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Comparison of nucleation and growth mechanisms in alloy solidification to those in metallic glass crystallisation - relevance to modeling

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Abstract

The development of microstructure during phase transformations is often best understood by considerations of nucleation in the parent material followed by growth of the new phase. This is a mature research field in alloy solidification, thanks to extensive investigations of nucleation and dendritic growth in cooling alloy melts. Bulk metallic glasses, on the other hand, typically do not form crystals on cooling from above the liquidus to below the glass transition temperature, resulting in very strong hard materials. As BMG toughness can be enhanced by a crystallising anneal, the study of nucleation and growth of crystals in viscous multi-component liquids has become an important topic for study. Such devitrification can lead to crystalline-glass composites or bulk nano-crystalline alloys, and the micro- or nano-structure is controlled by phenomena such as diffusion of solute and heat, and impingement dynamics. The relevance of solidification theories of nucleation, growth and impingement to crystallisation in amorphous alloys is discussed in this paper. The effects of the key differences between phase transformations in alloy casting processes and those in alloy devitrification on development of computational models for process simulation are highlighted.

Keywords

Thermodynamics, kinetics, bulk metallic glass, devitrification, Avrami, microstructure

Introduction

Apart from the exceptional diffusionless case, phase transformations in alloys are generally controlled by nucleation and growth processes, the slowest of which is the rate-limiting step. For thousands of years, casting has been used by mankind to fashion useful objects. The requisite solidification involves the nucleation and growth of crystals from the melt. On the contrary, it is only in the last two decades that the ability to create a bulk amorphous metallic alloy has been generated. This generally requires the relatively rapid cooling of a multi-component melt to below the glass transition temperature T_g in order to produce an amorphous structure. The properties of the resulting bulk metallic glass (BMG) can subsequently be engineered by a controlled heat treatment above T_g to cause at least partial crystallisation. As alloy solidification has a longer history, so too the theories and models of nucleation and growth of solid from the melt pre-date recent investigations into the phase transformations in BMG devitrification. This paper explores the relevance of the theories developed for alloy solidification to crystallisation in bulk amorphous alloys.

It is useful here to compare the temperature (T) vs. time (t) curves typical of both alloy solidification (AS) and metallic glass crystallisation (MGC), and this is illustrated in Fig. I, albeit the time scale for MGC is usually a lot longer than for AC. In solidifying castings, T typically drops below the liquidus temperatute (T_L) before nucleation of solid occurs, and the resulting latent heat release causes the recalescence often measured during equiaxed solidification. For MGC, the $T(t)$ plot starts below T_g, often at room temperature. When T_g is exceeded the material enters the supercooled liquid (SCL) range, which is metastable to crystal formation. Often an isothermal hold at a low temperature, to initiate copious nucleation, precedes a higher temperature plateau in $T(t)$ to encourage crystal growth, followed by a reduction in temperature to below T_g again. In order to compare and contrast the two technologically important processes of AS and MGC, we will first consider nucleation, then growth.

Nucleation

According to classical nucleation theory (CNT), in order for a random structural fluctuation in a liquid to lead to a stable crystal nucleus, an energy barrier (ΔG^*) to nucleation must be overcome, which relates to the energy needed to create the solid-liquid interface. For low values of undercooling ΔT ($=T_L-T$), this activation energy decreases with ΔT^2 [1]. In order for an embryonic crystalline cluster to reach the critical size needed to overcome ΔG^*, the requisite atoms must be transported through the liquid – and with this is associated another temperature-dependent activation energy, ΔG_d – that for diffusion. The net effect is that CNT predicts a nucleation rate I given by the expression

$$I = I_0 \exp\left[-\frac{(\Delta G^* + \Delta G_d)}{k_B T}\right] \qquad (1)$$

where I_o is a pre-exponential factor. It is the nature of the differences between ΔG^* and ΔG_d in AS vs. MGC that largely explains the differing nucleation behaviour in these processes. For heterogeneous nucleation, the value of ΔG^* can be very much reduced by the presence of impurities or inoculants in the melt. In AS this results in ΔG^* decreasing much more rapidly on cooling than does the available thermal energy, and the probability of nucleation increases rapidly with decreasing T [2]. This infers that over the small undercooling range typical in casting, ΔG_d could be considered a constant, in which case

$$I \propto \exp\left(-\frac{\Delta G^*}{k_B T}\right) \qquad (2)$$

Indeed I can increase rapidly towards a cascade with decreasing T, so that a certain fixed nucleation undercooling can be prescribed, assuming a thorough distribution of identical inoculants [2,3]. For a statistical distribution of inoculant parameters (e.g. size), there will be a corresponding spread in values of undercooling at which such particles activate a nucleation event [4]. The pre-exponential term may not be a constant if one discards the assumption that there will be no exhaustion of nucleation sites. Recalescence in AS can halt nucleation, but this may only be a temporary cessation [5].

