Free Solidification of Undercooled Eutectics

Mingjun Li¹,²,* and Kazuhiko Kuribayashi³

¹National Institute of Advanced Industrial Science and Technology, Materials Research Institute for Sustainable Development, Nagoya, 463-8560, Japan
²Japan Aerospace Exploration Agency, The Institute of Space and Astronautical Science, Tsukuba Space Center, Tsukuba, 305-8505, Japan
³Japan Aerospace Exploration Agency, The Institute of Space and Astronautical Science, Sagamihara Campus, Sagamihara, 229-8510, Japan

The traditional eutectic solidification theories always stress the role of eutectic growth and morphology selection. However, when a eutectic alloy solidifies freely from an undercooled state, the first step commences from nucleation and then follows eutectic growth. This paper reviews the free solidification behaviour of various undercooled eutectic alloys from the viewpoints of nucleation and growth. It is realized that an independent eutectic colony should be the basic unit when discussing eutectic solidification rather than a bulk sample, which urges us to re-examine the previous discussions and conclusions that were based on bulk solidification in which the role of nucleation was frequently ignored. Regarding to the eutectic growth after nucleation, particular emphasis is devoted to shedding light upon the physical mechanisms of the anomalous eutectic formation when the eutectic is undercooled beyond a certain critical undercooling. The interface attachment kinetics of terminal phases in a eutectic reaction is of great importance in yielding decoupled growth between a mobile interface and a sluggish interface. Further growth behavior after decoupled growth occurs is investigated when the effect of crystallization heat on solidification is considered.

Future work is briefly directed to improve current understanding on the free solidification from undercooled states.

(Received May 31, 2006; Accepted October 16, 2006; Published December 15, 2006)

Keywords: containerless processing, undercooling, nucleation, growth kinetics, anomalous eutectic

1. Introduction

A eutectic alloy at eutectic composition has two or more phases as its terminal components, which is of great potential as a composite material because of good mechanical properties. Moreover, alloys with the eutectic composition have good fluidity and castability, which enables the alloys a wide application in engineering.

The early pioneering work on regular eutectic growth should be attributed to Brandt,¹ Zener,² Tiller,³ and Hillert,⁴ who considered steady-state growth of coupled phases at constant velocity. Based on the pioneering work, Jackson and Hunt⁵ (JH model) developed a comprehensive model to illustrate the growth criteria of lamellar and rod eutectics when considering the diffusion field at a low growth rate. Trivedi et al.⁶ (TMK model) extended this model to large undercoolings for rapid solidification by releasing two critical restraints for small Peclet numbers. Kurz and Trivedi⁷ (KT model) further incorporated the effect of nonequilibrium solute trapping on eutectic growth at high growth velocity. Note that in all these theories only growth of coupling eutectics is considered under the assumption that terminal solid phases are already present so that growth of phases can further proceed, which is usually the case for directional solidification.

With respect to free solidification of eutectics from undercooled states, the earliest experimental work may be dated back to Tammann and Botschwar,⁸ who tried to determine the coupled zones of eutectic as a function of melt undercooling. In 1965, Powell and Hogan⁹ undercooled silver-copper eutectic alloys, in which they found copper particles imbedding into the continuous matrix of silver. From then on, many researches¹⁰–¹⁶ undercooled various eutectics to investigate the solidification behavior of this group of alloys. One of the most striking features in microstructure evolution has been verified in many non-faceted-faceted eutectics with eutectic compositions, i.e., with the increase of melt undercooling, the microstructural morphology experiences a transition from pure regular eutectics at low undercoolings and then a mixture of anomalous and regular eutectic at medium undercoolings and finally a unique anomalous eutectic when the alloy is deeply undercooled to exceed a certain critical undercooling. Accordingly, various models¹⁰–¹² have been proposed to account for the physical origin of the microstructure development, based on either dendrite growth within the entire volume of the alloy or the Karma model for dendrite fragmentation. However, as a poly-domain system, a eutectic alloy always implies nucleation, which is characterized by independent eutectic colonies. After realizing that nucleation plays a vital role in the eutectic systems, we have systematically investigated the free solidification of this group of alloys, including various oxide and metallic systems. In this paper, we will review the free solidification behavior of undercooled alloys after incorporating our recent research results.

