OSTWALD COARSENING UNDER CHANGING VOLUME FRACTION CONDITION①

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ABSTACT The mathematical model describing the Ostwald coarsening of the second phase particle in decreasing temperature process (the volume fraction of the second phase changes) have been put forward, and calculations have been carried out for the liquid-liquid phase transformation of Zn-Pb alloy. It was found that this model is in good accordance with LSW theory when the cooling rate is zero. With the increase of the cooling rate, the critical particle size decreases, and the coarsening rate of particle increases.

Key words: Ostwald coarsening second phase volume fraction

1 INTRODUCTION

Generally a first-order phase transformation process results in a two-phase mixture which consists of a dispersion phase in the matrix. The mixture is not initially in the thermodynamics equilibrium. The dispersion phase increases in its size scale to decrease the total interfacial area, and thus decrease the total energy of the two-phase system. This process is known as Ostwald coarsening. The first theoretical description of this coarsening behavior of systems with dispersive second phase droplets was made by Lifshitz-Slyozov-Wagner[1, 2]. This theory, often refered to LSW theory, can be used to describe the coarsening process when the second phase particles are infinitely separated and so the volume fraction of the second phase tends to zero. In recent years a lot of researches have been carried out to find out the effect of the volume fraction of the second phase[3-8]. But all studies before were undertaken for the constant temperature system (the volume fraction of the second phase does not change), and the degree of the supersaturation of the system is very small. In fact, most phase transformations take place during decreasing temperature process. Under this condition the theories above are not applicable. A mathematical model will be put forward to describe this coarsening process, and computer simulation will be carried out for the liquid-liquid phase transformation of Zn-Pb monotectic alloy.

2 MATHEMATICAL MODEL

Supposing a lot of particles (or droplets) of the second phase have been formed in the matrix after the beginning of phase transformation. According to the physical-chemistry theory, the concentration of the matrix in equilibrium with a particle with radius R can be given as follows:

$$X_R = X_\infty \exp\left(\frac{2\sigma_{L_1,L_2}V_e}{RR_gT}\right) \quad (1)$$

where X_R is the equilibrium concentration of the matrix at the boundary of a particle with radius R and matrix, X_∞ is the thermodynamic equilibrium concentration of matrix, σ_{L_1,L_2} is interphase surface tension, R_g is the gas constant, T is absolute temperature of the system, V_e is molar volume of the solute.

Generally the exponent is far smaller than unit, therefore eq. (1) can be indicated as:

① Supported by National Natural Science Foundation of China; Received Jul. 12, 1994

$$X_R = X_\infty(1 + \frac{\alpha}{R})$$

$$\alpha = \frac{2\sigma_{I_1,I_2}V_e}{R_gT} \quad (2)$$

If the volume fraction of the second phase is small and therefore the particle density in the matrix is not high, the diffusion current per unit area of solute toward a particle is given by[1]:

$$J = D\frac{\partial x}{\partial r}|_{r=R} = \frac{D}{V_m}\frac{X - X_R}{R} \quad (3)$$

where V_m is the average molar volume of the two-phase system, X is the concentration of the matrix.

The matrix surrounding a particle with radius R will transfer to the second phase for the solute diffusion, and according to the conservation law of solute, the molar number of the second phase newly formed can be related to J by the following equation[9]:

$$Y = \frac{J(1 - X_p)}{X_p - X} \quad (4)$$

where X_p is the concentration of the second phase.

Therefore the growth rate of the particle with radius R can be indicated as:

$$\dot{R} = \frac{dR}{dt} = \frac{V_e}{V_m}\frac{D(1 - X)}{X_p - X} \times \frac{1}{R}(\Delta - \frac{\alpha}{R}) \quad (5)$$

$$\Delta = X - X_\infty$$

Thus for every Δ value of the supersaturation there exists a critical radius $R_c = \alpha/\Delta$ with which a particle is in equilibrium with the matrix. Droplets with radius greater than R_c grows, while droplets with radius smaller than R_c dissolves.

Defining the particle distribution function as follows:

$$f(R, t) = n(R, R + \Delta R, t)/\Delta R \quad (6)$$

where $n(R, R + \Delta R, t)$ is the number of particle with radius between R and $R + \Delta R$ per unit volume at time t.

