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Undercooling and Nucleation Studies on Pure Refractory Metals by Drop Tube Processing: Comments on the Limit to Crystalline Nucleation of Cubic and Compact Metals[1]

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A graphic interpretation for homogeneous nucleation is discussed in the framework of the classical theory of nucleation. If the value of two-thirds of the melting temperature may be regarded as an ultimate limit for liquid undercooling, the physical limit is shown to be an intrinsic property of the element under consideration, as verified by undercooling experiments performed on refractory metals under ultrahigh vacuum conditions. The graphic interpretation also suggests elements for new experiments, since the likelihood of heterogeneous nucleation remains. Some of them could be relevant to a nucleation mechanism through metastable polymorphism as proposed for Zr.

KEY WORDS: containerless processing; crystalline nucleation; drop tube; refractory metals; surface tension.

1. INTRODUCTION

If the physical origin of liquid undercooling is well understood on the basis of Gibbs work, the question of its limit in temperature appears to provide no answer. It is, in fact, difficult to develop a quantitative theory of nucleation and to verify the occurrence of homogeneous nucleation, which cannot be claimed for the sole reason of a large amount of undercooling. Nonetheless, such a mechanism is observed for bulk samples of refractory metals

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processed in a high drop-tube facility [1], where ultimate undercoolings are mainly expected by dividing the melt into tiny discrete droplets [2]. The limit is shown to be an intrinsic property of the metal, in contrast with the speculation of a relatively well-defined unique normalized undercooling (referred to as the melting temperature T_m) for all metals. Since homogeneous nucleation is often considered fictitious, it is intended to have a fresh look at this subject and then to discuss new perspectives for nucleation studies on pure elements.

2. GRAPHIC INTERPRETATION FOR HOMOGENEOUS NUCLEATION

The Gibbs energy difference of a spherical nucleus in a melt, ΔG, is divided into a volume and an interface term,

$$\Delta G = \tfrac{4}{3}\pi r^3\,\Delta G_v + 4\pi r^2 \sigma_{LS} \tag{1}$$

where r is the radius, σ_{LS} is the solid–liquid interfacial energy, and ΔG_v is the free enthalpy change in forming a unit volume of solid from the liquid. Consequently, ΔG is shown to exhibit a maximum as a function of r, which forms an activation barrier of height,

$$\Delta G^* = \frac{16}{3}\pi\frac{\sigma_{LS}^3}{\Delta G_v^2} \qquad \text{with} \quad r^* = -\frac{2\sigma_{LS}}{\Delta G_v} \tag{2}$$

at a critical radius r^*. Any cluster that exceeds the critical size will become a nucleus and grow. So, initiation of solidification needs a finite amount of undercooling ΔT ($T_m - T_n$, where T_n is the nucleation temperature), which provides the driving force to surmount the energy barrier required to create a viable solid–liquid interface. In the framework of the classical theory of nucleation, Turnbull and Fisher [3] derive the following expression for the frequency J of formation of crystal nuclei per unit volume of an undercooled liquid,

$$J = K_v \exp\left(-\frac{\Delta G^*}{k_B T}\right) \tag{3}$$

where k_B is the Boltzmann constant. Limited by diffusion across the phase boundary, K_v is estimated to be close to $10^{40}\,\mathrm{s^{-1}\cdot m^{-3}}$. Since reaching $10^{35}\,\mathrm{s^{-1}\cdot m^{-3}}$ at the very most for heterogeneous nucleation, the determination of K_v is considered the clearest way to distinguish properly between homogeneous and heterogeneous processes. This can be undertaken by studying the effect of sample size on nucleation or, according to

Skripov [4], by analyzing the full width at half maximum of the distribution of nucleation events. The first method requires a significant variation of the sample volume, which needs different experimental conditions. The latter statistical method implies an accurate resolution of the nucleation temperature, as the critical undercooling can be quite narrowly defined. In fact, homogeneous nucleation can seldom be observed.

