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MICRO-DIFFERENTIAL THERMAL ANALYSIS TECHNIQUE WITH THE HOT-STAGE MICROSCOPE

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The construction and operation of a micro-differential thermal analyser in corporation with the hot-stage microscope are described. Based upon the use of two opposed, viewable thermocouple microfurnaces, the instrument provides a sensitive means of detecting heat effects with accompanying reactions which may occur when small quantities (<1 mg) of materials are rapidly quenched or undergoing programmed temperature change.

The differential thermal analysis technique is widely used as means of detecting thermal effects associated with chemical and structural changes in materials. For most application every analyser so far described[1] is based on a conventional furnace which is used to heat or cool a suitable container for both specimen and thermally inert substance, called the standard and when a reaction temperature is reached, the accompanying heat change in the material is registered as a temperature difference between the opposed thermocouples whose measuring junctions are embedded in the two materials. The majority of such instruments require microscopic quantities of materials and the total thermal capacities of these assemblies limit the rate of temperature change that can be imposed. It is unusual for heating or cooling rates higher than 20°C/min to be used; a generally accepted standard rate being 10°C/min.

There has recently been some development of micro-differential thermal analysis apparatus in order to improve the temperature definition by the removal of thermal gradients between the reacting materials and the thermocouples. A successful design is that of Maziers[2] who achieved both sensitivity and higher resolution. An arrangement that permits visual observation during thermal analysis has also been described by Hogan and Gordon.[3] Mercer and Miller [4,5] made considerable advances by combining high temperature microscopy with thermal analysis and by modifying the hot-stage microscope developed by Welch.[6,7] These modification provided a means for continuously monitoring and recording the cooling curves of microscopic quantities of materials, which are supported in the viewable thermocouple microfurnace of the hot stage microscope. In this form the apparatus has been used for high temperature phase studies in oxides and mineral systems, [4,5,8,9,10] where emphasis has been put on determining both equilibrium and non equilibrium behaviour in terms of variable thermal history.

The detail of the high speed thermal analysis has been published.[5,11] The introduction of two channel heating and oscilloscope monitoring of cooling curves extended the application of the technique to include microscopic thermal analysis between two pre-selected temperatures. The present high temperature microscope was also successfully used to study the effects of varying the cooling rate on the crystallization of beryllia containing melts.[4,5] These experiments were successful because beryl melts display large exothermic heat effects during rapid cooling and can be observed on curve of temperature versus time. But titanium containing slag exhibited no such large exothermic effects on the cooling curve although they did crystallise. An obvious refinement, therefore, would be the conversion of the high temperature microscope to differential thermal analysis with corresponding enhanced sensitivity. In order to incorporate the principle of differential thermal analysis into the high temperature microscope the following requirements had to be met.

(i) Retention of the facility for continuously observing the specimen.

(ii) The ability to control separately the upper and lower temperature of both thermocouples. This is necessary to annul temperature differences that would result if there is unequal thermal capacity; for example from difference in size and loading.

(iii) Simultaneous heating of sample and the standard and the measurement of sample temperature and differential temperature between the sample junction and inert junction.

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(iv) Common switching or programming of both couples between the selected limiting temperatures.

(v) Means of simultaneously recording the cooling curve and the differential curve, considering the desirability of more sensitive mV scale for latter curve.

Description of the Electric Circuit of the Micro-Differential Thermal Analyser.—Before the publications of Sommers and Co-workers, [11,12,13,14] there was not available any circuitry for such an instrument. All these circuits are based on the use of silicon rectifiers and synchronous converters. A micro-differential thermal analysis apparatus based on silicon rectifiers was constructed (Fig. 1). If the reference is made to the earlier circuit (Fig. 2) which permits only cooling curves to be registered, it will be seen that this micro-differential thermal analyser's circuit requires only the duplication of diode and synchronous converter arrangement.

