

An improved thermobalance for crystallization studies in fluxed melts

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This paper describes apparatus which has been specifically developed for crystallization studies by thermogravimetric analysis (TGA) and can also be readily adapted for crystal growth by top-seeding. Experimental data on the crystallization of DyPO_4 , TiO_2 , Fe_2O_3 and TmVO_4 are tabulated.

1. Introduction

Crystallization temperatures in fluxed melts can be determined by means of a thermobalance [1, 2] and the method has been used by various authors [3-10] to obtain solubility data for a variety of materials. In this method a platinum wire is suspended from the balance with its lower end immersed in the melt, which is heated in a temperature gradient, and crystallization occurs on the tip of the wire when the melt becomes supersaturated. The growth or dissolution of the crystals can then be monitored from changes in the apparent weight of the wire. A number of improvements in both apparatus and technique have been made since the method was first introduced and these are described below.

2. Apparatus

The apparatus is shown schematically in Fig. 1. An electrobalance type 2TS5 (CI Electronics), which accepts loads up to 5 g, is situated above a 5 cm bore vertical tube furnace and can be raised or lowered either manually or automatically. A platinum wire, 0.5 mm in diameter, suspended from the balance can thereby be readily introduced into the furnace. The balance is protected from accidental overloads by the simple arrestment shown in Fig. 2 and additional damping is provided by two aluminium cylinders immersed in silicone oil. An opaque enclosure prevents changes in the ambient light from affecting the balance photocell.

The fluxed melt is contained in a platinum

crucible which is supported by a movable pedestal. The position of the crucible can be adjusted by a rack and pinion and the depth of immersion of the platinum wire can be accurately determined by reference to a vernier. The wire passes through an aperture in a mirror mounted above the furnace and set at 45° to the horizontal. The lower end of the wire and the surface of the melt can thereby be observed either by eye or with the aid of a telescope. The effects of changes in air pressure in the extraction system on the suspended wire are reduced by a fine gauze (see Fig. 1). The furnace is heated by a Morgan Crusilite DM element and the temperature is regulated by a West Viscount controller. A Eurotherm twin-range or a Clarendon Laboratory programmer is used to provide heating and cooling rates in the range 1 to 150 K h^{-1} , and temperatures are measured by a Comark electronic thermometer. The temperature of the pedestal and the balance reading are displayed by a JJ Instruments twin-pen recorder or a Linseis three-pen recorder. The third pen is used to display the furnace temperature. The balance assembly is demountable and can be replaced by a seed-rotation mechanism. In this modified form the apparatus has been used for top-seeded solution growth [11].

3. Experimental procedure

Johnson Matthey crucibles of 20 cm^3 capacity and 0.25 mm wall thickness were used, one with a special re-entrant tube in the base for a Pt/Pt-13% Rh thermocouple, as shown in Fig. 3.

