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Microstructure formation during crystallization of immiscible phases

A. YU. DOVZHENKO, P. V. ZHIRKOV*, A. V. KOVALEVA, V. A. GORSHKOV
Institute of Structural Macrokinetics, Russian Academy of Sciences, 142432, Chemogolovka, Moscow, Russia

For composite materials such as metal–oxide, metal–ceramics, etc., the formation process of grain microstructure has been theoretically considered from the macrokinetic point of view. The interaction (mainly a thermal one) between two immiscible phases during crystallization was studied. Various types of grain-size distribution were found and distinguished.
A comparison with an experimental metallographic specimen of a metal–oxide system was made. Self-propagating high-temperature synthesis was used to produce the material ingots. Limits to the use of the model proposed are revealed.

1. Introduction

The problem of microstructure (texture) formation is an urgent and considerable one in material science [1, 2]. Recently, a number of the papers was published where the grain (particle) totality formation was studied for different materials in various processes (crystallization and precipitation of the refractory phase from the eutectic system melt [3–5], SVD layer covering [6], general models [7, 8]). It was shown that features of the system such as the phase diagram, essentially determine the course of the process and the microstructure of the particles formed.

In this connection, a system with immiscible components is of considerable interest. From the theoretical point of view, it is the ultimate case of the decrease in thermodynamic phase mixing (up to zero). In practice, it is a real class of materials, in particular the metal–oxide systems. The production of such material by conventional means is problematical, but self-propagating high-temperature synthesis (SHS) can solve this. SHS makes it possible to reach very high temperatures during several minutes followed by rapid cooling.

The technological possibilities of SHS are documented elsewhere [9, 10]. Using SHS various materials can now be produced: ceramics [10–13], intermetallics [14–16], gradient alloys [17], and composite materials (ceramic–ceramic, ceramic–metal, ceramic–intermetallic, intermetallic–metal [18–21]).

In the present work, an attempt was made to describe, from the macrokinetic point of view, the microstructure formation for the system of two immiscible phases, i.e. the formation of a refractory phase particle in a continuous matrix of the fusible phase. The dependencies of the grain-size distribution theoretically obtained were compared with those from the experimental metallographic specimen. The ingots tested were produced by SHS-casting for metal–metal oxide systems.

Crystallization of a pseudo-binary eutectic system was considered elsewhere [3–5]. It was assumed that the driving force of the process was the overcooling ΔT. Both the rate of nucleation and that of crystal growth (refractory grains) were proportional to ΔT. There exists a nucleation threshold $\Delta T = \Delta T_{\mathrm{MS}}$ (metastability range), beyond which the nucleation process starts. The study [3] revealed the existence of two types of grain-size distribution: "broad" and "narrow" depending on the ΔT_{MS} value. The grain structure formed was fixed by crystallizing the eutectic matrix. In fact, a monophase crystallization was considered.

In this work, we analysed the joint crystallization of two different phases following the approach suggested previously [3–5]. A simple, though interesting, example of such a system is that of two immiscible (mutually insoluble) phases (Fig. 1). The system is invariably heterophasic. In the liquid state, it can be emulsion (droplets in a continuous medium) or layer-structured. This work addressed the first case only. The interaction between two phases is sustained due to the heat released during the phase transition at the same temperature for both phases. A considerable interphase effect in this system could take place, when two parallel crystallization processes occur.

2. The formulation of the problem

The problem of bulk parameters alone is considered, i.e. the gradients of temperature and concentration are neglected. The grain-size distribution, $N(R)$, is the main parameter to be calculated. It should be noted that the results are valid for only one of the two phases (the continuous medium) and can be valid for the second one (set of drops) provided that the initial volume of droplets is much larger (10^3–10^4 times) than that of the final particle, or there is no hindrance to this phase

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* Author to whom all correspondence should be addressed.

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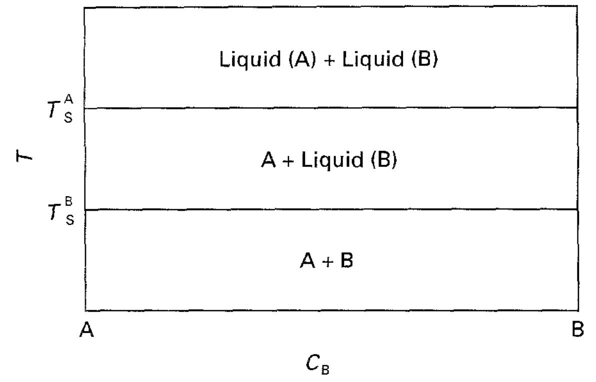

Figure 1 Phase diagram of the system of immiscible phases A and B.

transport through another phase. Keeping this in mind, we shall demonstrate both types of distribution.

