceeds as a growth of a second phase on the surface of the first one. This nucleation is a one way phenomenon [65]. This means that if the \( \alpha \)-phase promotes the \( \beta \)-phase to nucleate, the opposite phenomenon is not possible. The \( \alpha \)-phase is called as the leading phase while the \( \beta \)-phase is the wetting phase.

The undercooling of the \( \alpha \)-phase interface differs from that of the \( \beta \)-phase interface during solidification i.e.
\[ \Delta T^\alpha \neq \Delta T^\beta \]

Hence the temperature at both interfaces is not identical.
\[ T^\alpha_F \neq T^\beta_F \]

The fulfillment of the above conditions might be the reason that the wetting phase \( \beta \) is overtaken by the leading phase \( \alpha \).

The interaction between the nucleus and the catalytic site is taken into account in the nucleation rate expression through a variation of the interfacial surface tension \( \sigma_{SL} \) between the crystalline nucleus and the catalytic substrate. The contact angle \( \theta \), between the nucleus and substrate may vary from 180° (non wetting) to 0° (perfect wetting). Thus the interfacial term is modified by multiplying \( \sigma_{SL}^3 \) with the wetting function \( f(\theta) \).

For a spherical cap nucleus on a planar substrate the value of \( f(\theta) \) is given by
\[ f(\theta) = 0.25 (2 - 3 \cos \theta + \cos^3 \theta) \]  \hspace{1cm} \ldots (1.36)

The nucleation frequency or rate for heterogeneous nucleation is given by an expression
\[ J_a = \Omega_a \exp \left( - \frac{\Delta G^* f(\theta)}{k_B T} \right) \]  \hspace{1cm} \ldots (1.37)
\( \Omega_n \) is the prefactor term and can vary considerably. The nucleation rate is a relatively steep function of temperature whose magnitude is determined principally by the exponential term (involving \( \Delta G^* \)) and by the prefactor term. As such, the most important parameters for the nucleation rate are \( \Delta G_v \) and \( \sigma_{SL} \).

With increasing undercooling, the transition from heterogeneous nucleation to homogeneous nucleation is possible. By comparing the ratio of heterogeneous and homogeneous nucleation rates one can write

\[
\frac{J_H}{J_V} = \frac{\Omega_H}{\Omega_V} \exp \left[ \frac{\Delta G^*}{k_B T} (1 - f(\theta)) \right]
\]  

This condition can be examined as a function of contact angle \( \theta \) [64]. Since a sensible nucleation starts generally at a limiting value of \( \Delta G^* = 60 \, k_B T \), the ratio of heterogeneous to homogeneous nucleation can be obtained (Fig. 1.8).

1.6.1.3 Undercooling and Nucleation

The crystal growth from the pure melt depends upon two factors, namely volume and supercooling. Thus the limiting undercooling determines the energy barrier to homogeneous nucleation. The literature shows that the characteristics of nucleation from the melt are such that the following symmetry relations should be constant [57, 59].

\[
\xi = \frac{T_C}{T_m} \quad \frac{\Delta T}{T_m} = \frac{T_m - T_c}{T_m}
\]  

where \( T_m, T_C \) and \( \Delta T \) respectively are the liquidus, spontaneous crystallization and undercooling temperatures. \( \xi \) is a crystallographic factor which represents the fraction of the total number of neighbours situated in the newly formed layer. It is usually less than but almost equal to one.

In order to describe and predict the transformation products, knowledge of the thermodynamic properties of the undercooled liquid is most essential. Enthalpy, entropy and Gibbs free energy differences are important thermodynamic parameters between undercooled liquid and crystal. The differences in entropy \( \Delta S \), enthalpy \( \Delta H \) and free energy \( \Delta G = \Delta H - T \Delta S \) between undercooled liquid and crystalline solid are sufficient for explaining the thermodynamics of undercooled melt.
Fig 1.8: Relative magnitude of heterogeneous surface to homogeneous volume nucleation in 20μm dia. Droplet as function of contact angle $\theta$. 
1.6.2 Crystal Growth

Crystal growth may be defined as a process in which movement of solid-liquid interface occurs in a direction normal to the surface. The fundamental idea about the crystal growth has been given by Tamman [66]. The crystal growth from a pure melt depends upon two factors:

1. **Volume**
2. **Supercooling**

The mechanism of crystal growth in pure components, as well as in organic eutectic systems, have been nicely discussed [67]. Two types of crystal growth mechanisms have been suggested.

1. **Normal growth mechanism:**
   A normal growth generally occurs at a rough interface and the growth front of crystallization advances homogeneously in all sectors of the melt.

2. **Lateral growth mechanism:**
   In this type, the crystal growth occurs by lateral propagation of steps. This means that the growth is carried on with layer by layer mode resulting in side by side propagation.

Each mechanism of crystal growth has its own dependence on its growth velocity, \( v \) and the undercooling, \( \Delta T \). Hillig and Turnbull [68] have given an expression for the growth rate which is described in the following manner;

\[
v = k (\Delta T)^n \quad \ldots (1.40)
\]

where \( k \) and \( n \) are constants. If the crystal growth is governed by lateral growth mechanism then the dependence [69-72] follows the exponential law

\[
v = k_1 \exp \left[ -\frac{k_2}{T \Delta T} \right] \quad \ldots (1.41)
\]

where the values of \( k_1 \) and \( k_2 \) are different in different theories. For the formation of a crystalline nucleus, it is necessary to overcome an energy barrier and the growth velocity, is therefore, significant only after achieving the definite (threshold) undercooling.

In the case of the dislocation mechanism, the dependence [1, 59] of velocity on undercooling obeys the following parabolic law relationship

\[
v = k_3 (\Delta T)^2 \quad \ldots (1.42)
\]
In the case of the normal growth mechanism the dependence [46, 70, 71] satisfies the linear law:

\[ v = k_4 \Delta T \]  \quad \text{... (1.43)}

In the crystal growth process, role of the solid-liquid interface is important. Basically there are two types of solid-liquid interface. One is the atomically flat close packed interface in which the transition from liquid to solid occurs over a narrow transition zone (approximately one atom layer thick). The other type is an atomically diffused interface in which the transition from liquid to solid occurs over several atomic layers. These two types of interface migrate in quite different ways because of difference in atomic structure. Rough interfaces migrate by a continuous growth process while interface involving ledges migrate by lateral growth process.

The crystal growth of the constituent phases of eutectic system is dependent upon the nature of solid-liquid interface which can be predicted with the help of entropy of fusion value. Jackson showed that by using \( \alpha \)-factor (interface roughness parameter), given by Eq.(1.21) as described in section 1.4.1 of this thesis, the structure of solid-liquid interface can be predicted. It has been shown [48] that if \( \alpha > 2 \), the crystal liquid interface is atomically smooth, advances into the liquid by the propagation of atomic steps across the interface and the crystal will develop a faceted morphology. In some eutectic systems forming 1:1 addition compound with congruent melting point, the \( \alpha \) values were found [53] to be greater than 2. Jackson roughness parameters of some eutectic systems [21, 27] are given in Table 1.6. When \( \alpha < 2 \), the solid-liquid interface is atomically rough [73] and many preferable sites are continuously available for atomic attachment during crystal growth. Such crystal generally develops as a non-faceted morphology. Some more general theories are also proposed by Jackson [74, 75].

1.7 Crystal Growth Morphology

A bulk crystal may possess an infinite number of faces but the crystals which are grown practically possess a limited number of faces. Many attempts were made to correlate the morphological development of crystals with their internal structure and several theories were proposed [76-81].