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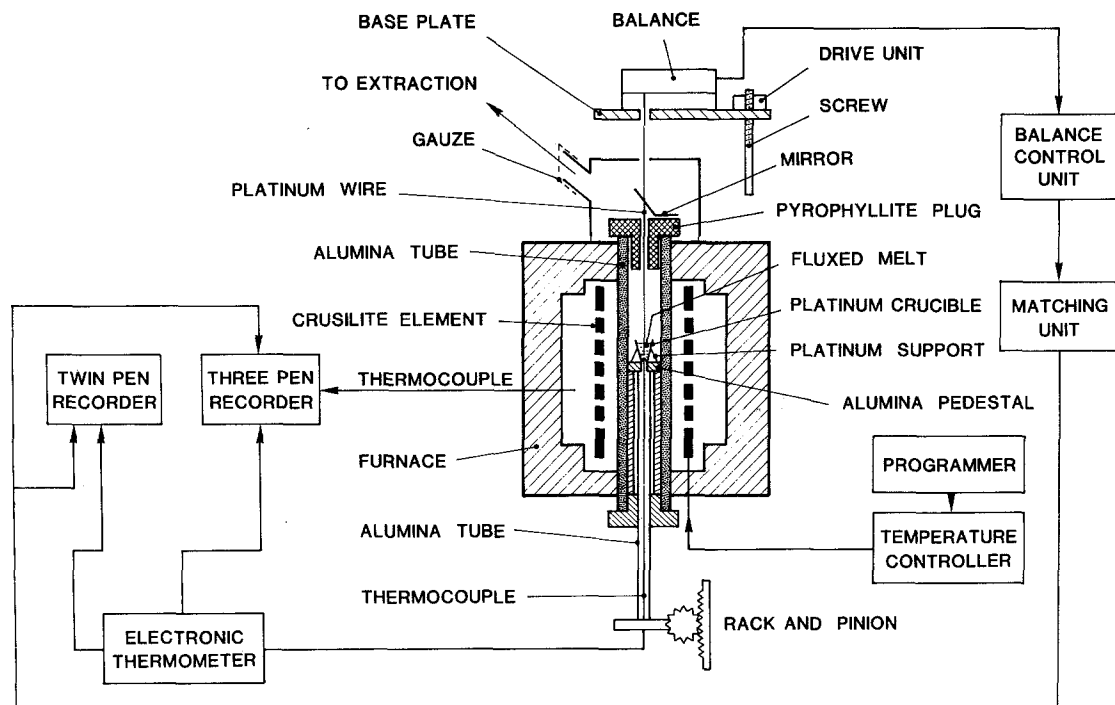


Figure 1 Schematic diagram of the thermogravimetric apparatus.

The chemicals were Rare Earth Products 99.9% rare earth oxides; Johnson Matthey "Specpure" Fe_2O_3 ; British Drug Houses "Analar" PbO , $\text{NH}_4\text{H}_2\text{PO}_4$, Bi_2O_3 , TiO_2 and silica gel (60 to 120 mesh); BDH laboratory reagent grade V_2O_5 . The materials were weighed to ± 0.05 g.

Fluxes were prepared by premelting weighed quantities of the constituents and then added calculated amounts of calcined refractory oxides. After heating to the required soak temperature for 12 to 24 h in the tube furnace, the platinum wire was immersed to a depth of 1 to 2 mm. At high temperatures, when the wire was prone to

disturbances caused by convection, it was replaced by several short lengths hooked one above the other to damp oscillations.

In the range 1000 to 1200°C, the vertical temperature gradient along the axis of the furnace was 4 K cm^{-1} , with the top of the crucible at the lower temperature. The vertical temperature gradient in the melt was typically 5 K cm^{-1} and the radial gradient about 2 K cm^{-1} . These conditions ensured that crystallization occurred preferentially on the tip of the platinum wire.

Crystallization on cooling and dissolution on heating were first observed during programming

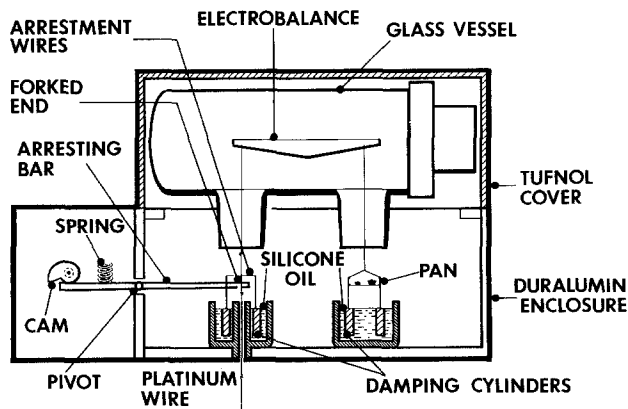


Figure 2 Schematic diagram of the balance with arrestment mechanism and fluid damping.