The variable dual track auto-transformer TR_1 and TR_2 (Fig. 1) separately controls the respective inputs to the primary windings of the transformer TR_3 and TR_4 between 0 and 220 volt A.C. at 50 cycles. The outputs of these last two transformers are controlled between 0 and 12 mV. The output of TR_3 is fed into two silicon rectifiers D_1 and D_2 wired in parallel. Identical considerations apply to the corresponding other half of the circuit involving the transformer TR_4 and silicon rectifiers D_3 and D_4. The function of the silicon rectifiers is to switch the output of the transformers TR_3 and TR_4 from A.C. voltage to half cycle D.C. voltage. Effectively continuous heating of the thermo couples takes place in the positive phase of the cycle, the negative phase being blocked by the rectifiers.

The contact of the synchronous converter SC_1 and SC_2 are so arranged that 3 and 7 are closed for $33\frac{1}{3}\%$ of the total cycle and 4 and 7 closed for the remaining $66\frac{2}{3}\%$ of the cycle. Contacts 3 and 7 are, therefore, used to switch in the measuring circuit during the period when the negative half cycles have been blocked from the heating circuit (Fig. 3). The convention adapted in opposing the polarities of the thermocouples is to

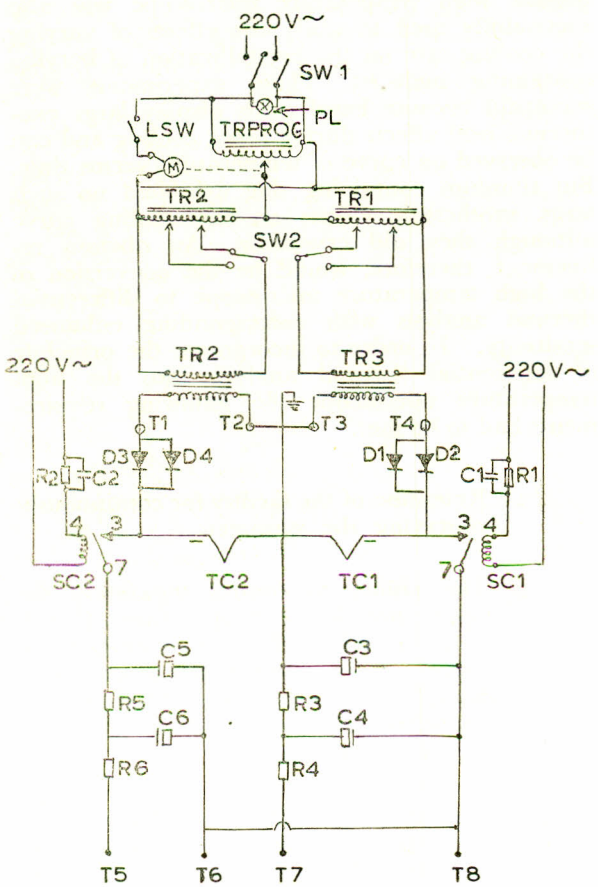
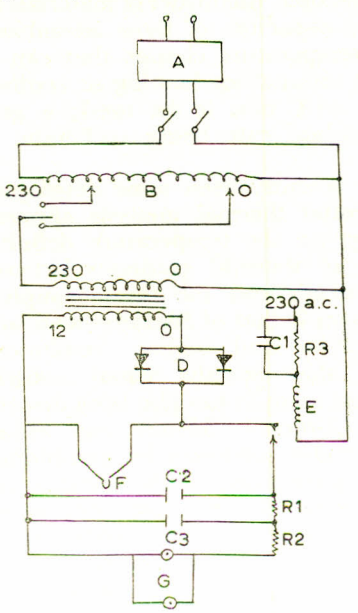


Fig. 1.— Block circuit diagram of the micro-differential analyser.



