Vol 12 No 11, November 2003
1009-1963/2003/12(11)/1266-06

Chinese Physics

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Rapid eutectic growth in undercooled Al-Ge alloy under free fall condition*

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(Received 14 March 2003; revised manuscript received 14 May 2003)

Eutectic growth in Al-51.6%wt Ge alloy has been investigated during free fall in a drop tube. With decreasing undercooling ΔT, the microstructural evolution has shown a transition from lamellar eutectic to anomalous eutectic. A maximum cooling rate of 4.2×10^4K/s and undercooling of up to 240K ($0.35T_{\rm E}$) are obtained in the experiment. The eutectic coupled zone is calculated on the basis of current eutectic and dendritic growth theories, which covers a composition range from 48%–59% Ge and leans towards the Ge-rich side. The two critical undercoolings for the eutectic transition are ΔT_1^*=101K and ΔT_2^*=178K. When $\Delta T \leq \Delta T_1^*$, the microstructure for Al-51.6% Ge eutectic shows lamellar eutectic. If $\Delta T \geq \Delta T_2^*$, the microstructure shows anomalous eutectic. In the intermediate range of $\Delta T_1^* < \Delta T < \Delta T_2^*$, the microstructure is the mixture of the above two types of eutectics.

Keywords: growth, morphology, undercooling, coupled zone, free fall
PACC: 6125M, 6150C, 6155H, 6470D

1. Introduction

Eutectic growth is an important subject in the field of condensed matter physics and materials science.[1−7] Binary eutectic growth involves the simultaneous nucleation and cooperative growth of two solid phases within one liquid phase. Under microgravity and containerless conditions, the liquid phase can be undercooled far from the equilibrium state. The resultant microstructure undergoes a "lamallar eutectic to anomalous eutectic" transition, which is controlled by an undercooling and a cooling rate. During the solidification of eutectic alloys, there also exists competitive growth between eutectics and dendrites. An entirely eutectic growth region which is called the eutectic coupled zone is determined by comparing the growth velocity of eutectics and dendrites. Models to deal with the rapid eutectic growth have been developed by TMK[8] treatments. And the LKT/BCT[9,10] model has been used to calculated the growth of primary dendrites.

The containerless state of an object can be achieved by several ways, such as glass fluxing,[11] levitation[12,13] and drop tube methods. Drop tube can not only accomplish rapid crystal growth under containerless condition and reduced gravity, but also has the advantage of combining high undercooling with rapid cooling.[14,15] Therefore, free fall process in drop tube is very suitable for the investigation of rapid eutectic and dendritic growth.[16,17]

The main objective of this work is to investigate the rapid growth characteristics of Al-51.6% Ge eutectic under containerless condition in drop tube. Special attention has been paid to "lamallar eutectic to anomalous eutectic" growth mechanism transition. The eutectic coupled zone is also calculated to obtain further understanding of eutectic microstructural evolution.

2. Experimental procedure

The experiments were performed in a 3m high drop tube. The gravity level during the free fall process is 10^{-2}–$10^{-3}g_0$ (g_0=9.8m/s^2). The master alloy with a mass of about 0.5g was prepared from pure Al (99.99%) and pure Ge (99.999%) in an arc-melting furnace under argon atmosphere. The sample was placed in a ϕ16× 150mm quartz tube with a ϕ0.3mm orifice at its bottom. The quartz tube was then installed on the top of the drop tube. After being evacuated to

*Project supported by the National Natural Science Foundation of China (Grant Nos 50221101, 50291015, 50201013 and 50271058).
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2.0×10^{-5}Pa, the drop tube was backfilled with a mixture of He and Ar gases to 0.1MPa. The sample was inductively melted and overheated by 200K, and then, the melt was ejected through the orifice and dispersed into many fine droplets by exerting a high pressure gas flow of Ar into the quartz tube. The temperature was monitored by an NQO6/11C3.4V250 infrared pyrometer during melting.

