Determination of the critical nucleation frequency in undercooled metal melt*

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Received April 12, 1999; revised May 10, 1999

Abstract By studying the effect of thermodynamic and kinetic factors on the nucleation frequency of undercooled metals, the expressions for heterogeneous and homogenous critical nucleation frequencies have been established. The results show that the homogenous critical nucleation frequency per unit volume is directly proportional to the ratio of the cooling rate to the volume of liquid metal. As the value of the equilibrium contact angle function $f(\theta)$ of the most effective catalyst is constant, the heterogeneous critical nucleation frequency per unit area of the catalyst surface is directly proportional to the ratio of the cooling rate to the sum of the surface area of the most effective catalyst surface (R_c/VS_v). When R_c/VS_v is constant, the heterogeneous critical nucleation frequency per unit area of the catalyst surface is inversely proportional to $f(\theta)^{0.53}$; the critical nucleation frequency per unit continuous mass of the metal melt for both the homogenous and heterogeneous nucleation can be expressed in terms of a general formula. The critical nucleation frequency is slightly influenced by the nature of the metal. The obtained theoretical result agrees well with the homogenous critical nucleation frequency estimated by Turnbull.

Keywords: **critical nucleation frequency, undercooling, cooling rate, catalyst.**

The theories of homogenous nucleation and heterogeneous nucleation that described the relationship among nucleation frequency, nature of metal, nature of catalyst and undercooling in metal melt were derived by Turnbull in 1950s[1]. It is the critical nucleation frequency at which the first nucleus forms in the metal melt that has immediate meaning to the nucleation process of metal. Not only can the related physical parameters of metal and the characteristics of catalyst be determined, but also the nucleation process of metal can be controlled in terms of the critical nucleation frequency[2—7]. Turnbull was the first to estimate the critical nucleation frequency, who assessed that the homogenous critical nucleation frequency per droplet of diameter 50 μm is $10^{-1\pm1}\cdot s^{-1}$[1]. Turnbull's method is imperfect in two aspects: first, lack of theoretical basis, the second is that the influence of technology factors on nucleation process was not considered. The accuracy of the result estimated by Turnbull has not been theoretically demonstrated yet. Another method of estimating the critical nucleation frequency is the calculating method[4—8]. Its basis lies on two formulas: I_v^* (homogenous critical nucleation frequency per unit volume) × V (volume of liquid metal) × t (nucleation time) = 1 or I_s^* (heterogeneous critical nucleation frequency per unit area of catalyst surface) × S (total area of

* Project supported by the National Natural Science Foundation of China (Grant No.59601011).

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catalyst surface) × t (nucleation time) = 1. The critical nucleation frequency of homogenous nucleation and heterogeneous nucleation can be calculated using these formulas. Willnecker and Herlach worked out the homogenous critical nucleation frequency per unit volume of Fe-based alloy with volume 8×10^{-8} m^3 is $10^{5.48}$ s^{-1}·m^{-3} [5]. Although this method had theoretical basis, but the effect of undercooling (or, nucleation time) on nucleation frequency was not considered. In fact, nucleation frequency increases exponentially with the increase of undercooling[1]. The actual critical nucleation frequency, therefore, is much greater than the critical nucleation frequency calculated according to the above formulas.

The purpose of this paper is, through studying the influence of thermodynamic and kinetic factors on the critical nucleation frequency, to derive the theoretical relationship among the critical nucleation frequency, the physical character of metal, the nature of catalyst, the volume concerned and the cooling rate of liquid metal.

1 Critical nucleation frequency per unit volume of homogenous nucleation

Suppose that the volume and cooling rate of metal melt are V and R_c, then, the undercooling ΔT^* at which the first nucleus forms in the melt can be calculated as:

$$1 = \int_0^{\Delta T^*} I_v \cdot V \cdot \frac{1}{R_c} \cdot d\Delta T, \tag{1}$$

where ΔT is the undercooling of metal liquid, I_v is the homogenous nucleation frequency per unit volume. I_v can be expressed as[1]:

$$I_v = A_v \exp\left[-\frac{\Delta G_A}{k(T_m - \Delta T)}\right] \exp\left[-\frac{\alpha\sigma^3 T_m^2}{k\Delta H_v^2 (T_m - \Delta T)\Delta T^2}\right], \tag{2}$$

where A_v is estimated to be a constant ($A_v \approx 10^{41\pm1}$ m^{-3}·s^{-1}), ΔG_A is the free energy of activation for transporting an atom across the liquid-solid interface, k the Boltzmann constant, T_m the melting point of the metal, α a factor determined by the shape of the nucleus (for spherical nucleus, $\alpha = 16\pi/3$), σ the interface energy between solid and liquid, and ΔH_v the latent heat of fusion per unit volume of metal.

