Decline of nucleation in the heating process with a high heating rate*

Yang Gao-Lin(杨高林), Lin Xin(林 鑫)†, Song Meng-Hua(宋梦华),
Hu Qiao(胡 桥), Wang Zhi-Tai(汪志太), and Huang Wei-Dong(黄卫东)

State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, *China*

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The effect of the heating rate on the nucleation of metallic glass in a rapid heating process starting from the glass transition temperature is investigated. The critical nucleus radius increases with the increase of the temperature of the undercooling liquid. If the increment rate of the critical nucleus radius, owing to the heating process, is higher than the growth rate of the nuclei, the nuclei generated at the low temperature will become the embryos at the high temperature. This means that the high heating rate can make no nucleation happen in the heating process. In consideration of the interfacial energy, the growth rate of the nuclei increases with the increase of their size and the growth rate of the critical nucleus is zero. Thus, the lower heating rate can also make the nuclei decline partially. Finally, this theory is used to analyze the nucleation process during laser remelting metallic glass.

Keywords: nucleation, growth rate, heating rate, bulk metallic glass

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1. Introduction

In the crystallization process of the undercooling liquid, nucleation is the premise of the crystallization.[1–4] According to classical nucleation theory, the nucleation rate is dependent on the temperature, but independent of its variation rate.[5] However, this is not correct for a rapid heating or cooling process as the critical nucleus will increase with the increase of temperature. In 1984, Fisher *et al.* presented an athermal nucleation theory, which indicated that an abrupt decrease of the critical nucleus radius caused by a rapid cooling process could make the embryos existing at high temperature change into the nuclei at low temperature.[6] Based on a similar principle, an inverse athermal nucleation is also possible. In a heating process, the nuclei formed at low temperature could come into the embryos at high temperature. This phenomenon could exist in laser remelting metallic glass. In the process, the metallic glass in the heat affected zone (HAZ) of the molten pool will be heated up to a temperature near the melting point rapidly, then cooled to room temperature rapidly again. The crystallization behavior of metallic glass during laser remelting metallic glass is important for laser solid forming and laser welding metallic glass. Therefore, it is necessary to study the decline of nucleation in the heating process of laser remelting metallic glass. In this paper, the decline of nucleation caused by the high heating rate is investigated, and it is used to analyze the nucleation behavior during laser remelting metallic glass.

2. Increment rate of critical nucleus radius in the heating process

The classical nucleation theory pertains to an undercooling phase transformation system. During a phase transformation, the production of the new phase releases Gibbs energy, whereas the creation of the interfaces between the old and the new phases costs Gibbs energy. The critical nucleus radius of the new phase in the classical nucleation theory is defined such that if the particle is of subcritical size, it costs energy to increase the size of the particle, whereas if the particle (nucleus) is of supercritical size, energy is released if the particle grows further.[1] The classical theory of nucleation gives the critical nucleus radius in undercooling liquid as[5]

$$r_{\mathrm{c}} = \frac{2V \cdot T_{\mathrm{m}}}{\Delta H} \cdot \frac{\sigma}{\Delta T}, \tag{1}$$

where V is the molar volume, ΔH is the melting enthalpy, T_{m} is the melting point, ΔT is the undercooling temperature, which is equal to T_{m}–T, T is the temperature, and σ is the interfacial energy which can be calculated by[7]

$$\sigma = \alpha \frac{\Delta S_{\mathrm{m}}}{N_0^{1/3} V^{2/3}} T = \alpha \frac{\Delta H}{N_0^{1/3} V^{2/3}} \cdot \frac{T}{T_{\mathrm{m}}}. \tag{2}$$

Here, N_0 is Avogadro's number, α is a constant, which is 0.71 for body-centered cubic crystal and is 0.86 for face-centered cubic or close-packed hexagonal crystal, and ΔS_{m} is the melting entropy. Thus, equation (1) can be rewritten as

$$r_{\mathrm{c}} = 2\alpha \frac{T}{\Delta T} \left(\frac{V}{N_0} \right)^{1/3}. \tag{3}$$

