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ARTICLE

Nucleation Dynamics of Rapidly Solidified Ternary Eutectic Au-19.25Ag-12.80Ge Brazing Filler

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Abstract: The nucleation of rapidly solidified Au-19.25Ag-12.80Ge ternary eutectic alloy was analyzed and discussed according to the classical nucleation theory. Then the relationship between the incubation period of each phase and the melting temperature was obtained. The results show that for rapidly solidified Au-19.25Ag-12.80Ge brazing filler, the incubation period of AuAg solid solution is much shorter than that of Ge phase, and AuAg phase is precipitated preferentially as the main nucleation phase in the rapid solidification process. According to the time-dependent transient nucleation theory, the critical nucleation temperature, critical nucleation undercooling and critical nucleation number of the brazing filler were calculated under continuous cooling conditions. It can be seen that with increase of the cooling rate, the initial nucleation undercooling required to trigger melt nucleation increases, and the critical nucleation number increases substantially too.

Key words: brazing filler; rapidly solidified; incubation period; nucleation

For rapidly solidified alloys with large initial undercooling, the competition of nucleation rate often plays a decisive role in phase selection^[1-3]. In order to determine the sequence of phase nucleation, the relationship between nucleation rate and undercooling of the competing phase must be calculated according to nucleation dynamics. The classical nucleation theory simplifies the difficulty of dealing with the nucleation problem and makes it a great success in describing the nucleation process^[4-7]. However, it can qualitatively and quantitatively describe nucleation phenomena because it neglects the effects of curvature and anisotropy of interfacial energy, and the density difference of the two phases is considered only. The step-by-step nucleation mechanism has been confirmed by a large number of simulation and experimental results in recent years^[8,9]. It is found that the nucleation process is carried out in two steps near the critical point of liquid-solid phase transition. The high density liquid phase first appears, and then the ordered crystalline phase

nucleates and grows in the high density liquid phase. Due to the limitations of research methods, the understanding of nucleation process step is still very restricted. The transition paths from metastable mesophase to stable crystalline phase and the underlying mechanisms leading to differences in nucleation paths in nucleation step during the rapid solidification process are far from being revealed.

The rapidly solidified ternary Au-19.25Ag-12.80Ge brazing filler was prepared by single-roller melt spinning technology. It can be widely used in the field of high reliability microelectronic devices and optoelectronic device packaging. It shows good wettability with Ni and Cu bases, and the shear strength of the welding joint which was formed by the rapidly solidified brazing filler is increased by 60% compared with that of the mother alloy^[10,11]. In this work, the relationship between nucleation time and temperature of competing phases in ternary eutectic Au-19.25Ag-12.80Ge brazing fillers during rapid solidification was calculated by time-dependent

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heterogeneous nucleation theory, and the step-by-step nucleation mechanism was preliminarily discussed.

1 Establishment of Time-Dependent Transient Nucleation Model

In classical models, it is assumed that the nucleation rate of alloy melt is independent of time, but this assumption is inconsistent with the reality. Under the condition of rapid solidification, the diffusion of atoms is restricted, which is not enough to ensure the equilibrium state of clusters^[12,13]. This makes the distribution of atoms much different from the steady state value. As the time-dependent nucleation rate varies continuously, some related problems were calculated and a time-dependent nucleation model was deduced.

The behavior of particles in the non-equilibrium system can be described by the Fokker-Plank equation:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial n} \left(\beta \cdot \frac{\partial C}{\partial n} \right) + \frac{1}{k_B T} \cdot \frac{\partial}{\partial n} \left(\beta C \frac{\partial \Delta G}{\partial n} \right) \quad (1)$$

