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EFFECT OF DIFFUSION ON THE CRYSTALLIZATION OF BINARY SYSTEMS

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The crystallization process for an Ni-TiC alloy of hypereutectic composition, as a binary system, is investigated. The influence of diffusion on the process and on the formation of the final structure of the product is considered. The conditions for implementation of a diffusional or kinetic mechanism of the growth of grains are estimated.

Introduction. Earlier we studied crystallization processes for binary systems in zero-dimensional [1] and one-dimensional [2] formulations. In the both cases a purely kinetic crystallization regime is investigated. From the general considerations it is clear that for large grain radii or a high rate of their growth the concentration field around grains will fail to keep pace with the motion of the grain boundary, i.e., diffusional constraints of transport of the crystallizing phase transform the process into the diffusional mode. The present work is devoted to an investigation of the influence of diffusional transfer on the final size distribution of grains of a high-melting phase.

For definiteness we shall deal with composite materials obtained by the SHS method [3]. Calculations are done for the TiC-Ni system studied earlier in [1, 2] (the phase diagram is shown in Fig. 1). The formulation of the problem and the physical assumptions are adopted from [1, 2].

Estimates. At first we make some estimates. We shall consider concentration changes on two different spatial levels: (1) with the scale l, i.e., the length of a zone in which a high-melting phase exists in both the solid and liquid states (Fig. 2) (in fact, the scale of the sample length is ~ 1 cm); (2) with the scale R, the grain radius (of about $\sim 10\,\mu$m).

In the literature [4], the rate of displacement of the crystallization boundary is determined as

$$V = \frac{K_V \Delta T}{1 + (K_V C_1 R)/D}. \tag{1}$$

As a boundary between the kinetic and diffusional modes, it is reasonable to take the condition $R_{cr} = D/(K_V C_1)$ when the rate of growth of the radius according to formula (1) is half that in a purely kinetic regime $V = K_V \Delta T$. For the processes considered $K_V \sim 10^{-4}$ cm/(sec·K), $D \sim 10^{-4}$ cm^2/sec, $C_1 \sim 2 \cdot 10^3$ K, whence $R_{cr} \sim 5\,\mu$m, which is within the range of considered (and observed in practice) sizes.

On the macroscale, the diffusion effect may be compared with the heat transfer, which is characterized by the Lewis number $\mathrm{Le} = a/D$. In our case, $a \sim 0.1 - 0.5$ cm^2/sec, i.e., $\mathrm{Le} \sim 200-1000$. Thus, it may be inferred that macrodiffusion, i.e., on a 1 cm scale, cannot exert a substantial influence on the process.

In principle, the rate of the process may have thermal constraints. Physically, they mean that the heat released upon crystallization has no time to be redistributed in space.

Analogously to diffusion, it may be written that [4]

$$V = \frac{K_V \Delta T}{1 + \dfrac{K_V RL/c}{a}}.$$

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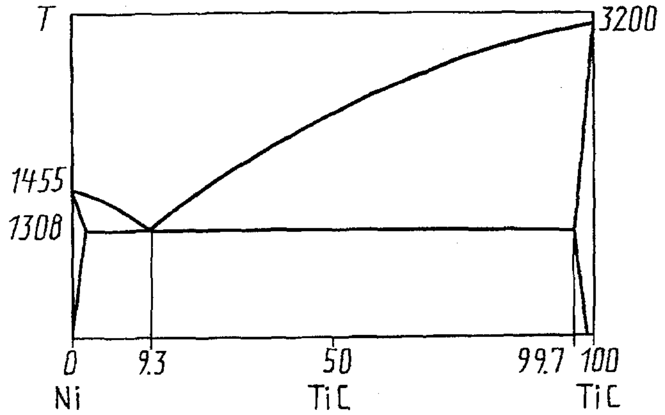


Fig. 1. Phase diagram of the Ni-TiC system. T, °C; TiC, wt.%.

