

CONTRIBUTION TO THE KNOWLEDGE OF THE EQUILIBRIUM
AND NON-EQUILIBRIUM BEHAVIOUR OF TITANIFEROUS
SLAGS

A dissertation presented to the Faculty of Engineering,
University of the Witwatersrand, in fulfilment of the
requirements for the Degree of Doctor of Philosophy by
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UNDERTAKING

I hereby certify that this is my own work and has not been submitted for a Ph.D. degree at any other University.

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It should be pointed out that the subject matter of this dissertation arose from previous tests and that the bulk of the present investigations was not of immediate interest to, nor initiated by, the above company.

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S Y N O P S I S

The phase equilibria in the slag system $(\text{CaO} + \text{MgO}) = 30.00$ per cent, $\text{SiO}_2 = 19.69$ per cent, $\text{Al}_2\text{O}_3 = 13.12$ per cent, and $\text{TiO}_2 = 37.19$ per cent were determined. Liquidus curves for titaniferous slags with $(\text{CaO} + \text{MgO})$ contents of 25.00 per cent and 35.00 per cent respectively were also drawn. These phase equilibria were determined on a high temperature microscope constructed in accordance with the design of Welch.

The phase equilibria of one of these titaniferous slags with increasing contents of SiO_2 were determined. Certain SiO_2 contents had the effect of causing the TiO_2 content of the slag to crystallize as rutile instead of as part of a much more complex oxide. This procedure could be used to facilitate extraction of the TiO_2 .

A new type of micro differential thermal analyser was constructed. On this instrument the behaviour of titaniferous slags was studied at high rates of thermal change such as simulated granulation plant tests and high-speed cooling tests.

Slags consisting of CaO , MgO , SiO_2 , and Al_2O_3 with various TiO_2 additions were subjected to devitrification tests on a conventional differential thermal analyser. The critical cooling rates required to achieve these slags in the glassy state as well as the liquidus temperatures were determined. It was found that the slags had to be in the massive form as opposed to a ground powder to obtain devitrification peaks characteristic of the actual devitrification process occurring.

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CHAPTER I.

INTRODUCTION.

1.1. The titaniferous magnetites of the Bushveld Igneous Complex.

Within the last decade an increasing interest has been shown in the exploitation of the Bushveld Igneous Complex for the production of ferrochrome and more recently for the large scale production of steel and vanadium.

The Bushveld Igneous Complex is the term applied to a suite of genetically connected volcanic and intrusive rocks which are believed to have been derived from a common magma. The complex is roughly oval in area and is situated in the central Transvaal, extending some 280 miles from Lydenburg in the east to Zeerust in the west, and from Pretoria in the south to Potgietersrus in the north.

The Bushveld Igneous Complex is regarded as consisting essentially of four phases which in sequence of events are :

- (i) an Extrusive Rooiberg Phase
- (ii) an Intrusive Sill Phase
- (iii) a Basic Intrusive Phase
- (iv) an Acid Intrusive Phase

It is in the Critical Zone of the Basic Intrusive Phase that the economic chromite bands and the pyroxenite and peridotite layers containing the platinum are found. Above this Critical Zone there occurs the Main Zone and it is near the upper limit of this zone that the extensive layers

of titaniferous magnetite occur as segregations in the gabbro body. These average 15 feet in thickness and have been traced for several hundred miles.

These titaniferous magnetites contain about 5 per cent by weight of ilmenite, which usually occurs as fairly large segregated particles. These particles may take the form of exsolution lamellae parallel to the octahedral planes of the magnetite. It is interesting to note that the ilmenite accounts for only about 18 per cent of the total TiO_2 content of the ore. The balance of the titanium occurs as ulvospinel and also enters into the structure of other constituent minerals.

The vanadium is thought to be present in the iron oxide phases due to isomorphous replacement of the iron. Furthermore, because an antipathetic relationship has been found to exist between the V_2O_5 and TiO_2 contents of the ore, it seems likely that the vanadium occurs in a titanium-poor iron oxide phase. The ilmenite-bearing fraction of the ore certainly does not contain any vanadium.

Microscopic examination has shown that the bulk of the ore consists of an extremely fine-grained exsolution intergrowth of different iron compounds with spinel structure (titanium-rich and titanium-poor magnetite?). The host material is magnetite (Fe_3O_4) or magnetite and gamma Fe_2O_3 - depending on the state of oxidation of the ore. This host material contains an abundance of minute inclusions of what is believed to be ulvospinel (ulvite), a spinel with the formula Fe_2TiO_4 . The intergrowth of magnetite and ulvospinel is so fine that grinding to a grain size of a few microns

would not produce monomineralic grains.