The energy barrier ΔG^* increases if the difference in volume Gibbs free energy between supercooled liquid and crystalline solid, ΔG_v, gets smaller. In metallic glass melts ΔG_v is smaller than for conventional alloys, because of their high packing density and tendency to form short-range order [6,7]. The term $\exp(-\Delta G_d/k_BT)$ on the RHS of Eq.(1) is an expression of the limitation to nucleation caused by atomic mobility in the liquid. At the relatively low undercoolings typical of heterogeneous nucleation in AS, this inhibition is relatively small, due to the high diffusivity of solute in simple liquid alloys of low viscosity. This is not the case for metallic glasses, however, where the retardation in transport to pre-nucleation embryo caused by high viscosity η and low mobility of atoms increases as T falls. Indeed the term is inversely proportional to the viscosity of the melt [8]. Near T_g, the effective diffusivity D_{eff} is directly related to the exponential term [6], as

$$D_{eff} \propto \exp\left(\frac{-\Delta G_d}{k_B T}\right) \tag{3}$$

The high values of ΔG^* and ΔG_d in metallic glass melts makes it possible to reach T_g prior to any significant nucleation, provided a critical cooling rate (R_c) is achieved – that necessary to avoid the crystallisation nose in the time-temperature-transformation (TTT) curve for the alloy. For example, a typical TTT curve for the commercial BMG alloy Vit 1 is depicted in Fig. II, where a high-R_c quench is necessary to avoid the nose. The fully amorphous material then becomes the starting point for MGC heat treatments, which are long-time processes carried out above T_g, as illustrated in Fig II. During such heat treatments the nucleation process may be sensitive to very small-scale features, such as a quenched-in distribution of pre-critical nuclei, and a subtle interplay between long-range diffusion and interfacial fluxes may occur early in MGC, as described, for example, in Kelton's cluster/shell model of nucleation [9], which has exhibited good agreement with some experimental devitrification studies [10]. The effects of a diffuse interface have also been considered [11].

Growth

Dendrites are the typical growth form at low undercooling in AS. For alloys this is typically diffusion-controlled, although the growth rate can be constant due to the relatively large diffusivity of solute in the liquid. Crystals forming from SCL in glass-forming alloys are usually faceted intermetallic compounds, and the temperature dependence of species diffusivity D can be estimated [8] from the Stokes-Einstein equation

$$D = \frac{k_B T}{3\pi\eta a} \tag{4}$$

where a is the average interatomic distance. The low value of D (high η) in MGC makes growth rates many orders of magnitude lower than in AS, like in sluggish solid state transformations. To complicate matters, a deviation from an average diffusivity for the different atoms in BMGs, pile-up formation of the larger atoms at the edge of nanocrytsals [12], and stress effects due to minor density differences between the parent and precipitate phases, can all hinder crystal growth.

In order to produce very fine crystals in BMGs, a low temperature hold is firstly done (see Fig. I) where the very large thermodynamic driving force for nucleation yields multiple nuclei, and this high density nucleation is assisted by the lack of growth due to very limited atomic mobility. Having established copious nucleation, the kinetic impediment to growth is then reduced by an isothermal hold at a higher temperature. The devitrified microstructure is then frozen in by rapid cooling.

Due to the high atomic mobility in the melt in conventional AS, growth can start immediately following the low ΔT heterogeneous nucleation events, so that nucleation and growth compete with one another to define the as-cast grain size. To minimise grain size in inoculated castings, a high rate of heat extraction is needed in order to activate as many inoculants as possible (each operating at a characteristic undercooling) before they are consumed by growth or made inoperable due to local undercooling reduction caused by recalescence or solute enrichment.

However, it can be seen that, in general, the theories of nucleation and growth developed for AS, are applicable, in modified form, to MGC and can be used to develop analytical and computational models of amorphous alloy devitrification.