The solidified droplets were sieved into several groups according to their sizes. Then, they were mounted, sectioned, polished, and, etched with 10% NaOH alcohol solution. The microstructures were analysed by XJG-05 optical microscope and an S2700 scanning electron microscope. And the latent heat of Al-51.6% Ge eutectic alloy has been measured by USA SDT2960 DSC apparatus.

3. Results and discussions

The phase diagram of the Al-Ge binary eutectic alloy system is shown in Fig. 1.[18] The equilibrium eutectic composition is Al-51.6% Ge. The eutectic transition L→(Al)+(Ge) occurs at 693.15 K for the composition range of 5.2%–99.6% Ge. The location of Al-51.6% Ge, the calculated coupled zone and the maximum undercooling achieved in the experiments are shown in Fig. 1.

3.1. Eutectic growth morphology

The size of droplets obtained in the drop tube ranges from 100μm to 1000μm in diameter, whose microstructures are shown in Fig. 2. The black phase is (Al) solid solute, and the white phase is (Ge) solid solute. Droplets larger than 500μm in diameter exhibit a complete coarse lamellar eutectics structure, as shown in Fig. 2(a). With the reduction of droplet diameter, most droplets show a mixed microstructure composed of lamellar and anomalous eutectics, and the volume fraction of anomalous eutectic increases. A complete anomalous eutectic whose microstructures look like nets was observed in the droplets with a diameter of 200μm, as illustrated in Fig. 2(b). Apparently, with the decrease in droplet size, a "lamellar eutectic to anomalous eutectic" structural transition occurs to Al-51.6% Ge eutectic alloy. This is due to increasing undercooling and cooling rate with decreasing droplet size. It has been demonstrated that the anomalous eutectic is the product of independent nucleation and growth of the two eutectic phases during rapid solidification and the lamellar eutectic results from slow solidification.

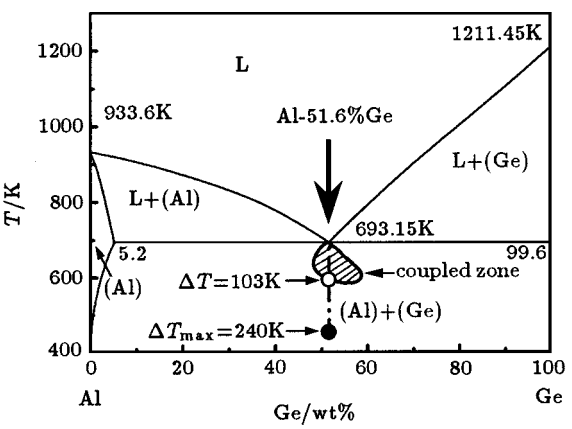


Fig. 1. Calculated coupled zone and experimentally achieved undercooling shown in Al-Ge phase diagram.

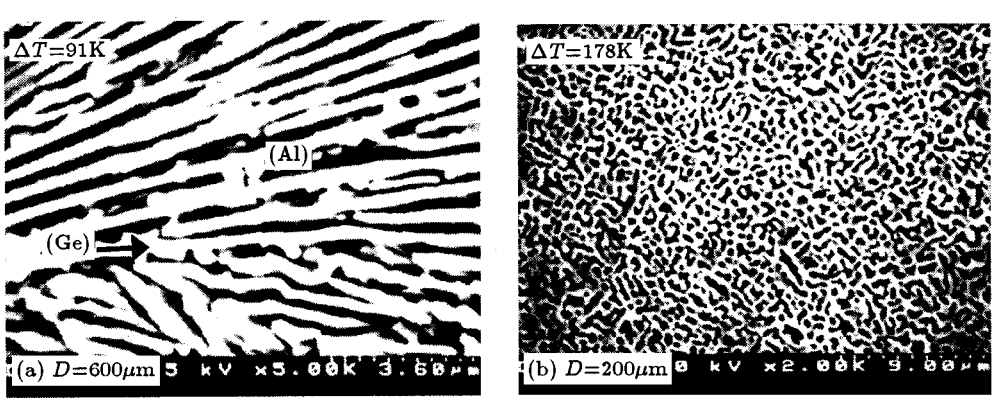


Fig. 2. Transition of eutectic growth morphology: (a) lamellar eutectic; (b) anomalous eutectic.

