

DIFFERENTIAL THERMAL ANALYSIS- STUDIES ON THE CRYSTALLIZATION OF STRONTIUM TUNGSTATE FROM SODIUM TUNGSTATE MELTS

KINETICS AND MECHANISM OF CRYSTAL GROWTH

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The kinetics of strontium tungstate crystallization from sodium tungstate melts in platinum crucibles were studied by differential thermal analysis at crystallization temperatures $T_0 = 800, 900$ and 1000° by continuous cooling at rates $R_T = 40, 120$ and 200° per hour. Heterogeneous nuclei that first formed on the metal platinate particles in the solution during the induction periods (\bar{t}) grew to small crystallites (\bar{l}). The main crystal growth started after the development of some excess solute concentration ($\Delta\bar{C}$) at the end of the induction temperatures (\bar{T}). For the first 80% crystallization, the average crystal lengths (l_c) varied with the growth time (τ) according to the relation $l_c^2 = (\bar{l})^2 + 4 \bar{k}_{D1} M \Delta\bar{C}$, where \bar{k}_{D1} is the diffusion rate constant at temperatures near \bar{T} , and M is the metal salt molecular weight. The initial growth rates and the ratios l_c^2/τ depended on $\Delta\bar{C}$ instead of R_T . The last 20% growth was controlled only by the rate of development of the excess solute concentration.

The kinetics of crystallization of several inorganic substances from melts and aqueous solutions under slow continuous cooling have been reported [1–8]. In some of these cases crystallization occurred practically immediately after the onset of cooling, while in other cases induction periods of various lengths were observed. In a crystallization, during an induction period only gradual development of excess solute concentration occurs. Therefore, at any time during an induction period the nucleation rate and the overall number of nuclei are very low; some very slow growth onto these early nuclei may take place. Eventually, however, at the end of the induction period, the number and the overall surface area of the nuclei become appreciable and a rapid growth surge occurs. The growth mechanism for systems with induction periods may become identical to that for systems without induction periods, but the kinetics relations will differ. Such kinetic relations for a system with induction periods depend on the length of the induction periods. Therefore, for a system with induction periods it would be interesting to study kinetic relations of crystal growth in terms of the induction periods.

The present work reports a differential thermal analysis study on the kinetics of crystal growth of strontium tungstate from sodium tungstate melts. This system exhibited moderate induction periods for all T_0 and R_T . The kinetics of the main crystal growth after the induction periods were analysed in terms of a diffusion-controlled growth from solutions of varying residual excess solute concentrations.

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Kinetic relations

For a diffusion-controlled crystal growth, the growth rate of metal salt crystals in unstirred solutions of low permeability is generally controlled by the diffusion rate of the metal salt ions into the growing crystal surfaces. The rate of the main growth of (the 'major' side of the main crystal face of) metal salt crystals at any growth time τ after the induction periods (\bar{i}) would be expressed by the relation [9, 10]

$$\frac{dl_{\tau}}{d\tau} = \frac{2(Sh)\Phi DM(\Delta C_{\text{sol}})_{\tau}}{l_{\tau}} (\rho_{\text{sol}}/\rho) \quad (1)$$

where Sh is the dimensionless Sherwood function;

Φ is an overall permeability factor;

D is the diffusion coefficient of the metal salt cations;

τ ($= t - \bar{i}$) is the actual growth time after the induction period, t being the total crystallization time from the onset of cooling;

$(\Delta C_{\text{sol}})_{\tau}$ is the residual excess solute concentration at τ ;

ρ and ρ_{sol} are the densities of the crystals and the solution, respectively;

M is the metal salt molecular weight.

