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DIFFERENTIAL THERMAL ANALYSIS OF FLUXED MELTS AND ITS APPLICATION TO THE SYSTEM $NiFe_2O_4-BaO-B_2O_3$

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The application of DTA to fluxed melts is discussed, and an apparatus for the determination of the solubility of crystalline materials in molten solutions is described. An exploratory study of the crystallization of nickel ferrite from barium borate fluxes is also described, and solubility curves are presented for fluxes which favour crystal growth. The heat of solution of nickel ferrite was found to be 73 ± 2 Kjoule $mole^{-1}$.

1. Introduction

Fluxed melt techniques [1, 2] are extensively used for the preparation of materials in the form of single crystals, particularly those which are difficult to grow from pure melts. In these techniques, the materials or their constituents are dissolved in suitable molten solvents, and crystals are formed when the solutions become supersaturated.

For the growth of crystals of a particular material from a fluxed melt, sufficient phase equilibrium data is required for the liquidus curve and the stability field of the material to be established, but a detailed analysis is unnecessary. DTA has seldom been used for the acquisition of such data for fluxed melts [3—8] and in only a few instances has the method been applied at temperatures above 1000° [3—6]. Few details of the apparatus which was used in these investigations have been reported.

In this paper the application of DTA to fluxed melts is discussed, and the construction of apparatus which has been developed for this application is described. Results of an investigation into the formation of nickel ferrite, $NiFe_2O_4$, in the system $BaO-B_2O_3-NiO-Fe_2O_3$ are presented. The flux system $BaO-B_2O_3$ was chosen for this investigation mainly because fluxes in this system are appreciably less volatile than most of the molten solvents in current use.

2. Basic problems

In the application of DTA to fluxed melts, a number of problems are encountered, the most important of which are summarised below.

(i) The samples are corrosive, molten solutions which can be contained only in crucibles of a chemically inert material such as platinum.

(ii) The interior of the sample holder is exposed to chemical attack by the samples, since fluxes tend to form films of liquid on the outer surfaces of the crucibles which contain them.

(iii) Since fluxes are often volatile at high temperatures, other parts of the sample holder assembly are also exposed to chemical attack, particularly those on which the fluxes remain in the liquid phase after condensation.

(iv) As a result of the high temperatures and the corrosive nature of the samples, the choice of thermocouple materials is restricted to platinum and its alloys. Since such thermocouples have small electromotive forces, the differential electromotive force is very small.

(v) Fluxed melts rarely contain more than 25% by weight of solute, only part of which may crystallize in a particular phase, and the variation of solubility with temperature can be small. The effect on ΔT of crystallization or dissolution of the solute may thus be minute.

(vi) Since crystal nuclei must exceed a critical size prior to growth, a fluxed melt must be supercooled before crystallization occurs, and the DTA curve for such a sample consequently indicates an erroneous value of the liquidus temperature. Although the magnitude of the error may be estimated by comparison of the curves which are obtained during heating and cooling, the problem of supercooling is ideally avoided by the addition of seed crystals at the liquidus temperature [9]. The adoption of this procedure, however, adds to the complexity of both the apparatus and the experimental technique.

(vii) Crystallization from fluxed melts is a slow process, and the rates at which melts may be cooled without becoming excessively supersaturated are limited to small values. Adequate time is thus available for the transfer of heat from the melt to the sample holder, and so ΔT remains small during crystal growth.

(viii) The thermal properties of samples vary with temperature, in particular as a result of the formation of a layer of solute on the inner surfaces of the crucibles during cooling. This phenomenon causes a progressive displacement of the ΔT base line as the thickness of the layer increases.

(ix) Convection currents can occur in that part of the sample which is in the liquid state and may cause spurious fluctuations of ΔT.

(x) Refractory insulators become electrically conductive at high temperatures and permit stray currents to enter the thermocouple circuits. These currents also produce spurious fluctuations of ΔT.

It is evident from (i)–(iii) above that apparatus for use with fluxed melts must be both resistant to chemical attack and easy to repair in the event of serious corrosion. It is also evident that the combination of restrictions enumerated in (iv), (v) and (vii) prevents the differential electromotive force from attaining other than small values. These must be considerably amplified before display if thermal events are to be detected.