The gravity level during free fall for Al-51.6% Ge droplets is $10^{-2} - 10^{-3} g_0$ (g_0=9.8m/s^2). However, the reduced gravity effect has little influence on the growth and distribution of eutectic phase in droplets since lamellar eutectic grows in different direction and anomalous eutectic shows a uniform net-like shape. The "lamellar eutectic to anomalous eutectic" transition is due to the large undercooling achieved in containerless conditions.

3.2.Undercooling and cooling rate

During free fall experiment, it is difficult to measure and record the temperature of large numbers of droplets with diameters of micrometre order. However, Lee[19] successfully described the thermal history of falling droplets by combining Newtonian heat transfer model[20] with the classical nucleation theory. In this model, the droplet is assumed to keep the spherical shape during free fall and the heat is mainly transferred by radiation and convection, neglecting thermal convection inside the droplet. The relationship between nucleation temperature T_N and droplet diameter D is described by two functions Φ and Ψ as follows:

$$\frac{\Psi(T_N, D)}{T_N \cdot \Delta T^2} = \ln \Phi(T_N, D), \tag{1}$$

$$\Phi(T_N, D) = \frac{\frac{\pi}{6} D^3 K_V \Delta T^3 T_N^2}{\Psi(T_N, D)(-\mathrm{d}T_d/\mathrm{d}t)(3T_L - T_N) + [\kappa + 2\varepsilon(T_N - T_g)]\Delta T^3 T_N^2}. \tag{2}$$

Here

$$\Psi(T_N, D) = \frac{16\pi\sigma_{SL}^3 T_L^2 f(D)}{3k_B \rho_d^2 \Delta H^2}, \tag{3}$$

$$\kappa = \frac{12 k_g}{\rho_d C_P D^2}, \tag{4}$$

where ΔT is the undercooling attained before nucleation, T_d the temperature of droplet, T_L the liquidus temperature, T_g the gas temperature in drop tube, ε the thermal convection coefficient of gas, k_B the Boltzmann constant, k_g the thermal convection coefficient, σ_{SL} the liquid-solid interfacial energy, ρ_d the density of droplet, C_P the specific heat of liquid and ΔH the heat of fusion. Parameters used in calculations are listed in Table 1.

Table 1. The thermophysical parameters used in calculations[21,22]

Parameter	Value
Eutectic composition /(wt%Ge)	51.6
Eutectic equilibrium temperature/K	693.16
Superheating/K	200
Thermal radiation coefficient	0.24
Specific heat of the melt/(J/mol·K)	30.6
Heat of fusion/(J/mol)	19361
Length of the eutectic line/(wt%Ge)	94.4
Solute diffusion coefficient/(m^2/s)	$2.16\times10^{-7}\exp(-36594/RT)$
Length scale for solute trapping/m	1.9×10^{-11}
Liquid-solid interface energy/(J/m^2)	0.39
Capillarity constant of (Al)/(m·wt%)	1.25×10^{-7}
Capillarity constant of (Ge)/(m·wt%)	1.41×10^{-7}
Gas density in drop tube/(kg/m^3)	1.249
Gas viscosity in drop tube/(Pa·s)	44.77
Thermal conductivity/(W/m·K)	126.3
Gas temperature/K	298

On the basis of Eqs. (1)–(4), the relationships of functions $\Psi(T_N, D)/T_N\Delta T^2$ and $\ln\Phi(T_N, D)$ related to nucleation temperature T_N are calculated, as shown in Fig. 3. The nucleation temperatures of the droplets with various sizes can be determined from the intersections. Furthermore, the corresponding undercoolings are available. The undercooling as a function of droplet size is given in Fig. 4.