In Eq.(1), β is the striking probability of clusters composed of n atoms by a single atom with the component C , k_B is the Boltzmann constant, T is temperature, and G is Gibbs free energy of forming an atomic cluster. The nucleation is related to the stable distribution of clusters in the process of nucleation dynamics, and the stable nucleation rate of time dependence is expressed by the following formula:

$$J = J_s \exp\left(-\frac{\tau}{t}\right) \quad (2)$$

where J_s in the upper formula is the stable nucleation rate, and it can be described as:

$$J_s = \beta^* Z C_n \exp\left(\frac{-\Delta G^*}{k_B T}\right) \quad (3)$$

In Eq.(3), ΔG^* is the critical nucleation free energy. Since the nucleation during the rapid solidification process is mostly heterogeneous, a shape factor should be added to the nucleation work. So the transient nucleation rate can be expressed as:

$$J = \beta^* Z C_n \exp\left(\frac{-f(\theta)\Delta G^*}{k_B T}\right) \exp\left(-\frac{\tau}{t}\right) \quad (4)$$

in which, the shape factor is described as follows:

$$f(\theta) = 0.25(2 - 3\cos\theta + \cos^3\theta) \quad (5)$$

2 Calculation Results and Discussion

2.1 Nucleating incubation period calculation

The predecessors have done a lot of work on the expression of incubation period. In this work, Feder's processing^[14] is used. Assuming that nuclei of atomic number ($n^* + \delta/2$) shrink without thermal fluctuation, the critical width is named as δ . The incubation period can be divided into two parts: t' , the time when a nuclear embryo reverses to a single atom within the scope from $n=0$ to $n=n^* - \delta/2$; τ_δ , the reverse contraction time of crystal nucleus from $n=n^* + \delta/2$ to $n=n^* - \delta/2$. These two parts are driven by different forces. Within the stage t' , the gradient of free energy is larger, which is also called instantaneous nucleation period as the driving force of growth.

The τ_δ stage is a stable nucleation stage with a little free energy gradient and approximate random walk. It can be described by the Einstein formula:

$$\delta = (2\beta^* \tau_\delta)^{1/2} \quad (6)$$

It is found that τ_δ is much larger than t' , so τ_δ is approximated as τ , and the expression of τ is derived as follows:

$$\tau \approx \tau_\delta = \frac{-4k_B T}{\beta^*} \left/ \left(\frac{\partial^2 \Delta G(n^*)}{\partial n^2} \right) \right. \quad (7)$$

where β^* still represents the diffusivity, which can be expressed by the product of the jumping frequency of liquid atoms and the number of atoms at the nucleation interface. For heterogeneous nucleation with a contact angle θ on a plane, the diffusivity can be expressed as follows:

$$\beta^* = D/\alpha^2 [2\pi(r^*)^2 X_{L,eff}(1 - \cos\theta)/\alpha^2] \quad (8)$$

where α is atomic transition distance (D/α^2 is the atomic transition frequency); D is self-diffusion coefficient of atoms; r^* is radius of critical nucleus; θ is contact angle of heterogeneous nucleation; $X_{L,eff}$ is concentration of effective alloy melt.

In the process of rapid solidification, when the stress at the solid/liquid interface is not taken into account, the change of Gibbs free energy at solid/liquid interface for globular nucleated embryos during heterogeneous nucleation is as follows:

$$\Delta G = V_a \Delta G_v n + \sigma [36\pi V_a f(\theta)]^{1/3} n^{2/3} \quad (9)$$

Among them, V_a is the average volume of atoms, ΔG_v is the difference of volume free energy between solid and liquid phases, and σ is the free energy of solid/liquid interface. The first term on the right side of Eq.(9) represents the change of volume free energy due to phase transition, and the second term represents the change of solid/liquid interface free energy. The number of atoms in the critical nucleus can be calculated according to Eq.(9):

$$n^* = \frac{32\pi f(\theta)}{3V_a} \left[\frac{\sigma}{\Delta G_v} \right]^3 \quad (10)$$

Eq.(11) can be obtained from Eq.(9) and Eq.(10):

$$\frac{\partial^2 \Delta G}{\partial n^2} = -\frac{V_a^2 \Delta G_v^4}{32\pi f(\theta) \sigma^3} \quad (11)$$

By substituting Eq. (8) and Eq. (11) into Eq. (7), the relationship between nucleation incubation period and the temperature can be deduced.

$$\tau = \frac{16k_B f(\theta)}{1 - \cos\theta} \cdot \frac{\alpha^4}{V_a^2 X_{L,eff}} \cdot \frac{\sigma T}{D \Delta G_v^2} \quad (12)$$

