Effect of droplet size on nucleation undercooling of molten metals

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The degree of undercooling is one of the important solidification parameters and has a vital effect on the solidification process. In 1950, Turnbull dispersed the liquid metal to microdroplets with the diameters of 10–100 μm during the investigation of homogeneous nucleation, confirming that the undercooling for homogeneous nucleation can reach about 0.18 T_m [1]. Subsequently, several investigations for the phenomena of undercooling have been carried out [2–7]. With the progress of modern fabrication techniques such as powder metallurgy and spray forming etc., it is found that the degree of undercooling depends not only on the purity of alloys, but also on the curvature of the microdroplets. By employing the method for the analysis of heat transfer suggested by Lee [8], Yao established an equation of undercooling for the droplets with large size through the research of Cu-Sb alloy [9]. However, a large deviation could be created by utilizing this equation when the microdroplet was small enough, therefore this model needs to be further modified. In this paper, a new mathematical model for microdroplets with infinitesimal size was established, and the size effect on the nucleation undercooling of solidification for molten metals was discussed.

Generally speaking, the coefficient of heat transfer can be considered as a constant. Nevertheless, an extreme non-equilibrium regime can be generated during the solidification owing to the infinitesimal size of microdroplets. Consequently, the size effect of droplets cannot be ignored. The relationship between the coefficient of heat transfer h and the droplet size D can be denoted by the following equation [8]:

$$h = \frac{k_g}{D}(2.0 + 0.6\sqrt{\mathrm{Re}}\sqrt[3]{\mathrm{Pr}}) \quad (1)$$

where k_g is thermal conductivity of gas, Re is Reynolds number, and Pr is Prandtl number of gas. Re and Pr are given by

$$R_e = \rho_g D \mu_g^{-1} |u_d - \mu_g| \quad (2)$$

and

$$P_r = C_{pg}\mu_g / k_g \quad (3)$$

with

$$u_d = u_0(T_N - T_g)/T_m \quad (4)$$

where ρ_g, C_{pg} and μ_g are the density, the specific heat, and the dynamic viscosity of gas respectively, T_g is the gas temperature, T_N is the nucleation temperature, T_m is initial melting temperature, u_d is the axial velocity of the droplet, and u_0 is the initial exit axial velocity of the gas, with the value $u_0 = 200\ \mathrm{ms}^{-1}$.

Whether for pure metals or alloys, the degree of undercooling is relatively large for homogenous nucleation process of the droplet solidification. The studies on pure metals and alloys show that the degree of undercooling can reach 0.2 times of their melting temperatures [10]. The smaller the droplet, the lower the possibilities for heterogeneous nucleation and larger of the undercooling. Attributing to the infinitesimal size, the solidification of microdroplets can be regarded as a process of homogeneous nucleation. Based on the classical nucleation theory, the nucleation frequency J_v at a given temperature T below T_L satisfies the following equation [8]:

$$J_v = K_v \exp\left[-\frac{16\pi\sigma_{SL}^3 T_L^2 f(\theta)}{3k_B T \rho_d^2 \Delta H^2 (T_L - T)^2}\right] \quad (5)$$

where K_v is the kinetic parameter with the value $10^{40}\ \mathrm{m}^{-3}\mathrm{s}^{-1}$, k_B is Boltzmann constant, ρ_d is the density of droplet, ΔH is the latent heat of solidification, T_L is the liquidus temperature, T is the solidification temperature, σ_{SL} is the solid-liquid interface energy, and $f(\theta) = (2 - 3\cos 2\theta + \cos 3\theta)/4$ is the factor of contact angle, with the value $f(\theta) = 1$ for homogeneous nucleation.

When the nucleation rate is small enough, we can assume that only one nuclear formed during the solidification process of the droplet, then the nucleation temperature in the continuous cooling process can be defined as [8]:

$$\int_{T_N}^{T_L} I(T_N)\mathrm{d}T_N \approx 1 \quad (6)$$

$I(T_N)$ is given by

$$I(T_N) = V_d J_{T_N} \big/ T \quad (7)$$

and

$$T = 6h(T_N - T_g)/\rho_d \quad (8)$$

where $I(T_N)$ is the nucleation rate, T is the cooling rate of solidification, C_L is the specific heat of liquid,

