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DIFFERENTIAL THERMAL ANALYSIS STUDIES ON THE CRYSTALLIZATION OF STRONTIUM TUNGSTATE FROM SODIUM TUNGSTATE MELT.
NUCLEATION MECHANISM AND INDUCTION PERIODS

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The nucleation mechanism, kinetics and induction periods in strontium tungstate crystallization from sodium tungstate melt in platinum crucibles were investigated by differential thermal analysis. Heterogeneous nuclei first formed on the metal platinate particles within the solution during the induction periods ($\bar{t}$); the main crystal growth started only after $\bar{t}$ and few new nuclei were then formed. At any crystallization temperature, $\bar{t}$ varied inversely with the cooling rate (R_T), and with the rate (R_c) of development of excess solute concentration according to the relation $\bar{t} = 1/(k_1 R_c^{\gamma})$, where k_1 and γ are constants. The critical temperature ($\bar{T}$), critical supersaturation ($\bar{S}$), k_1 and γ were evaluated.

Crystallization of many inorganic materials has been carried out from solutions in metal halide and other melts. Though the degree of supersaturation is the prime controlling factor for the deposition process, the condition of supersaturation alone may not lead to crystallization; crystallization can start only when very minute centres of crystallization (seeds or nuclei) are present or developed within the system. According to Volmer [1] and Becker and coworkers [2], the formation of a crystalline nucleus is a probability phenomenon: a nucleus comes into existence when the lattice-forming units collide in sufficient number so as to produce a particle big enough to be stable at any particular temperature. The shapes of nuclei as first formed are not definitely known, nor it is important to know their shapes to study crystallization; however, the study of the nucleation mechanism and kinetics in any crystallization is fundamental, because these aspects contribute greatly to the mechanism of growth of the final crystals. A survey of the literature reveals that there have been no detailed studies on the nucleation mechanism and kinetics in the crystallization of inorganic materials from solutions in metal halide and other melts; only a few semiquantitative studies have been reported [3, 4]. Heterogeneous nucleations in crystallizations of many soluble metal salts from aqueous solutions at low temperatures have been reported [5, 6].

This paper presents a detailed study of the nucleation process in the crystallization of strontium tungstate from sodium tungstate melt in platinum crucibles by differential thermal analysis. The system exhibited short induction periods;

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these induction periods were measured for different crystallization conditions. The main crystal growth generally started after a slow heterogeneous nucleation process during the induction periods. The kinetics of these heterogeneous nucleations were analysed and the induction periods were related to the cooling rates and nucleation rate-constants.

Kinetics of heterogeneous nucleation

The rate (R_n) of formation of heterogeneous nuclei for any cooling time would be expressed by the relation [7]:

$$R_n(= \mathrm{d}N/\mathrm{d}t) = (N_\infty - N_t)\exp\left[\frac{-f(\sigma_1)\,\Delta G_t^*}{RT}\right] \tag{1}$$

where N_∞ is the total number of potential heterogeneous nuclei in the solution;
N_t is the number of nuclei after any cooling time t;
ΔG_t^* is the free energy for the formation of critical (homogeneous) nuclei;
$f(\sigma_1)$ is the nucleator surface energy function $= \Delta\sigma/2\sigma = \dfrac{\sigma + \sigma_1 - \sigma_2}{2\sigma}$, where σ is the solute surface energy in contact with the solution; σ_1 is the nucleator surface energy in contact with the solute surface; and σ_2 is the nucleator surface energy in contact with the solution.

Since ΔG_t^* after any cooling time t depends on σ, T and the supersaturation S_t at t, we can express

$$\Delta G_t^* = \frac{\beta\sigma_t^3(M/\rho)^2}{2.3\,N_{av}(2.3\,RT_t)^2(\log S_t)^2} \tag{2}$$

where β is a function of the crystal numbers; M is the solute molecular weight; ρ is the solute density; and N_{av} is the average number of nuclei after any cooling time t. Equation (1) then becomes

$$\mathrm{d}N/\mathrm{d}t = (N_\infty - N_t)\exp\left[\frac{-f(\sigma_1)A_t}{(\log S_t)^2}\right] \tag{3}$$

