DIFFERENTIAL THERMAL ANALYSIS STUDIES ON THE KINETICS OF CRYSTALLIZATION OF CALCIUM TUNGSTATE FROM SOLUTIONS IN SODIUM TUNGSTATE MELTS

B. N. ROY* and S. APPALASAMI

School of Chemical Sciences, University Sains Malaysia,
Penang, Malaysia

The kinetics of calcium tungstate crystallization from solutions in sodium tungstate melts were studied in a platinum crucible by continuous cooling from an initial crystallization temperature $T_0 = 800°$ to $1000°$ to below the eutectic temperature at cooling rates $R_T = 0.67°$ to $3.3°$ min^{-1}. The main crystal growth was diffusion rate-controlled. The diffusion rate-constant (k_D) values for the growth along the major axis were estimated. Such values increased with the cooling rate and initial crystallization temperature. They were lower than those for diffusion-controlled growth of calcium tungstate from sodium tungstate melts in alumina crucibles. The experimental k_D values were compared with the theoretical k_D values.

Calcium tungstate is an important ceramic material. This material is prepared for various applications by crystallization from different suitable solvents [1 – 3]. Calcium tungstate crystallization from lithium chloride and other melts has been reported [4 – 6]. These works mainly reported studies on the nucleation processes and final crystal numbers and sizes in different crystallizations; some quantitative studies on the kinetics of crystal growth processes were also reported. The present authors have reported studies on the kinetics of crystal growth of calcium tungstate from solutions in sodium tungstate melts in alumina crucibles by continuous cooling [7]. Hitherto, however, there has been no reference in the literature to the kinetics of calcium tungstate crystallization from melts in platinum crucibles.

This paper presents a study on crystal growth kinetics of calcium tungstate from solutions in sodium tungstate melts in platinum crucibles by continuous cooling at different rates from initial temperatures $T_0 = 800°$ to $1000°$ to ambient temperature. The degree of crystallization, crystal lengths and growth rates were measured by differential thermal analysis. If proper experimental conditions are used, DTA measurements give reliable information about the kinetics and mechanisms of crystal growth.

* Present address: Department of Chemistry, University of Science and Technology, Kumasi, Ghana.

Experimental

Calcium tungstate was prepared in situ in sodium tungstate melts from equi-molecular mixtures of the metal carbonate and tungsten trioxide. The saturated solutions were prepared at temperatures slightly higher than the initial crystallization temperature, by heating for several hours inside a "Carbolite" electric furnace (No. 12−70−1173, Carbolite Co. Ltd., Sheffield, England). These solutions were then cooled down rapidly to room temperature; the solidified melt was ground well and dried at 100° for 24 hours to remove any moisture absorbed during grinding. Crystallization was carried out in a differential thermal analyzer (No. 990, E. I. du Pont de Nemours & Co., Wilmington, Del., U. S. A.) at initial temperatures $T_0 = 800°$ to $1000°$, using alumina as a standard. $0.20−0.50$ g of the above sample was taken in a small platinum crucible and the temperature was gradually raised to slightly higher than T_0 at a rate of $20°/min$. It was held constant at that temperature for half an hour to ensure complete melting. Then the temperature was gradually reduced at rates of (i) $40°/hr$, (ii) $120°/hr$ and (iii) $200°/hr$ according to a pre-assigned automatic cooling programme, down to below $300°$. The temperatures were recorded automatically on the chart.

From the DTA curves, the eutectic temperature (T_e) and the degree of crystallization (α_t) at different crystallization times were evaluated.

The eutectic temperature was determined as the initial melting temperature of the mixtures of metal tungstate and sodium tungstate.

The degree of crystallization at any crystallization time (t) is given by $\alpha_t =$
$= \Delta H_t / \Delta H_{total}$. But $\Delta H_t = KA_t$ and $\Delta H_{total} = KA_{total}$
where $\Delta H_t = $ enthalpy change at any time t;

$\Delta H_{total} = $ total enthalpy change during crystallization;
$A_t = $ area under ΔT vs. t plot at any time t;
$A_{total} = $ total area under ΔT vs. t plot;
$K = $ thermal conductivity of the sample.