Large undercooling amounts were obtained on small particles by Mendenhall and Ingersoll [5] at the turn of the century. Later, Turnbull and Cech [6] remarked that these amounts are roughly proportional to T_m and established that $\theta = \Delta T / T_m$ is a constant (0.18 ± 0.02) based on new experiments. Turnbull [7] assumed two approximations: ΔG_v is given by the product of the entropy of fusion ΔS_m and ΔT,

$$\Delta G_v = \Delta T \, \Delta S_m \tag{4}$$

and σ_{LS} is related to ΔS_m by

$$\sigma_{LS} = \alpha \frac{\Delta S_m T_m}{(N V_m^2)^{1/3}} \tag{5}$$

where N is the Avogadro number and V_m is the molar volume. Considering that ΔS_m is typically $8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, the coefficient of proportionality α is estimated to be 0.45. After reaching larger amounts of undercooling, especially on low-melting point materials [8], a shift of the limit up to 0.40 is proposed with different estimations of σ_{LS} and ΔG_v, leading to significant differences in predictions. Assuming Eq. (4), Perepezko and Paik [9] observed that, independently of σ_{LS} and ΔS_m values, J increases with θ and reaches a maximum for $\theta = \frac{2}{3}$, which is identified as an ultimate limit to liquid undercooling. The $\Delta T - T_m$ scaling allows comparisons between experiments (Fig. 1) but promotes the speculation of a defined, relatively unique normalized undercooling θ_{spec} for metals.

Nevertheless, if we consider the two basic hypotheses made on J (the critical nucleus is unique, i.e., $Jvt = 1$, where v is the sample volume and t is the characteristic time of the experiment) and K_v ($10^{40} \text{ s}^{-1} \cdot \text{m}^{-3}$ for homogeneous nucleation), the intervening term in the exponential is necessarily a constant for a given experimental configuration that we characterize by using the dimensionless number K_v^*:

$$Jvt = K_v vt \exp\left(-\frac{\Delta G^*}{k_B T}\right) \Rightarrow K_v^* \exp\left(-\frac{\Delta G^*}{k_B T}\right) = 1 \tag{6}$$

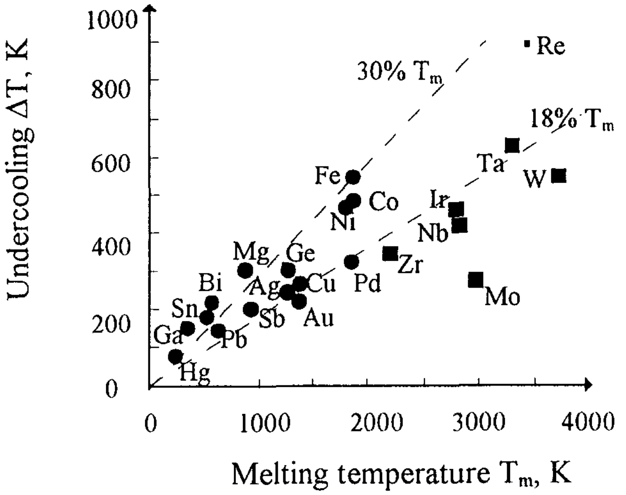

Fig. 1. Undercooling results using the classical ΔT–T_m representation; the black squares correspond to experiments performed on refractory metals by drop-tube processing.

K_v^* is typically 3×10^{31} for bulk droplets studied by containerless processing (drop tube, electromagnetic levitation) or 2×10^{27} for small particles prepared by the dispersion technique [8]. Indeed, K_v^* shows the dependence of nucleation on both specimen volume and cooling rate. By assuming the classical approximation for ΔG_v [Eq.(4)], the nucleation barrier can be rewritten using two dimensionless numbers, θ and C_n:

$$\frac{\Delta G^*}{k_B T} = \frac{C_n}{\theta^2(1-\theta)}, \quad \text{where} \quad C_n = \frac{16\pi}{3} \frac{V_m^2 \sigma_{LS}^3}{k_B T_m^3 \Delta S_m^2} \tag{7}$$

C_n is a characteristic parameter of the metal under consideration [1]. Finally, the explicit relation for $C_n(\theta)$ is expressed as

$$C_n = \theta^2(1-\theta) \log K_v^* \tag{8}$$

From a qualitative point of view, the graphic interpretation for homogeneous nucleation using the θ–C_n scaling (Fig. 2) shows that the absolute limit is an intrinsic property of the material as long as no relation is introduced between the thermophysical properties appearing in C_n. For a given material (i.e., a C_n number), arrow ① shows the dependence of undercooling on both specimen volume and cooling rate. The value of $\frac{2}{3}$ is clearly an ultimate limit for liquid undercooling, but not a universal limit.