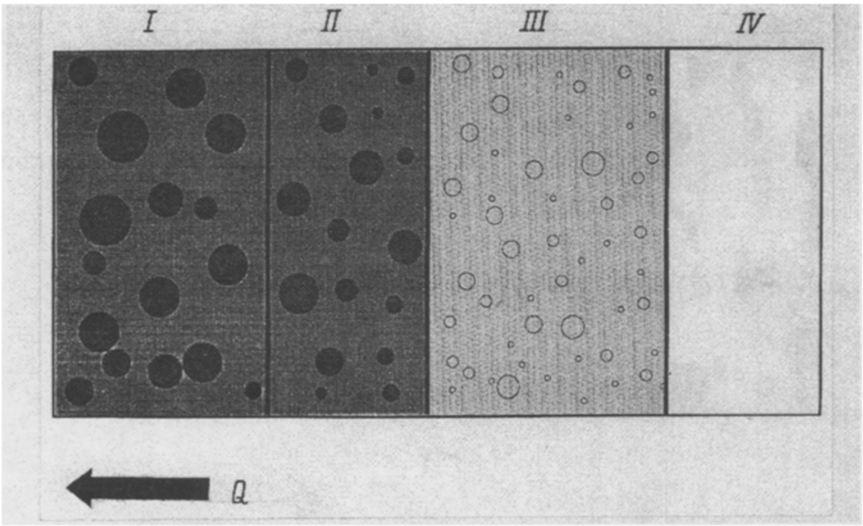


Fig. 2. Crystallization process in zones: IV, liquid melt; III, formation of grains and their growth; II, grain growth; I, crystallization of the eutectic matrix and formation of the final structure of the product.

For our case, $L \approx 300$ J/g, $c \approx 0.5$ J/(g·K). Then $R_{\text{cr}} = a/(K_V L/c) \approx 1$ cm, i.e., the grain radius at which thermal constraints start to appear is beyond the range of the investigated sizes.

Thus, the concentration field will be determined only by runoff of a substance onto the surface of the grains (in the kinetic regime) or into a boundary zone with the characteristic size $\sim R$ (in the diffusional regime).

We treat the crystallization process as follows. At first, mass crystallization of TiC occurs, and then as the temperature becomes lower than T_{eu}, a eutectic matrix begins to grow and to fix the formed structure of grains of the high-melting phase (Fig. 2).

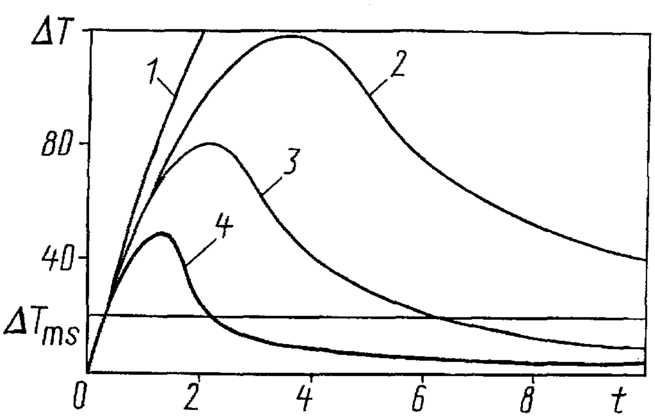
Formulation of the Problem. We consider the process in the zero-dimensional statement. Thus, the growth of grains is described only in the two-phase zone without account for temperature and concentration gradients.

The equation of heat balance is

$$\rho c \frac{\partial T}{\partial t} = L \rho_3 \frac{\partial V}{\partial t} - Q,$$

that of mass balance is

$$V = 1 - \exp \left[-\varphi \int_0^t V_N (\Delta T) \left[\int_{t^*}^t V_V (\Delta T) \, dt^* \right]^3 d\tau \right]$$



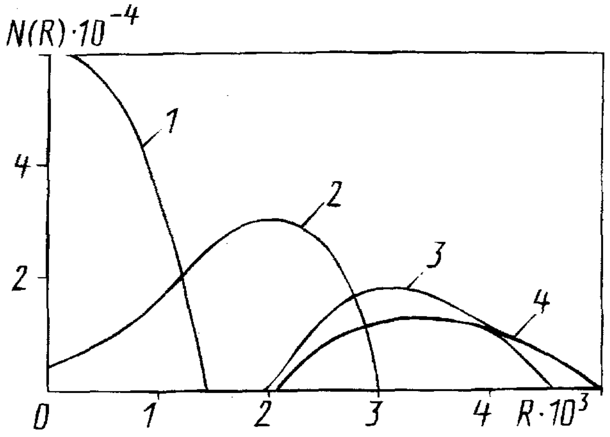


Fig. 3. Time history of supercooling at different diffusion coefficients: Q = 200 W/cm^{-3}; ΔT_{ms} = 20 K; K_V = $5\cdot 10^{-5}$ cm/(sec·K); K_N = 10^4 1/(cm^3·sec·K). The curves: 1, D = 10^{-1} cm^2/sec; 2, 10^{-4}; 3, 10^{-3}; 4, kinetic regime (D = ∞). ΔT, °C. t, sec.