where

$$A_t = \frac{\beta\sigma_t^3(M/\rho)^2}{N_{av}(2.3\,RT_t)^3}$$

Over the narrow ranges of supersaturation and excess solute concentration, Eq. (3) simplifies to [8, 9]:

$$\mathrm{d}N/\mathrm{d}t = k_n(N_\infty - N_t)(\Delta C_t)^p \tag{4}$$

$$= k_n(N_\infty - N_t)(R_c)^p \tag{5}$$

where ΔC_t is the excess solute concentration after any cooling time t; R_c is the development rate of excess solute concentration; k_n is the average "rate constant" for heterogeneous nucleation over the temperature range $T = T_0$ to T_t, T_0 being the initial crystallization temperature; and $p[= 2A_t(\log S_t)^2]$ is the average number of particles in the critical nuclei.

Equation (5) may be written as

$$N_t = N_\infty\left[1 - \exp\left(\frac{-k_n R_c^p t^{p+1}}{p+1}\right)\right]. \tag{6}$$

The nucleation rate would reach its maximum value at a time $t = t_{\text{inf}}$, which corresponds to the inflexion in the N_t *vs.* t relation, i.e. at $\mathrm{d}^2N/\mathrm{d}t^2 = 0$. Then, differentiating Eq. (5) and equating to zero for $t = t_{\text{inf}}$:

$$t_{\text{inf}} = (p/k_n R_c^p)^{1/(p+1)}. \tag{7}$$

Combining Eqs (6) and (7):

$$N_{t_{\text{inf}}} = N_\infty\{1 - \exp\left[-p/(p+1)\right]\}. \tag{8}$$

If p is high, Eq. (8) shows that few new nuclei are formed after $t = t_{\text{inf}}$ and the main growth surge would probably occur after this time. Therefore, the induction period $\bar{t}$ would be given by

$$\bar{t} \simeq t_{\text{inf}} = (p/k_n R_c^p)^{1/(p+1)} = 1/(k_1 R_c^\gamma) \tag{9}$$

where $\gamma = p/(p+1)$;

$k_1 = (\bar{k}_n/p)^{1/(p+1)}$, where $\bar{k}_n$ is the average "rate constant" for heterogeneous nucleation over the temperature range $T = T_0$ to $\bar{T}$, $\bar{T}$ being the induction temperature.

Experimental

Saturated solutions of strontium tungstate in sodium tungstate melt were prepared. Small amounts of saturated solution solid mixtures were than reheated in platinum crucibles in a "Du Pont" 990 Differential Thermal Analyser to initial crystallization temperatures $T_0 = 800, 900$ and $1000°$, and held at T_0 for half an hour to ensure complete remelting. The melts were then cooled down at constant rates $R_T = 40, 120$ and $200°$ per hour to the ambient temperature. The ΔT *vs.* T curves were retraced on millimetre graph-paper. The degree of crystallization (α_t) at different times (t) was estimated as

$$\alpha_t = A_t/A_{\text{total}} \tag{10}$$

where A_t is the area at any time t under the ΔT *vs.* T curve, and A_{total} is the total area under the same curve.

The rate (R_c) of development of excess solute concentration was then $R_c = aR_T$ mol/gh^{-1}, where $a(= dC/dT)$ was the variation of the solubility with temperature. Induction periods ($\bar{t}$) were determined by extrapolation of the linear parts of the crystal length (l_t) *vs.* t plots back to the t-axis [10]; the induction temperatures (or the critical temperatures) were then estimated as $\bar{T} = T_0 - R_T\bar{t}$.

Results

1. *Nucleation*

(A) Extents of crystallization: After different cooling times, these were measured by differential thermal analysis of the melts according to Eq. (10). Some typical $\alpha_T^{2/3}$ *vs.* t relations are presented in Figs 1 – 3. Generally, the α_t values were very low (< 0.055) until after some "induction period" ($\bar{t}$) at some "induction temperature" ($\bar{T}$). This indicated that there was no significant crystallization during the induction period. Immediately after the induction period, at cooling times $t > \bar{t}$, the α_t values increased regularly, and regular growth therefore occurred only after the induction periods.