The average composition of the titaniferous magnetite to be mined is given as follows :

Fe = 55.0 per cent

V_2O_5 = 1.6 per cent

TiO_2 = 13.1 per cent

MgO = 1.0 per cent

Al_2O_3 = 3.4 per cent

1.2 Proposed slag for pig iron production.

Until very recently, it was feared that the high titania content of these titaniferous magnetites would militate against their value as useful ores (1). However, the design of an integrated plant to produce both steel and vanadium improves the economic factors. Blast furnaces are not suitable for the production of the pig iron mainly due to the fact that for the economic extraction of the vanadium, the vanadium must enter the pig iron. This is only possible if the pig iron has a high carbon content. This in turn would necessitate an excessively high coke rate to supply the necessary highly reducing conditions in the blast furnace. A pig iron with the required carbon content can be produced under the highly reducing conditions obtaining in a submerged arc electric furnace.

For these reasons, the process to be adopted may be somewhat along the following lines. The ore together with coal will be passed through a rotary kiln at a temperature of $900^{\circ}C$ - $950^{\circ}C$. This step brings about a

55 per cent reduction of the iron oxide content of the ore and also serves to preheat the charge. The partially reduced ore together with the flux consisting of limestone, dolomite, and silica are then fed to submerged arc electric furnaces. The products from this smelting operation are a high-carbon pig iron containing the vanadium and a slag containing the gangue from the ore. The vanadium-bearing pig iron is then blown with oxygen in a shaking ladle and the vanadium enters the slag during the process. This slag is treated for the recovery of V_2O_5 and the pig iron is converted into steel.

Based primarily on preliminary pilot plant tests, on the experience of attempts to treat somewhat similar ores in other countries, and on the available raw materials as flux, it was found that additions of limestone, dolomite, and silica were required to produce slags of the required characteristics as regards liquidus temperatures and viscosities. Little is however known regarding the liquidus temperatures of these slags and variations in such temperatures with respect to changes in the slag composition. This lack of knowledge stems from the fact that at present there is no phase diagram relating to the slag components (CaO , MgO , SiO_2 , Al_2O_3 , and TiO_2) in the concentration in which they occur (* see page 5). During the pilot plant tests, the primary slags which were produced had the following compositions:

CaO	=	20 - 22 per cent
MgO	=	8 - 10 per cent
SiO_2	=	15 - 18 per cent
Al_2O_3	=	10 - 12 per cent

The flux used was a mixture of limestone, dolomite, and silica. These were added in amounts of 420, 400, and 120 lbs. respectively per ton of hot metal.

TiO_2	=	31 - 34 per cent
FeO	=	1 per cent
V_2O_5	=	0.3 per cent
Cr_2O_3	=	0.25 per cent

These slags had been found to be suitable but the question arose as to whether the limestone/dolomite mixture in the flux could be replaced by dolomite only, as dolomite is less expensive than limestone under the local conditions. With dolomite replacing the limestone/dolomite mixture in the slag, the composition of the slag could be expected to change (apart from minor changes in the other constituents) from a CaO = 22 per cent and MgO = 8 per cent content to a CaO = 16 per cent and MgO = 14 per cent content. These figures are based on theoretical mass balances involving the ore, dolomite, limestone, silica, and coal.

* The published phase equilibria which exist relating any three or more of the oxide components are:

Al_2O_3 - CaO - MgO	Fig. 596	"Phase Diagrams for Ceramists"
Al_2O_3 - CaO - SiO_2	Figs. 630 - 639	E.M. Levin, C.R. Robbins,
Al_2O_3 - MgO - SiO_2	Fig. 712	and H.F. McMurdie.
Al_2O_3 - MgO - TiO_2	Figs. 713 - 714	The American Ceramic Society
Al_2O_3 - SiO_2 - TiO_2	Figs. 768 - 771	Inc. 1964.
CaO - MgO - SiO_2	Figs. 598 - 610	
CaO - MgO - TiO_2	Fig. 612	
CaO - SiO_2 - TiO_2	Figs. 660 - 663	
MgO - SiO_2 - TiO_2	Fig. 723	
Al_2O_3 - CaO - MgO - SiO_2	Figs. 880 - 923	
Al_2O_3 - CaO - SiO_2 - TiO_2	Figs. 954 - 957	
CaO - MgO - SiO_2 - TiO_2	Figs. 930 - 934	

1.3. Possible uses of the titaniferous slags.

When an industry develops around a newly-exploited ore body and very large tonnages of slag are produced then automatically the question arises as to whether there are any products which could be derived, or made, from this slag. The special demands of such a large volume of slag can be embarrassing and recently because of demands for maximum exploitation of natural resources every product should at least be investigated for its market potential. An especial problem in this connection is raised due to the high TiO_2 content of these slags, which content exceeds 30 per cent. Thus, the normal avenues for the exploitation of an iron-producing slag are added to by the presence of this high content of TiO_2 ; and the question of the possibility of extracting this TiO_2 naturally arises.

