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RATE-CONSTANTS FOR DIFFUSION-CONTROLLED CRYSTALLIZATION OF BARIUM TUNGSTATE FROM SODIUM TUNGSTATE MELTS BY DIFFERENTIAL THERMAL ANALYSIS

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Variations of rate constants in diffusion-controlled crystal growth of barium tungstate from solutions in sodium tungstate melts in platinum crucibles were studied by continuous cooling from crystallization temperatures $T_0 = 800$ to 1000° to below the eutectic temperature at cooling rates $R_T = 0.67$ to 3.37° min^{-1}. During the induction periods ($\bar{t}$) heterogeneous nuclei slowly formed in the solution; the main crystal growth started only after the development of some excess solute concentrations (ΔC) at the end of $\bar{t}$. The diffusion rate-constants ($k_{D_{II}}$) for the growth increased with T_0 and R_T. These were much smaller than the real diffusion rate-constants $(k_{D_l})_{real}$ but higher than those for diffusion-controlled crystal growth of barium tungstate from sodium tungstate melts in alumina crucibles.

Crystallizations of barium tungstate from sodium tungstate and other melts have been reported [1–4] but these works were mainly on the nucleation process and final crystal numbers and sizes in different crystallizations. The present work reports a study on the variations of rate-constants for diffusion-controlled crystal growth of barium tungstate from sodium tungstate melts in platinum crucibles by continuous cooling of the melt from the initial crystallization temperature (T_0) to below the eutectic temperature. The system exhibited some induction period ($\bar{t}$); during these induction periods heterogeneous nuclei first formed slowly onto the metal platinate particles within the solution, and also some excess solute concentrations ($\Delta\bar{C}$) developed. The main growth started only after the end of $\bar{t}$ when sufficient $\Delta\bar{C}$ developed; the actual growth after $\bar{t}$ was diffusion rate-controlled.

The crystallization was studied by differential thermal analysis, and the degree of crystallization (α_t), the crystal lengths (l_t) and the growth-rates ($\mathrm{d}l/\mathrm{d}t$) were evaluated. The diffusion rate-constants (k_{D_l}) were estimated and the effects of the variations of T_0 and R_T on k_{D_l} were investigated.

Experimental

Equimolecular weights of barium carbonate and tungsten trioxide were thoroughly mixed. Then the requisite amounts of this mixture and sodium tungstate, necessary to prepare a saturated solution at the crystallization temperature, were

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mixed together and heated inside a "Carbolite" electric furnace to prepare a saturated solution. This saturated solution was rapidly cooled to the ambient temperature, ground and dried. 0.3 to 0.5 g of this saturated solid solution mix was heated (20°/h) in small platinum crucibles inside a "Du Pont" differential thermal analyser at a temperature (T') slightly higher than T_0 and held at that temperature to ensure complete solution. The crystallization was then carried out from $T_0 = 800$, 900 and 1000° down to below the eutectic temperature by slow continuous cooling at rates $R_T = 40$, 120 and 200° per hour according to a pre-assigned automatic cooling programme.

The degree of crystallization at any crystallization time (t) is given by

$$\alpha_t = \Delta H_t / \Delta H_{total}. \tag{1}$$

But $\Delta H_t = KA_t$ and $\Delta H_{total} = KA_{total}$, where

ΔH_t = enthalpy change at any time t;
ΔH_{total} = total enthalpy change during the entire crystallization;
A_t = area under the thermal curve at t;
A_{total} = total area under the thermal curve at the end of the process;
K = thermal conductivity;

Neglecting the variation of thermal conductivity and other possible factors with temperature,

$$\alpha_t = A_t / A_{total}. \tag{2}$$

The crystal length (l_t) at any crystallization time (t) is then given by

$$l_t = l_f \alpha_t^{1/3} \tag{3}$$

where l_f is the final crystal length at the end of the crystallization. The experimental DTA curves were traced on the standard millimeter graph papers and α_t and l_t were evaluated from Eqs 2 and 3. l_f values were obtained from separate runs in alumina crucibles as described earlier [1].