Neglecting the variation of thermal conductivity with temperature:

$$\alpha_t = A_t / A_{total} \qquad (1)$$

The DTA curves were traced on standard millimeter graph paper and α_t was calculated from Eq. 1. From these α_t values the length (l_t) of calcium tungstate crystals at any time t was estimated from the relation

$$\alpha_t = \left[\frac{l_t}{l_f} \right]^3$$

where l_f is the final crystal length. l_f values were measured by optical microscopy from separate crystallization runs in the "Carbolite" electric furnace mentioned above.

Results

Kinetics

(A) The α_t vs. t plots presented in Figs 1–3 show a regular increase. The α_t value reaches >0.9 in 6–8 hr for 40°/hr, 1.5–3.0 hr for 120°/hr and 1.5–4.0 hr for 200°/hr cooling rate. These plots are linear approximately up to $\alpha_t < 0.13$.

(B) l_t vs. t plots are presented in Figs 4–6. There is no induction period; regular growth occurred and reached the final size in about 7–10 hr for 40°/hr, 2–4 hr for 120°/hr and 1.5–2.5 hr for 200°/hr.

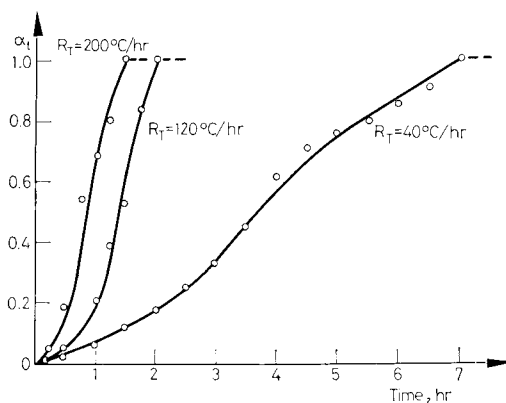Fig. 1. Crystallization of calcium tungstate from solutions in sodium tungstate melts. $T_0 = 800°$. Extents of crystallization after different times

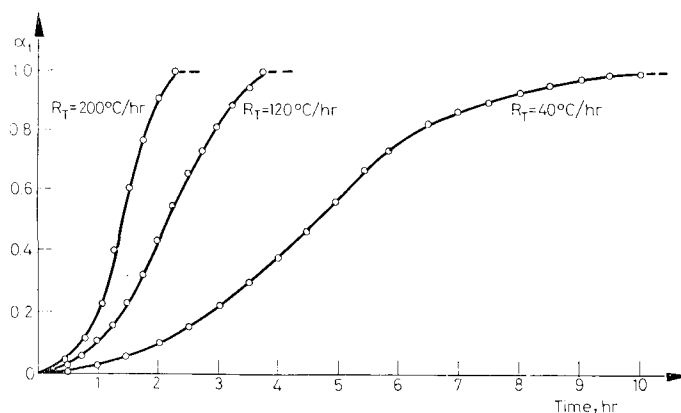

Fig. 2. Crystallization of calcium tungstate from solutions in sodium tungstate melts. $T_0 = 900°$. Extents of crystallization after different times
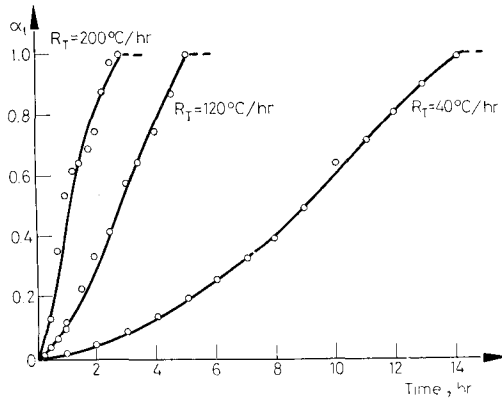
Fig. 3. Crystallization of calcium tungstate from solutions in sodium tungstate melts. $T_0 =$
$= 1000°$. Extents of crystallization after different times