Generally, all these theories are based on the atomic bonding energies in crystals and their relationship to the crystal morphology at thermodynamic equilibrium. However, a different group of crystal growth theories was proposed on the basis of...
Table 1.6: Values of Jackson’s roughness parameter (α) for various eutectic systems

<table>
<thead>
<tr>
<th>System</th>
<th>Jackson’s roughness parameter (Jmol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrene – <em>p</em>-Benzoquinone [21]</td>
<td></td>
</tr>
<tr>
<td>E₁ (eutectic)</td>
<td>3.1</td>
</tr>
<tr>
<td>E₂ (eutectic)</td>
<td>5.8</td>
</tr>
<tr>
<td>1:1 CTC</td>
<td>5.6</td>
</tr>
<tr>
<td>Pyrene – <em>m</em>-Dinitrobenzene [21]</td>
<td></td>
</tr>
<tr>
<td>E₁ (eutectic)</td>
<td>3.5</td>
</tr>
<tr>
<td>E₂ (eutectic)</td>
<td>5.0</td>
</tr>
<tr>
<td>1:1 CTC</td>
<td>4.8</td>
</tr>
<tr>
<td>Pyrene – <em>m</em>-Nitrobenzoic acid [21]</td>
<td></td>
</tr>
<tr>
<td>E₁ (eutectic)</td>
<td>4.6</td>
</tr>
<tr>
<td>E₂ (eutectic)</td>
<td>4.1</td>
</tr>
<tr>
<td>1:1 CTC</td>
<td>4.4</td>
</tr>
<tr>
<td>Phenothiazine – <em>m</em>-Nitrobenzoic acid [27]</td>
<td></td>
</tr>
<tr>
<td>E₁ (eutectic)</td>
<td>4.0</td>
</tr>
<tr>
<td>E₂ (eutectic)</td>
<td>4.7</td>
</tr>
<tr>
<td>1:1 CTC</td>
<td>4.3</td>
</tr>
<tr>
<td>Phenothiazine – <em>m</em>-Dinitrobenzene [27]</td>
<td></td>
</tr>
<tr>
<td>E₁ (eutectic)</td>
<td>5.3</td>
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<td>E₂ (eutectic)</td>
<td>5.6</td>
</tr>
<tr>
<td>1:1 CTC</td>
<td>5.9</td>
</tr>
</tbody>
</table>
crystallographic structure of crystals and an excellent account of kinetic and geometric
determination of the growth morphology of bulk crystals have been nicely reviewed by
Prywer [76]. According to Prywer during their growth, crystals adopt a variety of habits
due to differences in relative growth rates of faces of which the crystal is composed.
Most crystal growth theories suggest that the crystal morphology is dominated by the
slow growing faces because the fast growing faces may "grow out" and are not
represented in the final crystal habit.

It is reported that the seed faces may influence crystal morphology. Some seed
faces may cause a decrease in the size of the neighbouring face. It follows, therefore, that
the geometry of the seed and the crystal geometry plays an important role in the
formation of crystal habit. The influence of seed faces on the growth morphology also
depends on the growth time.

Prywer [76] has given an analytical view of the correlation between the crystal
geometry, the evolution of individual surfaces, their morphological importance and
morphological stability and the final crystal morphology. However, no consideration
about the type of bond or about dislocations, which may affect crystal growth and the
growth morphology, have been done.

1.8 Uncoupled and Coupled Growth

In the "uncoupled" growth, the two phases are formed independently; one grows
into the liquid well in advance of the other, which follows, filling in the space left by the
first. Therefore such growth is characterized, by a non-planar, non-isothermal solid-
liquid interface. On the other hand, "Coupled Growth", implies that the two phases are
formed from the liquid at a common interface, which is nearly planar and isothermal. In
this case, the process occurring at the interface of one phase is intimately related to that
occurring at the interface of the other phase. Coupled growth usually results in the
formation of either a lamellar or a fibrous microstructure. As reported [63,82,83] the
solidification of a eutectic, as a coupled growth process, must occur at a temperature
somewhat below the equilibrium eutectic temperature in order to provide a driving force
for the diffusion that is necessary for the "unmixing".
1.9 Microstructure of Eutectics

It has been observed that eutectics exhibit a wide variety of geometrical structures and may be broadly classified into two types.

1. Normal, or regular eutectics
2. Anomalous, or irregular eutectics

Regular eutectics [84, 85] are formed as a result of the coupled steady growth of the eutectic phases while the anomalous or irregular structures are formed as a result of separate or uncoupled growth of the eutectic phases. It is considered that the growth isotropy of phases having low $\alpha$-factors [48] leads to their easy branching and therefore to the formation of regular eutectic. In the system where one or both the phases have high $\alpha$-factors, the anisotropy of growth of crystals leads to the branching difficulties and consequently to the formation of anomalous eutectics. In regular eutectics, the roughness of one of the phase increases under the influence of the other phase and this surface which gets a rougher surface has easy branching and higher growth rate. This phase forms an envelope around the other phase and involves the other phase in coupled steady growth and therefore, regular eutectic structure is formed. Whereas, the phase which gets a smoother surface, has branching difficulties, less growth rate and difficulty in nucleation. The branching difficulties of both the phases do not allow the coupled steady growth to occur and as a result, anomalous or irregular eutectic is formed.

On the basis of the entropy of fusion of the two eutectic phases, Jackson and Hunt [83] have classified eutectics into three groups;

(i) Non-faceted - Non faceted type (NF-NF)

In this both the phases have entropy of fusion ($\Delta S$) less than $2R$ ($R$ being the universal gas constant). Examples of this type of eutectics are Pb-Sn, Cd-Zn, Cd-Sn, Cd-Pb, carbon tetrabromide - hexachloroethane systems.

(ii) Non-faceted - Faceted type (NF-F)

In this type one phase has the entropy of fusion less than $2R$ and the other phase greater than $2R$. For example Bi-Sn, Bi-Cd, Bi-Pb, Al-Si, succinonitrile-Borneol, cyclohexane-camphene, succinonitrile-hexachloroethane, carbon tetrabromide-azobenzene systems.
(iii)  

**Faceted - Faceted type (F-F)**

In this both the phases have entropy of fusion greater than 2R. Since most metals do not have high entropy of fusion, this type of eutectic is most common in non-metallic materials e.g. azobenzene-benzil system. In this category, the anisotropy of growth of the two phases leads to the branching difficulties and therefore, the irregular or anomalous type of structure is formed.

**1.9.1 Normal (Regular) Structures**

The regular type morphology of eutectics is formed as a result of coupled steady state growth. Regular eutectics are associated with two phases having low entropy of fusion (ΔS) and hence low α factor [64]. This will lead to their easy branching and therefore formation of regular eutectics takes place. In regular eutectics, a low volume fraction of one phase favours fibrous growth whereas a higher volume favours lamellar growth, this is because the interfacial area in lamellar eutectics independent of volume fraction, whereas in fibrous eutectics decreases with decreasing volume fraction. These NF-NF eutectics can be lamellar or fibrous type and are characterized by well defined constant interface spacing for a given constant growth rate. In the regular eutectics, the roughness of one phase increases in the influence of the other phase leads to easy branching, higher growth rate. Regular type eutectics are subject of continuing interest for the production of in situ composites. Thus, they have little tendency towards faceted growth. The lamellar and rod type structures are two main types of regular morphologies.