Results

Kinetics

(A) The system exhibited some induction period ($\bar{t}$); this corresponds to the induction temperature ($\bar{T}$). Some excess solute concentrations ($\Delta \bar{C}$) at $\bar{T}$ gradually developed during the induction period; there was no growth till the end of $\bar{t}$. The actual growth occurred only after the development of some excess solute concentration at the end of $\bar{t}$.

(B) α_t *vs.* t plots (Figs 1–3) were approximately linear up to $\alpha_t < 0.15$. The induction periods varied from 0.25 to 1.5 hours depending on the rate of cooling and the crystallization temperature. α_t attained the maximum value in about 1 to 12 hours.

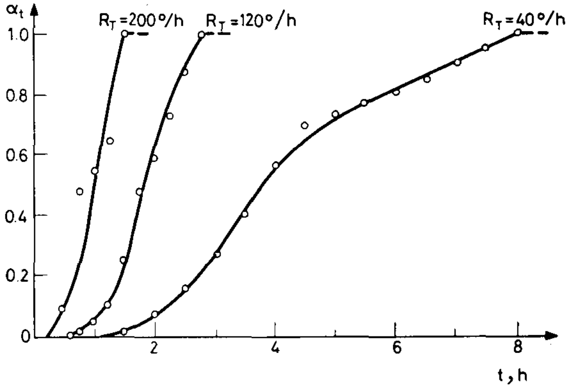

Fig. 1. Crystallization of barium tungstate from sodium tungstate melis at $T_0 = 800\ °C$. Extents of crystallization after different times

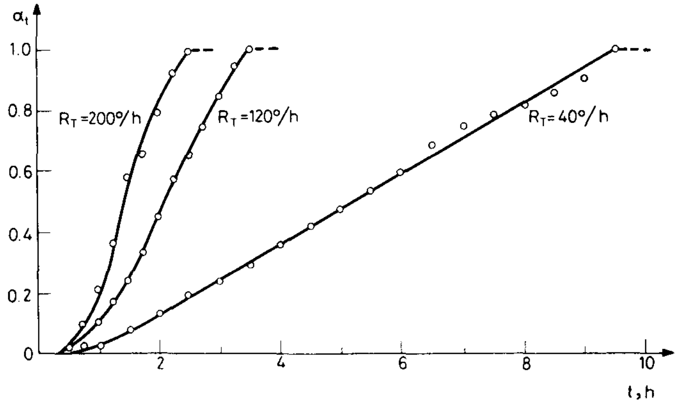

Fig. 2. Crystallization of barium tungstate from sodium tungstate melts at $T_6 = 900\ °C$. Extents of crystallization after different times

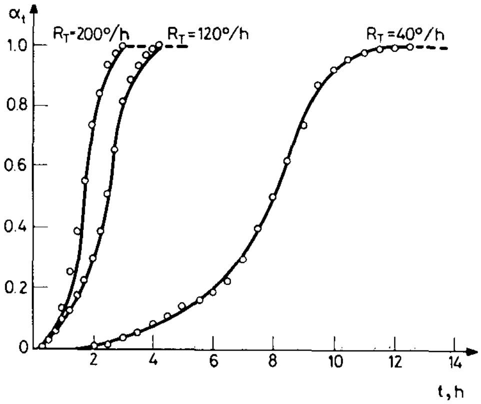

Fig 3. Crystallization of barium tungstate from sodium tungstate melts at $T_0 = 1000\ °C$. Extents of crystallization after different times

