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Relative supersaturation and supercooling in fluxed melt systems

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This paper reports the investigation of relative supersaturation and supercooling in solutions of Dy_2O_3 in $K_2O \cdot 2MoO_3$ and $K_2O_3 \cdot 3MoO_3$, which result in $DyKMo_2O_8$ crystals when cooled. It is shown that the relative supersaturation required for nucleation on platinum is higher in melts of the former compositions which yielded fewer, larger crystals. In each case, the degree of critical supercooling is proportional to the absolute saturation temperature, and it is shown that this also applies to the fluxed melt systems which yield $Ho_2Si_2O_7$ and $TbVO_4$. Measurements were made by thermogravimetric analysis (TGA), under conditions comparable to flux growth by slow cooling.

1. Introduction

The growth of crystals by the flux method has been extensively used, resulting in several reviews [1, 2] in recent years. However, a physical factor which is associated with the growth of few, large crystals rather than many small ones has not been identified as yet. Elwell *et al.* investigated the well-known beneficial effect of the addition of a few per cent of B_2O_3 to solutions of $PbO+PbF_2$, and showed that the viscosity and surface tension of the melts were scarcely altered [3].

It has been shown that in pseudoternary systems the flux growth of compounds consisting of a refractory and an acidic oxide is greatly affected by the ratio of basic oxide or oxide plus fluoride to the acidic oxide content of the melt [4]. When the acidic oxide content is decreased to the minimum excess required to produce the compound, the number of crystals obtained by spontaneous nucleation is greatly decreased, and often a habit change is observed. In a study of the Dy_2O_3–K_2O–MoO_3 system, it has been observed that solutions of Dy_2O_3 in $K_2O \cdot 3MoO_3$ yielded many platelets of $DyKMo_2O_8$ about 0.1 mm thick, whereas its solution in $K_2O \cdot 2MoO_3$ produced plates up to 3 mm thick [5], when experimental conditions were as similar as possible. Further increase in the K_2O concentration was not in question, since another primary phase, Dy_2MoO_6, then occurred.

Many studies of relative supersaturation and supercooling have been undertaken in the fields of aqueous and industrial crystallization; the present work represents the first such studies in high-temperature solution growth.

2. Experimental details

The chemicals used were: Rare Earth Products 99.9% pure Dy_2O_3; BDH "Analar" MoO_3 and K_2CO_3. The materials were weighed within ± 0.05 g, and the fluxes $K_2O \cdot xMoO_3$ ($x = 2$ and 3) were prepared separately by melting K_2CO_3 and MoO_3 in stoichiometric quantities at 550° C, to remove CO_2. There was no additional weight loss. Dy_2O_3 was calcined before use. The compositions used are given in Table I.

In addition to studies in the system Dy_2O_3–K_2O–MoO_3, similar experiments were carried out in this Laboratory in the systems Ho_2O_3–SiO_2–Bi_2O_3–V_2O_5 [6] and Tb_4O_7–PbO–V_2O_5 [7], yielding $Ho_2Si_2O_7$ and $TbVO_4$, respectively.

The TGA apparatus is based on that of Smith and Elwell in which the change in weight of a platinum wire, suspended with its free end in the melt, is monitored [8]. Modifications to this will be described elsewhere [6]. A Pt versus Pt–13% Rh thermocouple, sheathed in platinum, was calibrated and inserted in the melt to measure its temperature. Temperature measurement was estimated at ± 5° C. The crystallizing phase was

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TABLE I Melt compositions, saturation temperatures T^*, supercooling ΔT and reduced temperatures T_r

Crystal phase		Melt composition (mol%)				T^* (K)	ΔT (K)	T_r	Reference
		$DyKMo_2O_8$	K_2O	MoO_3					
$DyKMo_2O_8$	A (Fig. 1a)	3.74	33.32	62.94		1148	43	0.963	Present work
		8.36	33.32	58.29		1182	45	0.962	Present work
		16.26	33.32	50.41		1212	46	0.962	Present work
	B (Fig. 1b)	2.74	24.68	72.57		1098	40	0.963	Present work
		6.05	24.44	69.50		1143	41	0.964	Present work
		10.10	23.79	66.10		1173	44	0.962	Present work
		$Ho_2Si_2O_7$	SiO_2	Bi_2O_3	V_2O_5				
$Ho_2Si_2O_7$		8.20	9.15	65.80	16.85	1513	55	0.963	[6]
		9.14	7.44	66.41	16.99	1548	60	0.961	[6]
		11.25	9.95	62.74	16.06	1571	55	0.964	[6]
		16.50	8.36	59.83	15.31	1601	56	0.965	[6]
		$TbVO_4$	PbO	V_2O_5					
$TbVO_4$		1.37	49.25	49.37		1356	49	0.964	[7]
		1.72	49.10	49.20		1402	54	0.961	[7]

identified by its X-ray powder pattern. At the end of the experiment, the weight losses due to flux volatilization were determined.