(B) Crystal lengths: The crystal lengths (l_t) after different crystallization times (t) were evaluated from the relation $\alpha_t = (l_t/l_f)^3$, where l_f is the final crystal length. l_t^2 vs. t relations are presented in Figs 1 – 3 and Insets. Generally, very small crystallites grew shortly after the cooling commenced. These crystallites did not increase significantly during the induction period; their maximum lengths increased to values $\bar{l}$ at the end of the induction periods. These $\bar{l}$ values varied from about 0.003 to 0.01 cm, i.e. from about 0.03 to 0.1 l_f. Therefore, the maximum weights of these crystallites were about 0.004 to 1.0 percent of the maximum weights of the final crystals. Immediately after the induction period the main growth surge occurred; both maximum and minimum crystallites increased rapidly during the crystal growth. During these periods the distribution of maximum and minimum lengths probably remained unchanged. A comparison of Figs 1 – 3 and Insets shows that, at any time during the crystal growth, the l_t values were related to the α_t values according to the relation $l_t^2 = \alpha_t^{2/3} l_f^2$.

These experimental results indicated that the nuclei were first formed at the start of cooling, on metal platinate particles within the solution, and this process continued through the entire induction period. The early nuclei grew to the maximum lengths $\bar{l}$; concurrently, new nuclei were formed and grew to maximum lengths $< \bar{l}$. Then, at the end of the induction periods, regular growth occurred on all the nuclei formed during $\bar{t}$, and it is probable that no new nuclei were formed during the growth process. The slow crystallization probably occurred by a heterogeneous nucleation process similar to that observed in the crystallization of metal salts from aqueous solutions by slow cooling [5 – 7].

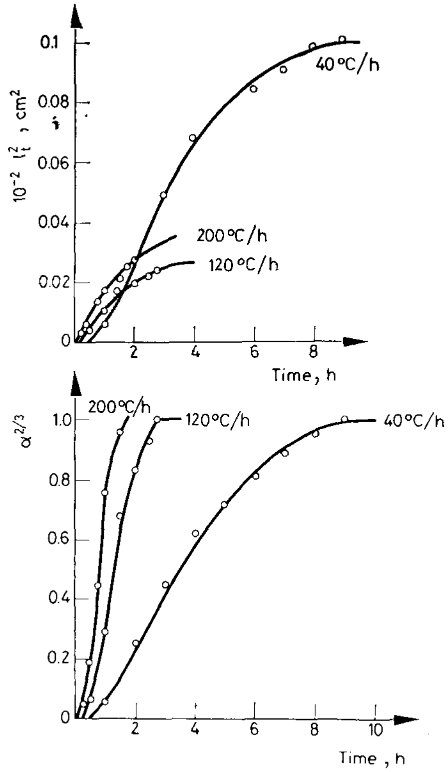

Fig. 1. Crystallization of strontium tungstate from sodium tungstate melt at $T_0 = 800°$. Extents of crystallization after different times

2. *Induction periods*

Strontium tungstate crystal growth from unstirred sodium tungstate melts was found to be diffusion rate-controlled. Therefore, for the initial growth immediately after the induction period, the $\alpha_T^{2/3}$ *vs. t* and the l_t^2 *vs. t* relations varied linearly (Figs 1—3 and Insets). The induction periods ($\bar{t}$), the critical temperatures or induction temperatures ($\bar{T}$) and the critical supersaturations $\bar{S}(= C_0/\bar{C}$, where C_0 and $\bar{C}$ are the solubilities at T_0 and $\bar{T}$, respectively) were estimated (Table 1). The $\bar{S}$ values varied from 1.16 to 1.50. The $\bar{t}$ values varied from 0.100 to 1.0 hour; for any cooling rate, these $\bar{t}$ increased with increasing T_0, but decreased regularly as the cooling rate, and hence the rate (R_c) of development of excess solute concentration, was increased (Fig. 4). $\bar{t}$ was related to R_c according to Eq. (9).The constant k_1 is related to the nucleation rate constant (k_n) and γ can be determined from the "nucleation rate" order [9].