A sharp vigorous non-equilibrium crystallization can be accompanied by a temperature increase because of the latent heat of phase transition. Hence we should take into account that the melting (complete or incomplete) of the phase being formed is highly probable. Although there are some published data available concerning the overheating of solids (from tenths up to tens of degrees Kelvin [22]), the fact is generally accepted that the overheating of a crystal is impossible (or negligibly low) [23]. It is assumed that all the heat released in (or flowing to) the system results only in melting, provided that the crystallization temperature is exceeded in calculation. The physical temperature during this melting is constant and equal to the melting point.

3. Equations and calculation procedure

The heat balance is

$$\rho_M C_M \frac{dT}{dt} = \rho_A L_A \frac{dV^A}{dt} + \rho_B L_B \frac{dV^B}{dt} - Q \quad (1)$$

where ρ is the density, C the heat capacity, L the heat of melting, and V the relative volume of solids. The indices used denote: M melt; A, B phases A and B. T is the current temperature, t the time, Q the heat flow (Q = constant or $Q = \alpha(T - T_{ENV})$ which are the II- or III-type of thermal boundary conditions), α is the coefficient of heat transfer, and T_{ENV} the environment temperature.

The mass balance (Kolmogorov–Avrami equation) is

$$V^k(t) = 1 - \exp\left\{-\varphi^k \int_0^t F_N^k(\Delta T^k) \times \left[\int_{t^*}^t F_V^k(\Delta T^k)\,d\tau\right]^3 dt^*\right\} \quad (2)$$

where k = A, B are the phase indices, φ is the form-factor, ΔT is the overcooling

$$\Delta T^k = T_S^k - T \quad (3)$$

where T_S^k is the melting point (temperature of crystallization), F_N and F_V are the kinetic functions of nucleation and growth, respectively. Following earlier work [3, 4], a simple linear shape is supposed

$$F_N^k = \begin{cases} K_N^k(\Delta T^k - \Delta T_{MS}^k) & \Delta T^k \geqslant \Delta T_{MS}^k \\ 0 & \Delta T^k < \Delta T_{MS}^k \end{cases} \quad (4)$$

$$F_V^k = K_N^k \Delta T^k \quad (5)$$

where K_N and K_V are kinetic constants, and ΔT_{MS} is the metastability range (threshold of nucleation).

In the course of crystallization, each subsequent step M (time interval) is followed by the occurrence of new grains $N_{(M)}^k$

$$N_{(M)}^k = F_N^k (1 - V^k)\,dt \quad (6)$$

Equation 6 is a normalization condition to account for narrowing of the free volume to nucleate.

The increase in radius, $\delta R = F^k dt$, for a multitude of grains can be rewritten as

$$\delta V^k = \sum_{i=1}^{M} \varphi^k N_{(i)}^k (R_{(i)}^k + \delta R^k)^3 \quad (7)$$

where δV^k should be determined by solving Equations 1–5. Because of difference between the $R(i)$ values, the final distribution $N^k(R)$ with equal steps along the radius can be obtained by an additional normalization.

The calculation procedure can bring up the situation when $\Delta T^B < 0$, which means the overheating of phase B. The above assumption states that the physical overheating is impossible and all surplus heat results in melting the low-temperature phase B. The melting volume is determined from the surplus heat. Then the radius decrease can be determined from Equation 7. This decrease results in the annihilation of the grains with shorter radii. A necessary number of such iterations is made, and a new distribution is determined with account made for changes of integrals (2).