2. Nucleation of Eutectics from Undercooled Melts

2.1 Traditional concepts on eutectic nucleation

In directional solidification of eutectics, the terminal phases can usually grow from a preset seeding crystal or an as-existed substrate in an epitaxial manner. However, in free solidification, either for a multi-phase eutectic alloy or a single-phase dendrite alloy, the first step to initiate crystallization is to create an effective nucleus, from which further growth may become possible.

To have a clear skeleton, let us first make a brief overview
of nucleation behavior in single-phase dendrite systems. In order to account for the physical mechanism of refined microstructures from deeply undercooled Ni melts, Walker\textsuperscript{17) first proposed that copious nucleation occurs at the large undercooling regions and thus generates a great number of nuclei, from which independent grains can grow to form refined microstructures. Obviously, such kind of nucleation behavior should result in a random distribution in texture, which is consistent with pole figure mapping by Lee et al.\textsuperscript{18) who attributed the refined microstructures of Ni\textsubscript{0.45}B\textsubscript{0.55} alloys to “dynamic nucleation” that is similar to copious nucleation, when alloys are solidified from deeply undercooled states. At medium undercooling range, this nucleation mechanism, however, becomes unviable and contradicts with observed microstructures, in which well developed dendrites grow from the nucleation site and then propagate throughout the entire sample, as have been confirmed in Fe-Ni,\textsuperscript{19) Ni-Cu,\textsuperscript{20)} and other single-phase alloys. Therefore, a traditional assumption has predominated over years in the undercooled solidification community, i.e., once an effective nucleus is formed in a deeply undercooled melt, it is sufficient to initiate the melt to crystallize immediately and thus recrystallization will complete within several micro seconds. In this case, the recrystallization boundary with a sharp contrast between the crystallizing bright solid and the undercooled dark liquid can be treated as the solid/liquid interface and thus the advancement rate of the recrystallization front can correspond to the growth velocity of the crystal, which is acquired by dividing the distance covered by the solid/liquid interface within a specific time interval. Following this assumption, the measured growth velocity versus melt undercooling, e.g., in Fe-Ni,\textsuperscript{19) Ni-Cu,\textsuperscript{21) Ni-Zr,\textsuperscript{22) Ni-B\textsuperscript{23) and Ni-C\textsuperscript{24) alloys, agrees well with dendrite growth theories\textsuperscript{25–27) in dendrite regions, which, in turn, strengthens the rationality of the one-effective-nucleus assumption in dendritic growth in single-phase alloys.

It is worth noting that this assumption has been extended to the solidification of double-phase eutectics without any convincing evidence that this extension is plausible. In the meanwhile, there has been much work that was based on this arbitrary extension, either directly or indirectly. The most distinct extension of the assumption is to measure eutectic growth velocity as a function of melt undercooling by using photo sensing diodes, similar to that as have made for single phase alloys. For example, Wei et al.\textsuperscript{28) and Geotzinger et al.\textsuperscript{29) measured growth velocities versus melt undercooling in Co-25.5 at% Sb and Ni-21.4 at% Si eutectic alloys, respectively, from which they\textsuperscript{28,29) discussed the influence of temperature dependent diffusion coefficients on eutectic growth. The other application of the arbitrary extension is to discuss the physical origin of anomalous eutectic formation from the viewpoint of dendritic growth.

Therefore, an important question arises as; whether or not it is correct to extend the analysis method for single-phase alloys to multi-phase eutectics by ignoring the role of nucleation.