Further approximation of Eq.(12) is needed for calculation. Here the relationship between the free energy of solid/liquid interface σ_m and the latent solid melting heat H_m can be approximately expressed as: $\sigma_m = N_0 d_{\alpha 0}^2 = 0.45H_m$, and $H_m = N_0 V_a H_v$; N_0 is the Avogadro constant and V_a is the average atomic volume of solid phase; $V_a = d_\alpha^3$, d_α is the average atomic diameter of solid phase, and it can be calculated

according to the formula $d_\alpha = \left(\frac{W_m}{N_0 \rho} \right)^{1/3}$; average molar mass of solids is W_m , and ρ is the density of the solid phase.

The expression of the relationship between incubation period and temperature is as follows:

$$\tau = \frac{7.2Rf(\theta)}{1 - \cos\theta} \cdot \frac{\alpha^4}{d_{\Delta}^2 X_{L, \text{eff}}} \cdot \frac{T_r}{D\Delta S_m \Delta T_r^2} \quad (13)$$

in which S_m represents the molar melting entropy of solid phase, and $T_r=T/T_m$, the degree of supercooling $\Delta T_r=T-T_m$. It can be seen from Eq.(13) that the three main factors affecting the incubation period are the degree of supercooling ΔT_r , diffusion coefficient D and atomic transition distance α .

Correct calculation of self-diffusion coefficient D is very important for the calculation of incubation period. However, it is difficult to directly measure the diffusion coefficient in the process of rapid solidification, so an approximate estimation can be made only. Considering the same magnitude order of diffusion activation energy and viscosity activation energy at solid/liquid interface during solidification of liquid metals, there is also a Stokes-Einstein relationship between viscosity coefficient and atomic self-diffusion coefficient:

$$\frac{\eta D}{T} = \frac{k_B}{6d_{\Delta}} \quad (14)$$

$$\eta = 10^{-3.3} \exp\left[\frac{3.34T_L}{T - T_g}\right] \quad (15)$$

The diffusion coefficient expressed by temperature is obtained based on Eq.(14) and Eq.(15):

$$D = \frac{10^{2.2} k_B T}{6d_{\Delta}} \exp^{-1}\left[\frac{3.34T_L}{T - T_g}\right] \quad (16)$$

Combining Eq. (13) and Eq. (16), the relationship between nucleation incubation period and temperature can be quantitatively calculated as follows:

$$\tau = \frac{7.2Rf(\theta)}{1 - \cos\theta} \cdot \frac{6\alpha^4}{d_{\Delta} X_{L, \text{eff}}} \cdot \frac{T_m \exp\left(\frac{3.34T_L}{T - T_g}\right)}{10^{3.3} k_B \Delta S_m (T - T_m)^2} \quad (17)$$

In which T_g is the glass transition temperature. For pure metals, it can be approximated as $T_g=0.25T_m$. For eutectic alloys, it can be approximated according to the molar ratio of each component according to Thompson and Spaepen as $T_g=0.25T_L$ (T_L is the liquidus temperature of alloys).

Based on the above formulas for nucleation incubation period, the relationship between nucleation incubation period and the temperature (namely TTT curve) of rapidly solidified Au-19.25Ag-12.80Ge brazing filler can be calculated. The relationship between nucleation incubation period and temperature of the phases is shown in Fig. 1, and the thermodynamic data are shown in Table 1.

As can be seen from Fig. 1, the nucleation incubation period of AuAg solid solution is much shorter than that of Ge phase for rapidly solidified ternary eutectic Au-19.25Ag-12.80Ge brazing fillers. The nucleation incubation period curve of AuAg solid solution completely envelops the curve of Ge phase. Therefore, it is considered that AuAg phase precipitates preferentially as the main nucleation phase during solidification.