A = CONSTANT VOLTAGE TRANSFORMER
B = DUAL TRAC VARIAC
D = RECTIFIER
E = CYNCHRONOUS CONVERTER
F = THERMOCOUPLE
G = SOCKETS TO OSCILLOSCOPE

Fig. 2.— Modified circuit diagram for cooling curve only after Mercer and Miller.

make the positive limbs the common junctions. The output generated across the ends of the thermocouple TC_1 is passed through a low pass filter consisting of condenser C_3 and C_4 and resistors R_3 and R_4. E.M.F. measurements were made across the terminals T_7 and T_8. Similar connections were made across the other part of the circuit containing the thermocouple TC_2 with condenser C_5 and C_6 and resistors R_5 and R_6.

Mode of Measurement and Recording of Thermoelectric e.m.f., Cooling and Differential Curves.— In earlier work on the microscopic thermal analysis [4,5,8,15] accurate thermoelectric e.m.f. measurements were made with a potentiometer capable of recording to 0.005 mV. The cooling curves are photographically recorded from a cathode ray oscilloscope connected in parallel with the potentiometer. This system of measurement has the disadvantage of pickup of stray signals by the oscilloscope. This draw back is overcome by the use of a high speed dual input chart recorder with pen speed of 0.4 sec over 10 inch deflection. There are two independent measuring circuits, one range (channel 1) being 12 mV. full scale deflection whilst the other (channel 2) can be altered either −1.0; 0; + 1 mV. full scale deflection or −0.5; 0; +0.5 mV. full scale deflection. This channel is used to register the differential curve of the sample. The chart speed can be varied between ¼″, 2½″, 1″, 2″ and 4″ per sec. The chart recorder can also function as millivolt recorder.

Mode of Temperature Programming.—To widen the versatility of the micro-differential thermal analyser, programmed temperature control is also introduced. This is effected by the introduction of a motor driven auto-transformer TR (Fig. 1) which controls the voltage across TR_1 and TR_2. With motor speed of 1 rev/hr and 1 rev/min respectively and gear system of 1:3, 1:1 and 3:1 it is possible to programme temperature over a wide range of rates.

The Description of the Modified Thermo-couple Cell for the Micro-differential Thermal Analyser.— The standard cell which has been adapted for general use in hot stage microscope[7] was not large enough to accommodate the differential thermocouple assembly. In modifying the cell, two cells are made for housing the two thermo couples separately. This permits better observation by reducing the thickness of cell wall and also reduces the thermal interference which arises when heating two thermocouples placed in the same cell. Arrangements are also made for applying water cooling to the thermo couple supports, so that the sensitivity with which the differential temperature is recorded may not be affected by the cold junction error. This also permits the use of various thermo couples in the apparatus irrespective of cold junction characteristics. The cell also allows the use of any desired atmosphere by providing with a gas inlet and outlet. Standard microscopic slide cover glass ⅞″ diameter is used as observation windows, sealed to the window openings by a thin polyethene washer. The details of the cell assembly are given in figure 4.

Thermocouples of the Micro-differential Thermal Analysis.—In differential thermal analysis, chrome-alumel wires are very satisfactory when used at temperatures below 1000°C, Grieg[16] found that a thermocouple of Au+40% Pd—Pt+10% Rh was five times as sensitive as Pt—Pt+10% Rh alloy but could not be used above 1400°C. But in micro-differential analysis, the most commonly

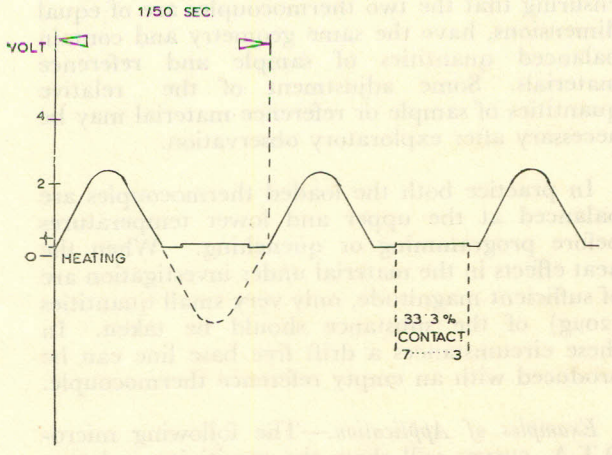


Fig. 3.— Diagramatic representation of heating temperature measurement principle.