Fig. 4. Final structure of the product (size distribution $N(R)$ of TiC grains). The parameters have the same values as in Fig. 3. R, cm.

The kinetic functions (the simplest form [1]) are:

$V_N(\Delta T) = K_N(\Delta T - \Delta T_{\text{ms}})$ is the rate of increase of the number of particles;

$$V_N\,(\Delta T \leq \Delta T_{\text{ms}}) = 0\,;$$

$V_N(\Delta T) = K_V \Delta T/1 + (K_V C_1 R)/D$ is the linear rate of growth of a particle.

Supercooling is

$$\Delta T = T^{00} - \frac{T^{00} - T_L}{1 - V} - T\,,$$

the initial conditions are

$$t = 0\,, \quad V = 0\,, \quad T = T_0 \geq T_L\,.$$

At each step a group of nuclei was recorded. The growth of each group was traced to the completion of the process, i.e., till the temperature T_{eu} was attained. Then we built the size distribution curves $N(R)$ for the grains. The substantiation of the formulation and the procedure for solving the mathematical problem are described in detail in [1]. The driving force for the crystallization process is the supercooling ΔT. The main kinetic parameter of the problem is the metastability interval ΔT_{ms} (the threshold of formation of particle a new phase).

In analyzing the problem, emphasis has been placed on the influence of diffusional transfer on the size distribution $N(R)$ of grains of the high-melting phase (TiC).

Results and Discussion. In the calculations, we varied the diffusion coefficient D. The supercooling ΔT does not differ qualitatively from that in the kinetic regime [1]: at first $\Delta T(t)$ increases drastically and then it smoothly relaxes. Depending on the metastability interval ΔT_{ms} the grain size distribution $N(R)$ may be of two qualitatively different types.

A narrow distribution $N(R)$ is formed if a small part of the curve $\Delta T(t)$ (near the peak, Fig. 3, curve 4) lies above ΔT_{ms}. A broad $N(R)$ is obtained when the entire cooling "tail," i.e., the quasistationary portion of the curve $\Delta T(t)$, is above ΔT_{ms} (Fig. 3, curve 2). A transition from the narrow to the broad distribution occurs in the comparatively narrow range $\Delta T_{\text{ms}} \approx 1-3$ K.

A decrease in the diffusional transfer may transform the supercooling substantially. The stronger the diffusional contraints, the more difficult it is for the system to relieve the supercooling. At very small D, a transition

TABLE 1. Influence of the Kinetic Constant K_N on the Weighted Mean Grain Radius. $K_V = 5 \cdot 10^{-5}$ cm/(sec·K); $Q = 200$ W/cm^3; $R_{cr} = 1.28 \cdot 10^{-3}$ cm

K_N	Purely kinetic regime ($D = \infty$)		Diffusional regime ($D = 10^{-4}$ cm^2/sec)	
	type of distribution	$R_{w.m}$, cm	type of distribution	$R_{w.m}$, cm
10^3	Narrow	$7.21 \cdot 10^{-3}$	Broad	$4.46 \cdot 10^{-3}$
10^4	"	$4.32 \cdot 10^{-3}$	Broad	$3.37 \cdot 10^{-3}$
10^5	"	$2.62 \cdot 10^{-3}$	Narrow	$2.23 \cdot 10^{-3}$
10^5	"	$1.61 \cdot 10^{-3}$	"	$1.46 \cdot 10^{-3}$
10^7	"	$1.00 \cdot 10^{-3}$	"	$9.46 \cdot 10^{-4}$
10^8	"	$6.36 \cdot 10^{-4}$	"	$6.16 \cdot 10^{-4}$