**1.9.1.1 Lamellar Structures**

The lamellar structure consists of alternate layers or lamellae which repeat in regular fashion and their interface is parallel to the solid-liquid interface [13]. The two phases solidify side by side as alternating lamellae (sheets). A schematic diagram of lamellar solidification from a eutectic melt is shown in Fig.1.9. During solidification, α-phase rejects the atoms of B and the β-phase rejects the atoms of A, where A and B are the components. Under the steady state growth conditions, the rate of rejection of the atoms of B by α-phase is equal to the rate of rejection of the atoms of A by the β-phase. Jackson and Hunt [83] analyzed this regular solidification by assuming it a steady state growth at constant freezing rate at a planar and interfacial undercooling.
In the lamellar growth, the undercooling at the interface ($\Delta T$) can be considered to be the sum of individual undercooling contribution viz. due to compositional differences ($\Delta T_D$) that exist across interface, curvature ($\Delta T_r$), kinetic ($\Delta T_k$), and thermal ($\Delta T_t$) terms [64]

$$\Delta T = \Delta T_D + \Delta T_r + \Delta T_k + \Delta T_t \quad \ldots (1.44)$$

For regular eutectic growth, at low velocities thermal and kinetic undercooling terms become negligible thus Eq. (1.44) can be represented as:

$$\Delta T = \Delta T_D + \Delta T_r \quad \ldots (1.45)$$

The undercooling, $\Delta T_D$ reaches a maximum at the centre of each lamella. This is shown in Fig. 1.10. This undercooling contribution may be calculated with the help of following expression (1.46) [86]

$$\Delta T_D = m (C_e - C) \quad \ldots (1.46)$$

where $m$ is the liquidus slope, $C_e$ is the eutectic composition and $C$ is the local liquid interface composition obtained from solution of the diffusion equation.

The second undercooling ($\Delta T_r$) due curvature, due to non-planar interface, is given by

$$\Delta T_r = \frac{a}{r(x)} \quad \ldots (1.47)$$

where $a$ is a constant given Gibbs Thomson relationship and $r(x)$ is the local curvature of the interface, $\Delta T_r$ reaches a maximum near the $\alpha - \beta$ interface.

Jackson and hunt [86] developed a theory for the growth of lamellar eutectics based on a diffusion model. The resultant equation derived by them is written as

$$\frac{\Delta T}{m} = \nu \lambda Q \frac{a'}{\lambda} \quad \ldots (1.48)$$

where

$$\frac{1}{m} = \frac{1}{m_o} + \frac{1}{m_p} , \quad \lambda = 2(S_{\alpha} + S_{\beta}) \quad , \quad Q = \frac{P(1+\xi)^2 C_0}{D_{e}}$$

and

$$a' = 2 \left(1 + \xi \right) \left[ \frac{a_{\alpha}}{m_o} + \frac{a_{\beta}}{m_p} \right]$$

Terms $P$ and $C_0$ appearing above are given by

$$P = \sum_{\nu=1}^{n} \left( \frac{1}{n \pi} \right)^3 \sin^2 \frac{n S_{\beta}}{S_{\alpha} + S_{\beta}} \quad \text{and} \quad C_0 = C_0^o + C_0^b$$

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Where $S_a$ and $S_\beta$ are the lamellar width of $\alpha$ and $\beta$ phases. $C_0^\alpha$ and $C_0^\beta$ are the amounts rejected, when the volumes of the $\alpha$ and $\beta$ phases freeze. $m_\alpha$ and $m_\beta$ are the slopes of corresponding liquidus lines defined in such a way that both are positive.

When the solid phase grows at the extremum, the parameters $\lambda$, $V$ and $\Delta T$ are related to each other by the following relations:

\[ \lambda^2 V = \frac{a^L}{Q^L} = \text{constant} \quad \ldots (1.49) \]

\[ \frac{\Delta T^2}{V} = 4 m^2 a^L Q^L = \text{constant} \quad \ldots (1.50) \]

Two types of faults [86] occur during lamellar growth. When the lamellar faults moves to the left, the average spacing decreases (Fig. 1.11) and when it moves to the right, the average spacing increases. Stables lamellar growth will, therefore, occur when the fault remains stationary.

1.9.1.1 Instabilities in Lamellar Growth

Jackson and Hunt [83] discussed the changes in lamellae spacing and instabilities. This occurs due to a change in composition at the interface resulting from the effect of a growth rate change on the boundary. The prediction of microstructure and interface pattern in alloys is important from the engineering point of view. During the last decade, phase-field modeling of eutectic solidification has been done by many workers [87-89]. The phase field model for single phase solidification, in pure or alloy melts, has been extended to multiphase systems [22, 91-93]. Recently Kim et al. [22] have reported a eutectic phase field model which successfully reproduces a variety of eutectic lamellar patterns under the real experimental conditions without any fitting parameters. A variety of eutectic lamellar patterns were observed in the experiments and characteristics of the pattern changed with lamellar spacing in both eutectic and hyper eutectic alloys.

Multiphase eutectic morphologies exhibits different distinct symmetry element which give rise variety of instabilities. Three distinct types of instabilities have been found in two dimensions. The first type of instability, which occurs for small spacings, is lamella elimination. This is long wavelength instability of the phase - diffusion type [94] i.e. it involves a large number of lamellae. The second type of instability is tilt instability, associated with a breaking of the left-right symmetry; all lamellae tilt in the same direction and drift laterally. The third type of instability is short- wavelength oscillatory
Fig. 1.9: A Schematic Diagram of Lamellar Type Structure.

Fig. 1.10: (a) Composition of liquid at a Lamellar Eutectic Interface, (b) Interface Undercooling due to Diffusion ($\Delta T_d$) and Curvature ($\Delta T_r$); $\Delta T$ is the Total Undercooling, and (c) Shape of Lamellar Interface [12]

Fig. 1.11: A Schematic Diagram of Lamellar Fault
instability in which all lamellae start to oscillate in phase (1 - \( \lambda \) - 0 instability) (Fig. 1.12a), or alternate lamellae of the minority phase oscillate out of phase, leading to a doubling of the spatial periodicity (2 - \( \lambda \) - 0 instability) (Fig. 1.12b). Both the tilt and oscillatory instabilities occur at large spacing. Kim et al. [22] have discussed the lamellar eutectic patterns observed in experiments on directional solidification of CBr\(_4\) - C\(_2\)Cl\(_6\) organic alloys. They focused on two dimensional instability i.e. tilt and oscillating pattern as a function of lamellar spacing in the eutectic and hypereutectic composition.

Lamellae start to deviate from its initial geometry, which is shown in (Fig. 1.13a and 1.13b). As discussed in Fig. 1.13 b, the lateral symmetry can be broken in various ways, distinguished by the discrete symmetry elements are preserved. In the first case, both mirror planes and the discrete translational symmetry survive which is denoted as 1-\( \lambda \) instability. And if only mirror planes is presented then the spatial period of the pattern is doubled will be denoted as 2- \( \lambda \) - \( \alpha \) and 2- \( \lambda \) - \( \beta \). Third type of instability is specific Zig-Zag type in which their both plane of symmetry is lost with unchanged periodicity.

Recently Parisi and Plapp [95] and Folch and Plapp [96] have studied the three dimensional eutectic structure and eutectic growth front by using organic alloys. In these experiments Zig – Zag (ZZ) instability is observed and characterized [97, 98].