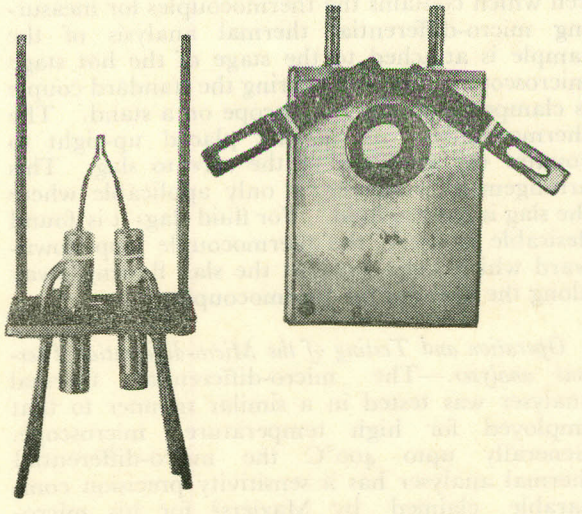


Fig. 4.— Photograph of the micro-D.T.A. cell with water cooled system.

used thermocouple has been 5% Rh+Pt—20% Rh+Pt alloy of 0.2 mm. diameter as a heating element which has been supported on 0.5 mm. diameter legs of the same alloys. The use of this couple is wide spread because of the almost negligible cold junction error. For temperature upto 1000°C, a high output couple which is a gold palladium alloy, known as "pallaplat" may be used. For higher temperatures the 6% Rh+Pt—30% Rh+Pt thermocouple was also used.

Reference Materials (standard).—The choice of reference materials is arbitrary and will depend largely upon the temperature regions over which the study is to be made. In conventional differential thermal analysis alumina is the usual choice being thermally inert at all temperatures but in the micro-differential thermal analyser, however, it is not possible to ensure that suitable amounts adhere firmly and uniformly in the loop at the junctions. If the heat effects of the sample are of sufficient magnitude, and only very small amount of test substance need to be taken, a satisfactory base line may be produced with an empty reference couple. This arrangement is most desirable, being independent of other materials. Alternatively, any materials which can be melted on to the junction and cooled without manifesting a heat effect can be used as reference substance. Where swift rates of cooling are involved, borax has been proved effective upto 1000°C at which temperature it begins to volatilise rapidly. At higher temperature albite feldspar is found most suitable since this mineral is well known for the difficulty with which it crystallises from its melt and glass.

Arrangement of Thermocouples in the Cell.—One cell which contains the thermocouples for measuring micro-differential thermal analysis of the sample is attached to the stage of the hot stage microscope. The cell bearing the standard couple is clamped near the microscope on a stand. The thermocouples are usually placed up-right to counter the tendency of the wire to slag. This arrangement, however, is only applicable where the slag is not too fluid. For fluid slags it is found desirable to insert the thermocouple loop downward which helps prevent the slag flowing away along the limbs of the thermocouple.

Operation and Testing of the Micro-differential Thermal analyser.—The micro-differential thermal analyser was tested in a similar manner to that employed for high temperature microscope. Generally upto 400°C the micro-differential thermal analyser has a sensitivity precision comparable claimed by Maziers[2] for his micro-differential thermal analyser, this was also confirmed by Sommers et al[14] when investigating the solid state changes in the sodium sulphate system. However, at higher temperatures (above 1000°C), there appears to be a loss of sensitivity in the micro-D.T.A. at the normal rates of cooling (10°C per min) probably due to the increasing radiation losses. This loss in sensitivity at high temperature can, to some extent be alleviated by passing through two thermocouples cells a gas of low thermal conductivity such as Argon, Xenon and Krypton.