Initial growth-rates (dl/dt) along the major axis in the early stages were measured. The excess solute concentration (ΔC_t) were estimated from solubility vs. temperature plots [7]. The crystal length increased regularly with the growth time and so also did the growth-rate as the crystallization proceeded. These values increased with increase in the initial crystallization temperature and the cooling rate. In all cases, l_t vs. t plots are approximately linear up to about 70% of the growth. This suggests that the growth of calcium tungstate crystals was probably diffusion-controlled.

The main growth

For a system with no induction period, the kinetics of slow crystal growth (rate-controlled by diffusion when growth times are small) may be expressed as [7]

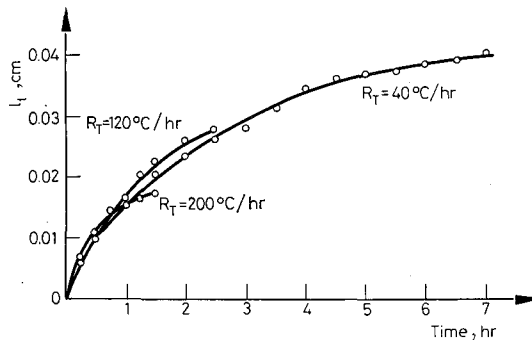$$dl/dt = (2k_{D_1}\Delta C_t)/l = (2k_{D_1}aR_T t)/l \qquad (2)$$

Fig. 4. Crystallization of calcium tungstate from solutions in sodium tungstate melts. $T_0 =$
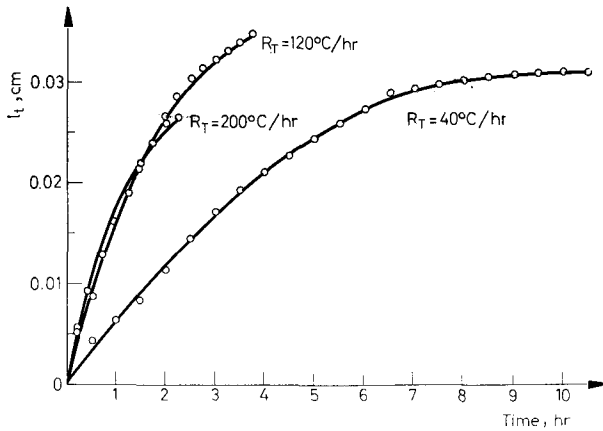$= 800°$. Maximum crystal lengths after different times

Fig. 5. Crystallization of calcium tungstate from solutions in sodium tungstate melts. $T_0 =$ $= 900°$. Maximum crystal lengths after different times
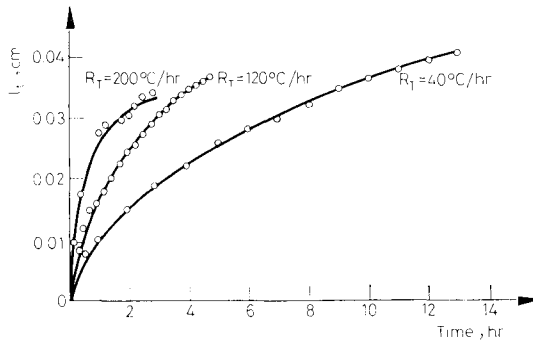

Fig. 6. Crystallization of calcium tungstate from solutions in sodium tungstate melts. $T_0 =$ $= 1000°$. Maximum crystal lengths after different times

where k_{D_1} is the diffusion rate-constant for the growth along the main axis, $a(= dC/dt)$ is the rate development of excess solute concentration by cooling and $R_T(= dT/dt)$ is the cooling rate. Then, from Eq. 2:

$$k_{D_1} = (dl/dt)_0^2/2aR_T \qquad (3)$$

The diffusion rate-constants for initial growth along the main axis were calculated from Eq. 3 and are collected in Table 1. a values were estimated from the solubility vs. temperature plots [5, 7].