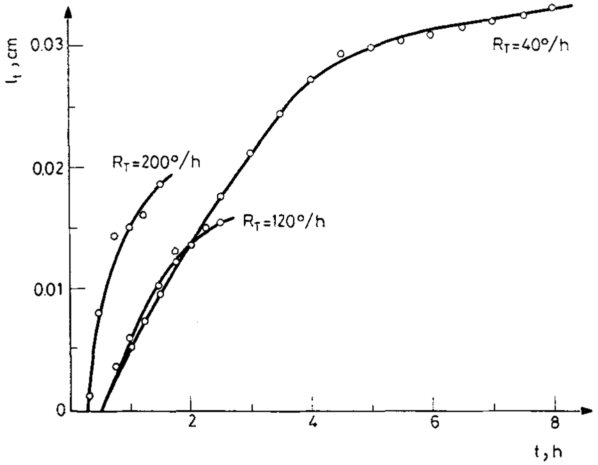

Fig. 4. Crystallization of barium tungstate from sodium tungstate melts at $T_0 = 800$ °C. Maximum crystal lengths after different times

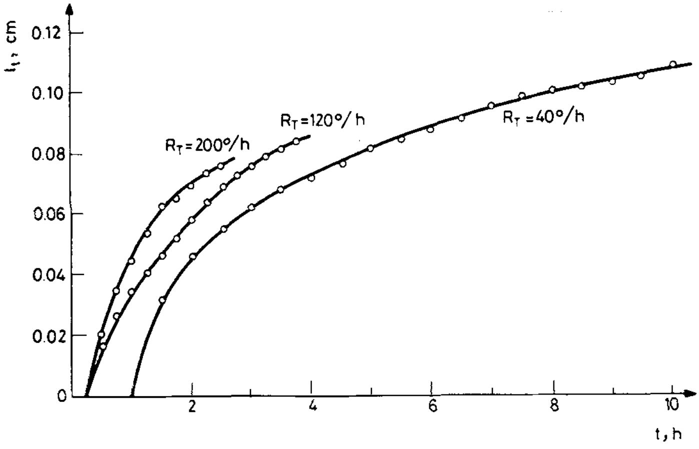

Fig. 5. Crystallization of barium tungstate from sodium tungstate melts at $T_0 = 900$ °C. Maximum crystal lengths after different times

(C) l_t *vs.* t plots (Figs 4–6) were linear up to $l_t \simeq 0.44\, l_f$. The induction periods were estimated by extrapolation of these plots back to the t-axis. There was virtually no growth during these induction periods; the actual growth occurred only after $\bar{t}$ and reached the final size in about 1 to 12 hours.

(D) In a system which exhibits induction periods, the development of excess solute concentration will precede the occurrence of the main crystal growth; the "induction value" of the solute concentration may be expressed as,

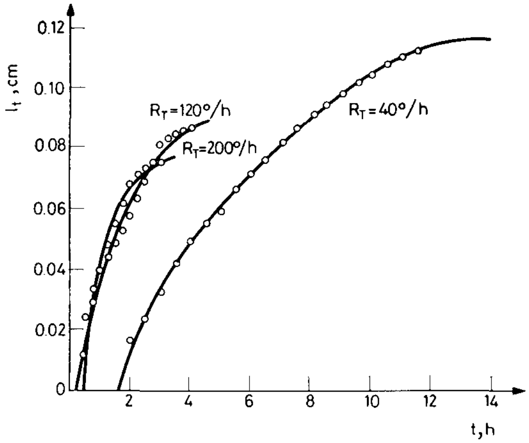

Fig. 6. Crystallization of barium tungstate from sodium tungstate melts at T_0 = 1000 °C. Maximum crystal lengths after different times

Table 1

Rate-constants for diffusion-controlled crystallization of barium tungstate from sodium tungstate melts by differential thermal analysis

Initial compositions (C_0) at different temperatures:

$(C_0)_{800^\circ}$ = 9 g/100 g solvent
$(C_0)_{90C^\circ}$ = 22 g/100 g solvent
$(C_0)_{1000^\circ}$ = 48 g/100 g solvent
Eutectic temperature (T_{eu}) = 570°
Eutectic composition (C_{eu}) = 135×10^{-6} mol/g sol.