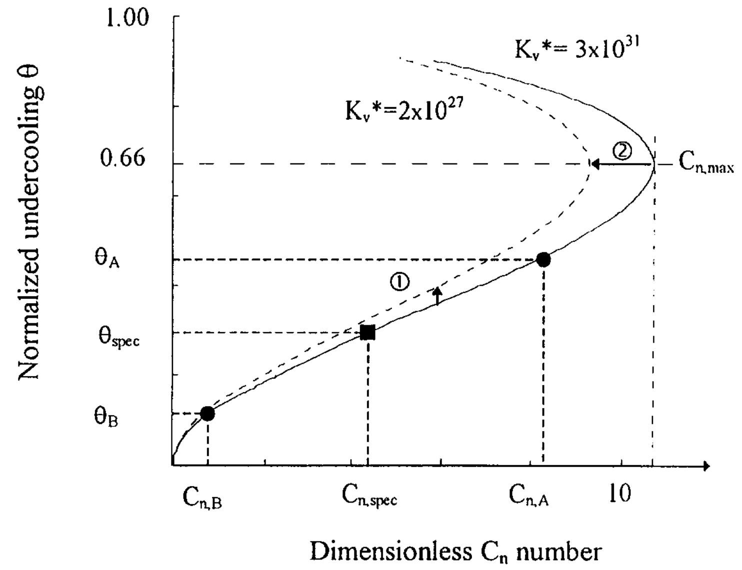

Fig. 2. Graphic interpretation using the θ–C_n scaling; K_V^* is typically 3×10^{31} for bulk droplets studied by containerless processing (drop tube, electromagnetic levitation) and 2×10^{27} for small particles prepared by the dispersion technique.

Considering that Eq. (5) furnishes a definition for a dimensionless interface energy α,

$$\alpha = \frac{(NV_m^2)^{1/3}}{\Delta S_m T_m} \sigma_{LS} \tag{9}$$

the C_n number is expressed as

$$C_n = \frac{16\pi}{3} \frac{\Delta S_m}{R} \alpha^3 \tag{10}$$

where R is the universal gas constant. Assuming, again, that ΔS_m is constant, the alternative is now the following: (i) the normalized amount of undercooling is an intrinsic property of the element, thus, for two metals A and B, $\theta_A \neq \theta_B \Leftrightarrow C_{n(A)} \neq C_{n(B)} \Leftrightarrow \alpha_A \neq \alpha_B$ [Eq. (10)]; (ii) there is a well-defined unique normalized undercooling, thus $\theta_A = \theta_B = \theta_{spec} \Leftrightarrow C_{n(A)} = C_{n(B)} = C_{n(spec)} \Leftrightarrow \alpha_A = \alpha_B = \alpha$. Consequently, the speculation on a well-defined unique normalized undercooling can be expressed as speculation on a constant coefficient of proportionality α (at least, a specific coefficient for a given structure, e.g., $\alpha_{bcc} \approx 0.71$ and $\alpha_{fcc,\,hcp} \approx 0.86$ [2]). This analysis is independent of the value assumed for the preexponential factor K_v; the question could only be its universality.

3. EXPERIMENTAL APPROACH

The Grenoble drop tube is a 48-m-high cylindrical enclosure, allowing 3.12 s of free-fall time under 10^{-9}-mbar vacuum. At the top of the facility, the droplets are formed using the pendant drop method with electron bombardment for heating [10]. The monitoring of recalescence, due to release of the heat of crystallization after nucleation, provides a determination of the nucleation temperature. The brightness of the droplet is tracked by a series of high-speed silicon diodes installed along the tube. Measuring the time between the droplet release and the nucleation event, T_n is calculated via numerical integration of the cooling rate