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†Corresponding author. E-mail: xlin@nwpu.edu.cn

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This equation means that the r_c will increase in a heating process. For the heating progress with a heating rate of $\beta(t)$, where t is the time, the increment rate of critical nucleus radius $v_c(t)$ can be gotten as

$$v_c(t) = \frac{dr_c(t)}{dt} = 2\alpha \left(\frac{V}{N_0}\right)^{1/3} \frac{T_m}{\Delta T(t)^2}\beta(t). \quad (4)$$

Equation (4) builds a relationship between the $\beta(t)$ and $v_c(t)$. At a certain temperature, $v_c(t)$ has a linear relationship with $\beta(t)$. The $v_c(t)$ also varies with the undercooling $\Delta T(t)$, the smaller undercooling leading to bigger $v_c(t)$.

3. Critical heating rate

For a heating process, the nuclei will grow up, but as previous analysis states, the critical nucleus radius will also increase. Assuming that when a heating process takes place from time t_1 to time t_2, the critical nucleus radius is r_{c1} and the radius of a nucleus is r_1 at t_1, and the critical nucleus radius is r_{c2} and the radius of the nucleus is r_2 at t_2, we can obtain

$$r_{c2} = r_{c1} + \int_{t_1}^{t_2} v_c(t)\,dt = r_{c1} + r_{gc},$$
$$r_2 = r_1 + \int_{t_1}^{t_2} v_g(t)dt = r_1 + r_{gr},$$

where v_g is the growth rate of nuclei, r_{gc} and r_{gr} are the growth parts of the critical nucleus radius and the nuclei radius respectively. Since the nuclei are formed by thermal fluctuation, the generation probability of the nuclei with the size much larger than the critical nucleus is low.[8] Therefore, the difference between r_{c1} and r_1 at the initial time t_1 should be small. If r_{gc} is larger than r_{gr}, the previous nucleus will decline at t_2. Therefore, if v_c is larger than v_g, most of the nuclei could decline. The heating rate, which causes v_c to equal v_g, can be defined as the critical heating rate β_c. The critical heating rate can be deduced from Eq. (4) and given as follows:

$$\beta_c(t) = v_g \frac{\Delta T^2}{2\alpha \cdot T_m}\left(\frac{N_0}{V}\right)^{1/3} = v_g(t)\frac{T(t)\cdot\Delta T}{T_m \cdot r_c}. \quad (5)$$

From Eq. (5), it can be seen that the larger undercooling will lead to a lager critical heating rate at a certain growth rate.

4. Variation of growth rate with the size of nucleus

The above discussion shows that the higher heating rate causes the increment of critical nucleus radius to be faster than the growth rate of the nucleus. Because of the effect of interfacial energy, the growth rate of the nucleus varies with the size of the nucleus.

According to the classical phase transformations theory, there are two growth patterns for the formed nucleus: volume diffusion controlled growth and interface-controlled growth. Interface-controlled growth is the faster one. Normally, it is reckoned that in the early stage, the nuclei grow by the interface-controlled growth. The growth pattern will change into the volume diffusion controlled growth when the nuclei grow bigger, which leads to the more severe solute segregation.[9] Therefore, the interface-controlled growth pattern is considered as the growth pattern of the nuclei in this paper. The growth rate v_g of the nuclei by the pattern of interface-controlled growth can be given as[1]

$$v_g = v_0 \exp\left(-\frac{\Delta G^a}{RT}\right)\left(1 - \exp\left(\frac{-\Delta G}{RT}\right)\right), \quad (6)$$

where v_0 is the pre-exponential factor for growth, ΔG^a is the activation energy for the transfer of atoms through the parent phase/new phase interface, and ΔG is the Gibbs energy difference per molar during the nucleus growth, which can be calculated from

