

Melt undercooling and nucleation kinetics



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ABSTRACT

While melt undercooling is often observed during solidification the control of undercooling and nucleation is difficult due to the numerous possible heterogeneous sites present in even high purity melts. The identification of active nucleation sites has been a continuing challenge that requires developing well planned experimentation. In samples with well-defined and controlled undercooling, the identification can be established for a number of the active sites and mechanisms that can act to catalyze nucleation. The sites and mechanisms that have been identified involve primary phases developed during cooling of alloy melts, liquid-added particle interfaces being modified (e.g. by adsorption or reaction) creating a particle type independent nucleation potency, dissolved impurities precipitating out of the melt at high undercooling or acting to alter local atomic arrangements in the melt to catalyze nucleation and nucleation sites resulting from residual solid preserved in cavities in inclusions or surface coatings. Recent advances in clarifying the structure of liquids reveal local atomic arrangements such as short range order, medium range order and cluster structures, but the role of these local heterogeneities on the undercooling and crystallization behavior is incompletely understood at present.

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1. Introduction

Liquid undercooling plays a central role in determining the solidification microstructure [1,2]. Even though the study of undercooling phenomena has a long history dating from the first report by Fahrenheit [3], undercooling behavior continues to attract increasing attention as new experimental methods, characterization techniques and modeling approaches have clarified the understanding of the liquid atomic structure and new applications such as nanomaterials [4] and phase change devices [5] have emerged that rely on undercooling and nucleation for their synthesis and functional operation. However, achieving reliable and reproducible control over the observed undercooling level has been a continuing challenge. Since only a single heterogeneous nucleation event is sufficient to initiate solidification in an undercooled melt and since there are numerous potential nucleation sites in an undercooled bulk melt, the identification of the active nucleant has been a difficult task with only limited success. For nucleant activity it is useful to consider two regimes. For example, in grain refining, the objective is to minimize the undercooling in order to allow the maximum number of grain refining particles to initiate grain formation [6] that is covered in the review by StJohn. Other examples

also indicate that at low undercooling solidification is initiated at pre-existing crystal sites [7]. At the opposite extreme, metastable and amorphous phases can be synthesized at high undercooling by rapid quenching [8] or by special melt treatments such as fluxing or containerless processing [9,10].

Another approach to achieve high undercooling is to employ the droplet sample method [11]. Upon subdivision of a melt into a large population of fine droplets a finite number of nucleants can be isolated into a few droplets to allow the nucleant-free droplets to exhibit large undercooling. In addition, the development of bulk metallic glasses has generated a renewed interest in the use of flux treatment of the melt where the flux acts to remove nucleants or to deactivate them to allow for large undercooling [12–14]. Associated with the experience on undercooling behavior there are many reports concerning the influence of melt superheat and thermal cycling, but a satisfactory explanation has not been available to account for these effects until recently. However, systematic studies of thermal cycling effects have provided new insight into the operation of a nucleant refining mechanism that promotes enhanced undercooling during flux treatment [14]. Moreover, advances in high rate calorimetry have provided a basis for a rational explanation for the effect of melt superheat on the subsequent undercooling [7]. In spite of the uncertainties regarding the action of specific nucleants, it is possible to provide insight into undercooling mechanisms and to achieve some measure of control through a systematic analysis of the crystallization kinetics

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behavior in undercooled melts and amorphous phases [14–20]. In fact, the activity has been so extensive that within the available coverage it is not possible to discuss all aspects satisfactorily. Instead the focus of the discussion is on undercooling, heterogeneous nucleation mechanisms and some aspects of nucleation analysis.

2. Nucleation catalysis by primary phases

Under most conditions, solidification is initiated by a heterogeneous nucleation event. While the study of homogeneous nucleation requires a sample free from all external nucleants, the study of heterogeneous nucleation requires a sample which contains only well-known and characterized nucleants. A proper examination of nucleation catalysis requires the full identification of the catalytic sites and solidification product structure as well as a characterization of the potency of the catalytic site in terms of the interaction energetics (i.e. contact angle) between the nucleus and catalyst. To circumvent the difficulties encountered in bulk systems, a droplet technique involving droplets on an “inert” substrate, droplet emulsions or entrained droplets has often been utilized to examine nucleation catalysis [11,21–25].