4. Calculation results (main results)

The Kolmogorov Equation 2 provides immediate evidence that the heat source is determined by a kinetic parameter $S^k = K_N^k (K_V^k)^3$. The following parametric values were chosen as basic:

$K_N = 10^2\,\mathrm{cm^{-1}s^{-1}K^{-1}}$; $K_V = 10^{-3}\,\mathrm{cm\,s^{-1}K^{-1}}$; $\rho_M = \rho^A = \rho^B = 8\,\mathrm{g\,cm^{-3}}$; $C_M = 0.5\,\mathrm{J\,g^{-1}K^{-1}}$; $L^A = L^B = 300\,\mathrm{J\,g^{-1}}$; $Q = 200\,\mathrm{J\,cm^{-3}s^{-1}}$; $\varphi = 4/3\,\pi$;
$\Delta T_{MS}^A = \Delta T_{MS}^B = 20\,\mathrm{K}$; $S^A/S^B = 1$.

Let us consider the modification of a physical picture of the process under the condition when the kinetic parameter S^A/S^B is decreased. The temperature–time dependencies are shown in Fig. 2. (Overcooling is the difference between T_S and $T(t)$.) In any case, an abrupt fall in temperature because of heat removal, Q, after "switching on" the heat release of crystallization, is changed with increase in relaxation.

When the rate of crystallization of phase A is not sufficiently high (large S^A/S^B value, curves 1 and 2), a quasi-stationary part of the process can exist near the melting point T_S^A: the rate of heat release decreases as liquid phase A is exhausted and the temperature

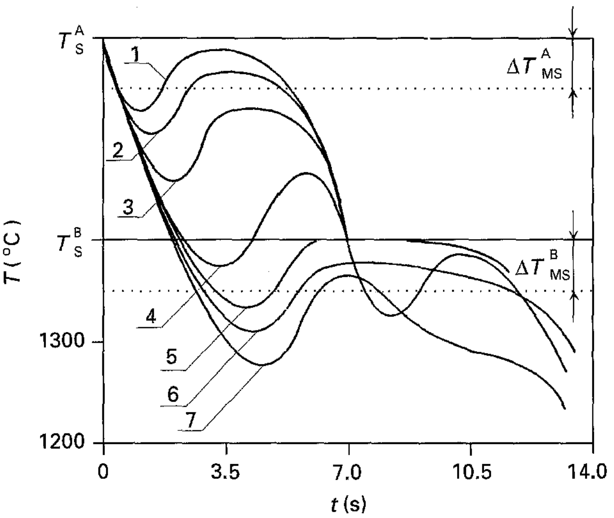

Figure 2 Temperature development. $S^A/S^B = K_N^A(K_V^A)^3/[K_N^B(K_V^B)^3]$: (1) 1, (2) 10^{-1}, (3) 10^{-2}, (4) 10^{-3}, (5) 10^{-4}, (6) 10^{-5}, (7) 10^{-6}.

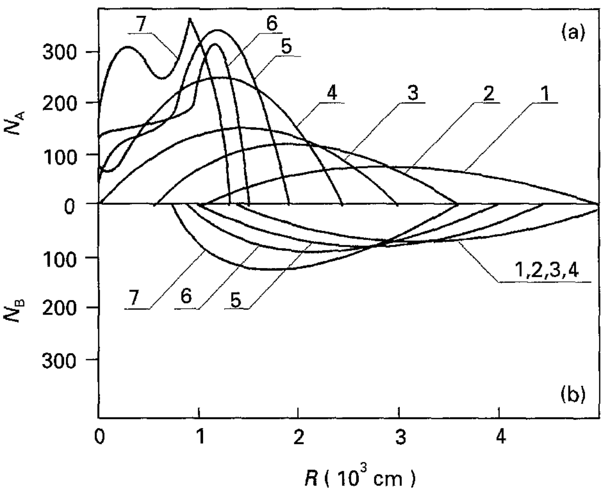

Figure 3 Size distribution. The numbers on the curves are as in Fig. 2. (a) Phase A, (b) phase B.

falls again. The presence of quasi-stationary results in the successive formation of almost equal numbers of grains with different radii, i.e. "extended" distribution takes place (Fig. 3, curves 1 and 2). It can also be referred to as "narrow" because the minimum radius $R_{MIN} > 0$.

The slowing down of the crystallization of phase A (low S^A/S^B) leads to a decrease both in temperature and the average grain size of phase A (curves 3 and 4, Figs 2 and 3). The heat released from the crystallization of phase A is insufficient to ensure an increase in the temperature to T_S^A. Curve 4 presents the case when (because of lowering temperature and consequently high overcooling, ΔT^A) the nucleation process proceeds to the exhaustion of liquid phase A, which gives rise to a "broad" distribution (with a fractional minimal radius $R \approx 0$). It should be noted that in this study, both "narrow" and "broad" distributions are observed as elsewhere [3, 5], but their formation mechanisms are different. The main parameter depending on distribution type is not ΔT_{MS}^A but S^A/S^B.