T_0 °C	R_T °C/h	$\bar{t}$ h	$\bar{T}$ °C	$\Delta\bar{C}$ (at $\bar{T}$) g/g sol	$(dl/dt)_{\bar{t}}$ cm/h	$(dl_\tau^2/d\tau)$ $\times 10^{-3}$ cm²/h	$dl_\Theta^2/d\Theta$ cm²/h	$10^{-6}k_{D1}$ cm²/s
800	40	0.50	780	0.0026	0.0144	—	0.0150	0.400
	120	0.50	740	0.0201	0.0600	—	0.1556	0.709
	200	0.25	750	0.0176	0.0560	—	0.1643	0.768
900	40	1.0	860	0.0900	0.0094	0.920	—	0.537
	120	0.25	870	0.0385	0.0115	—	0.6250	1.172
	200	0.25	850	0.0585	0.0350	—	1.443	1.501
1000	40	1.5	940	0.0869	0.0227	0.900	—	0.659
	120	0.25	970	0.0439	0.0667	—	0.8888	1.712
	200	0.25	950	0.0739	0.2000	—	1.966	1.848

$$\Delta\bar{C} = C_0 - C_E \qquad (4)$$

where C_0 is the initial melt composition and C_E is the equilibrium melt composition. But $C_E = aR_T\bar{t}$, where $a(= dC/dT)$ is the variation of concentration (C) with temperature near T_0. Thus $\Delta\bar{C} = C_0 - aR_1\bar{t}$. $\Delta\bar{C}$ values were evaluated from the solubility *vs.* temperature diagrams [3]. No clear variation of $\Delta\bar{C}$ with the changes in R_T or T_0 was noted.

(E) The initial growth-rates, $(dl/dt)_{\bar{t}}$, immediately after the induction periods were estimated from the l_t *vs.* t plots (Table 1). No clear variation of $(dl/dt)_{\bar{t}}$ with the changes in R_T or T_0 was noted.

Average crystal lengths (l_τ) at any growth-time $\tau(= t - \bar{t})$ after the induction periods were estimated from the l_t *vs.* t plots. These values were plotted against τ (Figs 7–9). l_τ varied linearly with τ at low τ values but at higher τ values these plots deviated.

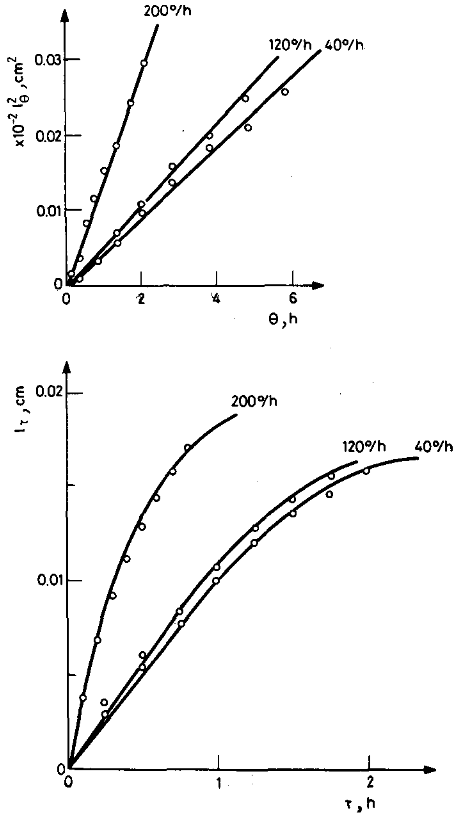

Fig. 7. Crystallization of barium tungstate from sodium tungstate melts at $T_0 = 800$ °C. Crystal lengths (l_T) at different growth times (τ)