Many studies have been conducted on binary alloys in order to determine the catalytic effect of crystals of a primary solid solution phase on the nucleation of the liquid where it has been demonstrated [26] that each characteristic contact angle between the nucleant and the liquid will yield a discrete, well-defined undercooling on nucleation which can be used to describe catalytic potency. However, for a given system different undercooling values have been observed in different investigations. Part of the cause for the disagreement between the observations of previous studies may be attributed to spurious effects introduced by the use of different types of substrates or materials to envelop the liquid metal [11,27]. For example, in the fabrication of samples for the entrained droplet method, the liquid droplets represent the final portion of the sample to solidify and as a result are the portions most likely to contain segregated concentrations of residual impurities. To permit a resolution of these differences, the droplet emulsion technique (DET) [11,27] was adapted to study primary phase catalysis in simple eutectic or peritectic alloy systems. The strategy of the approach is shown in Fig. 1. By using alloy emulsions that have been proven to exhibit a high undercooling before nucleation

and equilibrating alloys in the liquid + α or liquid + β two-phase field, the catalytic effect of α or β on subsequent nucleation of the liquid can be examined without the possible interference from a foreign substrate [28]. An important preliminary step in the application of the DET to the study of heterogeneous nucleation is the evaluation of the possible catalytic potency of the droplet surface coating and other possible sites. This was accomplished by determining the maximum undercooling ΔT_e below the eutectic to nucleation of a droplet emulsion which was initially completely liquid. Specially designed thermal cycles can be employed to demonstrate that the intended nucleation site is indeed the one that is operating [11]. This is not possible with other methods, but is of crucial importance in obtaining valid heterogeneous nucleation temperatures.

3. Nucleation catalysis by incorporated particles

In melts with incorporated particles such as in the solidification processing of particle reinforced composites most of the attention has been focused on the interaction between the particles and the solidification front. However, it is recognized that the particles can also act to catalyze nucleation. In bulk melts it is not possible to identify the catalytic action of individual particles separately even though substantial undercooling can be observed in melts with dispersed particles [29], but the identification can be accomplished with droplet samples and specific treatments [30,31].

In order to conduct experiments on added nucleants in a melt, it is first necessary to remove or isolate background nucleants. Breaking the sample into droplets achieves isolation of background nucleants to reveal the characteristic undercooling due to the added particles by containing them in only a portion of the droplets. Droplets without a potent background nucleant are able to reach large undercoolings or in the case where nucleants under investigation are added to the melt, reveal the added nucleant potency. As shown in Fig. 2a, a melt containing background nucleants and added particles forms small droplets when emulsified. Any given droplet may contain both a background nucleant and an added particle, either a background nucleant or an added particle, or neither. All droplets however will have a coating that is often an oxide that may serve as a nucleation site. Fig. 2b shows a schematic of four possible nucleation sites; (1) a background nucleant, (2) the droplet coating, (3) a compound site involving

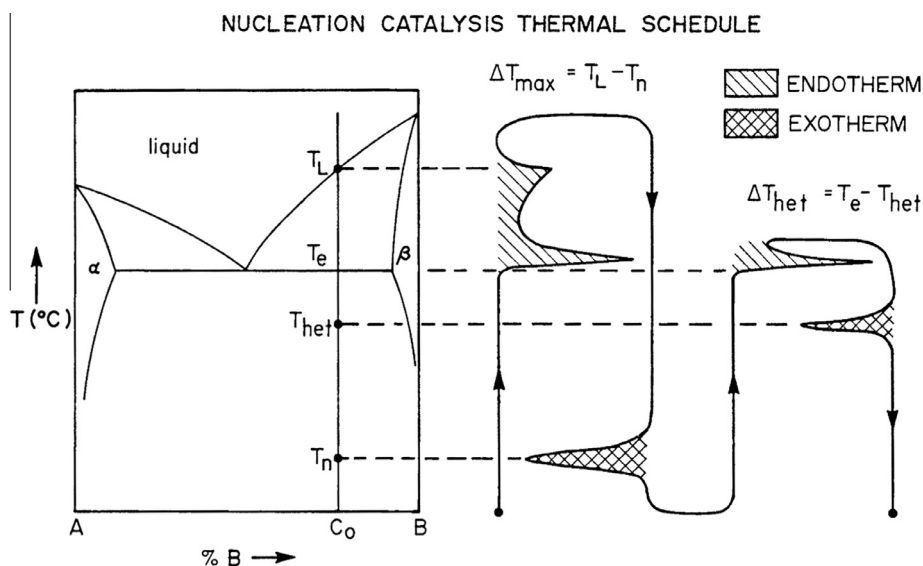


Fig. 1. General thermal treatment for solidification catalysis experiments with alloy droplets. Phase diagram related to schematic thermogram (on right).

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