Fig. 2 illustrates the difference in energy change and nu-

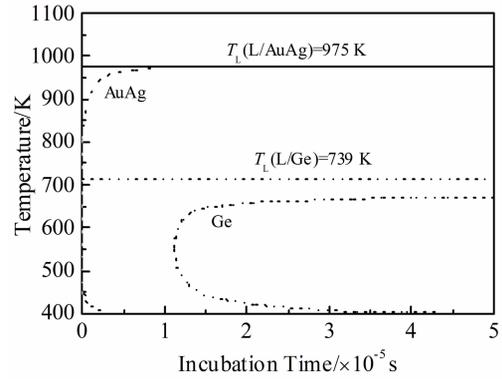


Fig.1 TTT curves of rapidly solidified Au-19.25Ag-12.80Ge brazing filler

Table 1 Thermodynamic data of the brazing filler

Element	Au	Ag	Ge
T_m/K	1337	1233.9	1210.4
$H_m/kJ \cdot mol^{-1}$	41.651	37.709	60.675
$S_m/J \cdot Kmol^{-1}$	97.813	90.885	97.339
$C_{PL}/J \cdot (mol \cdot K)^{-1}$	30.962	33.472	27.614
$C_{PS}/J \cdot (mol \cdot K)^{-1}$	24.317	24.407	23.355
$\rho_s/g \cdot cm^{-3}$	19.32	10.49	4.323

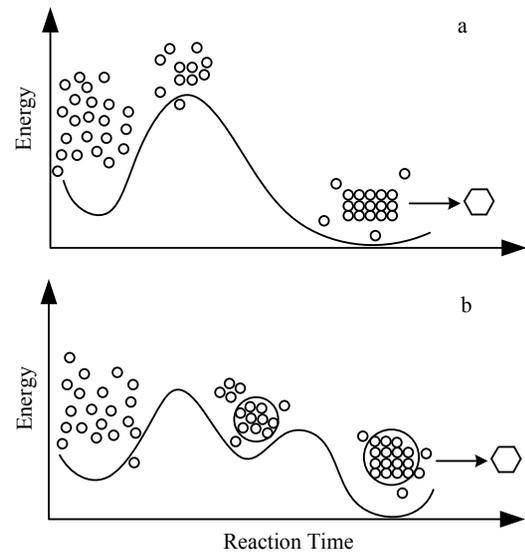


Fig.2 Nucleation pathways of two different nucleation mechanisms: (a) classical nucleation pathway and (b) two-step nucleation pathway

cleation pathway between classical one-step nucleation (Fig.2a) and two-step nucleation (Fig.2b). It can be seen that the two-step nucleation process through the intermediate state can significantly reduce the nucleation barrier, and it is a gradual process rather than a jump process in the classical nucleation theory. According to the two-step nucleation

mechanism, it is the core of metastable phase that forms firstly which is closest to the free energy of liquid phase, not the core of thermodynamic stable phase. That is, the nucleating process begins with the appearance of crystalline embryos which are similar to the melt structure, and then the crystalline embryos transform to stable nuclei through structural transformation.

The experimental results^[10] show that metastable phases form in the quenched ternary eutectic Au-19.25Ag-12.80Ge brazing filler during the rapid solidification process, and the metastable supersaturated AuAg solid solution which is more similar to the structure of liquid melt alloy forms firstly. After aging, metastable phase disappears and transforms into eutectic structure with more stable structure and high Ge content, consistent with the characteristics of two-step nucleation mechanism.

2.2 Nucleation dynamics analysis

For the rapid solidification process under continuous cooling conditions, it needs to be analyzed according to the time-dependent nucleation theory^[15-17]. The classical nucleation kinetics considers that when the total number of embryos formed in a unit volume melt $N_t(T)$ reaches a critical value N_{cnt} , the nucleation begins. At this time, the temperature is the nucleation temperature and the time is the nucleation starting time. Based on this, the nucleation criterion is obtained as $N_t(T)=N_{cnt}$, in which N_{cnt} is the critical number of nuclei per unit volume which is sufficient to trigger the nucleation process. As it is not convenient to observe and to measure N_{cnt} directly for the brazing filler melt, estimation according to the distribution of the primary phase grains of the sample is often carried out, which brings many uncertainties to the calculation results.