The k_{D_1} values increased with the initial crystallization temperature and cooling rate. In general, these values are higher than those for diffusion-controlled growth of calcium tungstate from sodium tungstate melts in alumina crucibles [7].

Diffusion rate-constants and diffusion coefficient

For crystallization by continuous cooling, the growth-rate of crystals at any crystallization time would be expressed by the relation [7]

$$\frac{dl}{dt} \simeq \frac{(4D\Phi\Delta C)}{l}\left[\frac{\rho_{sol}}{\rho}\right] \tag{4}$$

where D is the diffusion coefficient of the metal cations, Φ is the permeability factor, ρ_{sol} is the density of the solution and ρ is the density of the crystals.

From a comparison of Eqs 2 and 4, the minimum value of k_{D_1} for growth of one face would be $(2D\Phi)(\rho_{sol}/\rho)$.

The diffusion coefficients for self-diffusion of alkaline earth metal cations in sodium tungstate or alkali metal tungstate melts have not been reported. Only the work of Borucka [8] shows that for the self-diffusion of sodium in NaCl melts at 800° $D_{Na} = 9.62 \cdot 10^{-5}$ cm²/sec. With this value, the diffusion coefficient of calcium in melts at 800° may be approximated: $D_{Ca} = 92 \cdot 10^{-6}$ cm²/sec.

For crystallization in platinum crucibles by slow continuous cooling, the actual growth occurred at about 750°. As the actual diffusion coefficient depends on the viscosity (η) of the substance, the actual D value of calcium at 750° is [7] $D_{Ca} = 60 \cdot 10^{-6}$ cm²/sec.

The density of the solution at 800° was calculated as 5.63 g/ml. Therefore, the real value of k_{D_1} should be $111.60 \cdot 10^{-6}$ cm²/sec. The estimated k_{D_1} values are much lower than the $(k_{D_1})_{real}$ values. This is probably because of the low Φ value in the solution.

The rate-constants varied from 0.002 to 0.069 D_{Ca++} where D_{Ca++} is the diffusion coefficient of calcium cations at 800°.

Table 1

Crystallization of calcium tungstate at different temperatures
Initial growth-rates and diffusion rate-constants

Crystalliza-tion temperature (T_0), °C	Rate of cooling (R_T), °C/hr	Excess solute concentration (ΔC_t), g/g soln	$R_c\left(=\dfrac{dC}{dt}\right)=a\,R_T,$ g/g soln/°C	Initial growth-rates (dl/dt), cm/hr	$10^{-6}\,k_{D_1}$, cm²/sec
800	40	0.1168	0.0300	0.0059	0.183
	120	0.1168	0.0878	0.0114	0.228
	200	0.1168	0.0942	0.0135	0.291
900	40	0.1809	0.0131	0.0048	0.265
	120	0.1809	0.0449	0.0132	0.560
	200	0.1809	0.0612	0.0217	1.147
1000	40	0.3049	0.0263	0.0080	0.364
	120	0.3049	0.0783	0.0270	1.382
	200	0.3049	0.1300	0.0750	6.400

Discussion

The amount of material and the sizes of the crucibles used in this work were very much smaller than those in the case of crystallization in alumina crucibles [7]. Because of this, the growing crystals probably settled in the crucibles in a densely-packed manner, which in turn resulted in a low pore volume or inter-particle void space. Also, in this work the solutions were unstirred; because of the low free space there was probably very little or no convection in the bulk of the solution. Any convection in the solution was probably mainly due to the thermal agitation of the particles. Due to these factors, the permeability through the inter-particle void space to the reacting surface was possibly hindered.

A low pore volume leads to a low Φ value; consequently, diffusion of material into the reacting surfaces in a cluster of growing crystals is hindered. This makes the diffusion rate of material into the reacting surfaces somewhat lower and thereby decreases the rate-constant for crystallization. These factors were possibly responsible for smaller k_{D_1} values than those for crystallization of calcium tungstate from sodium tungstate melts in alumina crucibles [7].

