An Overview of the Progress in Solidification of Binary Monotectics

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Abstract- **The solidification mechanism of a monotectic alloy is quite complicated due to wide freezing range of temperature and large density difference of the two liquid phases involved. However, the diffusion model by Jackson and Hunt and the wetting model by Cahn, have been successfully applied to various metallic and organic systems to explain the solidification behavior of different monotectics. Using these models, in the present paper, a current status of solidification of binary monotectics of metal as well as that of organic origins has been described and various methods to overcome the problems associated with this have been highlighted. Due to low transformation temperature, ease of purification, transparency, minimized convection effects and wider choice of materials, organic systems are better than those of metallic systems for detailed investigation of the parameters which control the mechanism of solidification, which in turn, controls the properties of materials. Organic monotectic systems, suitable for experiments under reduced gravity condition, are potentially useful to explore new manufacturing techniques to get novel materials to cater the needs of modern civilization.**

Keywords- Monotectic Crystallization; Binary Monotectics; Binary Organic Solidification; Mechanism of Solidification

I.   INTRODUCTION

The modern age of science demands materials with diverse properties. The fundamental understanding of solidification [1-4] and properties of polyphase alloys is the key to develop new materials of technical and commercial importance. Chemistry of eutectics [5-10] and monotectics [11-27] has been a subject of potential investigation due to their unusual physical properties not normally shown by the parent components. Due to low transformation temperature, ease of purification, transparency, wider choice of materials, minimized convection effects, easy experimentation and possibility of visual observation, organic systems [6, 8, 11-23, 28-44] are being used as model systems for detailed investigation of the parameters which control the mechanism of solidification which, in turn, controls the properties of materials. It is well known that eutectic reaction is characterized by the isothermal decomposition of a eutectic liquid into two solids and monotectic reaction is associated with the decomposition of a monotectic liquid at an invariant temperature, into a solid and another liquid. The eutectic reactions have been examined in detail during the last four decades and their products are currently in wide practical applications. The freezing behavior of monotectic is more complicated. The main problem arises due to a wide freezing range and large density difference between two liquid phases. This results in low cast quality and de-mixing of liquid phases, which have delayed the potential use of monotectics as industrial material. A critical scanning of the existing literature [13-15, 25-33] has revealed that the segregation can be influenced and relaxed by directional freezing, vigorous stirring, chill casting and micro-gravity conditions.

In the present paper, the directional solidification behavior of monotectics, in general, and binary organic monotectics, in particular, has been reviewed and the current status of solidification is highlighted. On the basis of solidification behavior, the organic compounds have been classified as metallic and non-metallic. A list of eleven organic compounds solidifying like metal is reported earlier [45]. In comparison to this the number of organic compounds solidifying like non-metal is quite large. If both organic components of a monotectic system solidify like metal, the system is called as organic analogue of metal-metal system and when both components solidify like non-metal the system is known as organic analogue of non-metal-non-metal system. When one organic component of the system solidifies like metal and the other like non-metal, the system will be known as organic analogue of metal–non-metal system. Thus three types of binary combinations are possible. Details of all the above three types of organic monotectic systems dealing with their phase-diagram, solidification behavior, thermochemistry and microstructure are reported in the literature [28-43].

Various attempts have been made to classify the different types of microstructures that can be obtained by solidifying alloys of eutectic composition. Smith and co-workers [29, 46-47] have classified the eutectic microstructures in terms of parameters that influence the growth process. It was shown that many binary eutectics display closely similar range of morphology, permitting broad groupings such as normal (regular) eutectics and anomalous (irregular) eutectics. In normal structure, the two phases appear either as alternate lamellae, or as rods of the minor phase embedded in the other phase. During solidification, both the phases grow simultaneously behind an essentially planar solid-liquid interface. Several commercially important casting alloys show anomalous type of structures. When the primary phase is unable to serve as the nucleating agent for the secondary phase, eutectics with anomalous structure is formed. The secondary phase nucleates heterogeneously in the liquid and its randomly oriented particles grow rapidly to absorb the supercooling in an irregular fashion.