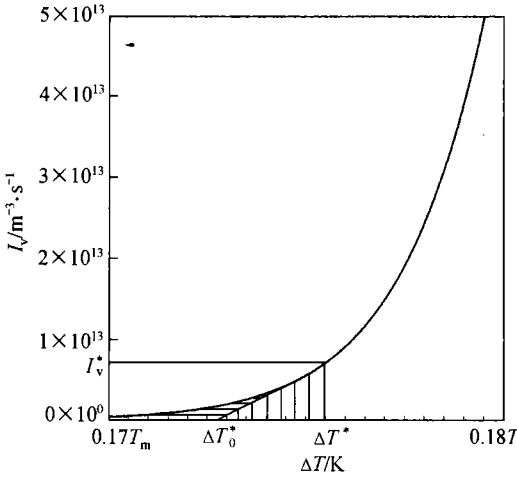

Fig. 1. Dependence of homogeneous nucleation frequency per unit volume on undercooling for copper.

The integral term in eq. (1) is related to the shaded area in fig. 1, but it can not be worked out directly. In order to calculate the shaded area, a tangent line to I_v curve at ΔT^* in fig. 1 is drawn. Thus, the shaded area is divided into two parts. Because the left shaded area is much smaller than the shaded area on the right side of the tangent,

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and because its effect on the undercooling is very small (the undercooling changes only 0.28% when the shaded area varies 50%), the whole shaded area can be replaced by the right shaded area approximately, i.e.

$$1 \approx \int_{\Delta T_0^*}^{\Delta T^*} \left.\frac{dI_v}{d\Delta T}\right|_{\Delta T=\Delta T^*} \cdot (\Delta T - \Delta T_0^*) \cdot V \cdot \frac{1}{R_c} \cdot d\Delta T$$

$$= \frac{1}{2} V(\Delta T^* - \Delta T_0^*)^2 \frac{1}{R_c} \left.\frac{dI_v}{d\Delta T}\right|_{\Delta T=\Delta T^*}. \tag{3}$$

From fig. 1, the following equation can be acquired:

$$\left.\frac{dI_v}{d\Delta T}\right|_{\Delta T=\Delta T^*} = \frac{I_v^*}{\Delta T^* - \Delta T_0^*}. \tag{4}$$

By differentiating eq. (2) with respect to ΔT, the following equation can be obtained:

$$\left.\frac{dI_v}{d\Delta T}\right|_{\Delta T=\Delta T^*} = \left[\frac{(2-3\xi^*)\psi}{(1-\xi^*)^2\xi^{*3}T_m} - \frac{\phi}{(1-\xi^*)^2 T_m}\right] I_v^*, \tag{5}$$

where,
$$\xi^* = \frac{\Delta T^*}{T_m}, \tag{6}$$

$$\psi = \frac{\alpha\sigma^3}{k\Delta H_v^2 T_m}, \tag{7}$$

$$\phi = \frac{\Delta G_A}{kT_m}, \tag{8}$$

and
$$I_v^* = A_v \exp\left(-\frac{\phi}{1-\xi^*}\right) \exp\left[-\frac{\psi}{(1-\xi^*)\xi^{*2}}\right] \tag{9}$$

is the critical nucleation frequency per unit volume of homogenous nucleation.

