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BEHAVIOR OF THE CRYSTALLIZATION PARAMETERS FOR ALLOYS OF THE SYSTEM Al-Si NEAR THE LYOTECTIC POINT

A. N. Chichko, N. P. Yurkevich, and V. F. Sobolev

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The character of growth of the nucleus for alloys of the system Al-Si is investigated using the Kolmogorov model. It is shown that the appearance of critical points on the phase diagram is related to maxima of the curves of the rate of growth and number of nuclei.

A search for critical points and the reasons for their appearance in alloys is one of the most important problems in the physics of metals. This is associated with the fact that it is precisely at the critical points that, for certain ratios of the components, anomalous phenomena may arise. In particular, it is of interest to elucidate the reasons for a decrease in the fluidity of alloys in the transition to wide-interval regions. For specific concentrations and systems there is no explanation at present for the decrease in fluidity at the lyotectic point from the point of view of nucleation theory.

The aim of the present work is to investigate the parameters of nucleation at the critical points of the system Al-Si.

To study the process of crystallization at the critical points, use was made of the Kolmogorov crystallization model [1]:

$$V_k(t) = V_0\{1 - \exp(-W(t))\}, \tag{1}$$

$$W(t) = \varphi_1 N_s \Big\{\int_{t_{cr}}^{t} v(\tau)\,d\tau\Big\}^3 + \varphi_2 \int_{t_{cr}}^{t} d\tau_1 n(\tau_1)\Big\{\int_{t_{cr}}^{\tau_1} v(\tau_2)\,d\tau_2\Big\}^3, \tag{2}$$

where $V_k(t)$ is the volume occupied by the solid phase (the Kolmogorov function), in m^3; N_s is the number of seeds in unit volume, in $1/m^3$; φ_1, φ_2 are the constants of the nucleus form; $v(\tau)$ is the linear rate of crystal growth, in m/sec; $n(\tau)$ is the nucleation intensity, in $1/(m^3 sec)$; t_{cr} is the time of onset of crystallization, sec; V_0 is the volume of the metal, in m^3.

The volume occupied by the solid phase $V_k(t)$ was calculated from the Nekhendzi-Girshovich model, based on the heat-balance equation

$$\frac{dQ}{dt} = \frac{dQ_c}{dt} + \frac{dQ_l}{dt}, \tag{3}$$

where dQ/dt is the rate of heat removal to the ambient medium, in W; dQ_c/dt is the rate of heat release by the melt, dependent on the variation in temperature and heat capacity, in W; dQ_l/dt is the rate of heat release of crystallization in the liquid-solid transition, in W.

The heat-balance equation is composed of the following components:

$$\frac{dQ}{dt} = AF\,[T(t) - T_m], \tag{4}$$

$$\frac{dQ_c}{dt} = -C\rho V_0 \frac{dT}{dt}, \tag{5}$$

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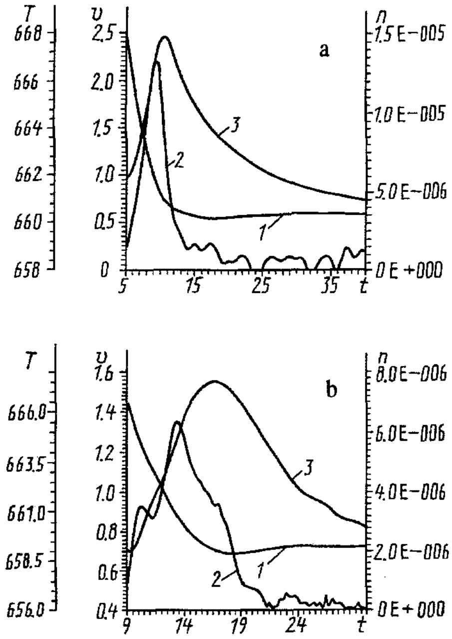

Fig. 1. Dependences of temperature (1), number (2), and rate of growth (3) of nuclei on time for aluminum (a) and the alloy Al-0.2% Si (b) T, °C; t, sec; v, 10^2 relative units; n, relative units.

$$\frac{dQ_l}{dt} = L\rho \frac{dV}{dt}, \tag{6}$$

here A is the specific heat transfer coefficient, in $W/(m^2 \cdot {}^\circ C)$; F is the heat-removing surface area, in m^2; C is the specific heat, in $J/kg \cdot {}^\circ C$; L is the specific crystallization heat, in $J/kg \cdot {}^\circ C$; ρ is the metal density, in kg/m^3; T(t) is the temperature as a function of time, in °C; T_m is the temperature of the medium.