To the sources of noise in (ix) and (x) must be added electromagnetic pick-up in the thermocouple circuits. Although the thermocouples may be screened, the elimination of pick-up is difficult because of the close proximity of the furnace element and the comparatively large currents which flow through it at high temperatures. The noise introduces spurious irregularities into thermograms, and these irregularities may mask or modify the peaks which are due to small thermal events.

Other problems which are encountered in the application of DTA to fluxed melts are not peculiar to this type of sample, but occur whenever an apparatus is operated at the limit of its sensitivity. These problems have been discussed by Mitchell [10] and two in particular are worthy of mention.

A temporary, small deviation from the linearity in the variation of the temperature of the furnace with time can produce a temporary variation in ΔT. This variation may be comparable with that which is due to a thermal event in the sample. A more prolonged deviation from linearity can produce a progressive variation in ΔT. This variation is observed as 'drift' of the base line and may be comparable with that which is due to a progressive change in the thermal properties of the sample. In both cases, real and apparent thermal events are not easily distinguishable.

3. Apparatus

The general features of the apparatus which was developed in this study are illustrated in Fig. 1. The sample holder, which is shown in more detail in Fig. 2, consisted of a mullite tube which was 34 cm in length and of 2.5 cm bore. Near one end of the tube was a cylindrical cavity, 3 cm in length, which contained a block of Morgan Morlite 28 insulation brick. The junctions of a matched pair of Pt/Pt$-$13%Rh thermocouples of 32 S.W.G. (0.27 mm diameter) protruded through holes in this block. The flat, upper surface of the block was covered with a protective sheet of platinum foil and served as a platform for the sample and reference crucibles.

The cavity was lined with platinum foil and the thermocouples were sheathed with platinum throughout the length of the mullite tube. When a platinum lid was placed over the cavity, the thermocouples were completely surrounded by a metal screen which was maintained at earth potential.

The crucibles were of Pt$-$5%Rh, cylindrical in shape, and each was provided with a deep thermocouple well in the base. The crucibles were of two sizes; the first was 5 mm in height and 5 mm in diameter, and the second was 8 mm in height and 6 mm in diameter. The latter size was found to give better results since a larger signal-to-noise ratio was obtained with the larger mass of sample.

A rectangular furnace, 30 cm in height, was constructed from Morlite 28 bricks on a square base of side 38 cm. The furnace enclosed a mullite tube, of 5 cm bore, which passed horizontally through two opposite walls and through a central cavity, 23 cm in length and 15 squ. cm in cross-section. The furnace was heated by four Crusilite elements, which were situated above the upper part of the tube as shown in Fig. 2. This configuration produced a vertical temperature gradient which contributed to the suppression of air currents at the crucibles and convection currents within the molten samples.

A minimum of insulation was used in the construction of the furnace so that cooling rates in excess of 5°/min could be obtained in the temperature range 800 – 1400°. The insulation was sufficient, however, for the maintenance of a heating rate of 4°/min in the same temperature range, despite a power limitation of 3 kW.