II.　REVIEW OF LITERATURE ON MONOTECTICS

Basically there are two models which explain the solidification behavior of monotectic alloys. These are (i) Diffusion model and (ii) Wetting model. Although the diffusion model was given by Jackson and Hunt [48] to describe the morphology of regular eutectics, it was successfully applied by different workers [4, 31, 49] to explain the morphology of regular monotectics. According to this model, during steady state eutectic solidification (Fig. 1), the β-phase rejects the atoms of A while the α-phase rejects the atoms of B where A and B are the components. These atoms reach the respective interface by diffusion through the liquid above the solid/liquid interface. Contrary to the eutectic where both components solidify in the solid form below eutectic temperature, a monotectic reaction is characterized by the breakdown of a liquid into one solid and one liquid phase. The Monotectic composition is determined by the intersection of a liquidus line and liquids miscibility gap as shown in Fig. 2. The directional solidifications of α phase, β phase and liquids phase are also shown in this Figure.
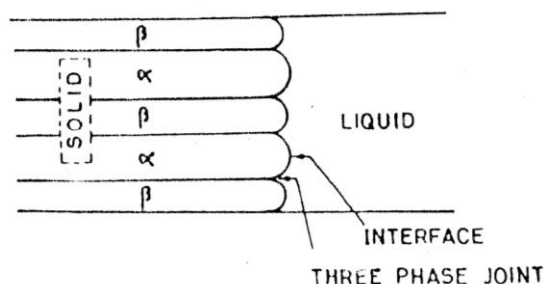

Fig. 1 Drawing of the steady state solid-liquid interface morphology
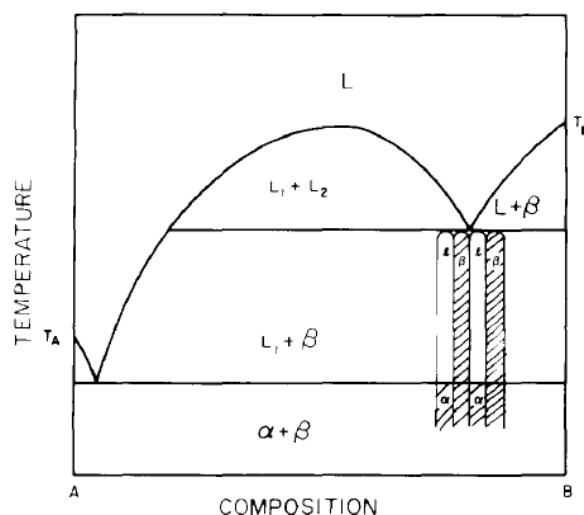

Fig. 2 Phase diagram of monotectic system and directional solidification of B components

The solidification behavior of Phenanthrene (Ph) − succinonitrile (SCN) monotectic system, studies by Singh et al. [31] report that the same monotectic melt produces the sphere or rode type structure depending on the supercooling. They have compared this microstructure to that of Al−Bi system reported by Schofer et al.[54] In case of Ph−SCN system the wetting condition, $\Upsilon_{SL2} < \Upsilon_{SL1} + \Upsilon_{L1L2}$ where Υ is the interfacial energy between the faces denoted by the subscripts, is applied. As such the Ph−SCN liquid wets the solidified Ph perfectly and SCN rich droplets are surrounded by SCN−PH liquid. Under this condition there is possibility of capillary instability of the type given in ref. [54]. As shown in Fig. 3a and 3b, if the cell depths are greater than the droplet circumference, capillary instabilities would develop SCN droplet and they will pinch off in to spheres. Repetition of this process produces an array of spheres. At low growth rate, the droplets are not long enough to develop capillary instability. This SCN droplet gets surrounded by solidified Ph in such a way that cylindrical rod of SCN freeze as the solidification proceeds.