When the melt solidifies under continuous cooling conditions, the embryo will grow up with the cooling of the melt, and the number of embryo will increase simultaneously. Therefore, in order to characterize the nucleation of continuous cooling process, it is unreasonable to consider only the number of embryo. The corresponding nucleation criteria need to be derived from the total volume of embryo formed in the process of liquidus continuous cooling.

Under continuous cooling condition, the number of embryo that can exist steadily at a given temperature can be calculated by integrating the time-dependent transient nucleation rate with temperature in Eq. (4). The critical radius of the stable embryo can be expressed as:

$$r_0 = \left(\frac{4\alpha^3 \Delta S_m k_B T_{cnt}}{R_g \sigma \Delta T_r^2 T_r} \right)^{\frac{1}{2}} \quad (18)$$

In order to characterize the volume change of embryos, Kelton's formula for the growth rate of embryos at nucleation stage is used here:

$$\frac{dr}{dt} = \frac{16D}{\alpha^2} \left(\frac{3v}{4\pi} \right)^{\frac{1}{3}} \sinh \frac{\Delta S_m \Delta T}{2RT} \left[1 - \left(\frac{1}{\zeta} \right)^{\frac{1}{3}} \right] \quad (19)$$

where r is the crystal embryo radius, v is atomic volume, ΔT is melt undercooling degree, ζ is the correction factor for the number of embryos and $\zeta=1.5$ is taken here. The radius of the

embryo corresponding to a certain temperature is obtained by the integration of the above formula:

$$r_t(T) = \int_t^{T_{cnt}} \left\{ r_0 + \frac{16D}{\alpha^2 \varepsilon(T)} \left(\frac{3v}{4\pi} \right)^{\frac{1}{3}} \sinh \frac{\Delta S_m \Delta T}{2RT} \left[1 - \left(\frac{1}{\zeta} \right)^{\frac{1}{3}} \right] \right\} dT \quad (20)$$

Accordingly, the embryo volume is:

$$V_t(T) = \frac{4\pi f(\theta)}{3} r_t(T)^3 \quad (21)$$

In summary, the volume fraction of phase precipitation during continuous cooling can be expressed as follows:

$$f_t(T) = \int_T^{T_{cnt}} \frac{J_t(T)}{\varepsilon(T)} V_t(T) dT \quad (22)$$

Under continuous cooling conditions, the critical nucleation temperature T_{cnt} , the critical nucleation supercooling ΔT_{cnt} and the critical nucleation time $t_{cnt} = \frac{\Delta T_{cnt}}{\bar{\varepsilon}}$ ($\bar{\varepsilon}$ is the average cooling rate) at the beginning of melt nucleation can be obtained by $f_t(T)=f_{cnt}$ when the cooling rate is $\varepsilon(T)$. f_{cnt} is the critical total embryo volume for triggering nucleation, and 10^{-6} is taken here. When the total volume of embryos per unit melt reaches this value, preferential nucleation will occur. By comparing the time (the incubation period) required for each phase to reach the critical embryo volume during solidification under continuous cooling condition, the preferential nucleation of each phase can be judged.

The critical nucleation supercooling degree and critical nucleation number of the rapidly solidified ternary eutectic Au-19.25Ag-12.80Ge brazing filler were analyzed under different cooling rates. The calculation results are shown in Fig.3 and Fig.4.

The wetting angle used in the calculation is $\theta=35^\circ$ and the potential nucleation number is $N_v=5 \times 10^{22}$. It can be seen from the figure that with the increase of cooling rate, the initial nucleation undercooling required to trigger melt nucleation increases, while the critical nucleation number to trigger nucleation increases significantly. When the cooling rate increases from 1.0×10^5 K/s to about 10×10^5 K/s, the nucleation

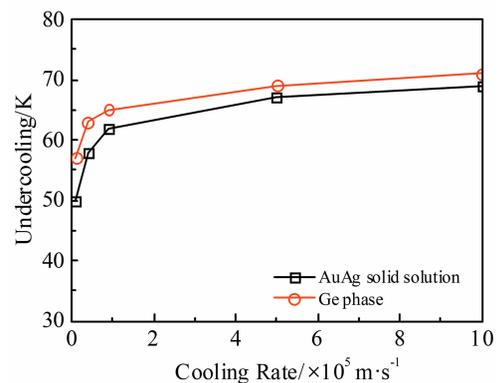


Fig.3 Relationship between cooling rate and undercooling of the phase in rapidly solidified brazing filler