From Eq. (3) in view of (4)-(6) we obtain

$$AF\,[T(t) - T_m] = -C\rho V_0 \frac{dT}{dt} + L\rho \frac{dV}{dt}. \tag{7}$$

We perform the following rearrangements of Eq. (7):

$$\frac{dV}{dt} - C/LV_0 \frac{dT}{dt} = \frac{AF}{L\rho} [T(t) - T_m], \tag{8}$$

$$\frac{1}{V_0} \frac{dV}{dt} = \frac{AFC/L}{V_0 \rho C} [T(t) - T_m] + C/L \frac{dT}{dt}. \tag{9}$$

We introduce the notation

$$\alpha = \frac{AF}{C\rho V_0}. \tag{10}$$

The quantity α is called the pace of cooling (the Newton-Richman constant). The physical meaning of can be ascertained as the reciprocal of the time during which the temperature is decreased by a factor of e. The dimensions of α are 1/sec. Then

$$\frac{1}{V_0} \frac{dV}{dt} = C/L \left[\alpha (T(t) - T_m) + \frac{dT}{dt} \right]. \tag{11}$$

We integrate (11):

$$\frac{V}{V_0} = C/L \left[\alpha \int\limits_{t_{cr}}^{t} [T(\xi) - T_m]\, d\xi + T(t) - T(t_{cr}) \right]. \tag{12}$$

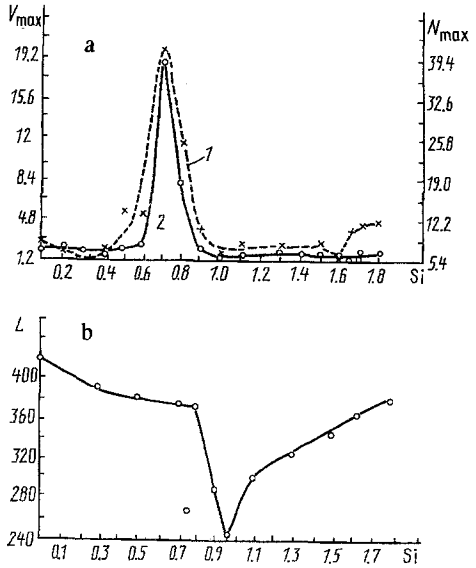

Fig. 2. Dependence of the parameters of crystallization N_{max} (1), V_{max} (2) (a) and the fluidity (b) of alloys of the system Al-Si on the silicon content. $V_{max} \cdot 10^{-2}$ relative units; $N_{max} \cdot 10^{-6}$ relative units; Si, %; L, mm.

Following rearrangements of (4)-(12) and from the condition $V(t) = V_k(t)$ we have that the growth function for the solid phase has the form [2]

$$\frac{V_k(t)}{V_0} = C/L\left[\alpha \int\limits_{t_{cr}}^{t} [T(\xi) - T_m]\, d\xi + T(t) - T(t_{cr})\right]. \tag{13}$$

The calculation of the linear rate of nucleus growth as a function of time v(t) was performed with the condition that the crystallization occurs mainly from seeds. The nucleation intensity as a function of time n(t) was calculated with the stipulation of the prescribed linear rate of crystal growth.

In the first stage of the investigation the cooling curves T(t) of silicon-alloyed aluminum were studied. The following silicon concentrations were investigated: 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; 0.9; 1.0; 1.1; 1.3; 1.5; 1.6; 1.65; 1.7; 1.8% (by weight). To determine the function T(t), use was made of thermoanalysis equipment consisting of a sampler, a V7-34A voltmeter, an interface, and an ES 1840.05 personal computer. The reading of a signal from a chromel-alumel thermocouple was performed in 0.25 sec, which enabled us to ensure a precision of measuring the temperature within 0.1%.