At present, the most common processes for the gainful use of iron-making slags are the use of air-cooled aggregate for concrete and roadmaking and the use of granulated slag in slag-cement. Also, recently there has been increased activity in the investigation of these slags as a possible raw material for the manufacture of slag-ceramics.

For the production of aggregate, the molten slag is tipped into pits in which the rate of cooling is controlled by the size of the pit and the schedule of filling. Depending on the chemical composition, which of course affects the mineralogical constitution, the highly crystalline slag thus obtained either has a mechanical strength comparable with that of rocks normally used for aggregate, or it can disintegrate into a powder. This unsoundness of air-cooled blast furnace slag is mainly caused by lime

unsoundness and magnesia unsoundness with relatively minor parts played by sulphur unsoundness. Lime unsoundness is attributed to the crystallization of dicalcium silicate and magnesia unsoundness is attributed to the crystallization of periclase (2), (3), (4).

When blast furnace slags are to be used for cement manufacture, they are subjected to a granulation treatment. Here the molten slag stream is subjected to the action of high pressure water jets which split the slag into small granules which cool extremely rapidly. This is done to achieve as high a glass content as possible, experience having shown that by this procedure the best cement quality is obtained for a given slag. In practice, the amount of crystalline material in granulated slags is generally between 2 and 20 per cent. As with the aggregate, one of the main problems is whether any of this crystalline material is periclase.

The various hydraulicity indices, which are often expressed in mathematical form are really various expressions indicating the basicity of the slag and it has been shown that these formulae can have serious limitations for predicting the hydraulicity of granulated slags. However, it is generally accepted that the amount of basic oxides must be high for suitable hydraulicity. Due to the high TiO_2 content, these titaniferous slags would probably display poor hydraulic properties. It has been shown that the high MgO content is not necessarily a disadvantage provided the MgO is not present as periclase but is part of the glassy slag (5), (6).

CHAPTER II.

PHASE EQUILIBRIA OF THE TITANIFEROUS SLAGS.

2.1. Survey of methods applicable to a study of phase equilibria.

The classical method of studying high temperature phase equilibria is well known. Essentially, small specimens in platinum containers are equilibrated at a particular temperature in an accurately controlled furnace and then the specimen is released and allowed to drop into water. By this means it is hoped that any non-crystallized material will be quenched into a glass and X-ray or mineralogical examination will permit identification of the phases in equilibrium at this temperature. This method is accurate but tedious, e.g. up to ten specimens are required to determine the liquidus temperature of a sample. Also certain doubt must exist as to whether the remaining melt has been quenched into a glass. If the remaining melt does crystallize during quenching the mineralogical examination of thin-sections usually identifies this quench product due to its different crystal morphology, characteristic of crystallization occurring during rapid quenching.

Dynamic methods of thermal analysis are indirect in that they rely upon the detection of heat effects accompanying phase changes. Transitions characterised by small heat effects may go unobserved but a more serious disadvantage in these methods is that they are of a non-equilibrium nature. This is particularly important in regard to sluggish systems, i.e. systems with larger contents of network-forming oxides may exhibit large degrees of non-equilibrium behaviour when subjected to programmed cooling or heating.

rates on a differential thermal analyser.

A comparatively new technique - that of high temperature microscopy - has been developed which, to a considerable extent, overcomes these difficulties. The high temperature behaviour of materials can now be continuously observed and defined as a function of accurately known thermal history.

The principle of heating a thermocouple by an alternating current filtered in such a way that the thermocouple electromotive force can be isolated and measured, was described in the literature (7), (8) as long ago as 1919.

In 1952, the field of high temperature microscopy received fresh impetus when Ordway (9) published his paper on techniques for growing and mounting small single crystals of refractory compounds using a thermocouple as a heating element, temperature measuring device, and specimen holder - the heating current being obtained from a 50 W audio amplifier. Welch progressively simplified the circuitry and described his experimental work, using the simplified circuits in a series of papers (10), (11), (12), (13), (14), (15), (16), (17), (18). The simple and effective circuit described in the paper published in 1961 (19), is now in extensive use in a number of research establishments and is similar to the one presented below.