Modelling

Analytical Modelling

The Johnson-Mehl-Avrami-Kolomogrov (JMAK) approach to predicting the development of phase transformations [2] has been adapted for use to model equiaxed AS – e.g. [13]. In its simplest 3D form, it predicts the temporal progress of volume fraction transformed (x), given a steady rate of nucleation I, and constant growth rate v of a spherical transformed grains, s.t.

$$x(t) = 1 - \exp\left(\frac{-\pi v^3 I t^4}{3}\right) \tag{5}$$

This version of JMAK also considers the geometric effects of impingement as the transformation proceeds. In a recent paper by the authors, we used a JMAK approach to equiaxed solidification [5] taking into account the fact that the fraction solid is not unity within each spherical equiaxed envelope, and using undercooling-dependent laws to replace the constants I for nucleation and v for dendrite growth. The more general form of Eq JMAK is

$$x(t) = 1 - \exp\left(-k\left(t - t_0\right)^n\right) \tag{6}$$

where k is a constant, t_0 is a delay time for nucleation onset, and n is the Avrami component [12], s.t.

$$n = n_I + dn_G \tag{7}$$

and n_I is ascribed to the nucleation process, being 1 for a constant nucleation rate, less than 1 for a decreasing rate (0 for site saturation or nuclei exhaustion [13]), d is the dimensionality of the growth, and n_G relates to the growth process, being generally 0.5 for diffusion-controlled growth and 1 for interface-controlled growth. Indeed the value of n can change as the transformation proceeds [13].

The JMAK approach has also been applied to MGC [6,8]. A complication here is that nucleation may be preceded by amorphous liquid phase separation (e.g. via spinodal decomposition), and one such phase may trigger primary nucleation. Schroers et al. [8] note a difference in nucleation mode between medium and high values of ΔT in the SCL; from a slow nucleation rate (possibly with an inherent delay t_o, as modelled by Kelton [9]) which finally triggers a chain-reaction like sequence of secondary nucleations at medium ΔT, to heterogeneous nucleation dominated by a fixed number of nucleation sites at high ΔT deep in the SCL. Such complex effects are difficult to characterise by JMAK expressions which are developed to yield a very geometrical understanding of the controlling phenomena, and fail to take account, for example, of the compositional and structural changes which may occur in the untransformed parent glass phase during MGC. Ambitions to model the complex physics more accurately, and build animations of microstructural evolution, can only be satisfied by numerical methods in computational models.

Computational Modelling

The last two decades have witnessed the increasing sophistication of models to simulate microstructural evolution in AS, which have used cellular automata (CA), front-tracking (FT) and phase field (PF) formulations, usually coupled to finite element or finite difference macro-models to describe process level transport phenomena. Although nucleation and growth considerations are different for MGC, it is clear that entirely new theories are not necessary to describe the fundamentals, and methods to simulate evolving microstructure during solidification are now being applied to MGC. Recent papers outline the development of rudimentary CA [12] and PF [14] models to simulate devitrification in detail. There are still a number of important microstructural features, like those resulting from multi-step nucleation, yet to be faithfully modelled in MGC.

Modelling Microstructure

The ability to model the nucleation and growth of grains in AS has led to simulations of technologically important casting phenomena such as single crystal growth, columnar growth, equiaxed solidification, and the columnar to equiaxed transition or CET (e.g. see[15]), whereby the competition (and the outcome) between different forms of growth is predicted. In such casting processes, thermosolutal convection and grain sedimentation in the liquid has a large effect on the as-cast material, and for this reason micro-gravity experiments have been carried out in space [16] The high η of SCL BMG, however, would rule out natural convection as a dominant effect in MGC. However, nucleation has been observed to occur at the outer surface of BMGs with crystal growth in towards the centre, and also within the bulk of the material, leading to sequences of events, as depicted in [17] which look very like the competition which causes CET in castings. Outside the traditional field of BMGs, understanding via modelling of the relative contribution of external and internal nucleation preceding recrystallisation of amorphous Te-based semimetallic alloys under the influence of a laser beam or a current pulse would assist the optimal deployment of such phase change materials for optical or electronic data storage [18]. The development of glass-ceramics for biomedical applications [19] is another field which could benefit from such simulations.

During AS in casting processes, the phase transformation goes to completion. Dendritic growth proceeds until individual grains impinge upon one another provided some other transformation of the remaining intergranular liquid (e.g. to eutectic) does not occur. Growth rates may slow due to soft impingement effects [20] – either solutal or thermal – which reduce the local undercooling. Crystal growth rates are so slow in MGC, however, that often the phase transformation does not go to completion prior to quenching, resulting in a crystalline-glass composite material. In such cases computational models may not need to treat impingement of crystals upon one another; in certain cases [12] growth is retarded by low-mobility atoms rejected to the periphery of nascent crystals to such an extent that nucleation is really the only part of the phase transformation that occurs. However it is of course possible to completely devitrify some BMGs, in which case the new models must also treat crystal impingement phenomena.