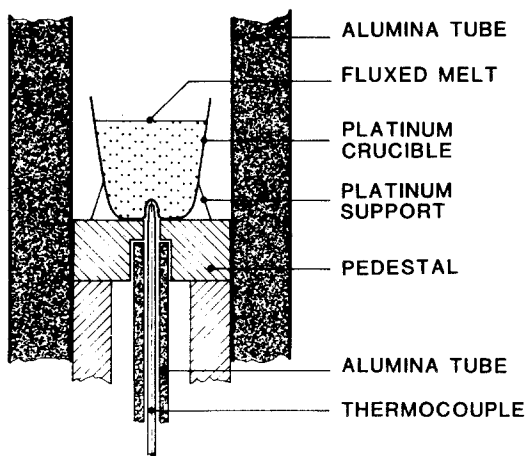


Figure 3 Platinum crucible with re-entrant tube and thermocouple.

at up to 30 K h^{-1} and then monitored with greater precision at $\leq 12\text{ K h}^{-1}$. The crystallization temperature T_c and the liquidus temperature T_l at the point of immersion of the platinum wire were obtained from the crucible base temperature shown on the chart with the aid of calibration measurements. These were made with a Pt/Pt-



Figure 5 Crystals of TmVO_4 .

13%Rh probe thermocouple enclosed in a thin platinum sheath. The accuracy of the thermocouple was checked periodically.

4. Results

A typical chart record is shown in Fig. 4. Crystallization is indicated by (a) a progressive increase in the apparent weight of the wire, and (b) irregular oscillations which increase in amplitude with further cooling.

Dissolution on heating is apparent from a pro-

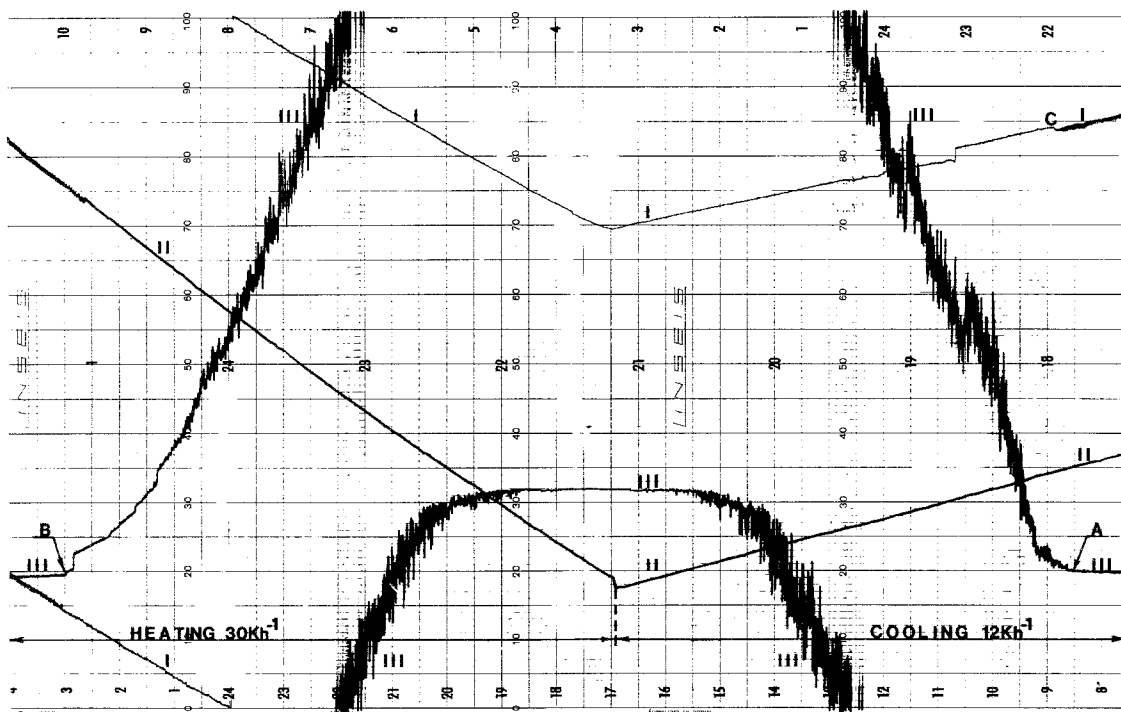
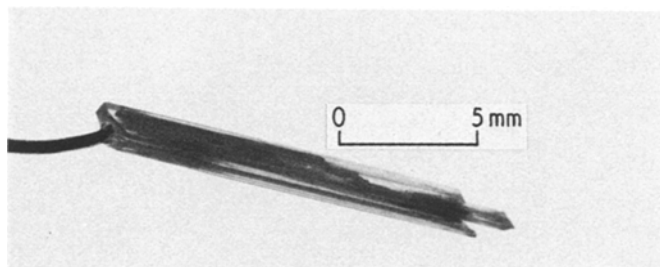