During the directional solidification of eutectic alloy the first three dimensional morphological stability is always Zig-Zag instability which becomes active with increasing lamellar spacing. Stable Zig-Zag pattern are formed when \( \lambda = \lambda_{TH} \) value become slightly above the threshold of the Zig-Zag one. Lamellar maze is formed with larger initial spacing (Fig. 1.13c). For off-eutectic composition lamellae break up into rods.

Popov et al. [99] have reported a two dimensional phase field method to observe the evolution of the composition field and the microstructure of lamellar eutectics caused by variations in the freezing rate. They studied solid-phase nucleation, lamella termination, and migration of the three-phase junction to elucidate the role of each in microstructure changes. They said that when the freezing rate is increased, the super saturation in front of the lamellae increases, causing formation of deep depressions, followed by nucleation of the other solid phase, instability and movement of the three phase junction. If the freezing rate is subsequently held constant, the microstructure eventually becomes stable. With a decrease in freezing rate, instability develops that...
Fig. 1.12: (a) 1-$\lambda$-O pattern; (b) a transient of 1-$\lambda$-O pattern to 2-$\lambda$-O pattern.

Fig. 1.13: (a) The development of an instability with time.

Fig. 1.13: (b) Possible instabilities in lamellar growth. The dashed lines indicate planes of mirror Symmetry.
Fig. 1.13: (c) The Development of 3-dimensional Zig-Zag instability at $\Lambda = 1.6$ [95].
changes the local growth direction and provokes changes in lamellar width followed by elimination of some lamellae. The morphological stability of lamellar eutectic coupled growth is investigated by Parisi et al [95] by means of quantitative three dimensional phase field simulations, both for a generic eutectic alloy with a symmetric phase diagram and for the transparent organic alloy carbontetra bromide - hexachloroethane. The instabilities that limit stable steady-state growth at large spacings are identified and compared to the instabilities known in thin samples.

B.L. Sharma [3] has investigated the anisotropic lamellae growth and hardness of the eutectic composite alloy Pb-Sn both at macro- and micro- levels in variable growth rate of solidification.

Eutectic-like α+β lamellar structures have been observed by F. Kohler et al [33] in near-peritectic composition alloys over several millimeters of growth. It was revealed by Electron backscattered diffraction measurements that bands and lamellae of a solid phase are continuous and originate from a single nucleus.

1.9.1.2 Rod (Fibrous) Structures

The second form of the normal structure is rod (fibrous) morphology which is shown in Figs. 1.14 and 1.15. Jackson and Hunt [86] proposed that the rod morphology should grow with lower undercooling than the lamellar morphology (and hence should be the stable growth form) when the volume fraction of one phase is sufficiently small. On varying the volume fraction of the two phases in a Pb-Sn eutectic it was found that the structure was lamellar [73] near the eutectic composition. When the volume fraction of the lead phase was reduced, the structure was fully rod like at a volume fraction of about 0.18.

According to Tiller [100], rods are produced in those eutectic systems where the proportions of the volumes of the two phases are large, since the interface boundary area can be lowered by the formation of rods. If a lamella is forced to bend away from its low energy interface, it loses the energy available to stabilize the structure and makes a transition possible [73]. Jackson and Hunt [86] gave a theory of rod eutectics based on diffusion model.

\[
\frac{\Delta T}{m} = V R Q^R + \frac{a^R}{R}
\]  

...(1.51)

where R is rod spacing, \(a^R\) and \(Q^R\) are given by the following relationships
Fig. 1.14: Rod Type Structure in Succinonitrile-Camphor Eutectic Alloy [15]

Fig. 1.15: Schematic Illustration of the Possible Shapes of Rods; (a) Lamellar Shape, (b) Circular Cylinder, (c) Elliptical Cylinder with the major axis in the direction of sample width, and (d) Elliptical Shape with the major axis along the sample thickness [15].
\[ a^R = 2(1 + \xi)\frac{a^R_a + a^R_\beta}{m_a + m_\beta} \]

\[ Q^R = \frac{4(1 + \xi)}{D^2} C_0 M \]

where \( a^R_a \) and \( a^R_\beta \) are surface energy terms, \( M \) is the tabulated function of the volume fraction[101]. On applying the extremum condition, one is able to write

\[ VR^2 = \frac{a^R}{Q^R} \quad \ldots (1.52) \]

and

\[ \frac{\Delta T^2}{V} = 4m^2a^R Q^R \quad \ldots (1.53) \]

The rod spacing is given by the equation

\[ R = (1/X) (A/N)^{1/2} \quad \ldots (1.54) \]

Where \( X \) is magnification and \( N \) is the number of rods in an area \( A \).

The growth and morphology of rod eutectic microstructures has been investigated in Succinonitrile - Camphor alloy by Teng et al. [15] and many workers [32,102-104].

1.9.2 Anomalous (Irregular) Structures

Sharma [1] has developed the structural model of faceted-faceted eutectic system vanillin-acenaphthene by analyzing the excess functions computed from its experimentally determined solidus-liquidus equilibrium data. Spontaneous nucleation model has been explored from the maximum limit of undercooling of the system and verified by the experimental evidences of dislocation mechanism governing the anisotropic velocity of crystallization determined at different undercoolings. The work is mostly an experimental introduction in the field of whisker growth, wherein attempts have been made to study eutectic solidification visually by watching the growth process.

The classical model on regular lamellar eutectic systems is due to Jackson and Hunt [86]. Among the several attempts to model irregular eutectic growth the most comprehensive is that of Magnin and Trivedi [105]. All models are based on JH model for lamellar growth. J. Liu and R. Elliott [106] have presented a numerical calculation for irregular eutectic growth which takes into account the increased difficulty of solute diffusion at a curved interface and the change in temperature of the interface with
position. They concluded that the planar interface assumption and steady state theory cannot be used to model irregular growth. It has been suggested that the different spacings in irregular eutectics may be characterized by different growth velocities or by different undercoolings.

Irregular structures are formed [107] when the primary phase is unable to serve as the nucleating agent for the secondary phase. The secondary phase nucleates heterogeneously in the liquid and its randomly oriented particles grow rapidly to absorb the supercooling in an irregular fashion. The anomalous structures are also formed when one or both the phases possess high entropy of fusion ($\Delta S$) and hence lead to a faceted growth. These structures show less coupling than the normal structures. The two phases are mixed intimately but grow without a uniform crystallization front.

Most of the eutectic alloys of technological and particle interest are irregular eutectics [108]. Generally, binary irregular eutectic consists of a faceted phase and a non-faceted phase. Experimentally it has been found that the actual average spacing and average interface undercooling of irregular eutectics are larger than those of regular eutectic under the same solidification conditions. These faceted – nonfaceted eutectics show varied morphologies which are characterized by a high level of branching and non-constant interface spacing even at a constant growth rate. The various morphologies that have been investigated in the class of irregular/Anomalous type eutectics are discussed below;

1.9.2.1 Broken Lamellar Type Structure

The broken lamellar structures are formed at a very low volume fraction [73]. The existence of broken lamellar structure has been reported by many workers [13]; the examples include those of Al-AlNi$_3$, Pb-Ag, Sn-Zn, Al-Al$_5$Co$_2$, Bi-Ag, Bi-Bi$_2$Mg$_3$, Cd-CdSb, Sb-CdSb and Al-Al$_3$Fe. The broken lamellar structures are formed at a very low volume fraction. The faceting phase forms the ribbons and the branching occurs within the plane of the ribbon as a result of the frequent occlusion of the minor phase of the matrix. The minor phase appears as broken lamellae microstructure. Fig 1.16 shows the broken lamellar type structure.