Conclusions

Thermodynamics and kinetics provide theories which are widely applied in nature, and can describe fundamental behaviour in all materials. The resultant theories of phase transformations – e.g those of nucleation and growth – should be able to describe a range of technologically important metallurgical processes, such as alloy solidification or devitrification of amorphous alloys, in which such phenomena occur. This is indeed the case, although the theories had been applied to AS long before their consideration as possible descriptors of MGC processes. Classical nucleation theory requires some modification, even to describe casting processes, and although it can be used to develop simple models of alloy devitrification, MGC is so much more complicated than AS that CNT quickly reaches its limitations when high fidelity simulations are required. Breaching the boundaries of what is possible with analytical models of nucleation and growth, and predicting evolving nano- or micro-structure during MGC, requires computational models like those already developed for describing AS in detail. Such a progression has recently begun, but it will be necessary to determine the key thermophyiscal properties of these multi-component alloys, such as the complex inter-diffusion tensors, in order for such models to be accurate and survive the tests of validation which will be needed.

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Figures

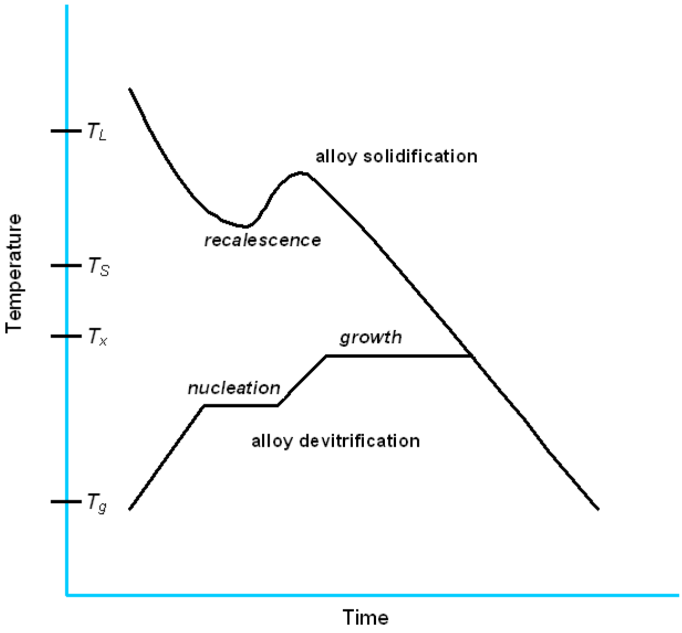

Fig. I. Temperature-time curves typical for alloy solidification and metallic glass crystallisation. Times for MGC may be shifted to the right.

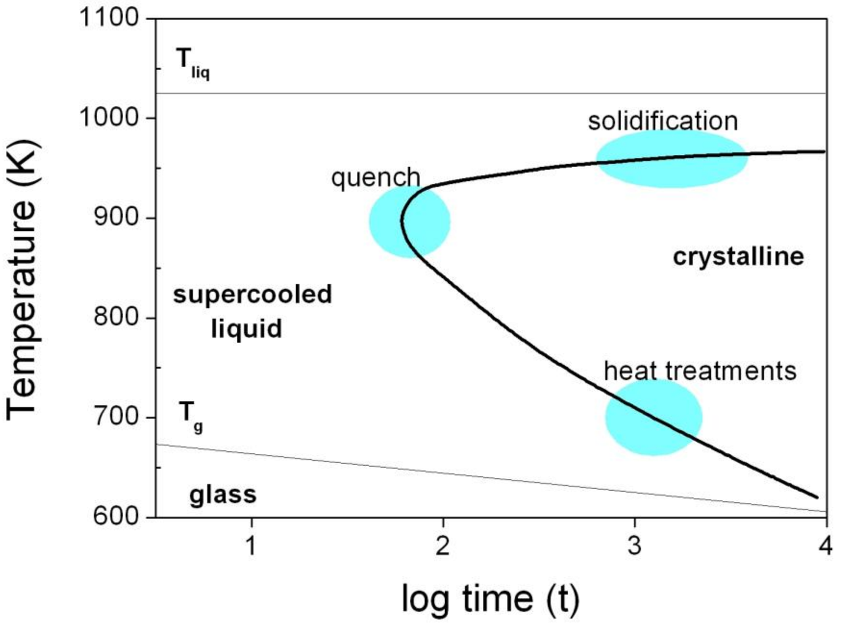

Fig. II. TTT curve typical of Vit1 BMG alloy. Solidification would occur at low undercooling. Quenching is needed to avoid crystallisation, and if this is done then the amorphous alloy can subsequently be heat treated to realise controlled devitrification.