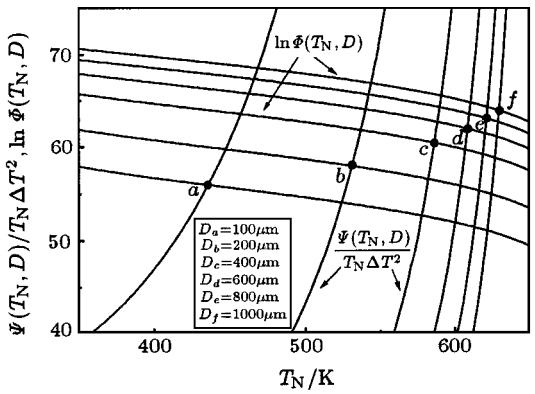


Fig. 3. Functions $\ln\Phi(T_N, D)$ and $\Psi(T_N, D)/T_N\Delta T^2$ versus nucleation temperature.

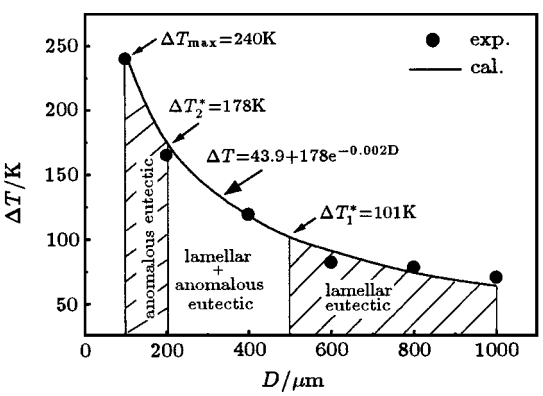


Fig. 4. Droplet undercooling and eutectic morphology versus droplet diameter.

Generally, the anomalous eutectic is the product of rapid growth during recalescence. Therefore, the undercooling can be estimated by measuring the volume fraction of anomalous eutectic f_a. Assuming the recalescence is an adiabatic process and the liquid specific heat C_P is a constant during this processing, the following Eq. (5) is obtained according to the energy conservation condition:

$$\Delta T = f_a \Delta H / C_P. \tag{5}$$

The value of ΔH for Al-51.6% Ge measured by DSC apparatus is 19361J/mol, as shown in Fig. 5. Hence, the relationship between undercooling and droplet diameter is estimated according to Eq. (5), as illustrated in Fig. 4.

From Fig. 4, it can be seen that the estimated undercooing in our experiment is in good agreement with the calculated undercooling. And, the undercooling is enhanced when droplet size is decreased. For droplets of 1000–100μm in diameter, the undercooling covers a range of 70–240K and fits for the formula:

$$\Delta T = 43.9 + 178\mathrm{e}^{-0.002D}. \tag{6}$$

The maximum undercooling attained is $0.35T_E$ (T_E is the eutectic equilibrium temperature). The two critical temperatures for the eutectic transition are ΔT_1^*=101K and ΔT_2^*=178K when droplet diameters are D_1=500μm and D_2=200μm respectively. The microstructure for Al-51.6% Ge eutectics shows lamellar eutectic when $\Delta T \le \Delta T_1^*$. The anomalous eutectics are unique morphology if $\Delta T \ge \Delta T_2^*$. In the intermediate range of $\Delta T_1^* < \Delta T < \Delta T_2^*$, the microstructure is the mixture of lamellar eutectic and anomalous eutectic.

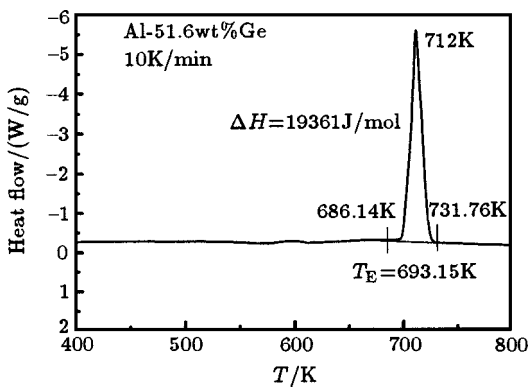


Fig. 5. DSC thermogram of Al-51.6%Ge eutectic alloy.