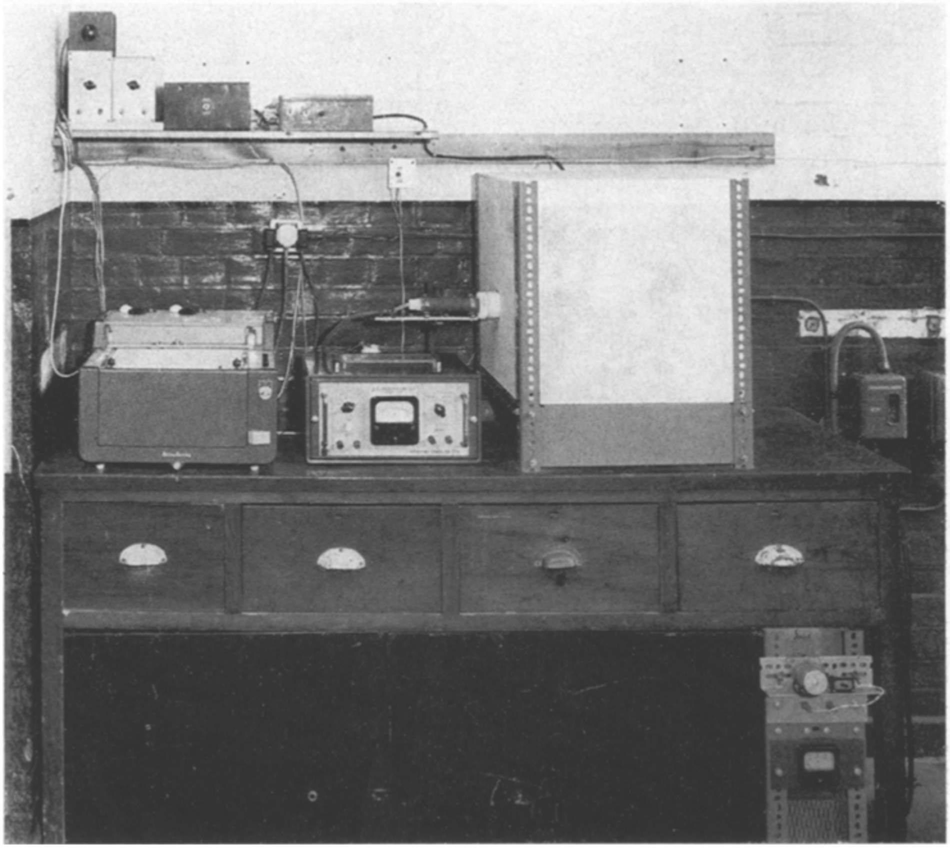

Fig. 1. DTA Apparatus

The temperature was regulated by a C. N. S. 'Sirect' Mk. I proportional controller. In this controller, a platinum resistance thermometer was used as the temperature sensor and the temperature was varied by rotation of a helical potentiometer. When the potentiometer was rotated by a synchronous motor, the rate of change of temperature was almost linear within the range of measurement (800° – 1400°).

A twin-pen Rikadenki Kogyo potentiometric recorder, model B24, was used for the display of both the temperature, T, and the differential temperature, ΔT, versus time. The maximum sensitivity of the recorder was 2.5 cm/mV, which was adequate for the measurement of T. The ΔT signal was amplified before display by a Rikadenki preamplifier, model A10, by means of which the sensitivity could be increased to 5 mm/μV. Zero suppression was available on both channels.

The measurements which are reported in section 5 were all made with this apparatus. In a recent modification, however, the crucibles were supported separately and no sample block was used. Each crucible was situated on a platform at the end of a horizontal alumina tube. The two tubes were parallel and were mounted, 1.5 cm apart, at one end of the furnace tube. Each of the alumina tubes contained a thermocouple, of which the junction protruded through the platform. This modification has contributed to a significant reduction in the noise content of the DTA curve, as a result of the elimination of the conductive path which had been provided between the thermocouples by the sample block.