1.9.2.2 Complex Regular Structure

In this one of the eutectic phases is faceting type. It is formed mostly in alloys containing a large volume of the faceting phase. It is assumed that an energy barrier
exists for the addition of a new solid layer during solidification, which proceeds by the lateral movement of steps across a specific crystallographic facet plane. The structural features of the complex regular class [73] are determined by the crystallographic features of the faceting phase and are also dependent on the velocity and temperature gradient in the systems that show thermal anisotropy. The complex-regular eutectic morphology has been observed [13] in a number of systems where one of the eutectic phases is faceting type and it occurs mostly in alloys containing a large volume of faceting phase.

The most common complex regular structures generally observed are of following three types.

(i) Cellular structure
(ii) Colony structure
(iii) Feather like structure. A feather like structure is shown in Fig. 1.17.

1.9.2.3 Dendritic Growth

When the composition of system is too far from the eutectic composition results in the formation of a dendrite morphology. These dendrites of one or the other primary phases grow ahead of the eutectic interface, producing a microstructure consisting of primary phase interspersed with lamellar eutectic. Such dendritic growth is shown in Fig. 1.18.

1.10. Modifications in Eutectic Morphology

Considerable research activities have been done in recent years for controlling and modifying the morphology of eutectic alloys. Modification of eutectic structures is important from the point of view of developing new types of materials. Eutectic modification is a common process performed in foundry alloys primarily to improve mechanical properties, particularly tensile elongation, by promoting a structural refinement of the inherently brittle eutectic phase. Modification has also been observed as a result of a change in the interfacial free energy.

Modification in eutectic structures can be done either by the addition of small quantity of impurity elements, or by changing the growth (solidification condition) and composition of the melt.

1.10.1 Effect of Impurities on Eutectic Microstructures

Considerable investigations have been done in understanding the microstructures of eutectic alloys which are important for developing new and advanced type of
Fig. 1.16: Broken lamellar structure

Fig. 1.17: Feather-like structure

Fig. 1.18: Dendritic structure
materials. Generally when trace amount of elements are added as an impurity, brings considerable improvement in the mechanical properties of the eutectic alloys and the eutectic microstructures are changed. A typical example of the modification of a eutectic structure is that of Al-Si alloy [13]. It is reported that the addition of elements such as Sr and Sb in trace amounts in Al-Si alloy results in modification of the eutectic silicon morphology from coarse and plate-like structure to a fine and fibrous structure [109]. The eutectic silicon morphology (a) unmodified, (b) Sr-modified, and (c) Sb-modified are shown in Fig. 1.19. Several rare elements are also known to cause varying degrees of modification. Eutectic modification may also lead to negative side effects such as porosity, hot tearing and poor surface finish and therefore, it is not always a recommended procedure. Dahle et. al. [109] studied the variation in eutectic nucleation and growth dynamics occur in Al- Si alloy as function of the type and amount of modifier elements added i.e. Sr and Sb. There was increasing nucleation difficulties after individual additions of Sr or Sb to an unmodified alloy. This was reflected in the eutectic grain sizes with the eutectic grains being largest in the Sr-modified alloys and of an intermediate size in Sb-modified alloys.

Zhao et. al. [110] studied the solidification of undercooled Ag–Cu eutectic alloy in the presence of Sb as an impurity. When Sb is added to Ag-Cu eutectic system, the eutectic dendrite tip is sharpened. Because of this, the growth is accelerated and recalescence rate is increased. With the increasing addition of Sb, the granular particles in the anomalous eutectics near the nucleation site become larger because of the increasing recalescence degree and recalescence rate.

1.10.2 Effect of Cooling Rates on the Eutectic Microstructures

Different cooling rates (solidification conditions) can affect the microstructures of the eutectics to a considerable extent. The microstructural changes during quenching of molten Al-(6.8%) Cu has been studied by Pompe and Rettenmayr [111]. They found that isothermal cooling of solid-liquid mixture yield a well defined microstructure, allowing separation of microstructural changes during quenching from the initial microstructure prior to the quench. It is reported that the microstructures depend on holding time and cooling rates. This is shown in (Fig. 1.20 a and b).

It has been hypothesized that in the process of solidification when the microstructure is fibrous, an increase in freezing rate causes the formation of new fibres
Fig. 1.19: Comparison of the Silicon Morphology in (a) Unmodified, (b) Sr-modified (300 ppm Sr) and (c) Sb-modified (200 ppm Sb), Al-Si alloys [109].
Fig. 1.20 (a): Microstructures of six samples quenched with 80 K/s
Fig. 1.20 (b): Microstructures of six samples held for 5000 s at 628 °C and then cooled to room temperature; cooling rates as indicated.
either by branching or by nucleation. A decrease in freezing rate would cause fibres to terminate by the over growth of the matrix phase. Directionally solidified MnBi / Bi eutectic has a quasi regular MnBi rod structure at freezing rate 9mm/h [112]. Similar to many other eutectic systems, the average rod spacing \( \lambda \) depends on the freezing rate \( V \) given such that \( \lambda^2 V = \text{constant} \).

If the eutectic mixture have lamellar microstructure during co-operative solidification the two phases solidifies side by side as alternating lamellae. The average spacing between the two lamellae also depends on the freezing rate. When the freezing rate is increased, the supersaturation in front of the lamellae increases causing formation of deep depressions, followed by the nucleation of the other solid phase, instability, and movement of the three-phase junction. If the freezing rate is subsequently held constant, the microstructure eventually becomes stable. With a decrease in freezing rate, instability develops which changes the local growth direction and provokes changes in lamellar width followed by elimination of some lamellae. With oscillating freezing rate, backmelting becomes important, especially for large lamellar spacing, large amplitudes, and low frequencies [100].

1.10.3 Dependence of Eutectic Microstructures on the Effective Entropy Change and Volume Fraction of the Eutectic Phases

The eutectic microstructures depend upon the effective entropy change and volume fraction of the eutectic phases [16]. Both these parameters are inter-related during eutectic solidification at low velocity, and the eutectic microstructures can be characterized based on the relationship between them. Eutectics may exhibit a wide variety of geometrical arrangements. Meng et. al [16] studied the effect of volume fraction and entropy change on the industrially important alloy systems: Al-CuAl2, Al-Si, Pb-Sn and Al-NiAl3. Al-Si system (Fig. 1.21 a) [113] belongs to irregular eutectics. In Al-Si system, the molar entropy change of the Si phase is high and there is small volume fraction of the faceted phase. In contrast, in the case of the Pb-Sn alloy, the molar entropy change of Sn rich phase is larger than the critical value 23 J mol\(^{-1}\)K\(^{-1}\), however such alloy still belongs to regular eutectics (Fig. 1.21 b) [114]. For regular eutectics, the volume fraction appears to merely determine whether a lamellar or rod structure ensues. Al - CuAl2 and Pb - Sn show lamellar structures owing to a larger volume fraction and
Al - NiAl$_3$ (Fig. 1.21 c) [115] show a rod arrangement or broken lamellar eutectics due to its lower volume fraction.
Fig. 1.21: Eutectic microstructures of Al-Si (a) [113] Pb-Sn (b) [114] and Al-NiAl₃ (c) [115] eutectics.
Part B: Reactions in Molten Eutectics

1.11 Introduction

A variety of useful materials have been prepared by solid state reactions, microwave synthesis, precursor methods, chemical methods, chemical vapour transport, sol-gel method, hydrothermal method etc. In these conventional methods, the main difficulty was to make the atomic level of mixing of the ingredients, thereby completely eliminating the possible impure phase contamination. These disadvantages were partially overcome by using the wet chemistry method such as sol-gel, hydrothermal and soft combustion [116-118]. But all these studies have certain disadvantages such as considerable difficulty in the removal of organic solvents that are used in the reaction, large particle sizes, wide range of particle size distributions and irregular morphologies. Preparation of crystals with specific size and morphology has recently attracted considerable interest [119,120], especially because the size and morphology of these materials can be designed according to the requirements of the devices, which have important value for the practical application of materials [121-125]. Synthesis of crystals with different morphologies, such as ZnO nanowires obtained by vapour-liquid-solid growth [126], PbCrO₄ nanorods and nanoparticles synthesized by using different surfactants and organic additives [127] and BaWO₄ crystals has also been prepared with different morphologies [128].