The main growth

(A) In this work the actual growth occurred only after the development of some excess solute concentrations at the end of $\bar{t}$. The lengths of the induction periods may vary depending on the crystallization temperature and cooling rates. For such crystallizations, it is probably more convenient to express results in terms of the actual growth time τ after the induction period. For a system where $\tau > 0.1\ \bar{t}$, the kinetics of slow growth (rate controlled by diffusion when growth times are small) may be expressed as,

$$\mathrm{d}l_\tau/\mathrm{d}\tau = \frac{2k_{\mathrm{Dl}}\Delta\bar{C}}{l_\tau} = \frac{2k_{\mathrm{Dl}}aR_{\mathrm{T}}(\bar{t}+\tau)}{l_\tau}. \qquad (4)$$

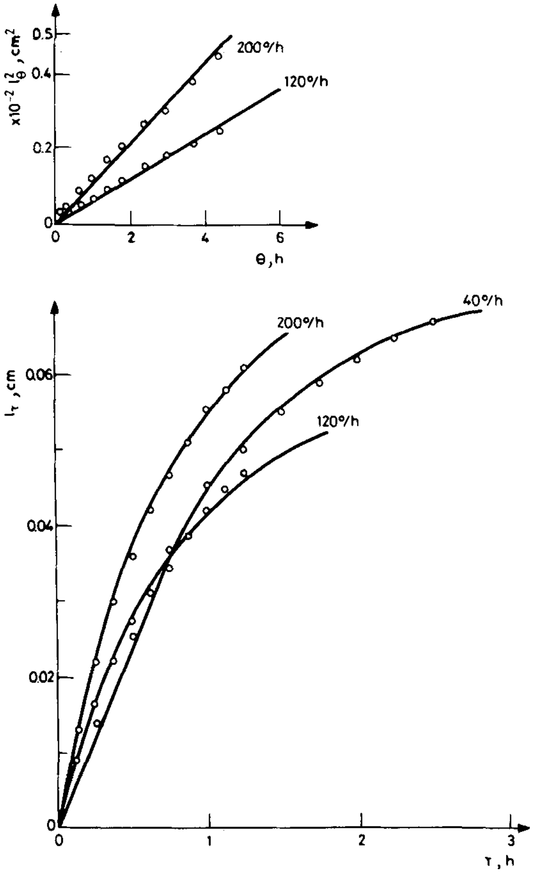

Fig. 8. Crystallization of barium tungstate from sodium tungstate melts at $T_0 = 900\ ^\circ\mathrm{C}$. Crystal lengths ($l_\mathrm{T}$) at different growth times (τ)

Integrating,

$$l_\Theta^2 = 4k_{\mathrm{D_l}} a R_\mathrm{T} \bar{t}\Theta \qquad (5)$$

where $\Theta = \tau(1 + \tau/2\bar{t})$

Hence,

$$k_{\mathrm{D_l}} = (\mathrm{d}l_\Theta^2/\mathrm{d}\Theta)/4\Delta\bar{C} \qquad (6)$$

$k_{\mathrm{D_l}}$ values for all T_0 and R_T (except $R_\mathrm{T} = 40°/\mathrm{h}$ for $T_0 = 900°$ and $1000°$) were evaluated from the slopes $\mathrm{d}l_\Theta^2/\mathrm{d}\Theta$ of the l_Θ^2 *vs.* Θ plots using Eq. 6 (Table 1).

(B) For a system with medium induction periods, i.e. $\tau < 0.3\ \bar{t}$, the diffusion rate-constants after the induction periods may be evaluated using the relation

$$k_{\mathrm{D_l}} = (\mathrm{d}l_\tau^2/\mathrm{d}\tau)_{\bar{t}}/4\Delta\bar{C} \qquad (7)$$

In this work the $k_{\mathrm{D_l}}$ values for $R_\mathrm{T} = 40°/\mathrm{h}$ at $T_0 = 900°$ and $1000°$ were evaluated from the slopes $\mathrm{d}l_\tau^2/\mathrm{d}\tau$ of l_τ^2 *vs.* τ plots using Eq. 7.