According to the wetting model [50-53] in the monotectic reaction ($L_1 \rightarrow S_1 + L_2$), the reaction constituents are in contact as given in Fig. 4. Chadwick [50] proposed that monotectic composites cannot be grown unless the relative surface energies are such that equilibrium contact between L_2 and S_1 occurs. As such when L_2 does not wet S_1, monotectic growth cannot take place. In this condition, Cahn [52-53] suggested monotectic growth in the light of critical wetting, critical velocity and disjoining pressure. The nucleation of liquid L_2 depends on the balance of interfacial tensions and as such the following three situations (Fig. 5) arise:
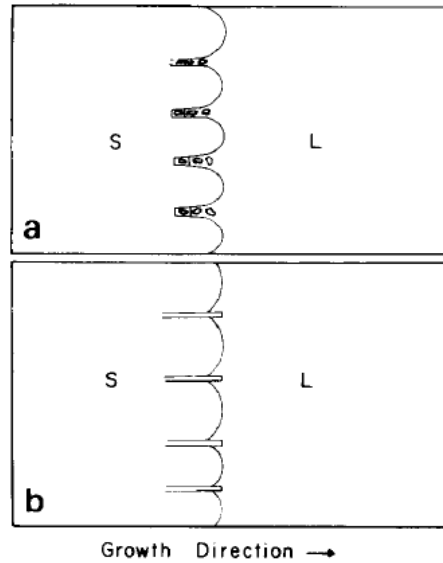
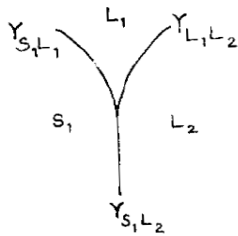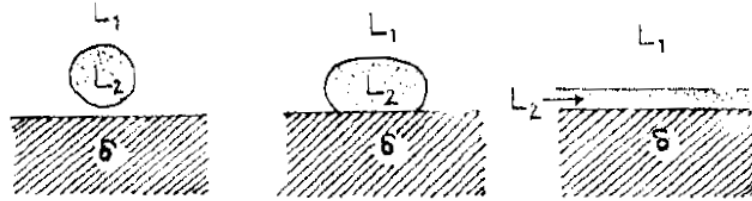Fig. 3 Formation of (a) sphere and (b) rods during the monotectic reaction

Fig. 4 Monotectic reaction components   Fig. 5 The nucleation of L_2 depends on the balance of interfacial tensions

A. If $\Upsilon_{S1L2} > \Upsilon_{S1L1} + \Upsilon_{L1L2}$, there will be non-wetting condition and a steady state growth of the monotectic will be observed.

On the other hand, if $\Upsilon_{S1L2} > \Upsilon_{S1L1} + \Upsilon_{L1L2}$, droplets of L_2 will be formed. They will sink or float is given by the Stokes formula,

$$V = 2gr^2 (D_1\text{-}D_2)/9\eta_1 \tag{1}$$

Where, V = liquid droplet float velocity

g = acceleration due to gravity

r = radius of droplet

D_1= density of liquid L_1

D_2= density of liquid L_2

η_1= viscosity of liquid L_1

R = solid-Liquid interface advance velocity

If V > R, L_1 will solidify at the bottom and L_2 will solidify at the top. On the other hand if V< R, steady state fibrous growth of L_2 will be observed.

B. If $\Upsilon_{S1L2} = \Upsilon_{S1L1} + \Upsilon_{L1L2} \cos\theta$, there will be partial-wetting. A steady state fibrous growth of L_2 will be obtained.

C. If $\Upsilon_{S1L2} < \Upsilon_{S1L1} + \Upsilon_{L1L2}$, there will be complete wetting. A steady state growth of L_2 will be observed.

Grugel and Hellawell [55] applied the wetting model [50-53] for Al-In, Cu-Pb, Cd-Ga, succinonitrile (SCN)-H_2O monotectics and realized the importance of upper consolute temperature (T_c), monotectic temperature (T_m) and the critical wetting temperature (T_w) when $\Upsilon_{S1L2} = \Upsilon_{S1L1} + \Upsilon_{L1L2}$, and suggested balanced wetting when $T_m < T_w$ and perfect wetting when $T_m > T_w$ (Fig. 6). According to them either $\Upsilon_{S1L2} > \Upsilon_{S1L1} + \Upsilon_{L1L2}$ or $\Upsilon_{S1L2} < \Upsilon_{S1L1} + \Upsilon_{L1L2}$ and $\Delta\Upsilon = \Upsilon_{S1L2} - (\Upsilon_{S1L1} + \Upsilon_{L1L2})$ may be positive or negative. If $T_m < T_w$, $\Delta\Upsilon = +$ ve, it will result steady state growth and high miscibility gap (Example: Al-In). If $T_m > T_w$, $\Delta\Upsilon = -$ ve, it will give non steady state growth and low miscibility gap (Example: Cu-Pb, Cd-Ga, and SCN-H_2O).
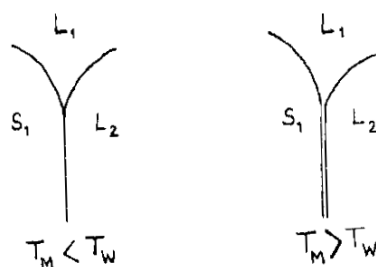
Fig. 6 Alternative wetting condition at S_1–L_1–L_2 monotectic growth front