For checking the sensitivity of the micro-differential thermal analyser more studies were made of the solid state changes of potassium sulphate and lithium sulphate i.e. their α and β transitions. The results obtained are in good agreement with previous results.

The material to be examined is made to adhere in the loop at the thermocouple junction. It is usual to melt specimens on to the thermojunction but if irreversible changes during heating are suspected transference as slurry is effective.

It has been experienced while working with the apparatus that a spurious differential heating effect can arise if the thermal capacities of the sample and the reference thermocouples differ. This spurious effect is easily recognised since it invariably takes the form of an immediate deviation from a straight base line when the system is being switched or driven between the operating temperatures. In cases where there was mismatching the genuine heat effects arising from reactions in the sample were clearly superimposed on the drifting base line, and visual examination safeguards against serious misinterpretation. However, it is clearly desirable to have a linear base line. Base line drift can be minimized by ensuring that the two thermocouples are of equal dimensions, have the same geometry and contain balanced quantities of sample and reference materials. Some adjustment of the relative quantities of sample or reference material may be necessary after exploratory observation.

In practice both the loaded thermocouples are balanced at the upper and lower temperatures before programming or quenching. When the heat effects in the material under investigation are of sufficient magnitude, only very small quantities (20μg) of the substance should be taken. In these circumstances a drift free base line can be produced with an empty reference thermocouple.

Examples of Application.—The following micro-D.T.A. curves will show the sensitivity and versatility of the apparatus. These curves are taken

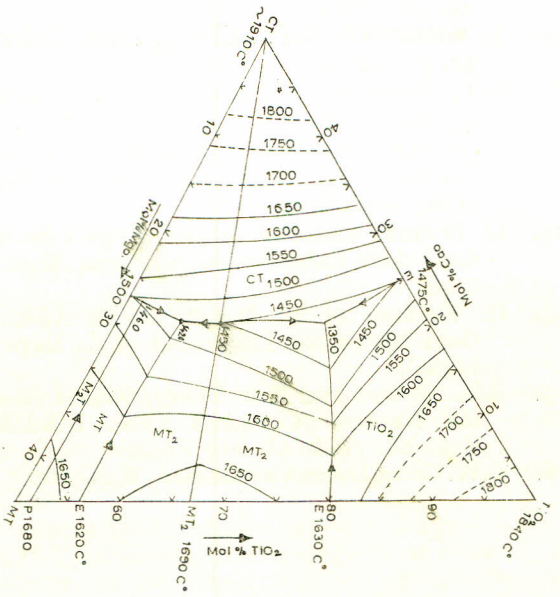


Fig. 5.— Isothern. M the system 'CT—MT—TiO_2'.

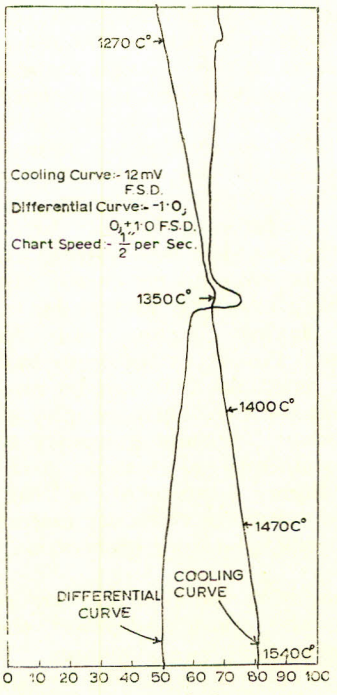


Fig. 6.— D.T.A. curves of slags in the composition triangle 'CT—MT—TiO_2'.