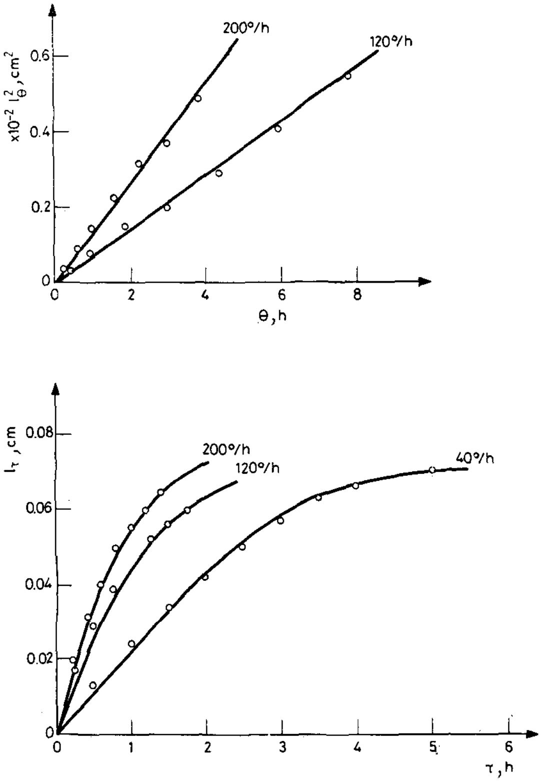

Fig. 9. Crystallization of barium tungstate from sodium tungstate melts at $T_0 = 1000\ °\mathrm{C}$. Crystal lengths (l_T) at different growth times (τ)

The diffusion coefficient

For crystallizations by continuous cooling, crystal growth-rates at any crystallization time would be expressed by [5]

$$\mathrm{d}l/\mathrm{d}t \simeq (4D\O\Delta\bar{C}/l)(\varrho_{\mathrm{sol}}/\varrho) \tag{8}$$

where D is the diffusion coefficient of the metal cations, $\O$ is the permeability factor, ϱ_{sol} is the density of the solution and ϱ is the density of the crystals. Comparing Eqs 4 and 8, the minimum value of k_{D_l} for growth along the major face would be $(3D\,\Phi)$ $(\varrho_{\mathrm{sol}}/\varrho)$.

The diffusion coefficient for self-diffusion of barium in barium tungstate at 800° has been reported [1] as $D_{\mathrm{Ba}} = 70\times10^{-6}$ cm^2/s. In this work the actual growth occurred at about 750°; therefore it is better to compare the diffusion coefficients at this temperature. Assuming that the actual diffusion coefficient depends on the viscosity of the substance [4], the actual D-value of barium at 750° would be $D_{\mathrm{Ba}} = 45.5\times10^{-6}$ cm^2/s. The density of the solution was 4.956 g/ml. Hence the real value of the diffusion coefficient, $(k_{D_l})_{\mathrm{real}}$, should be $82\times\times10^{-6}$ cm^2/s. The rate constants varied from 0.006 to 0.026 D_{Ba}^{2+}, where D_{Ba}^{2+} is the diffusion coefficient of barium at 800°.

Discussion

Temperature is a function of time and so is the diffusion coefficient (k_D). Ideally, the variation of k_D with time should have been considered in the integration of Eq. 5 from Eq. 4. However, since the k_D values are small, ignorance of this variation probably did not introduce any significant change in the final k_D values.

In all crystallizations k_{D_l} increased with increased crystallization temperatures and cooling rates. The estimated k_{D_l} values are higher then those for diffusion-controlled growth of barium tungstate from sodium tungstate melts in alumina crucibles [1], but they are very much smaller than the $(k_{D_l})_{\mathrm{real}}$ values.

The linearity of l_t *vs.* t, and l_τ versus τ plots at the early stages suggests that the barium tungstate crystal growth from sodium tungstate melts in platinum crucibles was probably diffusion rate-controlled as observed in the crystallization of the same system in alumina crucibles [1].

Because of the small size of the crucibles, probably the growing crystals settled at the bottom in a densely packed manner which resulted in the low inter-particle void space whereby the diffusion rate of material into the growing surfaces was hindered and the net result was the low k_D values.