$$\Delta G = \frac{\Delta H}{T_m}\Delta T. \quad (7)$$

It should be indicated that in Eq. (6), the effect of the interfacial energy has been ignored. However, in the size of the nucleus, the interfacial energy should be taken into account. The free energy difference Δg of the nucleus including interfacial energy is[5]

$$\begin{aligned}\Delta g &= -\frac{\Delta G}{V}\frac{4\pi}{3}r^3 + \sigma\cdot 4\pi r^2 \\ &= -\Delta G\cdot M + \sigma\cdot 4\pi\left(\frac{3M\cdot V}{4\pi}\right)^{2/3}, \end{aligned} \quad (8)$$

where r is the radius of the nucleus, and M is the number of moles of the atoms in the nucleus. The variation of Δg with the number of moles is

$$\begin{aligned}\frac{d\Delta g}{dM} &= -\Delta G + \sigma\cdot 4\pi\left(\frac{3V}{4\pi}\right)^{2/3}\cdot\frac{2}{3}M^{-1/3} \\ &= -\Delta G + \frac{2\sigma\cdot V}{r} = -\Delta G\frac{r - r_c}{r}. \end{aligned} \quad (9)$$

Therefore, the growth rate of the nucleus with considering surface energy v_{gr} can be obtained as

$$\begin{aligned} v_{gr} &= v_0 \exp\left(-\frac{\Delta G^a}{RT}\right)\left(1 - \exp\left(\frac{-\Delta G\frac{r-r_c}{r}}{RT}\right)\right) \\ &= v_0 \exp\left(-\frac{\Delta G^a}{RT}\right)\left(1 - \exp\left(\frac{-\Delta H\cdot\Delta T\frac{r-r_c}{r}}{T_m RT}\right)\right). \end{aligned} \quad (10)$$

In fact, equation (10) can be used for particles in all sizes. Equation (10) shows that the growth rate of the embryo, which is the particle smaller than the critical nucleus, is negative.

This means that the embryo will be remelted. It is reasonable because the embryo is thermodynamically unstable. The growth rate of the critical nucleus is zero. The growth rate of the nucleus increases with the increase of its size. Equation (10) is approximate to Eq. (6) when the nucleus is large enough. The growth rate generally mentioned is the growth rate of the large enough particle, which is the faster one in all growth rates of nuclei. So the heating rate calculated from Eq. (5) with this growth rate can make all nuclei decline. But a low heating rate can also make the nuclei smaller than a certain size of decline.

5. Decline of nucleation during laser remelting of the metallic glass

Table 1 shows the critical heating rates for some alloys with different initial undercooling degrees. The growth rates and melting temperatures shown in Table 1 are obtained from the published articles. The growth rates of Ni–Sn eutectic[10] and $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$[11] are experimentally measured results. The growth rate of $Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$[12] is the calculated result with a volume diffusion-controlled growth pattern. The molar volumes of the alloys are revaluated from the linear superposition of those of the constituent elements. It can be seen that the critical heating rate for the undercooling melt of Ni–Sn alloy at the undercooling of 140 K is 1.58×10^{10} K/s. This heating rate is too high to reach in the general heating process. However, the growth rate in the metallic glass is lower. The growth rate of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ amorphous alloy is only 1.1×10^{-8} m/s at the undercooling of 360 K, and the corresponding critical heating rate is 4.47×10^{3} K/s. This is easy to obtain during pulsed laser remelting of bulk metallic glasses.[13]

Table 1. Corresponding critical heating rates (CHR) for some alloys at certain initial undercooling degrees.