Treybal [10] has shown that when the natural convection in a solution is poor, $Sh \approx 2$. Then Eq. 1 becomes

$$\frac{dl_{\tau}}{d\tau} = \frac{4\Phi DM(\Delta C_{\text{sol}})_{\tau}}{l_{\tau}} (\rho_{\text{sol}}/\rho) \quad (2)$$

For crystallization under continuous cooling, for a system with induction periods where $\tau > 0.1 \bar{i}$, the kinetics of slow growth would be expressed by the relation

$$\frac{dl_{\tau}}{d\tau} = \frac{2\bar{k}_{D1} \Delta \bar{C}}{l_{\tau}} \quad (3)$$

where $\Delta \bar{C}$ is the excess solute concentration up to the induction period \bar{i} , and k_{D1} is the rate constant for diffusion-controlled growth of the 'wider' crystal side after the induction period. Comparing Eqs 2 and 3,

$$\frac{dl_{\tau}}{d\tau} = \frac{2\bar{k}_{D1} M(\Delta C_{\text{sol}})_{\tau}}{l_{\tau}} \quad (4)$$

For this equation, $\bar{k}_{D1} = (2 D \Phi)(\rho_{\text{sol}}/\rho)$. Generally, in the crystallization of any metal salt from melts, the excess solute concentration at any growth time (τ) would be

$$(\Delta C_{\text{sol}})_{\tau} = \left(\Delta C_{\tau} - \frac{W_{\tau}}{M} \right) \quad (5)$$

where ΔC_τ is the overall excess solute concentration developed up to τ , and W_τ is the weight of crystals developed at different τ . But ΔC_τ and W_τ are given by

$$\Delta C_\tau = \Delta \bar{C} + R_c \tau \tag{6}$$

and

$$W_\tau = N \rho f_s l_\tau^3 = M \beta l_\tau^3 \tag{7}$$

where $\Delta \bar{C}$ is the excess solute concentration up to \bar{l} ;

R_c is the rate of development of the excess solute concentration;

N is the number of crystals at time t in any crystallization;

f_s is a shape factor;

$\beta = N \rho f_s / M$ is a function of the crystal number. For final weights, β becomes $(\Delta C_f) / l_f^3$, ΔC_f being the final excess solute concentration and l_f being the final crystal length.

With the help of Eqs 6 and 7, Eq. 5 becomes

$$(\Delta C_{sol})_\tau = (\Delta \bar{C} + R_c \tau - \beta l_\tau^3). \tag{8}$$

Combining Eqs 4 and 8,

$$\frac{dl_\tau}{d\tau} = \frac{2 \bar{k}_{D_1} M (\Delta \bar{C} + R_c \tau - \beta l_\tau^3)}{l_\tau}. \tag{9}$$

Integrating this equation by Picard's iterative method up to the first approximation gives

$$l_\tau^2 = (\bar{l})^2 + (4 \bar{k}_{D_1} M \Delta \bar{C} - 4 \bar{k}_{D_1} M \beta \bar{l}^3) + 2 \bar{k}_{D_1} M R_c \tau^2 \tag{10}$$

or
$$l_\tau^2 = (\bar{l})^2 + A \tau + B \tau^2 \tag{11}$$

where \bar{l} is the maximum length of crystals up to the end of the induction periods;

$$A = 4 \bar{k}_{D_1} M \Delta \bar{C} - 4 \bar{k}_{D_1} M \beta \bar{l}^3$$

and

$$B = 2 \bar{k}_{D_1} M R_c.$$

For any T_0 and R_T , A and B are constants. If the residual excess solute concentrations remain approximately constant at $(\Delta C_{sol})_\tau = \Delta \bar{C}$, Eq. 4 simplifies to

$$\frac{dl_\tau}{d\tau} = \frac{2 \bar{k}_{D_1} M \Delta \bar{C}}{l_\tau} \tag{12}$$

Integration of this equation gives

$$l_\tau^2 = (\bar{l})^2 + 4 \bar{k}_{D_1} M \Delta \bar{C} \tau \tag{13}$$

or
$$l_\tau^2 = (\bar{l})^2 + A' \tau \tag{14}$$

where $A' (= 4 \bar{k}_{D_1} M \Delta \bar{C})$ is a constant for any T_0 and R_T ; it is a function of $\Delta \bar{C}$.