A very interesting method for synthesizing organic and inorganic substances was developed in which the synthesis is done through molten electrolytes and instead of using simple electrolytes, eutectic mixtures were used because of their low melting temperatures. In fact molten electrolytes are better and more effective solvents than water and other room temperature liquids. This method has several advantages over normal aqueous solvents, in respect of increased electrical conductivity, decomposition potential and temperature range for reactions. Several workers [129-132] have successfully used eutectic melts to study the decomposition of various inorganic substances. Preparation of mixed metals oxides through eutectic melts has also been done [133].

Organic reactions are generally carried out in conventional solvents, but the use of solvents may not always be advantageous; often it imposes a restriction on the yield and duration of the reaction, primarily due to (i) Influence of the dielectric constant of
the medium and (ii) The interaction of the solvent with the reactant and/or the products. An interesting alternative to the conventional method is to carry out the reactions in eutectic media where solids can be made to react at temperature much lower than their melting points.

Conventionally reactions taking place in solution require more time and their interaction with the reacting components also affect the reactivity. With the development of green chemistry, it has become essential to minimize the use of solvents during the reactions. An alternative way for the preparation of compounds without the use of solvents is through eutectic melts [134]. The process may be of much practical significance, since it may be possible to choose melts where the solvation of the reactants is minimized and the polarity of the medium can be controlled [135]. The decrease in volume and hence increase in concentration of the reactants during solidification would increase the rate of reaction resulting into enhanced yield.

A number of kinetic studies of reactions in melts have been reported in spite of the experimental difficulties [136,137]. Chlorine and acetylene together with CCl₄, as a diluents react in NaCl-AlCl₃-FeCl₃ melt at about 200 °C to give a mixture of ethylene chloride, tetrachloroethane and CCl₄. Vinyl chloride has been obtained either by reaction of ethylene, HCl, and O₂ in the ratio of 2:2:1 using CuCl₂ – KCl solvent or by thermal dehydro-halogenation of 1,1-and 1,2-dichloromethane using ZnCl₂ – KCl solvent. Five sets of reactions in organic eutectic melt have been studied by Rastogi [138]. The important of these reactions was that the reaction time is found to be very short and the yield of product is high. The reaction would be completed much below the melting point of either reactants and without the use of catalysts, since during solidification considerable amount of heat is evolved, the temperature automatically rises during the reaction and consequently the rate of reaction is considerably enhanced and the reaction time decreases.

N-benzyloxycarbonyl-l-aspartic acid ethyl ester-D-alanine amide, a derivative of alitame, was synthesized from a eutectic mixture of the substrates N-benzyloxycarbonyl-l-aspartic acid diethyl ester and D-alanine amide using a-chymotrypsin by Kim and shin [139]. A conversion yield of 70.3% was obtained at 37°C. Kim et al. [140] also synthesized kyotorphin precursor, N-carbobenzoxy-l-tyrosine-l-arginine amide (N-CBZ-l-Tyr-l-ArgNH₂), from the eutectic mixture of N-CBZ-l-tyrosine ethyl ester (N-CBZ-l-
TyrOEt) and l-arginine amide (l-ArgNH₂) by using α-chymotrypsin as a catalyst. Approximately 90% conversion was achieved from the substrate mixtures with substrate contents responsible for more than 80% of the total mixture.

Cooper et al. [141] synthesized new classes of zeolites (zeotypes)—such as aluminosilicate zeolites and zeolite analogues which are very important. Normally these materials are prepared hydrothermally with water as the solvent in a sealed autoclave under autogenous pressure. They have also reported the preparation of aluminophosphate zeolite analogues by using ionic liquids and eutectic mixtures. A choline chloride/urea eutectic mixture is also used in the preparation of a new zeotype framework.

Polypyrrole is prepared electrochemically from a room temperature ternary eutectic melt consisting of acetamide, urea and ammonium nitrate [134]. The temperature effects of conductivity of polypyrrole are analyzed to understand its conduction mechanism. The thermal degradation of both doped and undoped samples of the polypyrrole in air and nitrogen atmosphere has been followed using thermogravimetric and differential thermal analysis. The conductivity of polypyrrole was changed to 10⁻³ ohm⁻¹ cm⁻¹ by its electrodeposition from a novel ambient temperature ternary eutectic melt consisting of acetamide, urea, and ammonium nitrate [142].

Inorganic reactions such as decomposition of various transition metal salts have been studied by Kerridge et al. [129], Rastogi et al. [130] and Singh et al. [131,132] by using inorganic eutectic melts. With this method, metal oxides get precipitated at much lower temperatures and in many cases interesting reaction products are formed. It has been reported that that certain metal oxides prepared through molten electrolytes such as nitrate melts [143] were found to have lower particle size, higher surface area and as a result higher catalytic activity and reactivity. In recent years, greater attention is being given for the preparation of nanosized particles and nowadays, nanostructured materials such as (Sn₀.₂₅ Ti₀.₇₅)O₂ [144], CaWO₄ [145], CdWO₄ [146], Ni₃Al [147], Mn₅Si₃ [148], TiO₂ [149], CeO₂ [150], NiO [143,151,152] and ZnO [153] were prepared through molten salt methods. Nanocrystals of Bismuth tugustate (Bi₂WO₆) with different morphologies were successfully synthesized by a low temperature LiNO₃ –NaNO₃ molten eutectic melt [154]. The molten salt method has been reported to be one of the simplest techniques to preparing ceramic materials including composites oxides. Zhao et al. [155] proposed a newly developed molten salt method to obtain homogeneous and
pure LiNiVO₄ at a temperature as low as 350 °C for 2h without introducing any organic solvent. α- LiFeO₂ nanorods were synthesized by low temperature molten salt synthesis method [156].

Various types of inorganic eutectic melts have been used for synthesizing useful reaction products. Some of these are being discussed below:

### 1.12 Nitrate Eutectic Melt

Simple nitrates have comparatively low melting points and hence they have been extensively studied as non aqueous solvents in molten state. Several nitrates form eutectics with much lower melting temperature as compared to the individual components. Therefore, it is easier to use eutectic melts due to low melting points, rather than to use a simple nitrate compound. The system NaN₃-KNO₃ is probably the most studied binary nitrate salt systems [157].