References

1. B. N. Roy and V. K. Handa, J. Cryst. Gr., 47 (1979) 577.
2. A. Packter and B. N. Roy, Krist. Tech., 6 (1971) 39.
3. B. N. Roy and A. Packter, Krist. Tech., 8 (1973) 819.
4. A. Packter and B. N. Roy, J. Cryst. Gr., 18 (1973) 86.
5. B. N. Roy and S. Appalasami, J. Am. Ceram. Soc., 61 (1978) 38.

Résumé — On a étudié les variations des constantes de vitesse lors de la croissance, contrôlée par le diffusion, des cristaux de tungstate de baryum, en solution dans le tungstate de sodium fondu en creusets de platine. Le refroidissement en continu a été effectué depuis la température de cristallisation $T_0 = 800$ à 1000° jusqu'au-dessous de la température eutectique à des vitesses de refroidissement $R_T = 0.67$ à 3.37 °C.min^{-1}. Pendant les périodes d'induction ($\bar{t}$) des noyaux hétérogènes se forment lentement dans la solution; la croissance principale des cristaux ne commence qu'après le développement de concentrations quelque peu supérieures à la sursaturation de la substance en solution ($\overline{C}$), à la fin de $\bar{t}$. Les constantes de vitesse de diffusion (k_{D_1}) correspondant à la croissance augmentent avec T_0 et R_T. Elles sont bien plus petites que les constantes de vitesse réelles de la diffusion $(k_{D_1})_{\text{réel}}$, mais plus élevées que celles de la croissance des cristaux, contrôlée par la diffusion, du tungstate de baryum dans le tungstate de sodium fondu en creusets d'alumine.

Zusammenfassung — Die Änderung der Geschwindigkeitskonstanten bei dem diffusionsbedingten Kristallwachtum von Bariumwolframat aus Lösungen von Natriumwolframatschmelzen in Platintiegeln wurde durch kontinuierliches Kühlen von den Kristallisierungstemperaturen $T_0 = 800$ bis 1000° bis zur eutektischen Temperatur unter Anwendung von Kühlgeschwindigkeiten von $R_T = 0.67$ bis 3.37 °C min^{-1} untersucht. Während der Induktionsperioden ($\bar{t}$) bildeten sich in der Lösung langsam heterogene Keime; das Hauptkristallwachstum begann nur bei etwas übersättigter Konzentrationen der gelösten Substanz ($\overline{C}$) am Ende von $\bar{t}$. Die Diffusionsgeschwindigkeitskonstanten (k_{D_1}) des Wachstums nahmen mit T_0 und R_T zu. Diese waren viel niedriger als die wirklichen Diffusionsgeschwindigkeitskonstanten $(k_{D_1})_{\text{real}}$, jedoch höher als die des diffusionsbedingten Kristallwachstums von Bariumwolframat aus Natriumwolframatschmelzen in Aluminiumtiegeln.

Резюме — Были изучены изменения констант скоростей диффузионно-контролируемого роста кристаллов вольфрамата бария из растворов в расплавах вольфрамата натрия в платиновых тиглях путем непрерывного охлаждения от температур кристаллизации $T_0 = 800$ до 1000° и ниже температуры эвтектики при скоростях охлаждения R_Γ от 0.67 ыо 3.37° в минуту. Во время индукционного периода ($\bar{t}$) в растворе медленно образуются гетерогенные зародыши. Главный рост кристалла начинается только после достижения некоторого концентрационного избытка растворенного вещества (ΔC) в конце $\bar{t}$. Диффузионные константы скорости (k_{D_l},) роста увеличиваются с T_0 и R_T. Они намного меньше, чем действительные константы скорости (k_{D_l}) дейст., но выше, чем таковые для диффузионно-контролируемого роста кристаллов вольфрамата бария из расплавов вольфрамата натрия в алюминиевых тиглях.