Experimental

Experimental methods have been described in an earlier paper [11]. Saturated strontium tungstate solutions at initial temperatures $T_0 = 800, 900$ and 1000° in platinum crucibles were cooled down to ambient temperature at constant cooling rates $R_T = 40, 120$ and 200° per hour. The rates (R_c) of development of excess solute concentration were then $R_c = aR_T \text{ mol/g h}^{-1}$, where $a (= dC/dT)$ was the variation of solubility with temperatures. Induction periods (\bar{t}) were determined by extrapolation of the linear part of the crystal length (l_t) versus time (t) plots back to the t axis; the induction temperatures (or the critical temperatures) were then estimated as $\bar{T} = T_0 - R_T \bar{t}$. The actual growth time (τ) after the induction periods was given by $\tau = t - \bar{t}$. Overall excess solute concentrations (ΔC_t) at different τ were then estimated from the solubility versus temperature plots [12] as $\Delta C_t = (C_0 - C_t) \text{ mol/g soln}$, where C_0 was the initial concentration and C_t was the concentration at τ . The final overall excess solute concentrations (ΔC_f) at the eutectic temperature (T_{eu}) were then $(\Delta C)_f = (C_0 - C_{eu}) \text{ mol/g soln}$, where C_{eu} was the solubility at T_{eu} . The residual excess solute concentrations $(\Delta C_{sol})_t$ at any τ , and the total crystal weights W_t/M deposited after different τ , were estimated according to Eqs 5 and 7.

Results

Development of supersaturation

(A) *Overall excess solute concentrations.* The overall excess solute concentration (ΔC_t) increase was approximately linear with cooling time and reached the final value $(\Delta C)_f$ at T_{eu} (Figs 1 and 2).

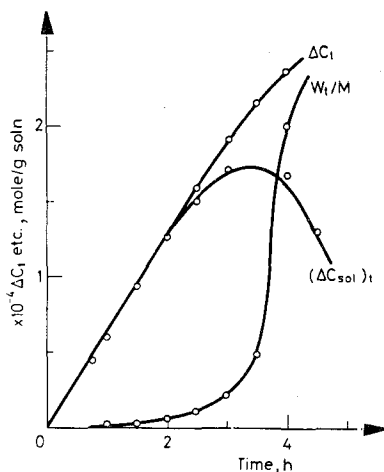


Fig. 1. Crystallization of strontium tungstate from sodium tungstate melts at $T_0 = 800^\circ$ and $R_T = 40^\circ/\text{h}$. Overall excess solute concentrations (ΔC_t), residual excess solute concentrations $(\Delta C_{sol})_t$ and total crystal weights at different times. (W_t/M has no dimensions)

(B) *Total crystal weights.* The total crystal weights increased significantly only after the induction periods. There was a discontinuity in W_t/M versus t plots at $t = t^*$, where t^* was the time after about 80% crystallization; W_t/M values then equalled ΔC_t .

(C) *Residual excess solute concentrations.* Significant crystallization started only after the induction periods (at $t > \bar{t}$) at critical temperatures (\bar{T}); very little material (or perhaps none at all) deposited on the early tiny crystallites until the excess solute concentrations in the solution attained some value $\Delta\bar{C}$. Then the residual excess solute concentrations $(\Delta C_{sol})_t$ in the solution at any cooling time t deviated more and more from the overall excess solute concentrations, gradually attained the maximum value and then deviated rapidly to very low values at $t = t^*$.

The ΔC_t and W_t/M values show that in the early stages the amount of material deposited on the growing crystals was far less than the amount of excess solute concentration developed by cooling. Total crystal weights increased gradually as the excess solute concentration increased with decreasing temperatures, and as this excess solute deposited on the increasing surface of the growing crystals. Then, probably after some time t^* , all the excess solute deposited on the growing crystals and it is assumed that no further growth occurred.