2.2 Reexamination of nucleation behavior in undercooled eutectics

A well defined melt undercooling can be achieved via several routines as the glass fluxing method, electromagnetic levitation, electrostatic levitation, aero-acoustic levitation, aero-dynamic levitation. For the fluxing technique, a metallic alloy is usually encapsulated in molten glass slag and then heated by rf induction. Because of a large viscosity and a high interfacial energy of the glass slag, the surface morphology of a solidified sample usually exhibits a mirror-like feature. Even when the sample surface was etched, Walder and Ryder\textsuperscript{30) only observed concentrated pellets crowding at the surface without any further details. In comparison, all the aforementioned levitation facilities can provide a containerless condition for processing metallic or non-conducting oxide materials, by which a direct observation of the original surface microstructures becomes possible. Meanwhile, it should be noted that although a drop tube can provide a containerless solidification condition as well, the small size and rapid motion of a molten droplet during free fall make it hard to measure accurately the droplet temperature and thus the melt undercooling upon recalescence is unclear, which does not favor a detailed analysis on the solidification behavior from the viewpoints of thermodynamics and kinetics. Furthermore, the stochastic nature of nucleation due to various fluctuations in a melt makes it ambiguous to correspond an undercooling value to a droplet with a specific diameter.

Figure 1(a) shows the surface microstructure of the binary Al\textsubscript{2}O\textsubscript{3}-36.8 at% ZrO\textsubscript{2} eutectic solidified spontaneously at an undercooling of about $\Delta T = 480 \text{K}$ on the aero-acoustic levitator (AAL) when a CO\textsubscript{2} laser beam was employed to heat and melt the oxide sphere. One can see that the sample surface consists of independent eutectic colonies and neighboring colonies have very clear contacting boundaries. Furthermore, each colony originates from a protruding site near the center of the colony, from which a radial structure develops. Based on the microstructure, it can be readily deduced that the protruding site is the starting point of the eutectic colony, which can act as the nucleation site of the colony. Considering that there are a lot of eutectic colonies at the sample surface, one can tell that copious nucleation or massive nucleation takes place in the bulk solidification of the oxide eutectic. In the meanwhile, it is worth noting that this kind of surface morphology has been observed in all samples solidified either spontaneously or by external seeding. Furthermore, a complete eutectic colony can be found near the sample edge, indicating that nucleation takes place not only near the surface, but also inside the sample, as depicted elsewhere in detail.\textsuperscript{30)

We would like emphasize that this kind nucleation behavior can be confirmed not only in the Al\textsubscript{2}O\textsubscript{3}-36.8 at% ZrO\textsubscript{2} eutectic, but also in the Fe\textsubscript{2}O\textsubscript{3}-16.5 mol% La\textsubscript{2}O\textsubscript{3}\textsuperscript{31) Y\textsubscript{2}O\textsubscript{3}-38 mol% SiO\textsubscript{2}, Nd\textsubscript{2}O\textsubscript{3}-33 mol% SiO\textsubscript{2}, Sm\textsubscript{2}O\textsubscript{3}-32.5 mol% SiO\textsubscript{2}, and Y\textsubscript{2}O\textsubscript{3}-35 mol% SiO\textsubscript{2} eutectic alloys.\textsuperscript{32) Figure 1(b) depicts the surface morphology of the ternary Al\textsubscript{2}O\textsubscript{3}-6 mol% ZrO\textsubscript{2}-68 mol% Y\textsubscript{2}O\textsubscript{3} eutectic solidified spontaneously on the aero-dynamic levitator (ADL) at an undercooling of about $\Delta T = 250 \text{K}$ when the CO\textsubscript{2} laser beam is blocked off to cool the sample rapidly. A similar microstructure feature to that of Fig. 1(a) can be identified with independent eutectic colonies. Further investigations on other eutectics with the compositions of Al\textsubscript{2}O\textsubscript{3}-19 mol% ZrO\textsubscript{2}-
16 mol% $Y_2O_3$ and $Al_2O_3$-10 mol% $ZrO_2$-53 mol% $Y_2O_3$ reveal almost the same microstructural characteristics as that in the as-studied binary and ternary eutectics; an individual eutectic colony is the basic unit in characterizing the microstructure.