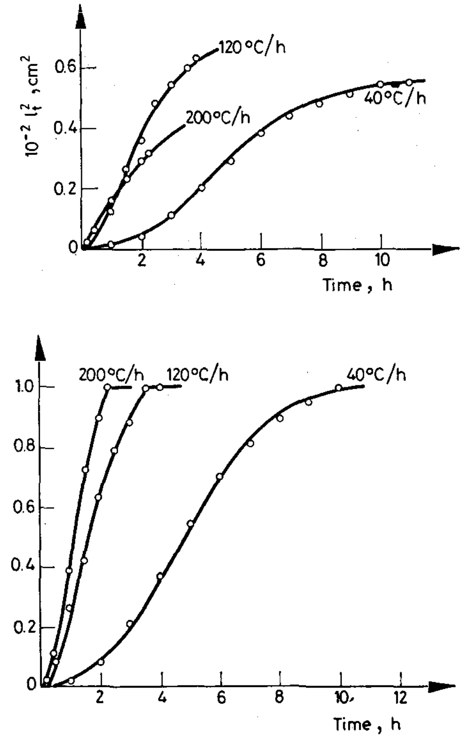

Fig. 2. Crystallization of strontium tungstate from sodium tungstate melt at $T_0 = 900°$. Extents of crystallization after different times

Table 1

Differential thermal analysis studies on the crystallization strontium tungstate from sodium tungstate melt

Induction periods ($\bar{t}$), induction temperature ($\bar{T}$), critical supersaturation ($\bar{S}$), etc.

T_0, °C	R_T, °C/h	R_c, g/g sol h^{-1}	$\bar{t}$, h	$\bar{T}$, °C	$\bar{S}$	γ	k_1, h^{-1}
800	40	0.022	0.50	780	1.20	0.5	15.0
	120	0.066	0.25	770	1.50		
	200	0.110	0.10	780	1.20		
900	40	0.022	0.50	880	1.15	0.5	14.0
	120	0.066	0.25	870	1.26		
	200	0.110	0.125	875	1.20		
1000	40	0.022	1.0	960	1.23	1.0	45.0
	120	0.066	0.25	970	1.16		
	200	0.110	0.25	950	1.31		

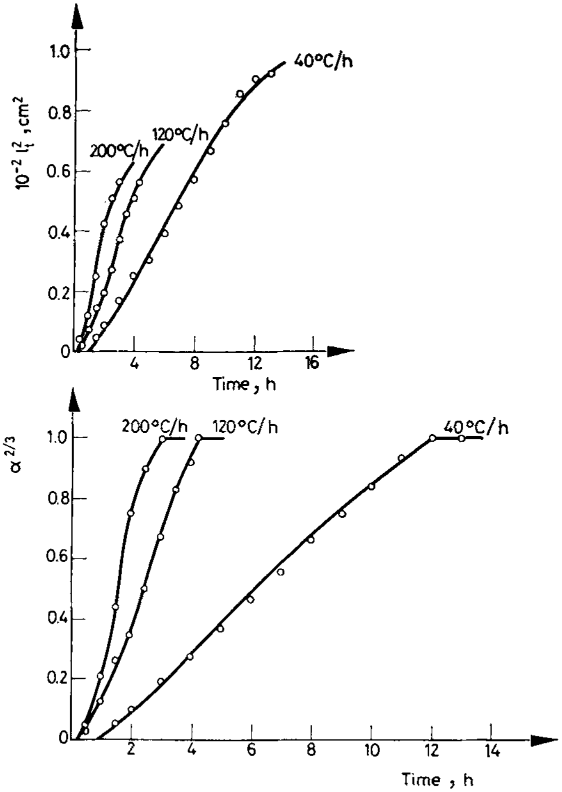

Fig. 3. Crystallization of strontium tungstate from sodium tungstate melt at $T_0 = 1000°$. Extents of crystallization after different times

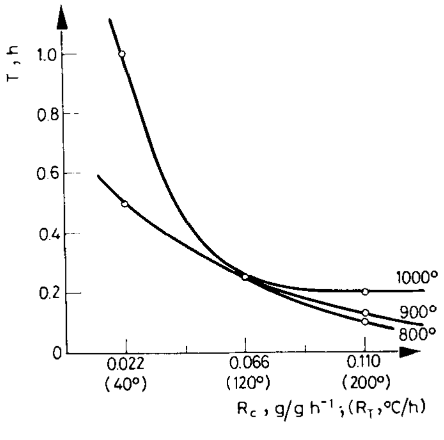

Fig. 4. Crystallization of strontium tungstate melt at different temperatures. Induction periods (t) at different cooling rates (R_T)

3. *Nucleation rate-constant*

k_1 and γ values (Table 1) were determined from $\bar{t}$ and R_c values using Eq. (9). The k_1 values varied from 14 to 45; the γ values were in the range $0.5-1.0$.