(D) *Critical time (\bar{t}), critical temperature (\bar{T}) and critical excess solute concentration ($\Delta\bar{C}$):* \bar{t} , \bar{T} and $\Delta\bar{C}$ values were estimated (Table 1); \bar{t} values decreased with increased rate of cooling, but $\Delta\bar{C}$ values increased with increased T_0 and R_T . Generally, $\Delta\bar{C}$ equalled 0.20–0.90 ΔC_f .

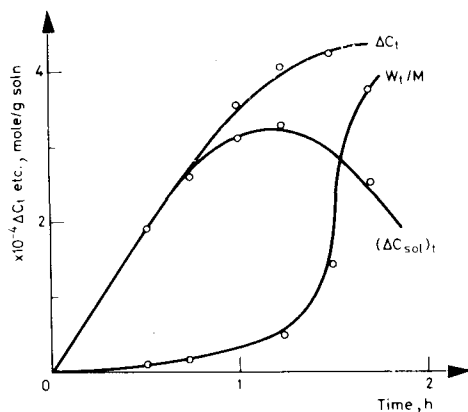


Fig. 2. Crystallization of strontium tungstate from sodium tungstate melts at $T_0 = 1000^\circ$ and $R_T = 200^\circ/\text{h}$. Overall excess solute concentrations (ΔC_t), residual excess solute concentrations $(\Delta C_{sol})_t$ and total crystal weights at different times. (W_t/M has no dimensions)

Kinetics of crystal growth after the induction periods

After the start of cooling, heterogeneous nuclei slowly formed onto metaplatinate particles within the solution during the induction periods. Probably very small crystallites developed onto these nuclei up to the induction periods; their average lengths increased slowly to values $\bar{l} = 0.003$ to 0.01 cm at the end of the induction periods. The kinetics of growth of these small particles were probably rate-controlled by a slow secondary mononuclear nucleation process [9]. The main crystal growth started only after the induction periods, when sufficient amounts of excess solute concentration had developed. Average crystal lengths (l_t) at any growth time (τ) after the induction periods were evaluated from l_t versus t plots; then l_t^2 values were plotted against the corresponding τ (Figs 3–5). l_t^2 generally varied linearly with τ according to Eq. 14 up to $l_t \approx 0.5 l_f$. The linearity of the l_t^2 versus τ relationships indicated that the strontium tungstate crystal growth from sodium tungstate melts was probably diffusion rate-controlled. The initial ratios l_t^2/τ were related to the excess solute concentrations in the solutions at the start of the growth.

The constant A' was evaluated for different crystallizations (Table 1). There was no correlation between these values and R_T .

Table 1

Differential thermal analysis studies on the crystallization of strontium tungstate from sodium tungstate melts. Kinetics and mechanism of crystal growth

Eutectic temperature (T_{eu}) = 565°

Eutectic composition (C_{eu}) = 102×10^{-6} mol/g solution

R_T , °C/h	T_c , °C	R_c , g/g h ⁻¹	\bar{l}_i , h	\bar{T}_i , °C	$\Delta\bar{C}$, g/g soln	A' , cm ² /h
40	800	0.0220	0.50	780	0.0066	1.0
	900	0.0220	0.50	880	0.0096	0.90
	1000	0.0220	1.0	960	0.0276	2.25
120	800	0.0660	0.25	770	0.0116	0.60
	900	0.0660	0.25	870	0.0136	4.70
	1000	0.0660	0.25	970	0.0286	2.75
200	800	0.1100	0.10	780	0.0120	0.90
	900	0.1100	0.125	875	0.0146	4.0
	1000	0.1100	0.25	950	0.0361	4.25

