Nucleation of Solidification as an Athermal Process

A. L. Greer
University of Cambridge, Department of Materials Science & Metallurgy, Cambridge CB3 0FS, UK.

Textbook treatments of nucleation normally consider it to be a stochastic process: through a series of bimolecular reactions, critical nuclei eventually arise. For both homogeneous and heterogeneous nucleation, the kinetics is commonly considered in terms of the rate of generation of critical nuclei on holding at a fixed temperature. In the practical processing of materials, heterogeneous nucleation is much more likely, and in the casting of alloys it is exploited to achieve grain refinement. Turnbull's pioneering studies of the nucleation of the freezing of metals focused on isothermal kinetics, but he also noted that in some cases the number of nuclei was not time-dependent on holding at a given temperature, but rather was dependent only on the maximum supercooling of the liquid [1]. This athermal process, important for heterogeneous nucleation, is the focus of this presentation. The process is deterministic, not stochastic. Under industrial processing conditions, the supercooling is small, and the critical nucleus radii are large enough to be clearly in the classical regime. These conditions are expressed in the 'free-growth model' [2–5] that is now widely accepted as a basis for quantitative prediction of grain size. The model highlights the importance of the size distribution of substrates upon which nucleation occurs. We examine recent in-situ observations [6], considering the extent to which they support this model. We also consider how the model may apply in very different cases such as ice-nucleating agents and the freeze tolerance of living systems [7]. We also consider how other factors, such as growth restriction by solute or by nanoparticles, can affect nucleation kinetics [8,9]. Finally, some priorities for future work are identified.

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