In the second stage for all the above-enumerated compositions the fluidity of silicon-alloyed aluminum was investigated. To measure the fluidity, a Nekhendzi-Samarin sample was used. The metal pouring temperature was 1013 K. The sample temperature was maintained equal to 353 K. Statistical analysis of the results obtained on the selected concentrations showed that the experimental error is no more than 5%.

In the third stage of the investigation for each of the experimentally measured curves T(t) of the alloys the nucleation intensities n(t) and the linear rates of nucleus growth $v(t)$ were determined according to the developed program. Figure 1 shows typical curves n(t) and $v(t)$, resulting from the calculation. As is evident from the figure, for the curves n(t) and $v(t)$ there are pronounced maxima in the supercooling zone, pointing to a maximal linear rate of nucleus growth and nucleation intensity in the temperature interval T_a and T_b. In this case the maxima of the functions n(t) and $v(t)$ do not coincide and are displaced with respect to the temperature that corresponds to the maximal supercooling. This fact is in complete agreement with the fundamental propositions of the Kolmogorov model.

The displacement of the maximum of the function n(t) with respect to the supercooling temperature (Fig. 1) suggests that the first nuclei in the alloy appear at the temperature corresponding to the divergence of T(t) from the exponential dependence, which agrees with the propositions of the Newton-Richman law.

Analysis of the calculated functions n(t) and $v(t)$ for the compositions with different silicon content showed that an increase of silicon in aluminum changes the locations of the maxima of the linear rate of nucleus growth and nucleation intensity. This is easily seen from Fig. 2a, where the dependences of the maximal linear rate of nucleus growth V_{max} and the maximal value of nucleation intensity N_{max} on the silicon content in aluminum are shown. Figure 2b shows the dependence of the fluidity of the alloy Al-x%Si (x is the silicon concentration) on the silicon content. Analysis of the results on experimental determination of the fluidity and calculated values of the parameters N_{max} and V_{max} permitted the conclusion that the maximal values of the linear rate of nucleus growth and nucleation intensity are found in the region of the fluidity minimum of the alloyed aluminum

This fact can be explained in the following manner. With an increase in the silicon concentration the maximal nucleation intensity and linear rate of nucleus growth that can be realized for the given system increase and attain limiting values at the nonequilibrium lyotectic point. A further change in the degree of alloying of the α-solution tends to decrease the values of V_{max} and N_{max}. A higher probability that the nuclei will separate from the liquid on addition of silicon is apparently associated with the fact that silicon-alloyed aluminum nuclei are thermally more stable as compared to those of pure aluminum. From the point of view of electron theory these nuclei tend to have a stable sp^3 configuration, which is stable from the point of view of the configuration model [3]. But adding large amounts of silicon probably decreases the importance of sp^3 atomic binding configurations in a liquid α-solution of aluminum and redistributes them in the direction of sp^4 atomic configurations. The latter configurations are not binding from the point of view of interatomic connection, which leads to a decrease in the nucleation intensity and correspondingly increases the fluidity of the melt.

The difference in the silicon concentrations corresponding to the maximum N_{max}, V_{max} and fluidity is related to the fact that the experimental measurements of the fluidity and the functions T(t) were performed at close but different cooling rates of the metal (from the technical point of view, it is difficult to attain complete equality of the cooling rates for the Nekhendzi-Samarin sample and the sampler for taking the curves T(t)).

Thus, use of the Kolmogorov and Nekhendzi-Girshovich model to calculate the process of nucleation enables one to explain the appearance of a critical point in the concentration region that corresponds to the solubility limit. This indicates the possibility of using nucleation theory to explain the critical points of the phase diagram of binary systems. The presence in the considered models of the functions T(t), which are determined experimentally, makes it possible to apply such an approach to the investigation of multiphase systems.

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