$V_d = \pi D^3/6$ is the droplet volume for assumed spherical droplet, and ρ_d, T_g, T_N, h, D are as in Equations 1–5. Furthermore, Lee obtained the following expression by modifying Equation 6 [8]:

$$-\frac{I(T_N)}{I(T_N)'} I(T_N) \approx 1 \tag{9}$$

and

$$I(T_N)' = d[I(T_N)]/dT \tag{10}$$

Substituting Equations 5 and 7 into Equation 9, we get

$$\frac{\Psi}{T_N \Delta T^2} = \ln \Phi(D) \tag{11}$$

here

$$\Psi = \frac{16\pi \sigma_{SL}^3 T_L^2}{3k_B \rho_d^2 \Delta H^2} \tag{12}$$

and

$$\Phi(D) = \frac{\frac{\pi}{6} K_v \rho_d C_L T_N^2 \Delta T^3}{6h\left[\Psi(3T_N - T_L)(T_N - T_g) + T_N^2 \Delta T^3\right]} \cdot D^4 \tag{13}$$

In view of

$$\Psi \frac{(3T_N - T_L)(T_N - T_g)}{T_N^2 \Delta T^3} \gg 1 \tag{14}$$

Hence, Equation 13 can be simplified as follows

$$\Phi(D) = \frac{\frac{\pi}{6} K_v \rho_d C_L T_N^2 \Delta T^3}{6h\Psi(3T_N - T_L)(T_N - T_g)} \cdot D^4 \tag{15}$$

TABLE I Thermophysical parameters of N_2 [8]

Specific heat C_{pg} ($Jkg^{-1}K^{-1}$)	Dynamic viscosity μ_g (Nsm^{-2})	Thermal conductivity k_g ($Wm^{-1}K^{-1}$)	Density ρ_g ($k_g m^{-3}$
1039	1.78×10^{-5}	2.6×10^{-2}	1.16

Substitution of Equation 15 into Equation 12 gives

$$\frac{\Psi}{T_N \Delta T^2} - \ln \Delta T^3 = \ln\left[\frac{\frac{\pi}{6} K_v \rho_d C_L T_N^2}{6h\Psi(3T_N - T_L)(T_N - T_g)} \cdot D^4\right] \tag{16}$$

Considering that $\frac{\Psi}{T_N \Delta T^2} \gg \ln \Delta T^3$, then the item of $\ln \Delta T^3$ can be ignored. As a result, Equation 16 can be generalized as

$$\frac{\Psi}{T_N \Delta T^2} = \ln\left[\frac{\frac{\pi}{6} K_v \rho_d C_L T_N^2}{6h\Psi(3T_N - T_L)(T_N - T_g)} \cdot D^4\right] \tag{17}$$

Based on the above deduction, the relationship between the degree of undercooling and the size of droplets is calculated for Al-4.5 wt%Cu alloy in N_2 atmosphere. The thermophysical parameters of N_2 and that of Al-4.5 wt% Cu alloy are listed in Tables I and II, respectively [8]. In light of Equations 1 and 17, the calculated results are tabulated in Table III.

Fig. 1 shows the relationship between the coefficient of heat transfer and the size of droplets. It is obvious that the values of h increase with the decrease of the sizes of droplets. And a dramatic change occurs for h vs. D when the size is smaller than 20 μm, which cannot be ignored when analysis of heat transfer is investigated during droplet solidification.

As shown in Fig. 2, the same tendency can be found from the relationship between the degree of undercooling and the size of droplets, furthermore, the relationship is not consistent with other research results obtained from Cu-Sb alloy in the range of 100–1200 μm