From eqs. (3), (4) and (5), the following equation can be derived:

$$I_v^* = \frac{2R_c}{T_m V} \frac{(2-3\xi^*)\psi - \phi\xi^{*3}}{(1-\xi^*)^2\xi^{*3}}. \tag{10}$$

By eliminating ξ^* from the simultaneous eqs. (9) and (10), a connotative relationship between I_v^* and V/R_c can be acquired. Substituting the related physical parameters of copper into eqs. (9) and (10), a curve representing the dependence of I_v^* on V/R_c can be obtained using Graphtool Software. Fig. 2 shows the dependence of $\lg(I_v^*)$ on $\lg(V/R_c)$ of copper. The result shows that $\lg(I_v^*)$ decreases linearly with the increase of $\lg(V/R_c)$, which conforms the following rule:

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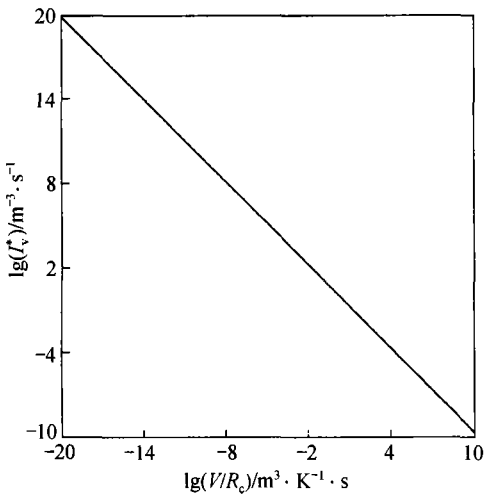

Fig. 2. Dependence of homogeneous critical nucleation frequency. Per unit volume I_v^* of copper on V/R_c.

$$\lg(I_v^*) + \lg(V/R_c) = c_v, \tag{11}$$

namely

$$I_v^* = 10^{c_v}\frac{R_c}{V}, \tag{12}$$

where c_v is a constant. Table 1 shows the calculated values of c_v and 10^{c_v} for some metals. It is worth to point out that the values of c_v and 10^{c_v} for different metals are almost constant, which shows that the critical nucleation frequency is influenced by the nature of metal only slightly.

The meaning of eq. (12) is that we can directly work out the critical nucleation frequency per unit volume I_v^* at a certain condition of solidification (e.g. when V and R_c are known). Furthermore, substituting the critical nucleation frequency per unit volume I_v^* into eqs. (9) and (10), the undercooling of metal at this solidification condition can also be calculated.

Table 1 Values of c_v and 10^{c_v} for some metals

	Metals					
	Cu	Au	Ag	Al	Fe	Ni
c_v	0.035	0.008	0.055	0.099	0.072	-0.080
10^{c_v}	1.08	1.02	1.13	1.26	1.18	0.83

2 The critical nucleation frequency of heterogeneous nucleation per unit area of catalyst surface

The heterogeneous nucleation process is influenced not only by the melt volume V, the melt cooling rate R_c, but also by the equilibrium contact angle function of effective catalyst $f(\theta)$ ($f(\theta) = (2+\cos\theta)(1-\cos\theta)^2/4$), and the surface area of the most effective catalyst per volume S_v. The heterogeneous nucleation frequency per unit area of catalyst surface I_s is obtained by substituting A_s ($A_s = 10^{31\pm1}\cdot m^{-2}\cdot s^{-1}$ [1]) and $\psi f(\theta)$ for A_v and ψ in eq. (2) respectively. Furthermore, substituting I_s and $S_v V$ for I_v and V in eq. (1) respectively and treating them in the same way as homogenous nucleation process, two equations corresponding to eqs. (9) and (10) can be obtained respectively, i.e.

$$I_s^* = A_s\exp\left(-\frac{\phi}{1-\xi^*}\right)\exp\left[-\frac{\psi f(\theta)}{(1-\xi^*)\xi^{*2}}\right], \tag{13}$$

$$I_s^* = \frac{2R_c}{T_m S_v V}\frac{(2-3\xi^*)\psi f(\theta) - \phi\xi^{*3}}{(1-\xi^*)^2\xi^{*3}}, \tag{14}$$

where I_s^* is the critical nucleation frequency per unit area of catalyst surface of heterogeneous nucleation.