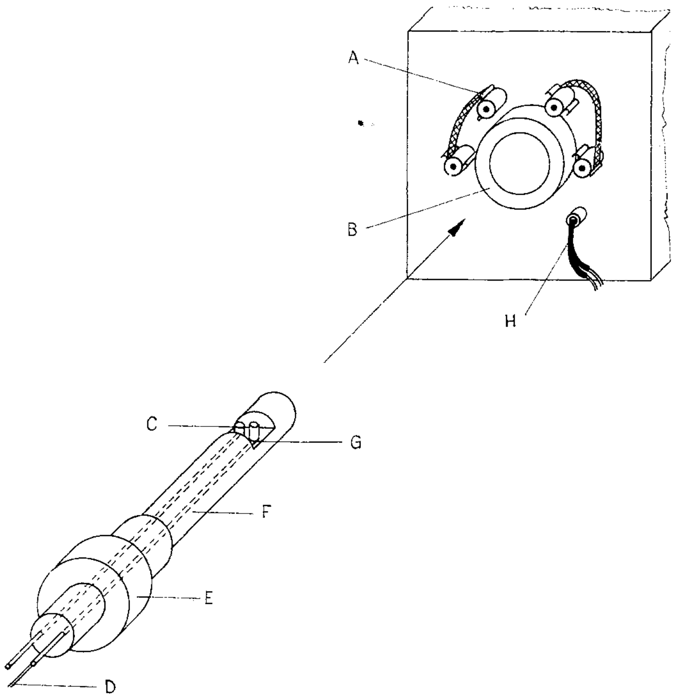

Fig. 2. Sample holder and furnace. A: Silicon carbide element, B: Alumina tube, C: Platinum crucibles, D: Thermocouples, E: Furnace plug, F: Mullite tube, G: Crucible platform, H: Platinum thermometer

4. Experimental procedure

Prior to use, the apparatus was calibrated against the melting point of BDH "Analar" grade sodium chloride. This material was chosen in the absence of accepted standards for the calibration of high temperature DTA apparatus.

On heating at 4°/min, ΔT deviated from the base line value at 800° and the peak displacement occurred at 815°. On cooling at 6°/min, ΔT first deviated at 815° and the peak occurred at 800°. The mean of either the peak or the initial displacement temperatures was thus 807°. The position of the recorder pen on the chart was, however, subject to an error of $\pm 0.5\%$ of full scale, which corresponded to a maximum error in temperature of $\pm 4°$. Since the initial adjustment of the pen was subject to a similar error, the melting point of common salt was determined to be $807 \pm 8°$. This is in satisfactory agreement with the accepted value [11] of 801°.

The fluxes which were used in the experiments were prepared from Koch Light 99.9% pure B_2O_3 and Barium Chemicals "high purity" BaO. Since these materials are hygroscopic, the powders were weighed rapidly so that the error which was introduced into the composition of the flux by the absorption of moisture from the air was negligible. The powders were thoroughly mixed in a planetary mill to ensure an intimate mixture of uniform composition.

In a typical experiment, a small quantity of the mixture was fused in a platinum crucible by heating with a coal gas-air flame. This procedure was repeated until the crucible was at least half full and the thermocouple well was completely covered. The mass of flux in the crucible was then determined. A predetermined quantity of a dry, homogeneous mixture of Johnson Matthey spectroscopic grade NiO and Fe_2O_3, in stoichiometric proportions, was added to the contents of the crucible. The crucible was again heated in the gas-air flame until the flux melted and the powders sank below the surface. The crucible was then weighed and the solute concentration was calculated. This procedure ensured that the presence of moisture in the oxide powders did not contribute to errors in the composition of the solution.

The crucible was placed on the sample block together with an identical crucible which contained powdered α-Al_2O_3, and the sample holder was inserted into the furnace. The furnace was heated to 800° and a curve was obtained as the temperature was increased at 2.5°/min to 1400°. After one hour the furnace was cooled to 800° at the same rate and a second curve was obtained. This sequence was then repeated and two more curves were recorded before the furnace was cooled to room temperature. All the experiments were performed in a static atmosphere of air.

Immediately after removal from the furnace, the samples were weighed and then immersed in hot dilute nitric acid. This reagent dissolved the flux and only minute, black faceted crystals remained. Most of the crystals adhered to the interior surfaces of the crucibles.

5. Results

The crystals which were obtained from DTA experiments were observed under a microscope and were found to exhibit octahedral morphology. Spontaneous magnetisation was evident when the crystals were exposed to a magnetic field.

Some of the crystals were ground to a fine powder and this produced an X-ray diffraction pattern which was consistent with that of the ferrimagnetic spinel $NiFe_2O_4$.

The curve which was obtained during the first heating programme was generally inferior to the others and its interpretation was difficult. However, subsequent curves possessed distinctive features from which deductions could be made. The peak of a typical curve which was obtained during the first cooling programme is shown in Fig. 3a. The peak was exothermic and was characterized by a small increase in ΔT which was maintained over a wide range of temperatures. The temperature, T_1, at which ΔT first deviated from the base line was found to depend on the concentration of $NiFe_2O_4$ in the sample, and thermogravimetric measurements [12] confirmed that this temperature corresponded to the initial crystallization of nickel ferrite.