Figure 1(c) reveals the surface microstructure of the binary Ni-18.7 at% Sn metallic eutectic solidified on the electromagnetical levitator (EML) at an undercooling of around $\Delta T = 100\, K$, which consists of separate eutectic colonies with clear contacting boundaries as well.\(^{33}\) Meanwhile, we have levitated and solidified other binary metallic eutectics, e.g., Ni-21.4 at% Si, Co-20.5 at% Sn,\(^{34}\) Co-23.1 at% Si, Co-25.5 at% Ge, and Co-25.5 at% Sb eutectics at various melt undercoolings, and confirmed that copious nucleation occurs in all of these alloys when solidified containerlessly from low undercoolings to high undercoolings attainable. Different from a single-phase alloy with a dendritic morphology that can propagate throughout the entire sample from the seeding area, we never found a eutectic colony that grows throughout the entire bulk sample to reach the opposite side of the nucleation area. Figure 1(d) shows a cross sectional microstructure of the Ni-18.7 at% Sn alloy solidified at an undercooling of around $\Delta T = 70\, K$, in which several eutectic colonies are included with a hybrid structure of anomalous eutectics and regular lamellar eutectics. The contacting boundaries can be discerned as that at sample surface, indicating that copious nucleation takes place not only at sample surface, but also in the internal area of the sample.

From our comprehensive investigation on microstructures of binary and ternary oxide eutectics and metallic eutectics, together with microstructural observation performed by Wei and co-workers in atomized droplets of Ag-Cu-Ge,\(^{35}\) Ni-Sb,\(^{36}\) Co-Sb,\(^{37}\) and Co-Ge\(^{38}\) eutectic alloys, one can readily tell that copious nucleation is the most striking feature characterizing this group of systems when they are freely solidified from undercooled states, indicating that a single eutectic colony should be the basic unit when discussing free solidification behavior of eutectics, rather than a bulk sphere.

Here it should be noted that all eutectic alloys in this review are with the equilibrium eutectic compositions in phase diagrams. However, when a hypoeutectic or hypereutectic alloy, with a composition far from the eutectic point, solidifies from an undercooled state, the primary phase may grow with dendritic morphology during recalescence and thus leaving remaining liquid to form regular eutectics after recalescence at plateau period, which is similar to single-phase alloys in nucleation behavior. In the meanwhile, we would like to stress that an independent eutectic colony from copious nucleation involves equilibrium terminal eutectic phases as its components in a bulk sphere, in which no other metastable reactions can be inferred. When there exists a metastable eutectic reaction below the equilibrium eutectic reaction, the metastable eutectic reaction may take place at high undercoolings instead of the equilibrium eutectic. A
2.3 Impact of copious nucleation on recalescence in undercooled eutectics

It is impossible to observe directly a solid/liquid interface at a low magnification by using a usual video camera or other photo sensing devices as the thickness of the solid/liquid interface is in a nanometer scale whereas the wavelength of visible light is in a micrometer scale, but the recalescence front with a sharp contrast of the bright crystallizing solid and the dark undercooled liquid is always regarded as the solid/liquid interface. The reason lays on the fact that the solidified microstructure, in particular at medium undercoolings, exhibits a well-developed dendrite when a single-phase alloy grows from an undercooled state, during which no secondary nucleation site can be identified. This is fundamental in measuring crystal growth velocity versus melt undercooling in single-phase dendrites.

From a macro viewpoint, a recalescence front, similar to that observed in single-phase alloys, can be captured by using a high speed video (HSV) as well, as obtained in Al$_2$O$_3$-36.8 at% ZrO$_2$, and Ni-18.7 at% Sn eutectics. However, for these eutectics without any metastable eutectic reactions, copious nucleation occurs. This indicates that the sharp contrast between the crystallizing bright solid and undercooled dark liquid cannot be regarded as a solid/liquid interface any longer but induced by the simultaneous thermal release of concentrated eutectic colonies during recalescence. Therefore, the advancement rate of the distinct recalescence boundary is not the growth velocity of the eutectics but the propagation speed of crystallizing eutectic colonies at the sample surface due to successive nucleation and subsequent growth. Hence, we should emphasize that in order to elucidate the origin of a recalescence front, it is essential to comprehend the solidified microstructures and alloy systems rather than using a simple recalescence image captured by a photo sensing device because copious nucleation may be the most striking feature for the eutectics solidified from undercooled states.

Obviously, the arbitrary extension of the nucleation concept from single-phase systems to double- or triple-phase eutectic systems is not applicable and thus the discussions and conclusions based on such an extension should be further deliberated with great care. For instance, several researchers have measured the so called “eutectic growth velocity” versus melt undercooling by photo sensing facilities, some of which show a good agreement between the measured “eutectic growth velocity” and the theoretical prediction, which may be due to a coincidence. Their further discussions and conclusions made on the relations obtained are of less scientific merits since the fundamentals are based on a misleading extension.