According to Newtonian model, the cooling rate for the falling droplets is described by the following equation:

$$-\frac{\mathrm{d}T_d}{\mathrm{d}t} = \frac{6h}{\rho_d C_{PL} D}(T_d - T_g) \approx [\kappa + \varepsilon(T_d - T_g)](T_d - T_g). \tag{7}$$

Based on Eq. (7), the relationship of cooling rate $-\mathrm{d}T_d/\mathrm{d}t$ and droplet diameter D for Al-51.6% Ge eutectic alloy is shown in Fig. 6. For droplets of 1000–100μm, the cooling rate ranges from 8.8×10^2 to 4.2×10^4K/s.

From the calculation of undercooling and cooling rate, it is obvious that undercooling and cooling rate have the similar tendency of increase when droplet diameter decreases. Both of them play an important role in eutectic growth.

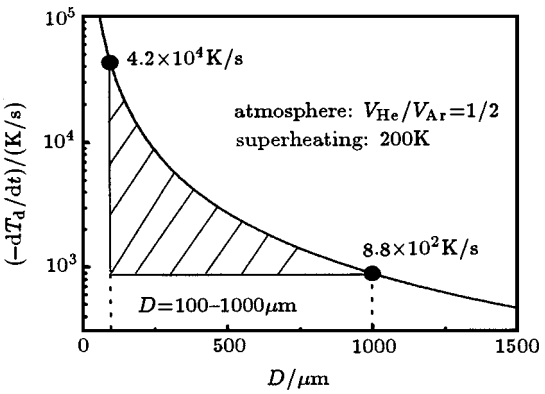


Fig. 6. Calculated cooling rate versus droplet size.

3.3.Eutectic coupled zone

Eutectic coupled zone is the growth temperature and composition region where the eutectic structure grows more rapidly than dendrites. This zone can be determined by comparing the eutectic growth velocity with dendritic growth velocity. The critical temperature is the temperature where eutectic growth velocity is equal to the dendritic growth velocity. For Al-Ge eutectic alloy, it is necessary to compare the growth velocity of Al-51.6% Ge eutectic with that of (Al) dendrite and (Ge) dendrite.

The eutectic growth velocity was calculated on the basis of TMK eutectic growth model. This model can be described by the following equations:[8]

$$\lambda^2 V = \alpha^{\mathrm{L}}/Q^{\mathrm{L}}, \tag{8}$$

$$\Delta T = \frac{2\overline{m}C_0^* P P_{\mathrm{e}}}{f_\alpha f_\beta}\left[1 + \frac{\lambda}{P\phi^2}\cdot\frac{\partial P}{\partial \lambda}\right], \tag{9}$$

where λ is the interlamellar spacing, V the growth velocity, ΔT the undercooling, $\phi = \overline{\lambda}/\lambda_{ex}$ the revised factor for faceted phase, $\overline{\lambda}$ the average interlamellar spacing, λ_{ex} the interlamellar spacing when the eutectic growth velocity is the smallest, α^{L} the capillarity length, Q_{L} the activation energy for solute diffusion, C_0^* the length of eutectic line; f_α and f_β are the volume fractions of α phase and β phase, and P_{e} is the Peclet number.