According to eq. (6), there exists the following relations:

$$N(t) = \int_0^\infty f(R, t)dR$$

$$\bar{R}(t) = \int_0^\infty f(R, t)RdR/N(t) \quad (7)$$

$$W_f(t) = \int_0^\infty f(R, t)4/3\pi R^3dR$$

where $N(t)$ is the number of all size particles per unit volume, $\bar{R}(t)$ the average particle radius, $W_f(t)$ the volume fraction at time t.

One can derive eq. (8) from the definition of the particle size distribution function:

$$\frac{\partial f(R, t)}{\partial t} + \frac{\partial[f(R, t)\dot{R}]}{\partial R} = 0 \quad (8)$$

If the initial particle size distribution is known, one can obtain the particle size distribution at any time by solving eqs. (5) and (8). But $W_f(t)$ is not a constant value in the cooling process. The supersaturation Δ at time t can be got through $W_f(t)$ and the volume fraction of the second phase under equilibrium condition $W_0(t)$[9]:

$$\Delta = \frac{V_m[W_0(t) - W_f(t)](X_p - X)}{V_e - V_mW_f(t)} \quad (9)$$

3 NUMERICAL CALCULATION FOR OSTWALD COARSENING DURING LIQUID-LIQUID PHASE TRANSFORMATION OF Zn-Pb ALLOY

Substituting eq. (5) into eq. (8), one can get the equivalent differential equation group of eq. (8) through partial differential equation trasformation:

$$\left.\begin{aligned}\frac{dR}{dt} &= \frac{V_e}{V_m}\frac{1 - X}{X_p - X}\frac{D}{R}(\Delta - \frac{\alpha}{R}) \\ \frac{df(R, t)}{dt} &= \frac{V_e}{V_m}\frac{1 - X}{X_p - X}\frac{D}{R^2}(\Delta - \frac{2\alpha}{R})f(R, t)\end{aligned}\right\} \quad (10)$$

Eq. (10) can be numerically solved by Runge-Kutta method.

Supposing the initial particle size distribution can be given by eq. (11):

$$f(R, 0) = A_0\exp[-\frac{1}{2}(\frac{R - \bar{R}}{\varepsilon R})^2] \quad (11)$$

where A_0 and ε are constants. If ε is given, one can get A_0 by solving eq. (7) according to the initial volume fraction of the second phase.

Fig. 1 is the phase diagram of Zn-Pb binary system. It can be seen that when the temperature goes below curve *mcb*, a homogeneous melt will transform to a two-phase mixture. For alloy whose content of Pb is less

than X_c, there will exist a lot of Pb-rich droplets in the matrix melt after the beginning of the liquid-liquid phase transformation, and the volume fraction of the Pb-rich phase increases with the decrease of the temperature. For Zn-5 wt.-% Pb alloy, supposing the initial average droplet radius and the constant ε equal 1 μm and 0.1 μm respectively, and melts are cooled from 530 ℃, the calculating growth of droplet with different initial radius is shown in Fig. 2. One can find that when the cooling rate is zero(the volume fraction of the Pb-rich phase is constant), droplets with radii smaller than $\bar{R}(t)$ dissolve, while droplets with radii larger than $\bar{R}(t)$ grow from the melt. That is droplet coarsening through the solute transfering from smaller ones to larger ones. This is in accordance with LSW theory. With the increase of the cooling rate, the degree of the supersaturation Δ of the melt increases and the critical radius R_c decreases, therefore some droplets which dissolved already become growing from the melt.

The relations between the cube of the average droplet radius $(\bar{R}(t)/\bar{R}(0))^3$ and the coarsening time for different cooling rates are shown in Fig. 3. The linear curve for zero cooling rate indicates that LSW theory is the special case of this model. When the cooling rate is not zero, the droplet coarsening does not obey LSW theory. The coarsening rate increases with the increase of the cooling rate.

Fig. 4 is the probability distribution of droplet radii after coarsening for 1 s. Calculations show that the droplet distribution width increases with the increase of the coarsening time and comes into stable state of distribution quickly when the cooling rate is zero. This is in accordance with the research results before. When the cooling rate is not zero, the main tendence is that the distribution width decreases with the increase of the cooling rate.