3. Growth of Eutectics from Undercooled Melts

3.1 Traditional growth mechanisms for the anomalous eutectic formation

After nucleation takes place, the growth of eutectic phases commences. Since the size of an effective nucleus is in a nanometer scale, the observed microstructure, in particular, within one eutectic colony, should result mainly from crystal growth of eutectic phases.

As mentioned above, anomalous eutectic will be yielded when the eutectic melt is solidified beyond a certain critical undercooling, which has attracted increasing attention for decades. After observing the microstructure of Ni-Sn eutectic, Kattamis and Flemings proposed that the anomalous eutectic originated from the dendritic growth of the supersaturated $\alpha$-Ni phase and subsequently, these $\alpha$-Ni dendrites decomposed into $\alpha$-Ni and $\beta$-Ni$_2$Sn phases. Jones suggested that anomalous eutectic formed in undercooled Ni-Sn and Ag-Cu alloys should be ascribed to the uncoupled simultaneous growth of the eutectic phases. Based on microstructures of Co-Sb eutectic alloys, Wei et al. assumed that cooperative dendritic growth of independent phases was responsible for the formation of anomalous eutectics. Note that from Jones to Wei et al., there is one important unanswered question; why decoupled growth can take place when the alloy is solidified beyond a certain undercooling. Assuming that possible growth patterns, i.e., regular eutectic lamellae, or dendrites of terminal eutectic phases, may compete, Wei and co-workers grouped the TMK eutectic growth model for directional solidification and the dendrite growth models developed by Lipton and Boettinger et al. (LKT model) and Boettinger et al. (BCT model) for free solidification to calculate the growth rates of these possible morphologies and then determine the coupled zone of the alloy, from which they concluded that regular eutectic would be formed in their calculated coupled zone while anomalous eutectic would be yielded once the alloy is solidified beyond the coupled zone. Their simple grouping of different models for different solidification conditions, together with some other misunderstandings as we commented, should be further deliberated though they seemed to persist in their approach. Considering the capillarity and solute effects as driving force, Goetzinger et al. proposed that the segmentation of primary eutectic lamellae took place during the semi-solid state in Ni-Si, Co-Sb and Ni-Al-Ti alloys and thus resulted in the anomalous eutectic when applying the Karma fragmentation model. This interpretation is subject to some open questions as we argued elsewhere.

3.2 Origin for the occurrence of anomalous eutectics when incorporating kinetics

Eutectic growth theories, from the comprehensive JH to
the modified TMK,\textsuperscript{5} and the latest KT\textsuperscript{7}) models, deal with the curvature and solute effects that contribute to interface undercooling. Thermal and kinetic parts have been ignored since no thermal undercooling can occur for directional solidification\textsuperscript{55}) and very small kinetic undercooling may be required at a low growth rate.\textsuperscript{5} Very recently, Li and Zhou\textsuperscript{56}) defined the thermal and kinetic undercooling for coupled growth from undercooled eutectics. Anomalous eutectic obviously results from decoupled growth of eutectic phases, which can be readily formed in a metallic eutectic alloy with a nonfaceted disordered solid solution and a well faceted ordered intermetallic compound as its terminal phases, as have investigated in many systems, e.g., Ni and Ni\textsubscript{3}Sn in Ni-18.7 at\% Sn eutectic, Co and CoSb in Co-25.5 at\% Sb eutectic. Since a pronounced difference exists in crystallographic feature of terminal eutectic phases, a significant difference arises in interface attachment kinetics regarding to the disordered nonfaceted solid solution and the ordered faceted intermetallic compound in that a collision-limited growth mode may permit a crystallization event with every effective collision of a liquid atom against the solid and thus corresponding high interface mobility for the disordered solution phase. However, a short-range diffusion-limited growth mode requires an atom to strike the interface in a correct sublattice and then attach onto the site via diffusion and thus resulting in a much more sluggish interface for the intermetallic compound.\textsuperscript{57}) Quantitatively, this difference in interface attachment kinetics for nonfacetted and faceted phases can be approximately reflected via the interface linear kinetic coefficient, $\mu$, which is expressed as below for collision-limited growth:\textsuperscript{58})