$$\dot{T} = -\frac{\varepsilon(T)\,\sigma}{C_p(T)}\,T^4 \left[\frac{36\pi}{m\rho_L^2(T)}\right] \tag{11}$$

which takes into account linear changes of the liquid density ρ_L, the heat capacity C_p, and hemispherical emissivity ε_t with temperature. σ is the Stephan–Boltzmann constant. Even if the typical accuracy of T_n is ±30 K, this approach allows a resolution in temperature of a few Kelvins due to the unusually high reproducibility under ultrahigh vacuum conditions of both the mass m (0.6%) and the initial temperature of the falling droplets. Indeed, the pendant liquid lends itself to small overheating and consequently to high reproducibility of the average initial temperature. As discussed elsewhere, the postrecalescence temperature is inferred from the height of the recalescence peak [11].

4. DISCUSSION

Statistical analysis according to Skripov [4] gives evidence for a homogeneous nucleation process in several refractory metals [1]. From a chemical point of view, heterogenous nucleation may be disregarded due to thorough purification under ultrahigh vacuum conditions. This mechanism is also not likely because many oxides of refractory metals (W, Re, Ta, Mo, Nb, Ir, etc.) are still volatile or dissolved at the measured nucleation temperatures. In this context, the study of refractory metals is of particular interest since they are shown to exhibit very different maximum normalized amounts of undercooling from Mo ($\theta = 0.10$) to Re ($\theta = 0.25$). Thus, it is concluded that the limit to liquid undercooling is probably an intrinsic

Table I. Experimental Results Compared with Model Predictions

	Solid–liquid interfacial energy σ_{LS} ($J \cdot m^{-2}$)					
	Mo	W	Ir	Nb	Ta	Re
Nucleation experiment	0.315	0.420	0.350	0.265	0.330	0.415
Structural model, Eq. (5)	0.839	0.725	0.760	0.448	0.500	0.630
β, Eq. (12)	0.160	0.181	0.164	0.144	0.179	0.165
α, Eq. (10)	0.268	0.385	0.397	0.405	0.480	0.580

property of the metal. This situation offers favorable conditions to test different predictions for the interface energy. Equation (5) is found to be inaccurate (Table I), especially when considering the values usually assumed for the coefficients of proportionality for cubic and compact structures (see Section 2). Conversely, an interesting agreement is found when using the semiempirical correlation,

$$\sigma_{LS} = \beta\sigma_{LV} \tag{12}$$

derived from Skapski [12], where σ_{LS} is expressed as a function of the liquid–vapor surface tension σ_{LV} at T_m, assuming that the solid is wetted perfectly by its own melt. The best fit is obtained with $\beta \approx 0.165 \pm 0.013$, while Eustathopoulos et al. [13] gave a value of 0.17. This agreement allows new insight into the treatment of the experimental results concerning other cubic and compact metals. The maximum undercoolings realized on bulk samples of Ni and Co by means of containerless processing appear to be related to a homogeneous process contrary to those reported for Pd, Ag, or Al, for example (Fig. 3).

The application of Eq. (12) to Zr leads to expected homogeneous nucleation for $\theta \approx 0.25$. If the nucleation of the modestly undercooled samples is well understood by the harmful action of the cubic $\gamma(ZrO_2)$ oxide, the formation of a nucleation center with sixfold symmetry observed by Cortella [14] on the deepest undercooled samples ($\theta \approx 0.17$) remains unclear. During rapid solidification of refractory metals and alloys, some brightness traces give evidence of two successive phase transformations [11, 15]; first-principle calculations of the structural stability in these systems are then developed to determine the possibilities of obtaining metastable phases. Calculations of different Zr structures [16] lead to excellent agreement between the measured nucleation temperature of the deepest undercooled Zr droplets (≈ 1780 K) and the deduced melting temperature for the simple hexagonal structure ω(Zr) (≈ 1775 K). It is then