Some of the reactions in different nitrate eutectic melts are given below:

#### 1.12.1 Decomposition Reactions

Decomposition of a number of metal salts such as those of zinc, titanium, zirconium, mercury, cadmium and cobalt, in LiNO₃-KNO₃ eutectic melt was studied by Kerridge et al. [158-162], using thermogravimetric technique. Decomposition of ZnCl₂ and ZnSO₄ take place in the following way [158];

\[
\text{ZnSO}_4 + 2\text{NO}_3^- \rightarrow \text{ZnO} + \text{SO}_4^{2-} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2
\]

\[
\text{ZnCl}_2 + 2\text{NO}_3^- \rightarrow \text{ZnO} + 2\text{Cl}^- + 2\text{NO}_2 + \frac{1}{2}\text{O}_2
\]

Compounds of Ti (III and IV) decomposed [159] in both pure molten LiNO₃-KNO₃ eutectic and basic nitrate melt solutions containing Na₂O₂, Na₂O or NaOH. Titanium dioxide as anatase and titanates of different basicities were produced, depending upon the concentration of base and temperature. When chloride was present, dinitrosyl hexachlorotitanate (IV) sublimed from the melt at 200 °C.

Zr (IV) sulphate reacted in LiNO₃-KNO₃ eutectic melt as a Lux-Flood acid in three stages. Initially, a soluble intermediate, possibly a basic nitrate was produced, secondly Zirconium dioxide could undergo a slow reaction at higher temperatures, probably forming Zirconate [160]. The overall reaction can be written as;

\[
\text{Zr(SO}_4)_2 + 2\text{NO}_3^- \rightarrow \text{ZnO}_2 + 2\text{SO}_4^{2-} + 4\text{NO}_2 + \text{O}_2
\]
The reaction of Hg(I and II) sulphate and Hg(II) oxide in pure LiNO$_3$- KNO$_3$ eutectic and in nitrate solution containing Na$_2$O$_2$, Na$_2$O and NaOH were studied and stoichiometries were derived [161]. The initial major reaction product of mercury sulphate was green schutteite HgSO$_4$.2HgO, which was converted to other brown HgO. At low base concentrations, yellow, white and grey sublimates, containing Hg(I) and nitrate were formed. Cadmium sulphate decomposed to give CdO and cobalt nitrate, chloride and bromide decomposed to give cobalt oxide in the NaNO$_3$ - KNO$_3$ eutectic melt.

Sodium hexanitrocobalt (III) reacted with LiNO$_3$- KNO$_3$ eutectic at 140 °C, forming a red brown melt [162]. At 220 °C, an olive green precipitate was obtained. It was identified as cobalt(II) oxide by X-ray diffraction technique. On heating further to 280 °C, a black precipitate of tricobalt tetraoxide was obtained.

Kerridge et al. [163-167] have also studied reaction of some lead, Tin (II), bismuth, chromium (III) and nickel (II), magnesium, aluminium, gallium and thallium compounds in LiNO$_3$- KNO$_3$ eutectic. Chromium(II) chloride and nickel(II) chloride was found to undergo a acid-base reaction from 320 °C to 450 °C and form corresponding oxides in molten LiNO$_3$-KNO$_3$ eutectic [166]. Stoichiometry of the reactions is as follows;

\[
\text{CrCl}_2 + 6\text{NO}_2^- \rightarrow \text{Cr}_2\text{O}_3 + 2\text{Cl}^- + 6\text{NO}_2 + 1.5\text{O}_2
\]

\[
\text{NiCl}_2 + 3\text{NO}_2^- \rightarrow \text{NiO} + 2\text{Cl}^- + 2\text{NO}_2 + 1/2\text{O}_2
\]

Bismuth trichloride reacted with nitrate and form white coloured low temperature product BiOCl$_3$ [165].

\[
\text{BiCl}_3 + 2\text{NO}_2^- \rightarrow \text{BiOCl}_3 + 2\text{Cl}^- + \text{NO}_2 + \text{NO}
\]

The reactions of Fe(III), Co(II), Ni(II) chlorides and Cu(II) compound were studied in sodium nitrite –sodium nitrate-potassium nitrate eutectic [168]. These reactions were found to undergo Lux-Flood acid base reactions to form their most stable oxides, which were insoluble, while copper (II) sulphate reacted to form a basic nitrate. FeCl$_3$,CoCl$_2$, NiCl$_2$ reacts with nitrate melt in the following stoichiometry;

\[
2\text{FeCl}_3 + 8\text{NO}_2^- \rightarrow \text{Fe}_2\text{O}_3 + 6\text{Cl}^- + 2\text{NO}_3^- + 5\text{NO} + \text{NO}_2
\]
\[ 3\text{CoCl}_2 + 8\text{NO}_3^- \rightarrow \text{Co}_3\text{O}_4 + 6\text{Cl}^- + 2\text{NO}_3^- + 6\text{NO} \]

\[ \text{NiCl}_2 + 3\text{NO}_2^- \rightarrow \text{NiO} + 2\text{Cl}^- + \text{NO}_3^- + 2\text{NO} \]

where Cu(SO_4) reacts in a following way

\[ \text{CuSO}_4 + 1.1\text{NO}_2^- \rightarrow \text{Cu}_{0.58}(\text{NO}_3)_{0.84} + \text{SO}_4^{2-} + 0.58\text{NO}_2^- + 0.58\text{NO} \]

Formation of copper oxide through NaNO_3-KNO_3 eutectic melt and its catalytic activity in the decomposition of ammonium perchlorate has also been studied by Singh et al. [169]. Reaction of Ni (II)Br and NiCO_3, 2 Ni(OH)_2, 2H_2O, CdCl_2 and CdBr_2 has been studied by Singh et al. [132,143]. Shurdumov et al. [170] synthesized alkaline-earth metal tungstates in NaNO_3 - M(NO_3)_2 (M = Ca, Sr, Ba) eutectic melts. The synthesis is based on the exchange reaction of calcium, strontium, or barium nitrate with sodium tungstate.

1.12.2 Oxidation Reactions

The reactions are generally classified as Lux-Flood acid-base reactions or oxidation-reduction reactions, according to whether the nitrate ion acts as a source of oxide or as an oxidant. The final products of an acid-base reaction, the conjugate base of acid, nitrogen dioxide and oxygen, are supposed to be produced through the reaction:

\[ \text{NO}_3^- + \text{Acid} = \text{NO}_2^+ + \text{Acid}^- + \text{O}_2 \]

\[ \text{NO}_2^+ + \text{NO}_3^- \rightarrow [\text{N}_2\text{O}_5] \rightarrow 2\text{NO}_2 + 1/2\text{O}_2 \text{ (slow)} \]

The Lux-Flood acids are commonly condensed anions, non metal oxides or transition metal cations, whose reactive strengths can be determined because of the slowness of the reactions. The oxidation of iodide ion in LiNO_3-KNO_3 eutectic melt was studied by Kerridge and Frouzanfar [171] when KI was added to the LiNO_3-KNO_3 at 145 °C containing dissolved copper nitrate, the following reaction was observed:

\[ \text{Cu(NO}_3)_2 + 2\text{I}^- \rightarrow \text{CuI} + 2\text{NO}_3^- + \frac{1}{2}\text{I}_2 \]

1.12.3. Reduction Reactions

Reduction of a number of metal ions in nitrate eutectic melts has been investigated using polarographic technique. Imman et al. [172] investigated the reduction of Cd^{2+}, Co^{2+}, Ni^{2+} and Pb^{2+} in LiNO_3-NaNO_3-KNO_3 eutectic by conventional polarography. The reactions and spectra of iron (III), cobalt (II), nickel (II) and copper (II) compounds in molten sodium nitrite - sodium nitrate - potassium nitrate eutectic, reactions and spectra of chromium (III) chloride and chromium (VI) compounds in
molten sodium nitrite - sodium nitrate - potassium nitrate eutectic and reactions of chromium (III) chloride and nickel (II) chloride in molten lithium nitrate - potassium nitrate eutectic were studied by Eweka and Kerridge [168,173,174].