$$\mu = \frac{\Delta H_i V_S}{R_g T_i^2}$$

where $\Delta H_i$ is the heat of fusion of the individual phase of interest and $T_i$ is the interface temperature of the growing crystal, and $R_g$ and $V_i$ are the gas constant and sound speed in liquid. For a single-component metallic material, although the interface temperature is always lower than its melting temperature, $T_i$ is usually, for simplicity, replaced by the melting temperature of the growing crystal, which makes it more operative in calculation. Regarding to the aforementioned double-phase eutectic, the equilibrium eutectic temperature of the alloy, $T_{E}$, should be a more reasonable approximant for $T_i$ from the viewpoint of driving force for crystal growth although we discussed separately the attachment kinetics of the nonfaceted and faceted phases. For diffusion-limited growth, the diffusion speed, $V_D$, corresponds the maximum ideal solidification rate and thus $V_D$ should be substituted for $V_S$ to calculate $\mu$. It is obvious that the $\mu$ value based on $V_D$ for compounds are two or three orders of magnitude lower than that of based on $V_S$ for metals and solid solutions ($V_S$ is about 1–10 km/s and $V_D$ is about 1–10 m/s for a usual metallic alloy).\textsuperscript{59}) It should be noted that for a solid solution or an intermetallic compound with a simple crystallographic lattice, the calculated $\mu$ value is in a relatively good agreement with experimental observations when proper parameters are determined. For example, the measured growth velocities of CoSi and FeSi compounds could be well fitted.\textsuperscript{60}) Note that Jackson\textsuperscript{61}) analyzed that interface kinetics should not depend strongly on chemical composition; the data $\mu$ derived from a stoichiometric compound or a solid solution can be used as an approximant for a multiple-phase alloy.

In order to simplify presentation, here we cite the Ni-18.7 at\% Sn eutectic with Ni and Ni\textsubscript{3}Sn as an example to elucidate the occurrence of decoupled growth. When Ni and Ni\textsubscript{3}Sn phases are yielded from the undercooled melt, these two phases may share similar planar interfaces upon immediate formation. The different interface attachment kinetics enables the Ni solid solution to grow faster than the Ni\textsubscript{3}Sn compound. When the melt is undercooled to exceed a certain undercooling, the overgrown distance covered by Ni is larger than the thickness of solute and thermal boundary layer. In this case, further growth of the Ni phase may be beyond the scope of the solute and thermal constraints. Therefore, the leading Ni phase may grow freely into the undercooled melt and decoupled growth takes place. Because of the chemical composition limitation of the eutectic alloy, it is difficult to form a complete dendrite since it requires sufficient diffusion for Ni atoms. Hence, the primary leading Ni phase may develop into an irregular network in a threedimensional view. When the microstructure is revealed, the anomalous eutectic grain exhibits a honeycomb-like structure at sample surface or an irregular network with a mosaic-like morphology at the cross section region.

In order to describe the occurrence of decoupled growth, we\textsuperscript{63}) recently presented a semi-quantitative model to consider the attachment kinetics of competing phases, in which a dimensionless undercooling is defined. It is worth noting that in this model, we considered the growth kinetics of eutectic phases separately, rather than treating two eutectic phases as a basic growth unit as in traditional eutectic theories. When this approach is extended to directional solidification of eutectics, we also find that it is this asymmetrical contribution in growth kinetics that enables the coupled eutectic composition shift to the faceted phase side so as to weaken the solute undercooling and balance the kinetic contribution for coupled eutectics.\textsuperscript{62})

### 3.3 Further growth of anomalous eutectics after the occurrence of decoupled growth

Asymmetrical effects in interface attachment kinetics for the nonfacetted and faceted phases result in the occurrence of decoupled growth. What happens after decoupled growth takes place? Powell and Hogan\textsuperscript{59}) found that the anomalous eutectic consisted of discontinuous copper particles in a continuous matrix of silver from the microstructural observation. Based on this microstructure, Hogan\textsuperscript{63}) proposed that the “discontinuous” minor phase in the anomalous eutectic was formed by repeated nucleation after being overtaken by the faster-growing phase. However, Kattamis and Flemings\textsuperscript{10}) concluded both eutectic phases in an anomalous Ni-Sn eutectic region were continuously interconnected along a polyhedral network after they successively polished and examined the parallel cross sections.