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Figure 3 shows the dependence of $\lg(I_s^*)$ of copper on $\lg(S_vV/R_c)$ at different values of $f(\theta)$ by means of Graphtool Software according to eqs. (13) and (14). The result shows that the variation of I_s^* with S_vV/R_c has the same characteristics as that of I_v^* with V/R_c. I_s^* decreases with the increase of S_vV/R_c, and conforms to the following rule:

$$\lg(I_s^*) + \lg(S_vV/R_c) = c_s, \qquad (15)$$

i.e.

$$I_s^* = 10^{c_s} \cdot \frac{R_c}{S_vV}, \qquad (16)$$

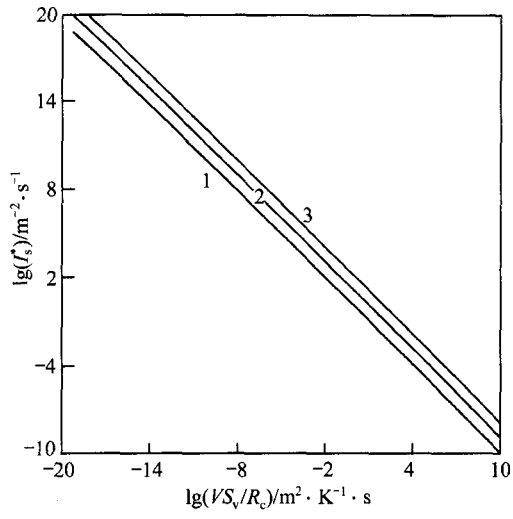

Fig. 3. The dependence of heterogeneous critical nucleation frequency. Per unit area I_s^* of copper on S_vV/R_c. 1, $f(\theta) = 1$; 2, $f(\theta) = 10^{-2}$; 3, $f(\theta) = 10^{-4}$.

where c_s is a constant. Table 2 shows the calculated values of c_s and 10^{c_s} for some metals. It can be seen that the values of c_s and 10^{c_s} are almost constant for different metals when $f(\theta)$ is constant. But the values of c_s and 10^{c_s} increase obviously with the decrease of $f(\theta)$ for the same metal. Through regression analysis, the following regression equation is obtained:

$$c_s = c_s^0 - m \times \lg[f(\theta)], \qquad (17)$$

where c_s^0 is the value of c_s as $f(\theta)$ is equal to 1, m is the regression coefficient.

Table 2 The values of c_s, 10^{c_s} and m for some metals

		Metals					
		Cu	Au	Ag	Al	Fe	Ni
c_s	$f(\theta) = 1$	0.08	0.05	0.10	0.18	0.13	-0.01
	$f(\theta) = 10^{-1}$	0.65	0.60	0.65	0.72	0.64	0.50
	$f(\theta) = 10^{-2}$	1.15	1.10	1.19	1.25	1.15	1.01
	$f(\theta) = 10^{-3}$	1.56	1.62	1.73	1.78	1.66	1.52
	$f(\theta) = 10^{-4}$	2.07	2.12	2.28	2.33	217	2.03
10^{c_s}	$f(\theta) = 1$	1.2	1.12	1.26	1.51	1.35	0.98
	$f(\theta) = 10^{-1}$	4.47	3.98	4.42	5.20	4.38	3.17
	$f(\theta) = 10^{-2}$	14.12	12.60	15.49	17.94	14.21	10.23
	$f(\theta) = 10^{-3}$	36.31	41.69	54.30	60.68	46.09	33.21
	$f(\theta) = 10^{-4}$	117.49	131.83	190.36	213.10	149.53	107.5
m		0.54	0.53	0.54	0.54	0.51	0.51

The values of m for some common metals are shown in table 2. It is worth to point out that the variations of m for different metals are insignificant. The slight discrepancies of values of c_s, 10^{c_s} and m for different metals illustrate that the effect of the nature of metal on the critical nucleation frequency is negligible.

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Substituting eq.(17) into eq.(16), the general equation of heterogeneous critical nucleation frequency per unit area of catalyst surface can be obtained:

$$I_s^* = \frac{10^{c_s^0}}{f(\theta)^m} \frac{R_c}{S_v V}. \tag{18}$$

S_v and $f(\theta)$ are usually unknown. But, if the undercooling of liquid metal at a concrete solidification and melting condition are determined, the values of $f(\theta)$ and S_v at this melting condition can be worked out according to eqs. (18), (14) and eqs. (13), (18)[9] respectively. When the values of $f(\theta)$ and S_v are known, the critical nucleation frequency and undercooling of liquid metal at different R_c and V can be forecasted according to eqs. (18) and (13) respectively.