Strong kinetic hindrances lead to a new situation. The minimum temperature is lowered below the nucleation threshold for the second phase, $T_S^B - \Delta T_{MS}^B$, and parallel crystallization of both phases occurs (curves 5–7). Increasing the temperature after the minimum point can cause the melting of solid phase B to occur (curve 5). A quasi-stationary portion of the $T(t)$ curve again appears owing to an intensive heat release resulting from the crystallization of both phases. The size distribution with an almost constant number of grains in the region of small radii, corresponds to this portion. A slight slope is explained by the reduction of the liquid phase volume (Equation 6).

Drastic deceleration of the crystallization of phase A could reverse the process, i.e. phase B (low-temperature) crystallizes first and then the crystallization of phase A takes place (curve 7). The peak of $N(R)$ corresponds to the joint process followed by the "usual" type of distribution.

Thus, four types of structure (size distribution) can be distinguished: I, a "narrow" distribution for separate crystallization (curves 1–3 for phase A and 1–7 for phase B); II, a "broad" distribution for separate decelerated crystallization (curve 4); III, a 'broad" one for joint crystallization (curves 5 and 6); and IV, a bimodal one for the reverse process.

The above-considered process was analysed assuming that the kinetic parameter S^A/S^B is subject to changes. A similar picture was observed when the ratio of the heats of melting L^A/L^B was changed. By decreasing L^A/L^B, we obtain the above-described situation (curves 1–4, Figs 2 and 3).

The effect of vigorous heat removal is analogous. An intensive cooling can give rise to the situation presented by curves 4–6. (The system passes T_S^B when the overcooling of phase A remains close to its maximum).

One more reason for kinetic hindrances to nucleation and grain growth (and corresponding change of $N(R)$) could be a wide metastability range of the first phase, A. If $T_S^A - \Delta T_{MS} \approx T_S^B - \Delta T_{MS}^B$ (see Fig. 1), both phases will begin to crystallize simultaneously. In this case, the driving force for phase A exceeds significantly that for phase B. Very rapid crystallization of phase A is observed. The result is type III of $N(R)$ for phase A and type II for phase B.

5. Experimental procedure

A conventional SHS-metallurgy technique [9] was used to prepare the following samples: (i) alloys of molybdenum with oxide ceramics Cr_2O_3, and (ii) chromium with chromium and silicon oxides. The volume of the samples was about 3–4 cm^3. The concentrations of molybdenum in the initial mixtures were 10 and 20 wt %, that of chromium was 15 wt %. Both metals are insoluble in oxide ceramics. The reactions are as follows

$$CrO_3 + Cr + Mo \rightarrow Cr_2O_3 + Mo \quad (8)$$

$$Cr + CrO_3 + SiO \rightarrow Cr + Cr_2O_3 + SiO \quad (9)$$

The temperature of combustion, $T_{COMB} > 3200\,°C$, was much higher than the melting points of all the final products ($T_{S(Mo)} = 2620\,°C$, $T_{S(Cr)} = 1890\,°C$, $T_{S(SiO_2)} = 1610\,°C$, $T_{S(Cr_2O_3)} = 2344\,°C$). In Reaction 8,