Using the electron backscattered diffraction pattern (EBSP) technique, we\textsuperscript{64}) recently observed the microtexture near the anomalous eutectic region of a Ni-18.7 at\% Sn alloy solidified at about $\Delta T = 50$ K, as depicted in Fig. 2. When
Ni$_3$Sn compound is indexed, the anomalous eutectic area contains several different sub-regions as indicated in Fig. 2(b) by the solid lines. Each sub-region shares one crystallographic orientation, indicating that the Ni$_3$Sn intermetallic is continuous in the area. When the Ni solid solution is indexed, as shown in Fig. 2(c), only independent Ni particles can be identified, indicating that Ni phase is discontinuous.

A further examination of misorientation relations among neighboring Ni grains within one anomalous eutectic region, e.g., in #1', #2', or #3' in Fig. 2(c), reveals that more than 70% grains have small misorientation angles less than 15°, indicating that these Ni grains are not due to repeated nucleation, as Hogan$^{53}$ suggested for copper-silver alloys, which should yield a random distribution in crystallographic misorientation. Kattamis and Flemings$^{10}$ might be misled due to the limitation of analysis approach, in which an optical micrograph or an SEM microstructure could not reveal the misorientation relation of grains; this may be why they considered that even the contacting grains were interconnected. Our present observations that Ni$_3$Sn compound is a continuous skeleton while Ni solution is discontinuous particles with small misorientation among neighboring grains in one anomalous eutectic unit indicated that the physical mechanism proposed by Goetzinger et al.$^{52}$ is of fatal error, which should result in a discontinuous distribution for both Ni and Ni$_3$Sn phases if the primary lamellae can really segment into spherical elements to form anomalous eutectics.

When solidification proceeds into undercooled liquids, crystallization heat is released to reheat the growing solids near the melting point. Note that the intermetallic compound Ni$_3$Sn has much higher entropy of fusion than solid solution Ni; this is why that Ni can be readily segmented into pieces whereas Ni$_3$Sn cannot according to the Karma fragmentation model.$^{55}$ The frame network constrains the free floating or rotation of fragmented Ni segments, which results in small misorientation angle for neighboring Ni particles within one anomalous eutectic skeleton.

The crystallization heat, in the other aspect, can increase the temperature of remaining liquid ahead of growing interface and thus lower the interface undercooling, which will terminate decoupled growth and enable regular eutectic lamellae to develop from the periphery of the anomalous eutectic grain, as depicted in Fig. 1(d) and observed in many other eutectic systems.$^{36-38}$ The regular Ni lamellae, as circled in Fig. 2(c), have the same orientation as that of the parent Ni grain, from which they grow. Considering that the Ni$_3$Sn lamellae have one orientation in this area as well, it is clear that fragmentation cannot occur for coupled growth of eutectics because of the absence of driving force when the alternative Ni and Ni$_3$Sn lamellae grow with a planar front.

4. Open Problems for Undercooled Eutectic Melts

Although we have investigated systematically the free solidification behavior of various undercooled eutectics from the viewpoints of nucleation and growth, there are still some open questions that are subject further clarification, as we$^{34}$ have addressed when discussing the origin of decoupled growth. Besides those questions, future work may be required to clarify other issues that are detailed as follows:

1. On the nature of nucleation in eutectics. In principle, nucleation can be classified as either homogeneous or and heterogeneous nucleation, which have been physically defined well. When simulating the binary crystal nucleation by a phase field theory, Granasy et al.$^{65}$ proposed that homogenous nucleation be more common in alloys than previously thought. Here we term the present nucleation phenomenon as “copious nucleation”. From the viewpoint of strict definition in physics, which kind of nucleation, homogeneous or heterogeneous, is it for the present “copious nucleation”? More delicate experiments should be tailored to reveal the nature of nucleation behavior since this issue is closely related to a further refinement of eutectic alloys regarding to the number of eutectic colonies.