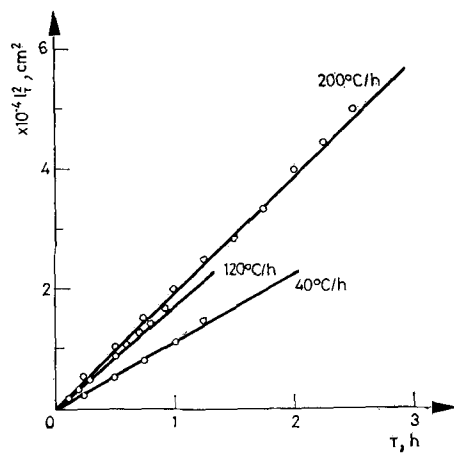


Fig. 3. Crystallization of strontium tungstate from sodium tungstate melts at $T_0 = 800^\circ$. Square of crystal lengths (l^2) at different growth times (τ)

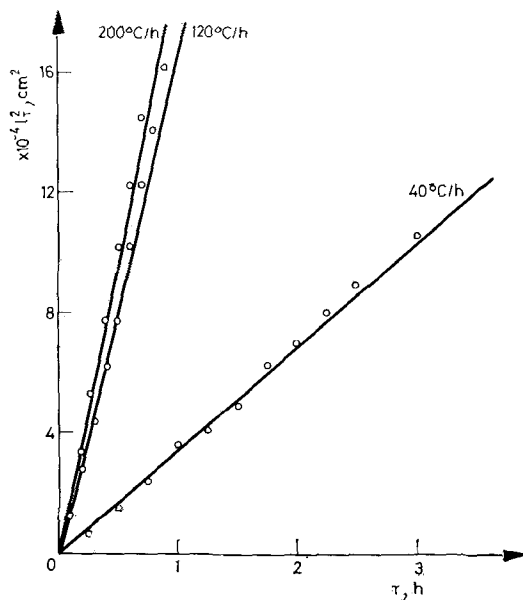


Fig. 4. Crystallization of strontium tungstate from sodium tungstate melts at $T_0 = 900^\circ$. Square of crystal lengths (l^2) at different growth times (τ)

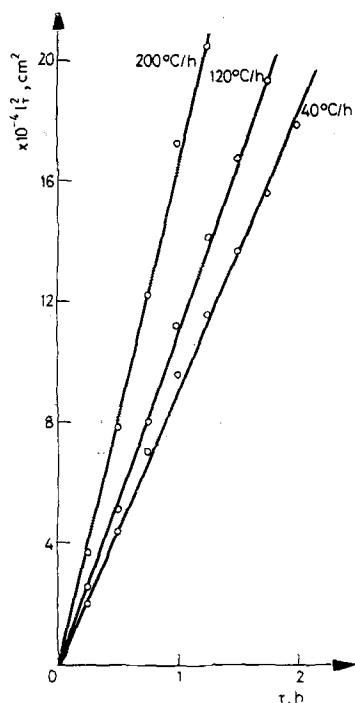


Fig. 5. Crystallization of strontium tungstate from sodium tungstate melts at $T_0 = 1000^\circ$. Square of crystal lengths (l_c^2) at different growth times (τ)

The final growth

At crystallization times $t > t^*$ (growth times $\tau > \tau^*$), all fresh solute released into the solution by further cooling was probably used up instantaneously and deposited onto the large crystals; the residual excess solute concentrations in the solution remained very low. Growth rates then depended only on the rate of development of further excess solute concentration by cooling. For this final growth,

$$\beta(l_c^3 - l^{*3}) = (\tau - \tau^*)R_c \quad (15)$$

or

$$l_c^3 = l^{*3} + b(\tau - \tau^*) \quad (16)$$

where $b = R_c/\beta$ is a constant. Then $l_c = l^*$ at $\tau = \tau^*$. This was observed experimentally.