Derby and Favier [56] have studied morphology of monotectics of Al-Bi, Al-In, Cd- Ga, Cu-Pb and Zn-Bi and reported that the systems do not obey wetting model. Their solidification behavior is explained satisfactorily by the Jackson-Hunt [48] diffusion model. They suggested that the regular monotectics dealing with lamellar or rod morphology is similar to regular eutectics and the irregular monotectics dealing feather or dendritic morphology are similar to irregular eutectics. This similarity is also reflected in the morphologies of the two reactions, both being able to form irregular and branching fibrous structures. Schaefer et al. [54] studied solidification behavior of Al-Bi monotectics and suggested that the morphology of monotectic is controlled by G/R ratio, where G is temperature gradient and R is growth rate. When G/R is large, rod monotectic and when G/R is small, monotectic gives rows of spheres. According to them the development of regularly spaced and regularly sized rods or spheres in a monotectic system can be understood in terms of interface breakdown and capillary instability mechanism between two liquid phases. The G/R ratio determines the depth of the intercellular nodes. When these nodes are shallow, rods are developed and spheres are produced when they are deep.

Grugel et al. [57] studied monotectics of both of metal and organic origin and suggested that the monotectic morphology depends on the ratio T_m/T_c. If $T_m/T_c = 0.9$, transition point and when $T_m/T_c < 0.9$, regular monotectic and if $T_m/T_c > 0.9$, irregular monotectic will be observed. On this basis they suggested regular microstructure for Al-In, Sb-Sb$_2$S, Al-Bi, SCN-H$_2$O, SCN-Glycerol and irregular morphology for Cu-Pb, Cd-Ga, SCN-C$_2$H$_5$OH systems. The significance of the transition temperature ratio is related to the idea of critical wetting temperature, T_w, suggested by Cahn. Above this temperature one liquid wets a third phase to the exclusion of the other and apparently precludes the development of a steady state growth front. Steady state growth in monotectic alloys seems to produce a slightly larger product for $\lambda^2 v$ (where λ = Inter-lamellar distance and v = Growth velocity) than in eutectic alloys. This may arise from a smaller entropy term for the liquid-liquid transformation and from enhanced diffusion brought about by mixing in the product liquid phase. Grugel and Hellawell[58] studied break down of fibrous structures of organic monotectics of SCN-Glycerol, SCN-C$_2$H$_5$OH and SCN-p-cresol systems and suggested regular arrangement of droplets, elongated droplets and fibrous morphology depending on temperature gradient and growth rate.

Growth morphology of organic monotectic systems was studied by singh et al. [31], Kaukler and Frazier [59] and Song and Hellawell [24] and they reported strong dependence of monotectic morphology on growth rate. In SCN-H$_2$O and SCN-Glycerol systems, steady state growth when growth rate < 1 μms^{-1} and in SCN-Benzene and SCN-C$_2$H$_5$OH systems non-steady state growth when growth rate > 0.1 μms^{-1} was reported by Song and Hellawell. In all cases when the growth rate is greater than 1 μms^{-1}, tubular morphology of monotectic was obtained. The ability of a monotectic reaction to proceed in a steady state manner and to produce an aligned structure does not depend on sample dimensions and is consistent with some critical ratio of the monotectic temperature to upper consolute temperatures, T_m/T_c. This temperature ratio may correspond to a critical wetting condition in any given system. Above a certain rate, steady state growth is not possible in any monotectic alloy, but in systems having a smaller T_m/T_c ratio, the upper rate limit is higher. W. F. Kaukler and D. O. Frazier [11, 59] reported the dependence of monotectic microstructure on various factors such as relative density of phases, interfacial tension and its variation with temperature and composition, thermal conductivities, fluid dynamics, interface morphology etc. in SCN-Benzene and SCN-H$_2$O monotectic systems. A review on binary phase diagram and microstructure is given by Voort [60] and a survey on constitution and thermodynamics of monotectic alloys is given by Predel [23]. Application of Jackson – Hunt model of diffusion has been discussed by B. Majumdar and K. Chattopadhyay [4, 25] in Zn-Bi monotectic system.