4 CONCLUSSIONS

A mathematical model describing the Ostwald coarsening during the process of decreas-

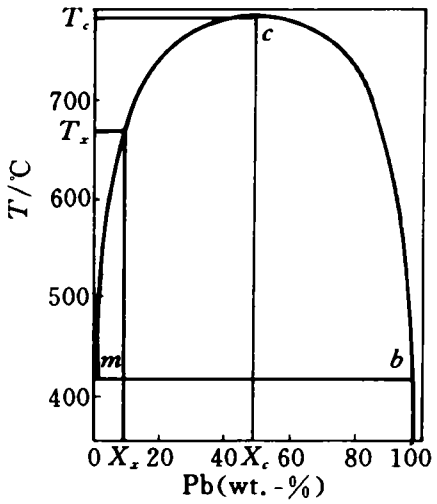

Fig. 1 Zn-Pb phase diagram

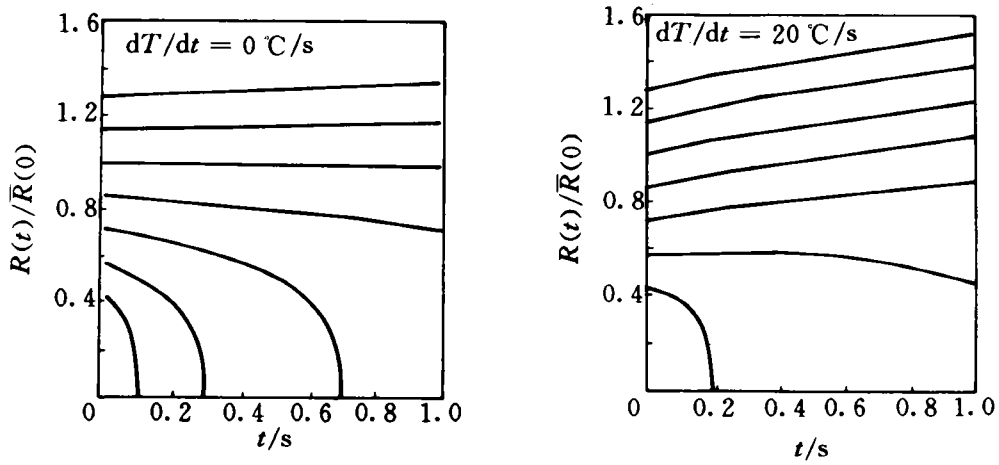

Fig. 2 Growth lines for droplets with different Radii

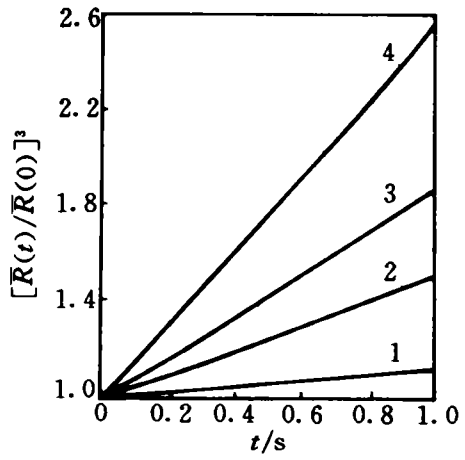

Fig. 3 Relation between average droplet radius and time

1— $\dot{T}$ =0 C/s; 2— $\dot{T}$ =5 C/s; 3— $\dot{T}$ =10 C/s; 4— $\dot{T}$ =20 C/s

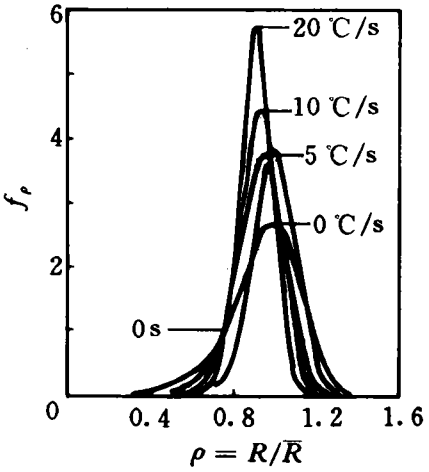

Fig. 4 Probability distribution of droplet radius

ing temperature (the volume fraction of the second phase changing) have been put forward. Calculations have been carried out of the coarsening of the second phase droplets during the liquid-liquid phase transformation of Zn-Pb alloy. It was found that this model is in accordance with LSW theory when the cooling rate is zero. But with the increase of cooling rate, the critical droplet radius R_c decreases and droplet coarsening rate increases. It was also found that the width of the droplet radius distribution decrease with the increase of the cooling rate.

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