Figure 4 Chart record showing crystallization and dissolution of TmVO_4 . I. Crucible temperature (sensitivity 20 K in^{-1}). II. Furnace temperature (sensitivity 16 K in^{-1}). III. Apparent weight of platinum wire (sensitivity 7.5 mg in^{-1}). A. Start of crystallization. B. End of dissolution. C. Displacement due to latent heat of crystallization. Chart speed 72 mm h^{-1} . Chart scales: 10 mm divisions (||) time axis. 25 mm (1 in) divisions (⊥) time axis.

Figure 6 Crystal of DyPO₄.



gressive decrease in the amplitude of these oscillations, and the liquidus is indicated by the point at which the weight signal returns to the base line value and the oscillations cease. The cessation of oscillations at the maximum apparent weight is the result of overloading the electrobalance. The oscillations are accounted for by the formation of small crystals, as shown in Fig. 5, which grow rapidly into the melt, where they are affected by convection currents. Filamentary crystals of TmVO₄ up to 10mm length and down to 0.01 mm thickness were recovered in some experiments. The cessation of oscillations can thus provide a very sensitive indicator of complete dissolution. At slow cooling rates a single crystal can be grown, as shown in Fig. 6.

Fig. 4 also shows that the use of a crucible with a re-entrant tube and thermocouple in the base allows latent heat effects to be displayed simultaneously. In this way thermobalance measurements can be confirmed. The sensitivity of the electrobalance is, however, far greater. In systems of low volatility accurate results can be obtained under near equilibrium conditions.

The apparatus has been used in a variety of investigations concerned with the crystallization of

simple and complex oxides, and some results are given in Table I. The chief use has been to determine starting compositions for flux growth experiments and to assess the possibilities of gradient transport or top-seeding, rather than the determination of phase diagrams.

5. Conclusion

The thermobalance has proved useful in studies of crystallization, solubility, supercooling [10] and gradient transport [11]. It has also been used to investigate changes in the crystal habit of DyPO₄ accompanying changes in the composition of PbO–P₂O₅ fluxes [10], and the growth of DyKMO₂O₈ [8]. When used in conjunction with the demountable seed-rotation assembly [11], optically clear crystals of DyVO₄, TbVO₄ and TmVO₄ were grown. The fact that the electrobalance and seed-rotation assembly can be interchanged when the furnace is hot is an advantage.

Recent studies with the thermobalance have shown that measurements of crystallization temperature are affected by the previous treatment of the platinum wire. Details of this work will be published elsewhere.

TABLE I Starting composition and crystallization temperatures for some oxide crystals

Starting composition (mol %)	Crystal	Soak temperature (° C)	Crystallization temperature (° C)	Evaporation loss (wt %)
1.5 Dy ₂ O ₃ 64.7 PbO 33.8 Pb ₂ O ₅	DyPO ₄	1090	1035 ± 2.5	< 1
12.8 TiO ₂ 55.7 PbO 31.5 V ₂ O ₅	TiO ₂	1060	986 ± 3	< 1
6.0 Fe ₂ O ₃ 53.7 PbO 40.3 V ₂ O ₅	αFe ₂ O ₃	1050	957 ± 3	0.8
0.8 Tm ₃ O ₃ 49.2 PbO 50.0 V ₂ O ₅	TmVO ₄	1180	1098 ± 1.5	0.9

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