III. METALLIC MONOTECTICS

It is well known that solidification is influenced by gravity through buoyancy-driven thermosolutal convection, Stocks flow and hydrostatic pressure. The thermal gradient is an important source of density gradient responsible for natural convection in the liquid. This convection can be avoided not only by eliminating gravity but also by unidirectional solidification in a vertical configuration with solidification anti-parallel to gravity in which the less dense hotter liquid will be located at the top. Alternative by, a density gradient can be caused by a solute gradient resulting solutal convection. The thermal and solutal density gradients when combine together they result in thermosolutal convection. In the case of monotectic alloys when monotectic liquid is cooled below monotectic temperature, it decompose to give the primary grown phase and in the case of density deference it lead to Stock's flow or gravity driven flotation acting on the free surface. Lastly, the hydro or metallostatic

pressure does not exist in absence of gravity. As a consequence, a source of stress is removed, making the shape of liquid drops to be determined by the surface tension and influencing the porosity in the casting. The absence of hydrostatic pressure in a microgravity environment allows liquid to be confined solely by surface tension and it offers the possibility of melting and solidifying materials without physical contact with the container walls. The latter possibility eliminates major source of heterogeneous nucleation sites, namely the wall of the container.

In binary invariant eutectic or monotectic reactions, coupled growth leads to a periodic concentration profile in the liquid close to the interface that decays in a direction perpendicular to the interface much faster than in single-phase solidification. For binary or multi-component alloys, the redistribution of the solute occurs over a much longer distance and perpendicular to the solid/liquid interface. In the case of monotectic growth, the effects of liquid flow are more important as one of the phases growing in monotectic reaction from liquid is another liquid phase. As such the L_1/L_2 interface with a low energy interface with high mobility represents a high diffusivity path. In general the monotectic composition is low and close to the higher melting point components such that the monotectic reaction resulting second liquid phase minimizes it's interfacial energy to the growing interface. In summary, the effect of liquid flow driven by buoyancy, density differences and capillary effect on confined growth of binary eutectic and monotectic alloys is not fully understood till date.

Several aluminium based alloys, namely, Al-Pb, Al-In, Al-Bi and Al-Cd are potential material for bush wearing applications in mobile industry. These are produced currently by spray forming technique [61-62]. In this process the monotectic melt is atomized from temperature above the liquid immiscible boundary of the system. The cooling rate of the droplets often exceeds $10^6 \, Ks^{-1}$. The high cooling rate minimizes separation of Al and Pb rich droplets. Subsequently, during deposition state a highly turbulent fluid flow condition on the deposition surface further promotes fragmentation of lead rich liquid. The preform thus produced exhibits the dispersion of ultra fine lead particles in Al-matrix. Such microstructures are desirable for their superior wear properties. In general, wear rate decreases with increasing lead content and hardness of the base alloy, but friction does not decrease beyond a certain concentration of lead. Pb-Al alloys are characterized by low wear rates, anti friction and anti seizure characteristics. Lead present in aluminium alloys acts as a solid lubricant and reduces friction and wear between the mating planes. Lead is extruded during service and forms a thin layer of low shear strength spread over a stronger substrate.