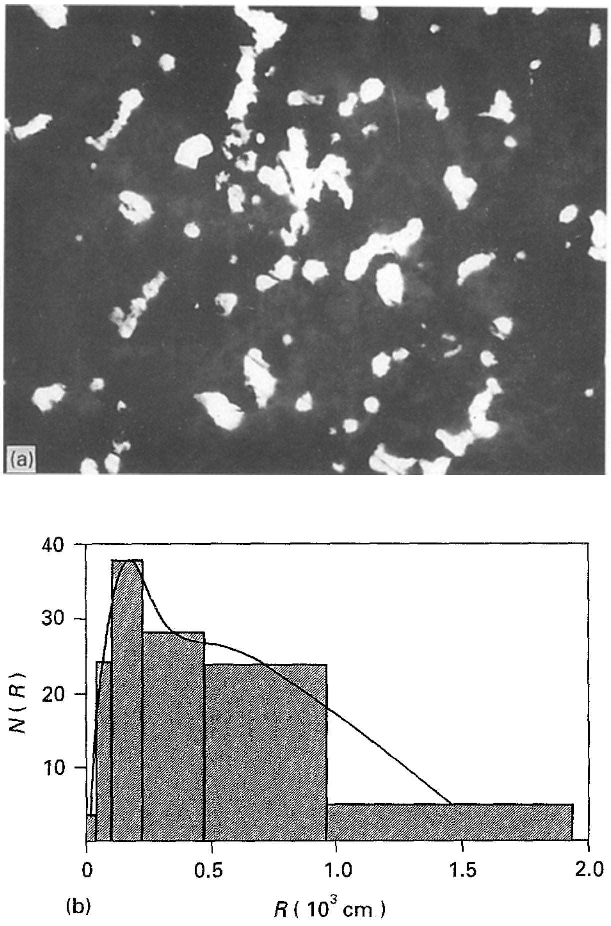

Figure 4 (a) A metallographic specimen of the system molybdenum + ceramics. (b) Size distribution.

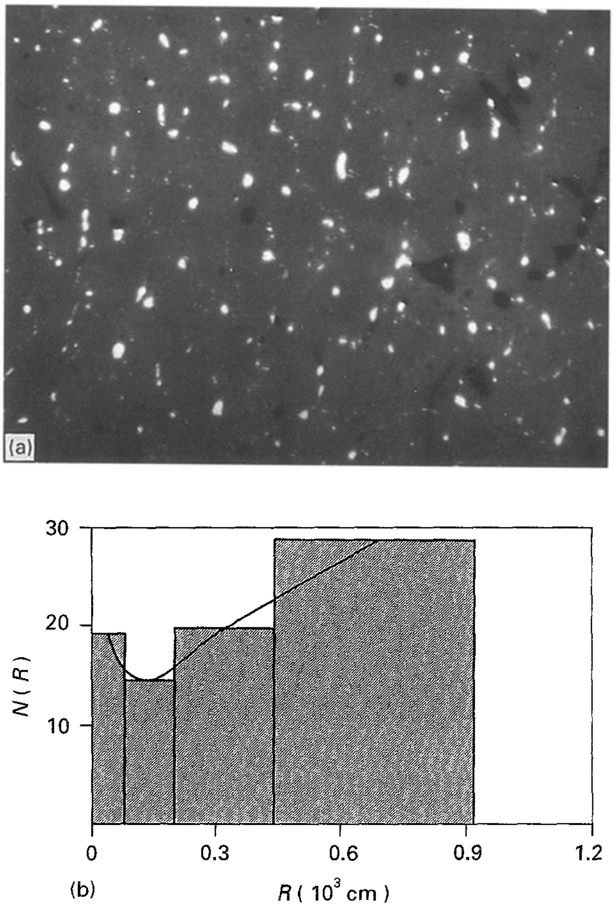

Figure 5 (a) A metallographic specimen of the system chromium + ceramics. (b) Size distribution.

the high-temperature phase was metallic molybdenum, in Reaction 9 this phase was layered ceramics.

Typical metallographic specimens for both systems are shown in Figs 4 and 5. In Reaction 8 the experimental size distribution agrees with that predicted theoretically, i.e. with separate crystallization without considerable kinetic (or other) hindrances.

A different distribution pattern is exhibited by Reaction 9. In this system metal is the last component to be crystallized on the boundaries of solidified ceramic grains. Hence the physical mechanism of the process is obviously different. The developed model cannot be used for this system.

Unfortunately, quantitative comparison of theoretical and experimental results is impossible because of the absence of kinetic crystallization parameters.

6. Conclusion

A simple model has been suggested for crystallization of two immiscible phases. The high-temperature phase must be a liquid continuous medium at the initial stage of the process (otherwise, there must be no hindrance to the mass transport).

As a rule, the phases crystallize separately. However, when the rate of crystallization of the high-temperature phase is very low, the simultaneous crystallization of both phases is possible. Four different types of size distribution (including a bimodal one) for various mechanisms of the process have been distinguished.

It is shown that the model developed can be used to describe the crystallization of a refractory metal in a ceramic matrix.

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