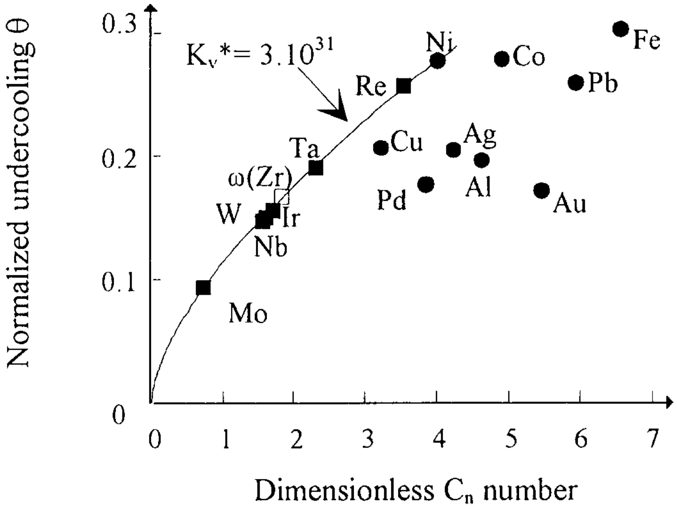

Fig. 3. Experimental results for refractory metals (■) in the θ–C_n scaling; Other cubic and compact metals are plotted (●) versus a theoretical C_n determined using the semiempirical correlation; (□) the case of ω(Zr) using the value estalbished for K_v^* in Ref. 17.

remarkable that this interpretation can support the anomalous high value of K_v ($10^{43}\,\mathrm{m}^{-3}\cdot\mathrm{s}^{-1}$) obtained by statistical analysis on nucleation events of Zr droplets processed during the last flight of the TEMPUS facility aboard the space shuttle *Columbia* [17]. Let us assume that the metastable polymorphism acts as a "topological impurity" leading to a more deterministic nucleation behavior. Other metals showing the hcp → ω → bcc sequence (Hf, Ti) could be relevant for such a metastable nucleation path; perhaps this is also the case for unexpectedly poorly undercooled elements, such as Au and Pt.

The θ–C_n scaling is of practical interest as long as the approximation for ΔG_v can be used. Experiment indicates that its universality cannot be taken for granted for relative undercoolings higher than 0.3; the behavior of the entropy of fusion must be described via a more complex formulation, which involves mainly the discontinuity of specific heat between liquid and solid. But this formulation may only reinforce the idea of an intrinsic limit and does not change the qualitative features of the scaling. Finally, the original result of Turnbull is probably a good estimation for cubic and compact metals, with a coefficient α of approximately 0.45.

The discussion of undercooling results obtained on semimetallic elements is beyond the scope of this paper. Nonetheless, the case of Ga is certainly more exciting, as this is the only element that occurs very near to the nose of the θ–C_n curve, when using the dispersion technique [8]. Since the maximum value for C_n (i.e., $C_n^{\theta=2/3}$) diminishes with K_v^* (see Fig. 2, arrow ②), the scaling supports the possibility for very small Ga droplets, through favorable characteristic times, to say liquid (i.e., to bypass the nose) under cooling to the temperature of liquid nitrogen as realized by Koverda et al. [18].

The classical theory assumes that critical crystalline nuclei form through successive additions of single atoms to a preexisting distribution of subcritical embryos. An alternative mechanism has been proposed by Desré et al. [19], who argue that nuclei of critical size can form directly within thermally activated density fluctuations of appropriate amplitude by a diffusionless transformation. It is remarkable that the latter approach leads to a nucleation barrier and a preexponential factor for the nucleation rate which are similar to those obtained by the so-called classical nucleation theory. In other words, this study verifies only the consistency of an equivalent formulation of the nucleation rate, and not the mechanism for critical nucleus formation.

5. CONCLUSION

Since a large population of small impurities could give a large nucleation rate at large undercoolings which may be misinterpreted as homogeneous nucleation, let us assume that the demonstration of such a mechanism will remain much debated. However, the self-consistency obtained between the classical nucleation theory approach and undercooling experiments performed on cubic and compact metals can hardly be considered fortuitous. In particular, these results show that the limit to liquid undercooling is an intrinsic property of the metal under consideration. The use of θ–C_n scaling helps to define an experimental strategy by indicating elements for which the likelihood of heterogeneous nucleation remains. However, some of them could be relevant for a nucleation mechanism through metastable polymorphism as proposed for Zr. First-principle calculations can be used as a guide to identify the corresponding elements.

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