from the micro-differential thermal analysis of composition on the termary phase diagram of the system 'CaO. TiO_2—MgO.TiO_2—TiO_2' (Fig. 5). From the position of the thermal arrests, the liquidus, binary phase separation, ternary eutectic

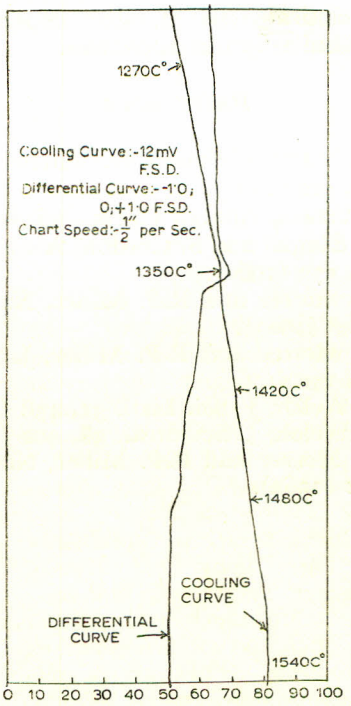


Fig. 7.— Micro-D.T.A. curve of slag in the composition triangle 'CT—MT_2—TiO_2'.

and solid state transition temperatures were determined.

(a) Figure 6 shows the micro-D.T.A. curve of the melt having composition CaO—25, MgO—5, and TiO_2—70 mole percent. The above composition is on the primary phase field of CaO. TiO_2. The differential curve shows the changes at liquidus temperature at 1470°C, binary separation of phase CT (CaO.TiO_2) and TiO_2 at 1400°C and a large thermal arrest at 1350°C showing the ternary solidification. The solid state change of αCT (CaO.TiO_2) to βCT (CaO.TiO_2) is distinctly shown in the differential curve at 1270°C.

(b) Figure 7 shows a micro-D.T.A. curve obtained from the composition CaO—15, MgO—10, and TiO_2—75 mole percent. This composition is on the primary phase field of TiO_2. This curve shows the liquidus temperature at 1480°C, binary separation of TiO_2 and MT_2 (MgO. 2 TiO_2) at 1420°C and large thermal arrest at the eutectic temperature at 1350°C. There is also a weak indication of the solid state change of CT (CaO. TiO_2) in the differential curve at 1270°C.

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References

1. R.C. Mackenzie and B.D. Mitchell, Analyst, **87,** 420 (1962).
2. C. Maziers, Analyst Chem., **36,** 602 (1964).
3. V.D. Hogan and S. Gordon, Analyst Chem., **32,** 573 (1960).
4. R.A. Mercer and R.P. Miller, Nature, **197,** 4868 (1963).
5. R.A. Mercer and R.P. Miller, J. Sci. Inst., **40,** 352 (1963).
6. J.H. Welch, J. Sci. Inst., **31,** 458 (1954).
7. J.H. Welch, J. Sci. Inst., **38,** 402 (1961).
8. R.A. Mercer and R.P. Miller, Nature, **202,** 581 (1964).
9. R.A. Mercer and R.P. Miller, Mineralog., **35,** 250 (1965).
10. L. Glasser and R.P. Miller J. Chem. Educ., **42,** 91 (1965).
11. R.P. Miller and G. Sommer, J. Sci. Inst., **43,** 293 (1966).
12. G. Sommer and R.P. Miller, Report South African Govt. Met. Labs. Project No. 46/64 Rept. I (1964).
13. G. Sommer and R.P. Miller, Report South Govt. Met. Labs. Project No. 46/64 Rept. 2 (1965).
14. G. Sommer et al; Report South African Goct. Met. Labs. Project No. 46/64 Rept 3 (1966).
15. R.A. Mercer and R.P. Miller, Report from the National Chemical Labs. D.S.I.R. England. NCL/AE 213 (1962).
16. T.W. Grieg J. Am. Ceram. Soc., **8,** 465(1925).