Theoretical analysis of Eq. (9) suggests that induction periods at any cooling rate would be determined by some function of k_n. However, since k_n would be dependent on the initial crystallization temperature and also on the function $f(\sigma_1)$, $\bar{t}$ would then be dependent on T_0 and $f(\sigma_1)$. Variations of $\bar{t}$ with T_0 confirmed this phenomenon.

$\bar{t}$ values were rather low for crystallizations at $T_0 = 1000°$ for all R_T. A low $\bar{t}$ suggests a high k_n, i.e. $\sigma_1 \to 0$, $\sigma_2 \to \sigma$ and $\Delta\sigma \to 0$. This means that the nuclear particles were probably adequately wetted during the nucleation. On the other hand, the comparatively high $\bar{t}$ at $T_0 = 800°$ for all R_T suggests low k_n values, i.e. $\Delta\sigma \simeq 2\sigma$ and the nucleator particles were probably inadequately wetted by the solute during the nucleation.

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Résumé — On a étudié par analyse thermique différentielle le mécanisme de nucléation ainsi que la cinétique et les périodes d'induction de la cristallisation du tungstate de strontium, à partir des bains fondus de tungstate de sodium, dans des creusets de platine. Des noyaux hétérogènes se forment d'abord sur les particules de platinate métallique dans la solution, au cours des périodes d'induction (τ): la croissance principale des cristaux ne commence qu'après τ et il se forme alors quelques noyaux nouveaux. A une température quelconque de cristallisation, τ varie de façon inverse avec les vitesses de refroidissement (R_T) et les vitesses de développement (R_c) de concentrations de sursaturation de la substance en solution, selon la relation $\tau = 1/(k_1 R_c^{\gamma})$, où k_1 et γ sont des constantes. On a évalué la température critique ($\bar{T}$), la sursaturation critiques ($\bar{S}$), k_1 et γ.

Zusammenfassung — Der Keimbildungsmechanismus, sowie die Kinetik und die Induktionsperioden wurden bei der Kristallisation von Strontiumwolframat aus Natriumwolframatschmelzen in Platintiegeln durch Differentialthermoanalyse untersucht. Die heterogenen

Kristallkeime wurden zuerst während der Induktionsperiode (τ) an den Metallplatinat-Teilchen in der Lösung gebildet: das Hauptkristallwachstum begann erst nach τ und nachfolgend wurden einige neue Keime gebildet. Bei jeder Kristallisationstemperatur änderte sich τ umgekehrt proportional zu den Abkühlungsgeschwindigkeiten (R_T) und den Geschwindigkeiten (R_c) der Bildung überschüssig gelösten Materials, entsprechend der Gleichung $\tau = 1/(k_1 R_c^{\gamma})$, wobei k_1 und γ Konstanten sind. Die kritische Temperatur ($\bar{T}$), die kritische Übersättigung ($\bar{S}$), k_1 und γ wurden bewertet.

Резюме — С помощью дифференциального термического анализа изучен механизм образования центров кристаллизации, кинетика и индукционные периоды кристаллизации вольфрамата стронция из расплавов вольфрамата натрия в платиновых тиглях. Сначала образуются гетерогенные зародыми кристаллов на металло-платинированных частицах в самом растворе во время индукционных периодов ($\bar{t}$). Основной рост кристаллов начинается только после $\bar{t}$ и тогда образовывалось несколько новых центров кристаллизации. При какой-либо температуре кристаллизации, $\bar{t}$ изменяется обратно пропорционально скорости охлаждения (R_T), а скорости развития (R_c) избытка концентрации растворенного вещества подчиняется уравнению $\bar{t} = 1/(\kappa_1 R_c^{\gamma})$, где κ_1 и γ — константы. Определены критическая температура ($\bar{T}$), критическое сверхнасыщение ($\bar{S}$), κ_1 и γ.