Seeger [9] has examined diffusion problems associated with crystal growth from dilute solutions. He suggested that a diffusion-controlled growth-rate can be expressed more exactly by the relation

$$\mathrm{d}l/\mathrm{d}t = \frac{(k_{D_1})_{\text{real}}\,(\varDelta C)_{\text{eff}}}{l} \qquad [(5)$$

where $(\varDelta C)_{\text{eff}}$ is the effective excess solute concentration. Then

$$\frac{\mathrm{d}l}{\mathrm{d}t} = \frac{(k_{D_1})_{\text{real}}\,(f \cdot \varDelta C)}{l} \qquad (6)$$

where f is a factor < 1.

Therefore, $(k_{D_1})_{\text{experimental}} = f \cdot (k_{D_1})_{\text{real}}$.

The results suggest that the factor f varies with the initial excess solute concentration. f is low for high $\varDelta C$. Probably, at very small $\varDelta C$ and rate of cooling, $f \to 1$ and $(\varDelta C)_{\text{eff}} \to \varDelta C$.

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RÉSUMÉ — La cinétique de la cristallisation du tungstate de calcium à partir de ses solutions dans le tungstate de sodium fondu a été étudiée dans un creuset de platine au cours du refroidissement continu depuis la température initiale de cristallisation $T_0 = 800$ à $1000\,°$C jusqu'à température inférieure à celle de l'eutectique, avec des vitesses de refroidissement allant de 0.67 à $3.3\,°$C $\cdot$ min^{-1}. La croissance des cristaux est contrôlée principalement par le processus de diffusion. Les valeurs de la constante de vitesse de diffusion (k_D) ont été estimées pour la croissance le long de l'axe principal. Ces valeurs augmentent avec la vitesse de refroidissement et la température initiale de cristallisation et sont plus faibles que les valeurs correspondantes en creusets d'alumine. Les valeurs expérimentales et théoriques de k_D sont comparées.

ZUSAMMENFASSUNG — Die Kinetik der Kristallisation von Calciumwolframat aus Lösungen von Natriumwolframatschmelzen wurde im Platintiegel durch kontinuierliches Kühlen von der Anfangskristallisationstemperatur $T_0 = 800°$ bis $1000°$ bis unter die eutektische Temperatur, bei Abkühlgeschwindigkeiten von $R_T = 0.67°$ bis $3.3°$ min^{-1}, untersucht. Das Hauptkristallwachstum wurde durch die Diffusionsgeschwindigkeit bedingt. Die Werte der Diffusionsgeschwindigkeitskonstante (k_T) in Richtung der Hauptachse wurden geschätzt. Diese Werte nahmen mit der Abkühlgeschwindigkeit und der Anfangskristallisationstemperatur zu. Sie waren niedriger als jene des diffusionsbedingten Wachstums von Calciumwolframat aus Natriumwolframatschmelzen in Aluminiumtiegeln. Die experimentellen k_D-Werte wurden mit den theoretischen k_D-Werten verglichen.

Резюме — Изучена кинетика кристаллизации вольфрамата кальция из растворов расплавленного вольфрамата натрия в платиновом тигле путем непрерывного охлаждения от начальной температуры кристаллизации $T_0 = 800°$ до $1000°$ ниже температуры эвтектики при скорости охлаждения от $R_T = 0.67°$ до $3.3°$ мин$^{-1}$. Рост кристаллов контролируется скоростью диффузии. Установлены константы скорости (k_D) диффузии роста кристаллов вдоль их главной оси. Эти величины увеличиваются с увеличением скорости охлаждения и начальной температуры кристаллизации. Они были более низкими по сравнению с теми, которые были установлены в случае диффузно-контролируемого роста вольфрамата кальция из расплавов вольфрамата натрия в тиглях из окиси алюминия. Экспериментальные значения k_D были сопоставлены с теоретическими.