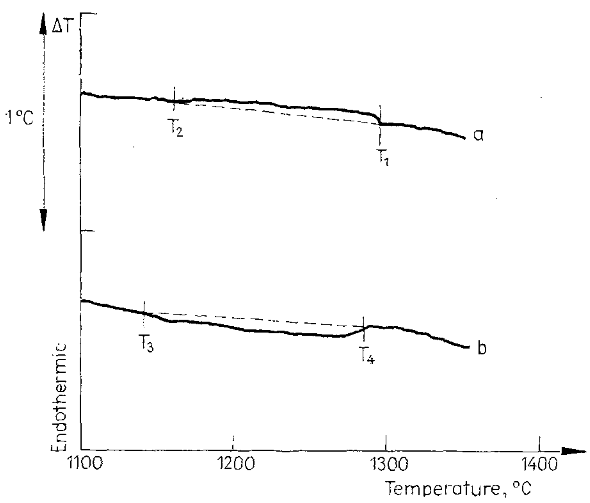

Fig. 3. DTA curves for 20% $NiFe_2O_4$ in BaO · 0.62 B_2O_3. *a)* cooling, *b)* heating

The height of the peak varied little with temperature. This indicated that the rate at which heat was evolved in the sample was almost independent of temperature, a phenomenon which is consistent with crystallization from solution. Ultimately, however, ΔT was reduced to a value which was indistinguishable from that of the base line. The temperature, T_2, at which this occurred was taken to be that below which crystallization could not be detected. T_2 was found to be independent of the concentration of $NiFe_2O_4$.

An endothermic peak of comparable magnitude was present in the curve which was obtained during the second heating programme. The shape of the peak is evident from Fig. 3b. The temperature, T_3, at which ΔT deviated from the base line was in fair agreement with T_2 and the temperature, T_4, at which the displacement became insignificant was in agreement with T_1 to within 5° under favourable conditions.

It was noted that T_4 was generally less than T_1. This was to be expected since the thermal gradient between the thermocouple and the outer wall of the crucible was reversed on changing from a cooling to a heating programme. If, however, the sample had been supercooled to a significant extent during the cooling programme, T_4 would have been greater than T_1. It was thus evident that supercooling was relatively small, and that the mean of T_1 and T_4 could be taken as the liquidus temperature of the sample.

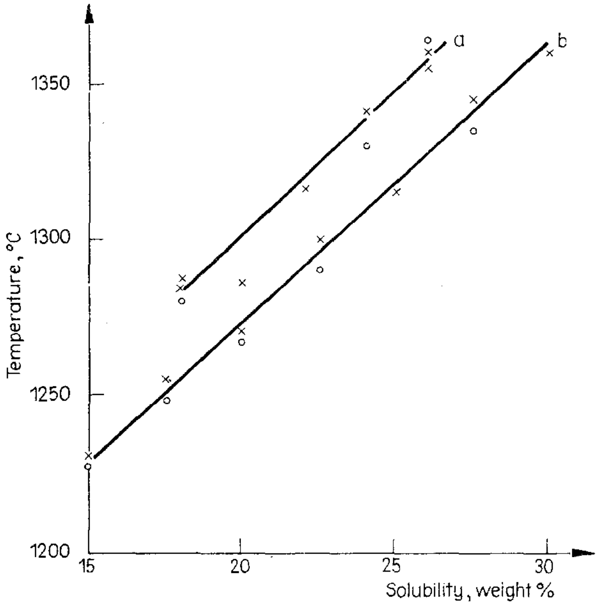

Fig. 4. Solubility of nickel ferrite in *a)* BaO · 0.5 B_2O_3, *b)* BaO · B_2O_3; × = T_1, ○ = T

The results were confirmed by analysis of the curve which was obtained during the final cooling programme. Good agreement was normally observed between the values of T_1 which were obtained from this and from the previous cooling programme, although the values of T_2 were often only in fair agreement.