Curiotto et al. [63] determined the metastable monotectic diagram of Cu-Co, Cu-Fe and Cu-Co-Fe systems and the data on these systems were confirmed by determining new phase diagram using differential scanning calorimetry and comparing them in the calculated phase diagram. Silva et al. [64] studied cooling rate, growth rate, temperature gradient, interface spacing and diameter of the Pb-rich phase for a hypomonotectic Al-0.9 wt. % Pb and a monotectic Al-1.2 % Pb alloy, directionally solidified under study-state flow condition. For both cases, it was shown that from the cooled bottom of the casting up to a certain position along the casting length, the microstructure was characterized by well-dispersed Pb-rich droplets in the aluminium-rich matrix, followed by a region of morphological transition and finally by a mixture of fibbers and strings of perls for positions closer to the top of the casting. The phase diagram of pseudobinary Ag-TiO$_2$ system, determined by differential thermal analyser, gives two monotectic with melting temperatures 930 ^{o}C and 538 ^{o}C with 8 and 52.5 % mole percent of TeO$_2$, respectively. This system also gave one eutectic at 523 ^{o}C with 42 mol % TeO$_2$, and two miscibility gaps with critical temperatures 965 ^{o}C at 20 mol % of TeO$_2$ and 555 ^{o}C at 47.5 mol % TeO$_2$. Silva et al. [65] also studied a hypomonotectic Al-5.5 wt % In alloy directionally solidified non-steady-state flow conditions. Tip growth rate, microstructural feature, such as cell spacing and interface spacing, have been experimentally determined and data have been compared with theoretical predictions given by Hunt-Lu model [66].

Boettinger et al. [67] have given a critical account of solidification science with emphasis on interface dynamics, peritectic growth, convection effects, multicomponent and numerical technique. It is also shown as to how the new mathematical technique coupled with powerful computers allow modelling of complicated interface morphologies, taking into account steady state and non steady state phenomena. Chen et al. [68] studied directional solidification and convection of Pb-2.2 wt % Sb alloy in 1, 2, 3 and 7 mm diameter crucibles. Under plane-front condition, the resulting macrosegregation along the solidified length show that the convection persists even in the 1 mm diameter crucible. Al-2 wt % Cu alloy expected to be stable with respect to convection indicated the presence of convection. Simulations performed for both alloys show that convection persists for crucibles as small as 0.6 mm of diameter. Norris et al. [69] have given a detailed account of faceted interfaces in directional solidification describing process of freezing a liquid by pulling it through an externally induced temperature gradient. At high pulling speeds, this gradient steepens sufficiently to create instability, replacing normal planar interface with more complicated cellular or dendritic structures which is more common in organic alloys. Directionally solidified aluminum-7 wt pct Si alloy sample grown from $< 100 >$ oriented single crystal seeds were examined to investigate the detachment of tertiary arms and growth of spurious grains during steady state solidification [70]. This study shows that the tertiary arms, which appear to be attached and aligned with respect to their neighbours in optical microscope views, can be significantly misaligned when examined by electron back scattered diffraction. The extension of tertiary arm displacement appears to depend on a complicated interplay between gravity driven thermosolutal convection and gravity independent phenomenon effect such as capillarity.

IV.   ORGANIC MONOTECTICS

It is well known that direct observation on solidification of transparent organic systems has been the most useful technique for unravelling the mysteries of solidification. It is evident from the available literature [11, 24, 29, 31, 33-43] on organic monotectics that there are two groups of workers. One group [11, 24, 29] is involved in the study of phase diagram and morphology of monotectic systems (SCN-H$_2$O, SCN-Glycerol, SCN-Benzene, SCN-C$_2$H$_5$OH) and effect of various parameters on it. Today, one can observe the solidification process of a transparent model system and generalize to metallic systems, which produce similar casting patterns. In view of this SCN-H$_2$O monotectic system phase diagram was re-determined [29] using current methods and a difference of 11.4 % in monotectic composition and 1.7 % variations in monotectic temperature were reported. In addition, worm-like monotectic solidification interface morphology was observed by Kaukler and Frazier [11] in this system. The other group [31, 33-43] is involved in the investigation of phase diagram, growth kinetics and thermochemistry of binary organic monotectics. However, Singh et al. [31] have justified the applicability of Jackson-Hunt theory by giving experimental data on phenanthrene-succinonitrile binary organic system. Neither diffusion model nor wetting model is able to explain all experimental observations satisfactorily. The solidification behavior of metal monotectic is quite complicated and it is more difficult to control the microstructure of a monotectic in comparison to a eutectic. The main problem during monotectic growth arises due to a wide freezing range and large density difference between its phases. In view of this Rai and co-workers [31, 33-43] have studied phase diagram, growth kinetics, thermochemistry and microstructure of the following systems:

S. No.	Systems
[1]	Carbontetrabromide - Succinonitrile (SCN)
[2]	Acenaphthene - SCN
[3]	Diphenyl - SCN
[4]	Hexamethyl benzene - SCN
[5]	1,2,4,5 -Tetramethyl benzene - SCN
[6]	Pyrene - SCN
[7]	Phenanthrene - SCN
[8]	4,4-Dibromobenzene - SCN
[9]	4-Bromochlorobenzene - SCN
[10]	1,4-Dibromobenzene - SCN
[11]	Pentachloronitrobenzene - SCN
[12]	1,4-Diidobenzene - SCN
[13]	TCB - m-Aminophenol
[14]	TCB - Resorcinol
[15]	1,2,4,5-Tetramethylbenzene (TMB) - Resorcinol
[16]	TMB - Pyrogallol
[17]	TMB - m-Aminophenol
[18]	1,4-Dibromobenzene(DBB) - m-Aminophenol
[19]	DBB - Resorcinol
[20]	Urea - p-Chloronitrobenzene
[21]	1,4-Diiodobenzene - Resorcinol
[22]	4-Bromochlorobenzene (BCB) - Resorcinol (R)
[23]	2-Cyanoacetamide - 4-Choloronitrobenzene
[24]	Urea and 1,3-Dinitrobenzene
[25]	Urea - 4-Bromo-2-nitroaniline
[26]	Biphenyl - 3-Hydroxybenzaldehyde
[27]	1,4-dibromobenzene - Pyrogallol

While S. No. 1 is organic analogue of metal-metal system those of S. Nos. 2-12 are organic analogues of metal-nonmetal systems and the remaining S. Nos. 13-27 are organic analogues of nonmetal–nonmetal systems. While growth data obey square relationship between growth velocity and undercooling, those of thermochemical investigations suggest the applicability of Cahn wetting condition in these systems. In most of the cases the Cahn wetting condition has been successfully applied and a rod type or arrays of spheres type microstructures were observed. The systems, in which the wetting condition is not applicable, an irregular morphology was obtained. The basic aim of the present overview is to give to scientific community a large number of potential monotectic systems suitable for study of mechanism of monotectic solidification due to minimized convection effects and, due to their transparent nature, the possibility of direct observation on solidification.

In many cases gravity driven convection and fluid flow are very important and microgravity experiments could be employed to understand these problems. In general, convection and fluid flow are of great importance for understanding the complexity of solidification phenomena and developing crystal growth techniques. In the microgravity environment it is expected that bulk diffusion and interfacial effects will dominate and that fluid convection can be suppressed to a negligible extent. In the absence of convection, it is possible to control the other process variables such as temperature, composition, etc. very precisely. Dendritic morphology of pivallic acid and succinonitrile was studied by Singh [49] and he reported that growth

velocity varies as a function of orientation with respect to gravity vector. The solidification mechanism of monotectic dendrites, poly phase materials, is quite complicated and needs exhaustive studies for unravelling the mysteries of their crystallization.