TABLE 2. Influence of Heat Transfer on the Weighted Mean Grain Radius. $K_V = 5 \cdot 10^{-5}$ cm/(sec·K); $K_N = 10^6$ 1/(cm^3·sec·K); $R_{cr} = 1.28 \cdot 10^{-3}$ cm

q, W/cm^2	Purely kinetic regime ($D = \infty$)	Diffusional regime ($D = 10^{-4}$ cm^2/sec)
	$R_{w.m}$, cm	
200	$1.61 \cdot 10^{-3}$	$1.46 \cdot 10^{-3}$
400	$1.45 \cdot 10^{-3}$	$1.32 \cdot 10^{-3}$
600	$1.38 \cdot 10^{-3}$	$1.25 \cdot 10^{-3}$
800	$1.34 \cdot 10^{-3}$	$1.20 \cdot 10^{-3}$
1000	$1.30 \cdot 10^{-3}$	$1.18 \cdot 10^{-3}$

to an infinitely increasing ΔT is possible, i.e., the system does not reach the quasistationary cooling section of the curve (Fig. 3, curve 1) (this case cannot be described quantitatively within the framework of the present model).

The influence of the coefficient D on the curve $\Delta T(t)$ is also directly manifested in the shape of the distribution $N(R)$ (Fig. 4). Diffusional hindrances slow down the growth of large grains, thus leading to a pronounced narrowing of $N(R)$ (Fig. 4, curves 4 and 3). Enhancement of diffusional hindrances may result in a qualitative transition, namely, from the typical narrow (curves 3, 4) to the broad distribution $N(R)$ (curve 2).

As for the influence of the other parameters, a decrease of K_V or an increase of K_N leads to a decrease of grain sizes and an increase of their total number. It is possible that their size does not exceed R_{cr} and then grains grow in a kinetic regime and even for small D diffusion does not exert a substantial influence on $N(R)$ (see Table 1).

An increase of the number of grains and, correspondingly, a decrease of their mean sizes may be induced by intense removal of heat at the initial stage of the process, and then with slow cooling of the melt it is possible to remain in the region of kinetic growth.

The influence of heat removal, with the heat flux Q being unchanged in time, is shown in Table 2. The increase of the heat removal entails an insignificant decrease of $R_{w.m}$. A form of the distribution $N(R)$ does not change. At very high Q values, the process passes to the kinetic regime (in Table 2, at $Q > 400$ W/cm^3 $R_{w.m} < R_{cr}$).

We have solved the problem in the one-dimensional statement (diffusion is considered on a macrolevel). In this case, account for diffusional transfer has not changed the process qualitatively. All the regularities of motion of the fronts, the supercooling waves, the development of concentration fields, and, finally, the distribution $N(R)$ do not change their form, i.e., as would be expected from the estimates obtained, the diffusion effect on the scale of the sample (the two-phase region) is negligible in the range of reasonable D ($D \leq 10^{-3}$ cm^2/sec). At $D =$

10^{-2}, the maximum change of the concentration fields does not exceed 2–5% and only at $D = 10^{-1}$ does the process undergo qualitative changes. However, such high D values correspond to turbulent, not molecular, diffusion (or powerful convective flows), which necessitates consideration of another adequate physical model of the process.

Conclusions. Diffusion on a microlevel (on the scale of the scale grain) exerts a pronounced influence on the course of crystallization and the material structure (grain size distribution).

Diffusional hindrances may change the distribution $N(R)$ qualitatively: the narrow distribution may turn into the broad one.

Diffusional transfer of a substance on the scale of the sample (~ 1 cm) does not affect the process within $D \leq 10^{-2}$, i.e., the change of the concentration field is determined only by the mass crystallization.

The process may be affected both in the kinetic and the diffusional regime by changes of the heat removal conditions, regulating the structure of the forming solid phase.

NOTATION

T, T_L, T^{00}, T_{eu}, current temperature, equilibrium liquidus temperature at the initial concentration, melting point of pure TiC, and eutectic temperature, respectively; K; V, relative volume of the solid phase; ρ, ρ_3, density of the melt and the high-melting phase, respectively, g/cm^3; Q, volumetric heat-removal, W/cm^3; φ, form factor, $\varphi = 4/3\pi$ for spherical grains; ΔT_{ms}, metastability interval, K; K_N, formation factor, 1/(cm^3·sec·K); D, diffusion coefficient, cm^2/sec; L, latent heat of crystallization, J/g; c, heat capacity, J/(cm^2·K); a, thermal diffusivity, cm^2/sec; Le, Lewis number; l, length of the sample, cm; t, time, sec; R, R_{cr}, $R_{\text{w.m}}$, grain, critical, and weighted mean radii, cm; C_1, slope of the liquidus in the phase diagram, K; $N(R)$, distribution of grains with the radius R.

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