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RÉSUMÉ — On a étudié par analyse thermique différentielle la cinétique de la cristallisation du tungstate de strontium à partir du tungstate de sodium fondu dans des creusets de platine à des températures de cristallisation: $T_0 = 800^\circ$, 900° et 1000° sous refroidissement continu à des vitesses $R_T = 40$, 120 et 200° par heure. Les noyaux hétérogènes formés initialement sur les particules de platinate du métal dans la solution pendant les périodes d'induction (\bar{t}) grossissent en petits cristallites (\bar{l}). La croissance principale des cristaux commence après le développement d'une concentration d'excès de la substance solubilisée ($\Delta\bar{C}$) à la fin des températures d'induction (\bar{T}). Pour les premiers 80 p. c. de cristallisation, les longueurs moyennes (l_τ) des cristaux variaient avec le temps de croissance (τ) selon la relation: $l_\tau^2 = (\bar{l})^2 + 4\bar{k}_{D_1}M\Delta\bar{C}$, où \bar{k}_{D_1} est la constante de vitesse de la diffusion à des températures proches de \bar{T} et M est le poids moléculaire du sel métallique. Les vitesses de croissance initiale et les rapports l_τ^2/τ dépendent de $\Delta\bar{C}$ et non de R_T . La vitesse des derniers 20 p. c. de croissance n'est contrôlée que par la vitesse du développement de l'excès de concentration de la substance solubilisée.

ZUSAMMENFASSUNG — Die Kinetik der Kristallisation von Strontiumwolframat aus Natriumwolframat-Schmelzen in Platintiegeln wurde durch Differentialthermoanalyse bei den Kristallisationstemperaturen $T_0 = 800^\circ$, 900° und 1000° unter kontinuierlichem Kühlen bei Geschwindigkeiten $R_T = 40^\circ$, 120° und 200° pro Stunde untersucht. Die heterogenen Kerne, welche sich auf den Metallplatinat-Teilchen in der Lösung während Induktionsperioden (\bar{t}) zuerst gebildet hatten wuchsen zu kleinen Kristalliten (\bar{l}) heran. Das Hauptkristallwachstum begann nach der Entwicklung einer überschüssigen Konzentration an gelöster Substanz ($\Delta\bar{C}$) am Ende der Induktionstemperaturen (\bar{T}). Für die ersten 80% der Kristallisation variierten die durchschnittlichen Kristalllängen (l_τ) mit der Wachstumszeit (τ) dem Zusammenhang $l_\tau^2 = (\bar{l})^2 + 4\bar{k}_{D_1}M\Delta\bar{C}$ entsprechend, wobei \bar{k}_{D_1} die Geschwindigkeitskonstante der Diffusion bei Temperaturen in der Nähe von \bar{T} ist und M das Molekulargewicht des Metallsalzes. Die anfänglichen Wachstumsgeschwindigkeiten und die Verhältnisse l_τ^2/τ waren von $\Delta\bar{C}$ abhängig anstatt von R_T . Die letzten 20% des Wachstums waren nur durch die Entwicklungsgeschwindigkeit der überschüssigen Konzentration der gelösten Substanz geschwindigkeitsbedingt.

Резюме — С помощью дифференциального термического анализа изучена кинетика кристаллизации вольфрамата стронция из расплавов вольфрамата натрия в платиновых тиглях при температурах кристаллизации $T_0 = 800^\circ$, 900° и 1000° путем непрерывного охлаждения со скоростью $R_T = 40^\circ$, 120° и 200°C в час. Гетерогенные ядра, первоначально образующиеся в растворе на металл платинированных частицах в течении скрытого периода (\bar{t}), вырастают до небольших кристаллитов (\bar{l}). Главный рост кристаллов начинается после накопления некоторого концентрационного избытка растворенного вещества ($\Delta\bar{C}$) в конце скрытой температуры (\bar{T}). Для начальной 80% кристаллизации средняя длина кристалла (l_τ) изменяется с временем роста согласно уравнения $l_\tau^2 = (\bar{l})^2 \pm 4\bar{k}_{D_1}M\Delta\bar{C}$, где \bar{k}_{D_1} — диффузионная константа скорости при температуре около T , а M — молекулярный вес соли металла. Скорости начального роста и отношения l_τ^2/τ зависят от $\Delta\bar{C}$, вместо R_T . Последние 20% роста контролировалось только скоростью накопления избыточной концентрации растворенного вещества.