In a typical experiment, a 20 cm^3 crucible of pure platinum was filled with a mixture of Dy_2O_3, K_2CO_3 and MoO_3 corresponding to the compositions shown in Table I. The melt was held for 16 h at a temperature high enough to ensure complete dissolution prior to immersion of the end of the platinum wire. The melt was cooled at 15 K h^{-1} and the apparent weight of the wire recorded. A change in weight of ± 0.1 mg could be detected. The cooling was continued until a discontinuity in the rate of change of the weight with temperature was observed and the corresponding melt temperature was taken as the crystallization temperature of the compound. The difference in crystallization temperatures when the rates of cooling were 30 and 6 K h^{-1} was typically below 3° C, and within the error in measuring the temperature. Thus it was not expected that further decrease to the slower rates usual in flux growth would materially affect the temperature of crystallization. The melt was then heated at 6 K h^{-1} and the temperature at which the last traces of crystalline material disappeared was taken to be the solubility temperature, as observed by a discontinuity in the weight and by visual inspection of the wire.

3. Results

The starting compositions of $DyKMo_2O_8$ chosen for solubility studies are given in Table I. At the temperatures and starting compositions with which this study is concerned, $DyKMo_2O_8$ is the primary phase. Solutions of Dy_2O_3 in $K_2O \cdot 2MoO_3$ and $K_2O \cdot 3MoO_3$ resulted in thick and thin crystals respectively, after slow cooling of the solutions [5]. The solubility and the crystallization temperatures as a function of molar concentration

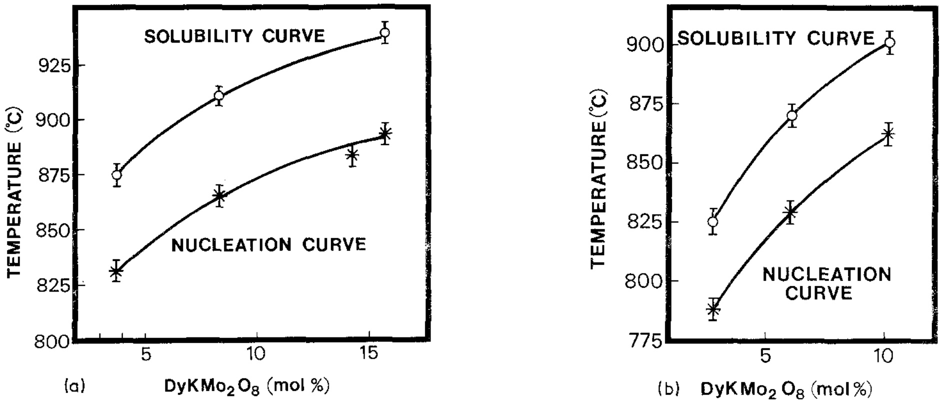

Figure 1 Solubility and crystallization temperatures of $DyKMo_2O_8$ (a) in $K_2O.2MoO_3$ and (b) in $K_2O.3MoO_3$.

of $DyKMo_2O_8$ in the two pseudobinary flux systems are shown in Fig. 1a and b. The starting compositions which yielded $Ho_2Si_2O_7$ and $TbVO_4$ are given in Table I.

The main errors in the solubility determinations were errors in weighing the starting compositions, in temperature control, and those owing to flux volatilization. The total error in the measurements is estimated at approx. ± 7.5% at low concentrations, and ± 5% at high concentrations.

4. Discussion

4.1. Solubility

The solubility expressed as mol% $DyKMo_2O_8$ (see Table I) increased with the concentration of MoO_3, as shown in Fig. 1. Similar increases have been observed in systems containing $A_2O–MoO_3$ for $ZrSiO_4$ (A = Li, Na, K) and for Be_2SiO_4 (A = Li, Na) [9]. The crystallization temperatures are in good agreement with those estimated by the viscosity method for the same starting compositions [10].