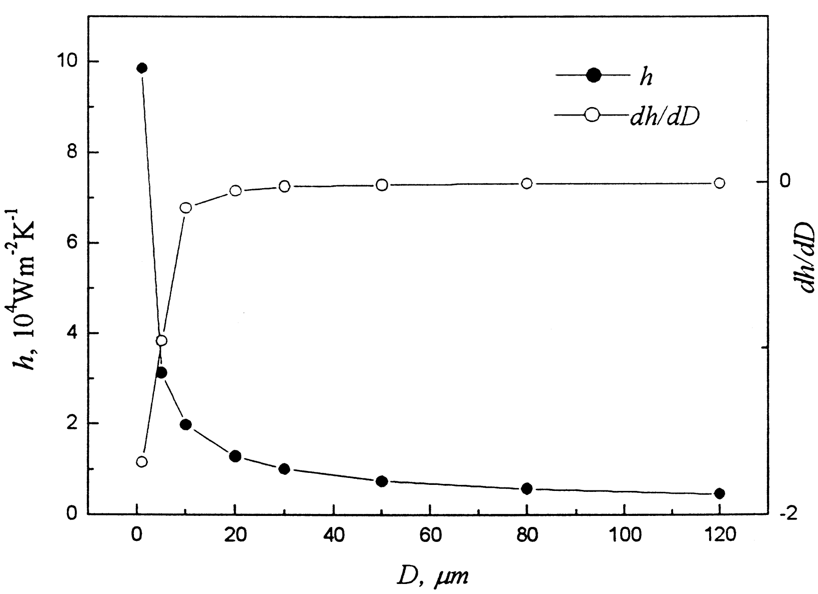

Figure 1 Relationship between the coefficient of heat transfer and the size of droplets.

TABLE II Thermophysical parameters of Al-4.5 wt%Cu alloy [8]

Specific heat of liquid C_L ($Jkg^{-1}K^{-1}$)	Density of droplet ρ_d (k_gm^{-3})	Interface energy σ_{SL} (Jm^{-2})	Latent heat of solidification ΔH (Jkg^{-1})	Liquidus temperature T_L (K)	Melting temperature T_m (K)
982	2800	0.131	3.48×10^5	919	934

TABLE III Calculated results of the degree of undercooling and the coefficient of heat transfer for Al-4.5 wt%Cu alloy in N_2 atmosphere

Size of droplets (μm)	1	5	10	20	30	50	80	120
Coefficient of heat transfer (10^4 Wm^{-2} K^{-1})	9.86	3.13	1.99	1.30	1.02	0.76	0.59	0.47
Degree of undercooling (K)	224.2	175.2	162.4	152.0	146.7	141.0	136.2	132.5

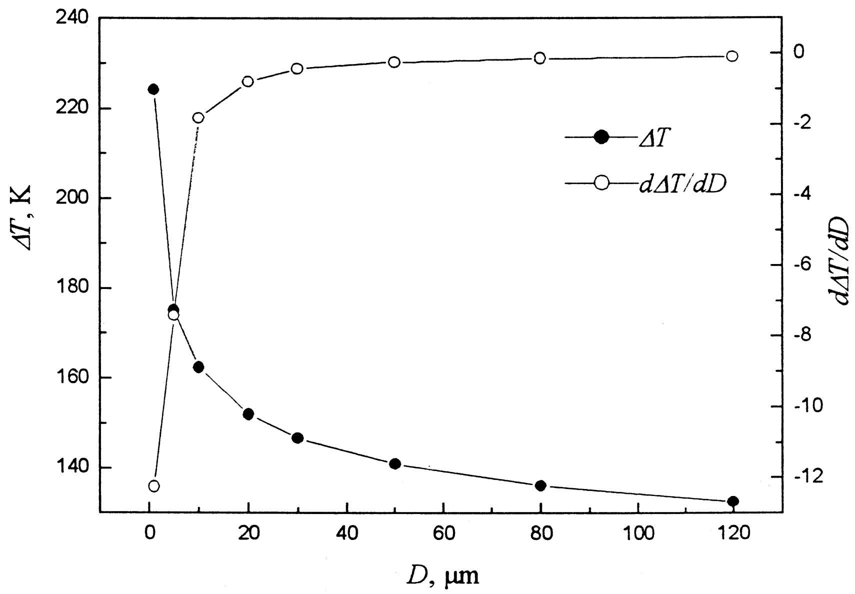

Figure 2 Relationship between the degree of undercooling and the size of droplets.

when $D < 20$ μm [9]. The degree of undercooling can reach $0.23T_m$ when the droplet with the size of 1 μm, exceeding the maximum undercooling of homogeneous nucleation. That is to say, *size effect creates* owing to the infinitesimal size of droplets.

In summary, the coefficient of heat transfer h and the degree of undercooling ΔT are evidently influenced by the size of microdroplets D. When the size of droplets is larger than 20 μm, an approximative linear relation exists among them. However, size effect generates obviously when the size is smaller than 20 μm, and their relationship does not obey the traditional law any more.

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