V.   FUTURE PROSPECTS

The updated literature [11, 24, 29, 31, 33-43] on monotectic solidification illuminates that monotectic systems with a large miscibility gap in the liquid state have received less attention despite many alloys of monotectic group offer interesting potential applications. The solidification behavior of monotectic is highly complicated and it is more difficult to control the microstructure of a monotectic in comparison to a eutectic. The main problem during monotectic growth arises due to a wide freezing range of temperature and a large density difference between two liquid phases. These parameters result in low cast quality and de-mixing, which cause inhomogeneity in resulting alloy material. These drawbacks have delayed the wide use of metal monotectics as industrial material to date. In order to overcome the problem associated with the monotectic systems, various methods such as directional freezing [31, 47, 55, 57], squeeze casting [44], vigorous stirring, heating, spray forming [61-62], flow casting, rheo casting, powder metallurgy, alloy preparation under reduced gravity condition and under ultrasonic vibrations [71] are being exploited. Due to minimized convection effects and possibility of direct observation of solidification, the organic monotectic systems will prove to be of immense importance to study the effect of various parameters such as relative density of phases, interfacial tension and its variation with temperature and composition, interface morphology, fluid dynamics, acceleration due to gravity, viscosity of monotectic liquid, solid-liquid advanced velocity, radius of droplet, temperature gradient, ratio of monotectic temperature with consolute temperature etc. on monotectic morphology. The commercial and technical use of monotectic composites to cater the needs of novel materials for modern civilization for practical application will depend on the success of study of the above parameters and knowledge of their role on the mechanism of monotectic solidification.

VI.   APPLICATONS OF SPACE PROCESSING

The microgravity can be exploited to understand and control various aspects of materials processing. In the studies of the solidification characteristics of materials one can observe various types of solidification morphology [49] whenever supercooling or supersaturation exists ahead of the solid-liquid interface. For example, the dendritic morphology is very common and well known in many materials. When a very pure melt freezes this way, the latent heat of fusion flows from the moving solid-liquid interface into the supercooled melt. This heat transfer produces a thermal field around the growing dendrite. The presence of this thermal gradient is responsible for so-called diffusion heat flow. The direct observation of dendritic morphology and growth velocity was made by Glicksman [28] and the results were compared with the existing theories in the area. The materials used for the studies were transparent organic compounds, namely, pivallic acid, cyclohexanol and succinonitrile. Extremely careful experiments showed that beyond a critical supercooling, dendritic growth is dominated by the transport, and convection effects are negligible. However, at lower supercooling the gravity driven natural convection strongly influences heat transport. The morphological evolution in binary systems in which dendritic growth occurs is much more complex and it is controlled by diffusion even in earth's gravitational field, if the reasonable precautions are taken to choose convectively stable geometry and maintain good control of growth velocity and temperature in a layer near the interface that is much thinner than the boundary layer for convective flow under 1-g condition. Details of several NASA flight experiments on materials from organic as well as metal origins dealing with effects of mass transport and various thermo-physical properties on the solidifications behavior under reduce gravity condition are described earlier [72-75].

The influence of surface energy on solidification morphology in the monotectic systems are of potential importance. These systems consist of a liquid which, on cooling transforms to solid and a liquid of differing composition. Due to lack of information on surface energies and complications due to wetting phenomena, the choice of systems for the study is limited. Generally, the solidification of monotectic alloys produce two different fibrous morphologies characterized as regular and irregular. Direct observation of the freezing interface of transparent organic systems such as succinonitrile-water and succinonitrile-phenanthrene systems have been used to reveal details of the solidification structure. The second type of morphology, termed, worm like, was observed in the succinonitrile-water system. Shuttle experiments on these systems will unfold various mysteries such as wetting behavior, quality of dispersed in-situ composites, nucleation behavior in immiscible region, and morphological changes.

VII.   CONCLUSIONS

Transparent binary metallic alloy models are importance in material and metallurgical science as they permit visual observation of the processes during solidification. The monotectic temperature in a binary mixture is the temperature at which two immiscible solutions of the same components form phases in equilibrium with the solid phase of one of the components. The growth of unique and high perfection crystals for optical and electronic devices depends on the compositional uniformity, crystal defect density and mass heat-transfer conditions during growth, especially in the vicinity of solid-liquid interface. Slight perturbations in the conditions of equilibrium at the fluid-crystal interfaces cause the instabilities, which lead to interfacial convection resulting acceleration of material exchange by hydrodynamic coupling and density instabilities. The basic questions regarding crystal growth are: What is the thermal stability of the system? What is the thermal gradient at the interface? Are the facets developed at the interface? Is the interface, convex, planar, or concave on a microscopic scale? The space experiments

would provide the advantage that gravitationally induced transport phenomena could be separated from those that predominate in the microgravity environment. Secondly, space experiments will provide a relationship between diffusional transport mode and the compositional and structural defects in the crystals.

ACKNOWLEDGMENT

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