4.1. Supercooling

The supercooling, ΔT, of a melt or solution is defined as:

$$\Delta T = T^* - T$$

where T^* and T are the melting or saturation temperature and the nucleation temperature, respectively. The nucleation rate depends upon the degree of supercooling and the reduced temperature [11, 12] where the reduced temperature $T_r = T/T^*$.

Values of T_r have been reported to be 0.82 for metals and alkali halides [13], and between 0.93 and 0.97 for *n*-alkanes [14, 15]. In practice, crystallization is usually a result of heterogeneous nucleation, and thus the degree of supercooling is less, since the substrate affects the nucleation rate.

Turning to solutions, Brice [12] has listed data for aqueous solutions, which have a median value for T_r of 0.97. However, the value of the reduced temperature has not previously been investigated for molten salt solutions. Table I shows the reduced temperatures for a number of molten salt solutions investigated here. The data for the molten salt systems indicate an average value for T_r of 0.963 and this conformity may relate to the following facts: (1) In all cases, the substrate on which heterogeneous nucleation occurred is platinum. (2) The rates of cooling were similar. (3) At the temperatures in question, it can be expected that all inorganic impurities will have dissolved. (4) The compound crystallizing from each system studied contained small, highly charged metal ions such as Si^{4+}, V^{5+} and Mo^{6+}, all of which tend to form complex ions of the type $(M^{x+}O_4)^{(8-x)-}$ in solution.

Applying this relationship to crystal growth from molten salt solutions, it is now evident that after a "soak" period, perhaps 20 or 30° C above the saturation temperature, it is necessary to cool the melt to a crystallization temperature which is about 40° C below the saturation temperature before nucleation commences on the platinum surface, for saturation temperatures in the range 1100 to 1260° C. It would thus be reasonable to cool from the soak temperature to 40° C below it at a relatively rapid rate (say, at $50\,K\,h^{-1}$) without risk of nucleation, and then to continue cooling at the lower rates, near $1\,K\,h^{-1}$, usual in flux growth.

4.3. Relative supersaturation required for nucleation on platinum, σ_n

The relative supersaturation, σ_n, at a given temperature t is defined by the relationship

$$\sigma_n = \frac{c - c^*}{c^*}$$

where c is the solution concentration at t and c^* is the equilibrium saturation, or solubility, at t. As shown in Table II, σ_n remains almost constant over the temperature range studied. At 860° C, the relative supersaturation for $DyKMo_2O_8$ in $K_2O\cdot 2MoO_3$ is 1.8, whereas that relating to $K_2O\cdot 3MoO_3$ is 0.92. Thus the relative supersaturation for the melts which produced fewer,

TABLE II Solution concentration c, equilibrium saturation or solubility c^*, and relative supersaturation σ_n at given temperatures.

T (° C)	C (mol%)	C^* (mol%)	σ_n	Composition range
880	11.4	4.1	1.78	flux $K_2O\cdot 2MoO_3$
870	9.2	3.3	1.78	
860*	7.5	2.7	1.77	
860*	9.8	5.1	0.92	flux $K_2O\cdot 3MoO_3$
850	8.4	4.3	0.95	
840	7.2	3.6	1.0	
830	6.1	3.0	1.0	

*Values taken from extrapolated curves of Fig. 1a and b.

thicker crystals is higher by 100% than for those which produced many thin crystals.

A recent study has shown that the viscosities of the melts investigated in this work lie between 1 and 6 cP [16] (extremely low compared with other flux systems, where the viscosity is typically in the range 1 to 100 cP [1]). Such small differences in viscosities are unlikely to affect nucleation or supersaturation. Whether or not the number and habit of crystals obtained by flux growth are, in general, related to the relative supersaturation required for nucleation will be revealed by further investigations now in progress at this laboratory.

5. Conclusions

(1) It is shown that in the several fluxed melt systems investigated, where the actual supercooling varies from 40 K at 1100 K to 56 K at 1600 K, the temperature of nucleation is proportional to the saturation temperature, with a reduced temperature, T_r, of 0.963.

(2) It has been shown that in the system Dy_2O_3–K_2O–MoO_3, the relative supersaturation required for nucleation is much higher in the melts producing thick crystals as compared to those producing thinner crystals.

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