Material	ΔT/K	T_m/K	Growth rate/(m/s)	r_c/nm	CHR/(K/s)	v_g/(10^{-6} m^3/mol)
Ni–Sn eutectic	140	1403	0.45	3.98	1.58×10^{10}	12.6
$Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$	360	1100	1.1×10^{-8}	0.89	4.47×10^{3}	11.8
$Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$	43	1028	1.94×10^{-3}	9.31	8.96×10^{6}	9.87
$Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$	188	1028	4.8×10^{-5}	1.53	4.82×10^{6}	9.87

The nucleation rate and growth rate have the same variation trend with temperature. Both of them first rise to a maximum and then decline with temperature increasing. But the temperature at the maximum nucleation rate T_n is generally lower than the temperature at the maximum growth rate T_r.[12] For example, for $Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$, T_r is 985 K and T_n is 840 K. Table 1 shows that the growth rates at these two temperatures have a difference of two orders of magnitude, and the critical nucleus radius at T_r is about six times that at T_n. However, the critical heating rates at these two temperatures are similar.

Considering two experiments with single pulsed laser remelting of $Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$ metallic glass, the single pulsed energy of the first experiment is 30 J and the pulse duration is 0.1 ms, while the single pulsed energy of the second experiment is 119 J with a pulse duration of 3 ms. The temperature distribution during laser remelting of the metallic glass can be simulated by the software of Comsol. The simulation results are shown in Fig. 1. The temperature–time profile is for the point which is 0.076 mm below the center of the molten pool surface. The maximum temperature of this point is 1009 K, which is close to but below the melting temperature. This point is in the heat affected zone.[13] Figure 1(a) shows the first rapid heating process and then a relatively slow cooling process. The heating rate at T_n is 9.4×10^{6} K/s, which is higher than the critical heating rate at T_n. The heating rate at T_r is 1.3×10^{6} K/s, which is lower than the critical heating rate at T_r. This situation means that the declining effect of nucleation in the heating process with such a high heating rate makes the metallic glass hardly nucleate at the temperature of the maximum nucleation rate. The heating rate at the temperature of the maximum growth rate of the nuclei cannot stop nucleation, but the nucleation rate should be too small at this temperature. So the metallic glass could hardly crystallize in the whole heating process due to the absence of nucleation.

In previous heating/cooling asymmetry theory, it is reckoned that the cooling process causes less crystallization than the heating process.[12] This theory makes sense when the heating rate is low, because the heating process passes first through T_n and then through T_r while the cooling process passes first through T_r and then through T_n, the cooling process generates less crystallization due to the absence of nucleation. But for a rapid heating process, the declining effect of nucleation will also make the nucleation absent while the athermal nucleation can also generate nucleation in a rapid cooling process. Therefore, the heating/cooling asymmetry theory should not be suitable for describing the rapid heating/cooling process.

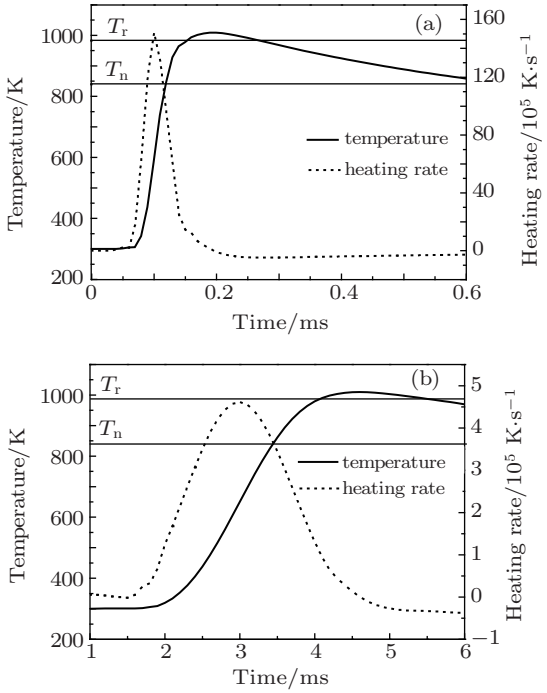


Fig. 1. Temperature–time profiles of laser remelting metallic glass. (a) Single pulsed energy of laser is 30 J with a pulsed duration of 0.1 ms. The point is 0.076 mm below the center of the molten pool surface. (b) Single pulsed energy of the laser is 119 J with a pulsed duration of 3 ms. The point is 0.5 mm below the center of the molten pool surface. Both panels (a) and (b) have similar maximum temperatures of about 1009 K.