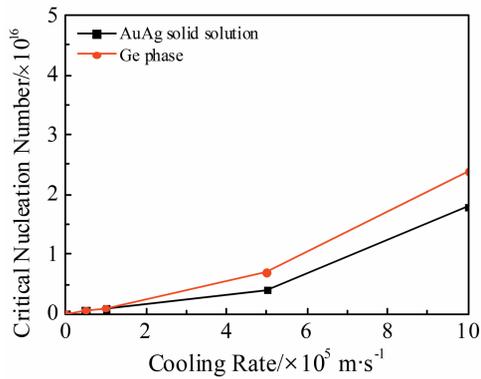


Fig.4 Relationship between cooling rate and critical nucleation number of the phase in rapidly solidified brazing filler

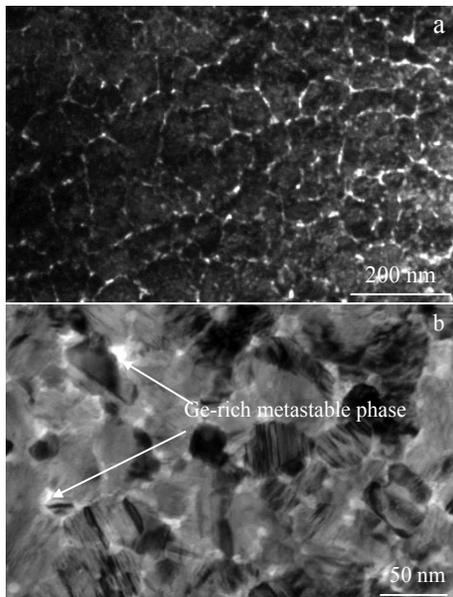


Fig.5 TEM images of rapidly solidified Au-19.25Ag-12.80Ge alloy with different cooling rates: (a) $6.5 \times 10^5 \text{ K/s}$ and (b) $1.3 \times 10^6 \text{ K/s}$

supercooling of AuAg solid solution increases from 51 K to 68.8 K, and the critical nucleation number increases from 3.55×10^{15} to 2.52×10^{16} . This is consistent with the result of the number of grains observed in the microstructure, as shown in Fig.5.

It can be seen from Fig.5 that the grain number increases greatly and the grains are refined obviously when the cooling rate is increased from $6.5 \times 10^5 \text{ K/s}$ to about $1.3 \times 10^6 \text{ K/s}$.

3 Conclusions

1) By the formula of nucleation incubation period, the

relationship between the nucleation incubation period of the rapidly solidified ternary eutectic Au-19.25Ag-12.80Ge alloy and melting temperature can be obtained.

2) The nucleation incubation period of AuAg solid solution is much shorter than that of Ge phase, and AuAg phase precipitates preferentially as the main nucleation phase in the solidification process.

3) With the increase of cooling rate, the initial nucleation undercooling required to trigger the rapidly solidified melt nucleation increases, while the critical nucleation number increases substantially.

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快速凝固三元共晶 Au-19.25Ag-12.80Ge 钎料合金的形核动力学

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摘要: 利用经典形核理论中孕育期计算公式对快速凝固 Au-19.25Ag-12.80Ge 三元共晶合金的形核进行了分析, 得到了各相形核孕育期与熔体温度的关系。从计算结果可以看出, 对于快速凝固 Au-19.25Ag-12.80Ge 钎料, AuAg 固溶体的形核孕育期远短于 Ge 相, AuAg 相优先析出, 是快速凝固过程中的主要形核相。根据时间依存的瞬态形核理论, 对连续冷却条件下的钎料合金临界形核温度、临界形核过冷度和临界形核数进行了计算。结果表明: 触发熔体形核所需的初始形核过冷度随着冷却速度的增加而增大, 同时临界形核数量也增加明显。

关键词: 钎料; 快速凝固; 孕育期; 形核

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