2. On the time scale for the occurrence of decoupled growth. In our semi-quantitative model,$^{34}$ we defined a critical condition under which decoupled growth occurs when relating the melt undercooling and a time scale. Theoretically, decoupled growth can take place provided that the growth period is sufficiently long so that a nonfaceted phase may overgrow the competing faceted phase even at a very low undercooling. However, this critical undercoolings upon the formation of anomalous eutectic in nonfacetted-faceted metallic eutectics are always around $\Delta T = 50$ K in practice, as we have referenced in many systems.$^{34}$
effort may be necessary to clarify whether or not there is a specified time scale for the occurrence of decoupled growth, which is essential in developing a quantitative model to interpret the state-of-art results.

(3) *On coarsening of anomalous eutectic.* Experimentally, the critical undercooling for the formation of a fully anomalous eutectic is about \( \Delta T = 150 \text{ K} \) when a nonfaceted-facetted metallic eutectic alloy is solidified from an undercooled state, as many researches investigated.\(^{12,28,33,36,52}\) This undercooling is much lower than the hypercooling limit, usually \( \Delta T_{\text{hyp}} \approx 400 \text{ K} \) for a typical metallic eutectic, at which undercooled melts can completely crystalize without any remaining liquid upon recalescence for an isenthalpic process. This indicates that more than 50% anomalous eutectic is yielded after recalescence due to coarsening. The coarsening kinetics and morphology selection at the semi-solid state within a short time interval are of great concern in furthering our understanding on the anomalous eutectic formation.

### 5. Concluding Remarks

We reviewed the state-of-the-arts of the free solidification from undercooled eutectics from the viewpoints of nucleation and growth. To have a clear skeleton on the issue, we presented a brief chart, as indicated in Fig. 3, in which the main differences between the traditional treatments and our present treatment have been listed from nucleation to growth and then final continuity features of anomalous eutectics.

Microstructural observations in various oxide and metallic eutectic systems reveal that copious nucleation takes place in these eutectics regardless of melt undercooling. The basic unit in discussing the free eutectic solidification should center

---

**Fig. 3** A brief comparison chart to elaborate the differences between the traditional treatments and our present treatment on the free solidification of undercooled eutectics.
on a single eutectic colony rather than a bulk specimen. The as-existed conclusions, from nucleation to anomalous eutectic formation, should be further deliberated with great care if they were based on the arbitrary extension of the one-effective-nucleus assumption for single-phase alloys.

Diffusion-limited growth kinetics for a well ordered faceted intermetallic compound yields a sluggish interface whereas collision-limited growth kinetics for a nonfaceted disordered solid solution yields a mobile interface. This remarkable difference in attachment kinetics enables the nonfaceted phase to grow faster than the faceted phase. When the overgrown distance is beyond the thickness of solute and thermal boundary layer at a certain melt undercooling, decoupled growth occurs. Further growth of the decoupled phases will result in the formation of anomalous eutectics.

The crystallization heat can remelt the primary nonfaceted phase into pieces due to lower entropy of fusion than that of competing faceted compound and thus making the nonfaceted phase exhibit discontinuous particles while the faceted phase have a continuous network within one anomalous eutectic grain, as we revealed in the Ni-18.7at% Sn alloy by the EBSP technique. This observation is of great significance in revealing the physical mechanisms and solving the arguments on the continuity feature of anomalous eutectics upon crystallization. Open questions suspending are briefly outlined to give a guideline in future work on free solidification of eutectics from undercooled states.

Acknowledgements

The work presented in this overview was mainly completed when one of the authors (M. Li) held a postdoctoral fellowship from the Japan Society for the Promotion of Science, foreign research fellow from the Japan Aerospace Exploration Agency (formerly the Institute of Space and Astronautical Science, was renamed the Japan Aerospace Exploration Agency after it was merged with the National Space Development Agency of Japan and National Aerospace Laboratory of Japan), and project researcher fellowship from the Japan Aerospace Exploration Agency. Sincere thanks are due to Dr. K. Nagashio for many technical helps, valuable discussions, and constructive comments throughout the entire accomplishment of the present work.

REFERENCES