According to the LKT/BCT dendritic growth model,[9,10] the interrelationship between growth velocity V, dendrite tip radius R, and undercooling ΔT is uniquely determined by the following two coupled equations:

$$\Delta T = \Delta T_{\mathrm{c}} + \Delta T_{\mathrm{t}} + \Delta T_{\mathrm{r}} + \Delta T_{\mathrm{k}}, \tag{10}$$

$$R = \frac{\Gamma/\sigma^*}{\dfrac{\Delta H}{C_{\mathrm{PL}}}P_{\mathrm{t}}\xi_{\mathrm{t}} - \dfrac{2m'_{\mathrm{L}}C_0(1-k_{\mathrm{v}})P_{\mathrm{c}}}{1-(1-k_{\mathrm{v}})I_{\mathrm{v}}(P_{\mathrm{v}})}\xi_{\mathrm{c}}}, \tag{11}$$

where ΔT_{c} is the solutal undercooling, ΔT_{t} the thermal undercooling, ΔT_{r} the curvature undercooling, ΔT_{k} the kinetic undercooling, Γ the Gibbs–Thomson coefficient, P_{c} the solutal Peclet number, P_{t} the thermal Peclet number, σ^* the stability constant, m'_{L} the actual liquidus slope under nonequilibrium conditions, ξ_{c} the solutal stability function, ξ_{t} the thermal stability function and the k_{v} the solute partition coefficient.

The growth velocities of (Al) and (Ge) dendrites have been calculated according to the above Eqs. (10) and (11). The physical parameters used in calculations are also given in Table 1.

The calculated coupled zone of Al-Ge system covers a composition range from 48 to 59% Ge and leans to the Ge-rich side, as shown in Fig. 1. It is obvious that the eutectic structure shows lamellar eutectic when ΔT is less than 103K, otherwise the lamellar eutectic cannot be obtained. This result is consistent with the calculation of undercoolings.

The interrelationship of eutectic growth velocity V, interlamellar spacing λ and undercooling ΔT for Al-51.6% Ge eutectic is calculated on the basis of TMK model, as illustrated in Fig. 7. The maximum growth velocity of lamellar eutectic is 107 mm/s. The λ-ΔT relationship measured in experiments is $\lambda\Delta T^{0.95}$=10.79, as described also in Fig. 7. It can be seen that the values of interlamellar spacing measured in experiment are larger than the calculated results although they have the similar variation tendency. This may be due to the coarsening of lamellar eutectic during cooling process.

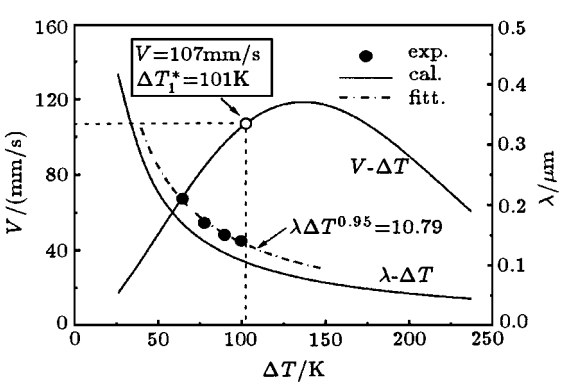


Fig. 7. Eutectic growth velocity and interlamellar spacing versus undercooling.

4. Conclusions

1. The rapid growth of Al-51.6% Ge eutectic has been investigated during free fall experiment. The structural evolution undergoes "lamellar eutectic to anomalous eutectic" transition with decreasing the droplet size. The critical undercoolings ΔT_1^* and ΔT_2^* are 101K and 178K, respectively. This transition is due to the large undercooling and rapid cooling rate. The reduced gravity effect has little influence on the growth morphology transitions.

2. The calculated undercooling and cooling rate range from 70 to 240 K and 8.8×10^2 to 4.2×10^4K/s corresponding to the droplet diameter changing from 1000 to 100μm, respectively. With decreasing droplet size, both undercooling and cooling rate show an increasing tendency.

3. The coupled zone calculated on the basis of TMK eutectic growth theory and LKT/BCT dendritic growth model covers a composition range from 48% to 59% Ge and leans to the Ge-rich side. The critical temperature of lamellar eutectic to anomalous eutectic transition coincides with the lower boundary of the calculated eutectic coupled zone.

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