3 Discussion

If the nucleation frequency per unit continuous mass of metal melt is expressed as R_n, according to eqs.(12) and (18), the homogenous critical nucleation frequency per unit continuous mass of metal melt R_{nv}^* and the heterogeneous critical nucleation frequency per unit continuous mass of metal melt R_{ns}^* can be obtained respectively as follows:

$$R_{nv}^* + I_v^* V = 10^{c_v} R_c, \tag{19}$$

$$R_{ns}^* + I_s^* V S_v = \frac{10^{c_s^0}}{f(\theta)^m} R_c. \tag{20}$$

As mentioned above, the values of the constant term 10^{c_v} in eq. (19) and $10^{c_s^0}$ in eq. (20) vary in a very small range around 1, they are almost equal for different metals. If the values of 10^{c_v} and $10^{c_s^0}$ are assumed to be 1, and the value of m ($m = 0.51$—0.54) is assumed to be 0.53, a general expression for the homogenous and heterogeneous critical nucleation frequency per unit continuous mass of metal melt can be obtained as:

$$R_n^* = \frac{R_c}{f(\theta)^{0.53}}, \tag{21}$$

where the unit of R_n^* is s^{-1} and it stands for the homogenous critical nucleation frequency per unit continuous mass of metal melt when $f(\theta)$ is 1; and stands for the heterogeneous critical nucleation frequency per unit continuous mass of metal melt when $f(\theta)$ is less than 1.

Equation (21) shows that the homogenous critical nucleation frequency per unit continuous mass of metal melt depends only on the cooling rate of liquid metal, but the heterogeneous critical nucleation frequency per unit continuous mass of metal melt depends not only on the cooling rate of liquid metal, but also on the contact angle of catalyst. Therefore, the homogenous critical nucleation frequency per unit continuous mass of metal melt can be calculated only if the cooling rate of liquid metal is known. But if we want to determine the heterogeneous critical nucleation frequency per unit continuous mass of metal melt, not only the cooling rate of liquid metal, but also the contact angle of catalyst must be known.

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Substituting the experimental parameters ($R_c = 0.5\ Ks^{-1}$, $V = 6.5 \times 10^{-14}\ m^3$) used by Turnbull into eq.(21), the homogenous critical nucleation frequency per unit continuous mass of metal melt R_{nv}^* can be calculated as $10^{-0.3} \cdot s^{-1}$, i.e. I_v^* is $10^{12.9}\ m^{-3} \cdot s^{-1}$. The calculated result agrees well with the result ($10^{-1 \pm 1} \cdot s^{-1}$) estimated by Turnbull. Substituting the experimental parameters ($R_c = 8\ Ks^{-1}$, $V = 8 \times 10^{-8}\ m^3$) used by Willnecker into eq.(21), the homogenous critical nucleation frequency per unit continuous mass of metal R_{nv}^* and per unit volume I_v^* can be calculated as $10^{0.90} \cdot s^{-1}$ and $10^8\ m^{-3} \cdot s^{-1}$ respectively. The obtained I_v^* is almost 10^3 times higher than the result ($10^{5.48} \cdot s^{-1} \cdot m^{-3}$) estimated by Willnecker et al.[5]. As stated above, this difference is caused by that the variation of nucleation frequency with undercooling was not considered in the formulas[4—8] used by Willnecker et al.

4 Conclusion

(i) The homogenous critical nucleation frequency per unit volume I_v^* is directly proportional to the ratio of cooling rate to volume of liquid metal; the heterogeneous critical nucleation frequency per unit area of catalyst surface I_s^* is in direct proportion to the ratio of the cooling rate to the sum of the area of the most effective catalyst surface in the liquid metal (R_c / VS_v) as $f(\theta)$ is constant; when R_c / VS_v is constant, the critical nucleation frequency of heterogeneous nucleation per unit area of catalyst surface I_s^* is in inverse proportion to $f(\theta)^{0.53}$.

(ii) The critical nucleation frequency per unit continuous mass of metal R_n^* is influenced by the cooling rate of liquid metal and the equilibrium contact angle of the catalyst. It increases with the increasing cooling rate and decreases with the increase of equilibrium contact angle. The homogenous and heterogeneous critical nucleation frequency per unit continuous mass of metal melt can be expressed by a general equation: $R_n^* = R_c \cdot f(\theta)^{-0.53}$.

(iii) The critical nucleation frequency is slightly influenced by the nature of metal.

(iv) The obtained theoretical result agrees well with the homogenous critical nucleation frequency estimated by Turnbull.

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