Figure 1(b) shows the temperature–time profile of the experiment with a pulse duration of 3 ms and single pulsed energy of 119 J at the point which is 0.5 mm below the center of the molten pool surface. The heating rates at T_n and T_r are 3.7×10^5 K/s and 1.0×10^5 K/s respectively. Both of them are below the critical heating rate. But this does not mean that the heating rate does not affect the nucleation. Since the growth rates of the nuclei vary from zero to v_g, there must exist some nuclei whose growth rates are less than the v_c, and they will decline in the heating process. As the growth rate corresponds to the nucleus size, the sizes of all these nuclei which will decline must be below a new marginal nucleus size. The new marginal nucleus is the nucleus whose growth rate is equal to v_c. The v_c corresponding to a certain heating rate can be calculated from Eq. (4). Then the new marginal nucleus size can be calculated from Eq. (10). Therefore, at a certain heating rate, only the nuclei which are larger than the new marginal nucleus can grow. Figure 2 shows the relationship between the growth rate and size of the nuclei at the temperature of T_n which is calculated from Eq. (10). The growth rates of $Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$ shown in Table 1 are calculated with a volume diffusion-controlled growth pattern, which are smaller than the growth rates of interface-controlled growth. The growth rates of the interface-controlled growth of $Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$ cannot be figured out because there is not enough necessary parameter. If the growth rate of $Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$ at 840 K shown in Table 1 is equal to the growth rate of interface-controlled growth, the new marginal nucleus radius of $Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$ in the heating process at a heating rate of 3.7×10^5 K/s is 3.97 times larger than r_c. This means nuclei smaller than 3.97 r_c will decline. If the interface-controlled growth rate is twice as large as the growth rate shown in Table 1, the new marginal nucleus size becomes 1.56 r_c. The smaller v_{gr}/v_g leads to a smaller new marginal nucleus size. Generally, the interface-controlled growth rate is a constant for a certain heating process. Therefore, the heating rate less than the critical heating rate can also reduce the nucleation rate and the lower heating rate leads to a smaller reduction in the nucleation rate.

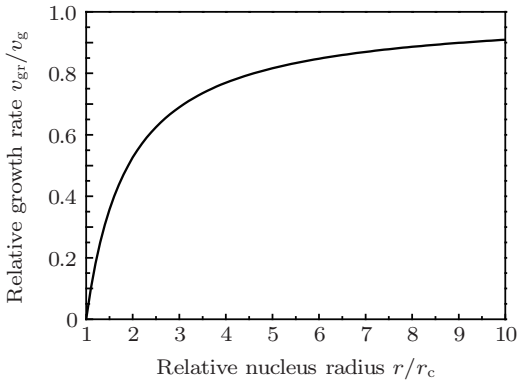


Fig. 2. Variation of the growth rate with the size of the nucleus in $Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$ undercooled liquid at 840 K. r_c is the critical nucleus radius, r is the radius of the nucleus with the growth rate of v_{gr}. v_g is the growth rate of the particle that is large enough.

6. Conclusion

In summary, there is a critical heating rate for the heating process of the metallic glass and the undercooling liquid. The heating rate larger than the critical heating rate renders the increment rate of critical nucleus radius higher than the growth rate of the nuclei, and causes no nucleation to happen in the heating progress. The growth rate of the nucleus is closely related to the size of the nucleus due to the effect of interfacial energy. A larger nucleus has a larger growth rate. The growth rate of the embryo is negative and the growth rate of the critical nucleus is zero. The lower heating rate can also make the nuclei smaller than a marginal nucleus decline.

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