1.12.4 Mechanism of Reactions

Rastogi and coworkers [130] have studied the decomposition of a number of metal salts in nitrate eutectic melt and have divided the reactions into two categories:

(I) Homogeneous Reactions
(II) Heterogeneous Reactions

In the first category the metal salts dissolve in the salt whereas in the other they do not dissolve. A brief description of these reactions is given here.

1.12.4.1 Homogeneous Reactions:

In this category of the reactions, decomposition of the following type of salts has been discussed [131]: ZnSO₄, CdSO₄, HgSO₄. The decomposition of CdSO₄ and HgSO₄ obeys first order rate law. The reaction can be represented in ionic form as follows:

\[ M^{2+} + SO_4^{2-} + 2B^+ + 2NO_3^- \rightarrow B_2SO_4 + M^{2+} + 2NO_3^- \]
\[ M^{2+} + NO_3^- \rightarrow MO + NO_2^+ \]
\[ NO_3^- + NO_2^+ \rightarrow 2 NO_2 + 1/2O_2 \]

Where \( M = \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Hg}^{2+} \) and \( B = \text{Na}^+, \text{K}^+ \)

1.12.4.2 Heterogeneous Reactions:

In this category, the metal salts do not dissolve in eutectic melt and a solid liquid reaction occurs [130]. The decompositions of the following metal salts have been studied:

CoSO₄, NiSO₄, CuSO₄, CoCl₂, NiCl₂, CuCl₂.

The mechanism of such reactions can be understood by considering a solid-liquid interface between the solid metal salts and liquid (molten) nitrate eutectic. At the first instance, the nitrate ions of the melt surround the solid granules of the metal salts and then the counter-diffusion of the NO₃⁻ and SO₄²⁻/ Cl⁻ ions between the liquid and the solid particles may take place.

As a result of the counter-diffusion of the ions, sulphate/chloride salt of sodium and potassium are formed and the metal cation \( M^{2+} \) comes in contact with NO₃⁻. These two ions interact together and NO₃⁻ decomposes with the evolution of NO₂ and O₂ gases and formation of porous metal oxides. The overall reaction can be expressed as:

\[ MCl₂ + 2B^+ + 2NO_3^- \rightarrow 2BCl + M^{2+} + 2NO_3^- \]
\[ M^{2+} + NO_3^- \rightarrow MO + NO_2^+ \]
\[ NO_3^- + NO_2^+ + \frac{1}{2}O_2 \rightarrow 2NO_2 + 1/2O_2 \]
(M= Ni\textsuperscript{2+}, Cu\textsuperscript{2+}, B= Na\textsuperscript{+}, K\textsuperscript{+})

1.13 Thermal decomposition of nitrate melts

It has long been reported that alkali metal nitrates loose oxygen and form nitrates at higher temperatures in following manner,

\[ NO_3^- = NO_2^- + \frac{1}{2}O_2 \]

The NaN\textsubscript{O}\textsubscript{3} / KNO\textsubscript{3} system: the position of the solidus and sub – solidus was discussed by Berg et al. [157]. Singh et al. [132] have studied the thermal decomposition of Nickel (II) Bromide in sodium nitrate – potassium nitrate eutectic melt. Salaha et al. [175] have reported a number of reactions involving the oxidation of lead (II) in molten nitrates (Li\textsubscript{N}O\textsubscript{3}, Na\textsubscript{N}O\textsubscript{3}, K\textsubscript{N}O\textsubscript{3}, Li\textsubscript{N}O\textsubscript{3}/K\textsubscript{N}O\textsubscript{3}, Na\textsubscript{N}O\textsubscript{3}/K\textsubscript{N}O\textsubscript{3}) at higher temperatures.

1.14 Reaction in Halide Eutectic Melt

Novoselova et al. [176] investigated the redox potentials of Yb\textsuperscript{3+}/Yb\textsuperscript{2+} in a eutectic melt of sodium and cesium chlorides relative to a chlorine reference electrode in the temperature range 823–973 K. The electrochemical study of Yb (III) ions in molten alkali metal chlorides in the temperature range 723–1073 K was done by Smolenski et al. [177].

Castrillejo et al. [178] studies of rare earth oxides and oxohalides have been carried out in the eutectic LiCl–KCl melt at 450 °C and the equimolar CaCl\textsubscript{2}–NaCl mixture at 550 °C. The direct electrochemical reduction of Nb\textsubscript{2}O\textsubscript{5} was achieved by electrolysis in the CaCl\textsubscript{2}–NaCl eutectic melt at 1123 and 1173 K, respectively, at a controlled potential of 3.1 V, below the decomposition potential of the salts [179]. Oxoacidity reactions in equimolar molten CaCl\textsubscript{2}–NaCl mixture at 575 °C has been studied [180]. The reversibility of a membrane oxygen electrode Pt (O\textsubscript{2}) | ZrO\textsubscript{2} (Y\textsubscript{2}O\textsubscript{3}) and acid–base reactions in molten LiCl–KCl at 700°C have been studied by the potentiometric method [181]. The reduction and oxidation processes on platinum and glassy carbon electrodes in molten LiCl–KCl eutectic containing UCl\textsubscript{3} were investigated by cyclic voltammetry (CV), chronopotentiometry and electrochemical impedance spectroscopy (EIS) in the temperature range 660–780 K [182]. In view of increasing trend of performing solvent free reactions, reactions in molten eutectics are becoming more important. The reactions in eutectic melts occur at a lower temperature and are
more ecofriendly. These eutectics can be easily prepared either by using organic compounds or inorganic salts. Reactions in inorganic molten eutectics have been studied extensively, but very less work on the reactions in molten organic eutectics have been reported. Therefore, it was thought worthwhile to prepare reaction products through organic eutectic melts.

In the present investigation reactions between some metal carbonates (Zn, Cd and Cu) and 8-Hydroxyquinoline have been performed in the eutectic melt of 8-Hydroxyquinoline and naphthalene.

Objective of the Present Thesis

Eutectic systems are used as model systems for predicting various properties of metallic alloys and producing materials having controlled two phase microstructure forming in situ composites. Therefore, the present work has been aimed to develop and study some new eutectic materials which may offer better properties specially for producing high strength composite materials. Metallic composites are opaque in nature and thus it is not possible to carry out the visual observations on their growth fronts crystallizing from the melt. The problem of visual observation can be overcome by choosing transparent analogs of the metallic systems. In view of this, some new binary organic systems viz; Benzamide – Benzoic acid, Benzoic acid – o-Chlorobenzoic acid, Benzamide – o-Chlorobenzoic acid and Naphthols – m-Dinitrobenzene which form simple eutectics and congruent melting compounds were chosen for detailed investigation in the present thesis.

Reactions in molten eutectics are becoming more important due to increasing trend of performing solvent free reactions. The reactions in eutectic melts occur at a lower temperature and are more ecofriendly. These eutectics can be easily prepared either by using organic compounds or inorganic salts. Reactions in inorganic molten eutectics have been studied extensively, but very less work on the reactions in organic eutectic melts have been reported. Therefore, it was thought worthwhile to prepare reaction products through some suitable organic eutectic melt. Thus, in the present investigation reactions between metal carbonates viz; zinc carbonate, cadmium carbonate and copper carbonate and 8-hydroxyquinoline have been performed in the 8-hydroxyquinoline and naphthalene eutectic melt.
1.15 References