Experiments were performed with fluxes of composition BaO · B_2O_3, BaO · · 0.5 B_2O_3 and BaO · 0.62 B_2O_3, which is a eutectic composition. The temperatures T_1 and T_4 were measured and are displayed in the form of solubility versus temperature curves in Figs 4 and 5. The results indicate that the solubility of nickel ferrite increases slightly with increasing B_2O_3 concentration but is rather insensitive to the ratio of BaO to B_2O_3 in the composition range which was investigated.

Although straight lines were drawn to indicate the approximate variation of solubility with temperature, the results may be fitted, within experimental error, to the relation for an ideal solution, namely $n \propto \exp(-\phi/RT)$, where n is the solubility and ϕ is the heat of solution. A value of 73 ± 2 Kjoule mole^{-1} was obtained for the heat of solution of nickel ferrite in the three fluxes.

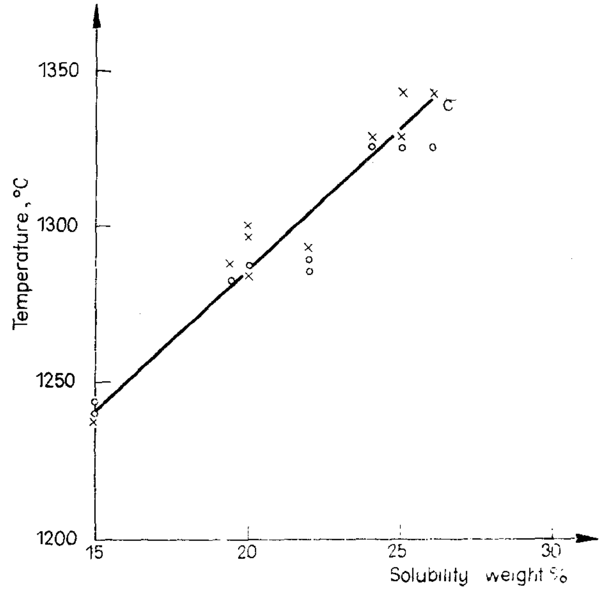

Fig. 5. Solubility of nickel ferrite in BaO · 0.62 B_2O_3; $\times = T_1$, $\circ = T_4$

6. Conclusions

It is concluded that, although the signal-to-noise ratio is small for crystallization or dissolution in molten solutions, DTA is a viable method for the study of fluxed melts, and is convenient for the determination of the essential solubility data for crystal growth experiments. The method is most simply applied to melts of low volatility, but could be applied to volatile melts if these were contained in sealed crucibles.

Apparatus for the DTA of fluxed melts in various atmospheres at pressures greater than atmospheric is currently under construction.

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Résumé. — On a décrit l'application de la méthode ATD à l'étude des fusions avec fondant et un appareil adapté à la détermination de la solubilité des substances crystallines dans les fondants. On a étudié la cristallisation de ferrite de nickel des flux de borate de baryum. Des courbes de solubilité pour des flux favorisant les grossissement des cristaux sont présentées. La chaleur de solution du ferrite de nickel a été trouvée 73 ± 2 kjoule mole^{-1}.

Zusammenfassung. — Es wurde über die Anwendung der DTA Methode bei der Untersuchung von Flußmittel enthaltenden Schmelzen berichtet und ein Apparat zur Bestimmung der Löslichkeit von kristallinischen Substanzen in Flüssen beschrieben. Eingehend wurden die Kristallisation von Nickelferrit aus Bariumborat-Flüssen untersucht und Löslichkeitskurven für den Kristallwachstum begünstigende Flüssen gegeben. Die Lösungswärme von Nickelferrit betrug 73 ± 2 Kjoule Mol^{-1}.

Резюме. — Обсужден вопрос о применении ДТА расплавленных металлов и описан прибор для определения растворимости кристаллических веществ в расплавленных растворах (в расплавах). Изучена кристаллизация феррита никеля из расплава бората бария и показана кривая растворимости для расплавов, способствующих увеличению кристаллов. Теплота растворения феррита никкеля составляет 73 ± 2 кдж моль$^{-1}$.