The introduction by Mercer and Miller (20), (21) of two-channel heating and oscilloscope monitoring of cooling curves extended the application of the technique to include microscopic thermal analysis between any two pre-selected temperatures. It has recently been shown that a high-speed

millivolt chart recorder is a superior means of obtaining heating and cooling curves.

An understanding of the possible applications of high temperature microscopy is best gained by enumerating, in Appendix i, some of the research work conducted in the past decade on this type of apparatus. It was during this work that the various modifications in this instrument and technique were developed.

2. Construction of the high temperature microscope.

The electronic circuit is presented in Fig. 1.

Stabilised main supply passes via a constant-voltage transformer to two parallel interswitched variacs controlling the input to a 12 V transformer. The output from this transformer supplies the variable low voltage to the thermocouple through silicon diodes which pass only the positive half-cycles. This still provides sensibly continuous heating as proved in Appendix ii. The synchronous converter is phased to tap off the thermoelectric e.m.f. during part of the chopped negative half-cycles.

The heating current is varied and controlled by means of the two parallel interswitched variacs. The e.m.f. produced by the thermocouple is measured on a potentiometer and/or recorded continuously on a high speed millivolt recorder.

Because of the d.c. nature of the heating current the Peltier effect will produce, depending on the direction of current flow, a slight absorption

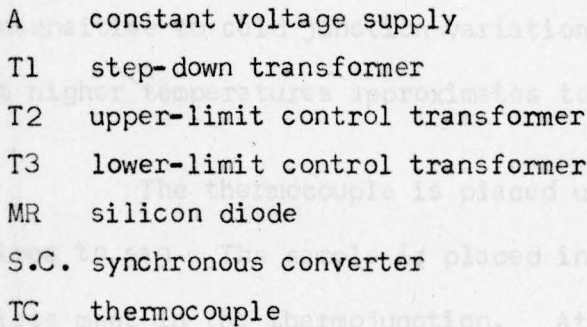


Fig. 1. Electronic circuit for the high temperature microscope.

or liberation of heat in the immediate vicinity of the thermojunction. It was recommended (10) that the direction of current flow be arranged to produce local cooling of the junction.

The heated portion of the thermocouple consists of two $1\frac{1}{2}$ cms. lengths of 0.2 mm. diameter wires, 5 per cent Rh-Pt and 20 per cent Rh-Pt, welded to each other at one end. The open ends are welded to supporting wires $3\frac{1}{2}$ cms. long and 0.5 mm. diameter. The supports are of the same composition as the thin wires making up the thermocouple cum heating portion. The thick supports are connected to terminals in the base plate of the cell which is attached to the stage of a polarising stereoscopic microscope with magnification of 50X and 100X. Cold junction errors can be neglected when using the 5 per cent Rh-Pt/20 per cent Rh-Pt combination since this is very insensitive to cold junction variation between 0°C - 50°C although the output at higher temperatures approximates to that of conventional thermocouples.

The thermocouple is placed upright to prevent the tendency of the wires to sag. The sample is placed in the loop at the apex where the two wires meet in the thermojunction. At this point the wires must be parallel and about 0.15 mm. apart. Under these conditions the temperature gradient throughout the specimen will be less than 5°C .

The cell in which the thermocouple is housed is a small rectangular container with a removable base plate carrying fittings designed to hold the thermocouple. This cell is attached to the microscope stage by means of movable arms so that the thermocouple can be centred in the optic system of

the microscope. On each side of the cell are two $\frac{7}{8}$ in. diameter holes covered with microscope slide covers. Fittings are provided for a controlled flow of gas.

A view of the high temperature microscope apparatus showing the incorporation of the high speed millivolt chart recorder is presented in Fig. 2.

The ease of determining the liquidus temperature will depend on the mobility of the melt and the relative ease of crystallization. To obtain the liquidus temperature for simple systems having mobile melts, the temperature is lowered and raised after melting until near the thermojunction a very small crystal remains in the melt without showing signs of growth or decay. Crystallization from viscous melts can be very sluggish and more patience has to be exercised in determining the liquidus temperature. Experience of crystal habit, crystal growth characteristics, birefringence, and general behaviour allow the observer repeatedly to recognise in a melt crystals which he has previously seen. This evidence of crystal identity is not available in other methods employed in studying phase equilibria. Naturally, where initial identification and final confirmation is required, the sample must be subjected to X-ray analysis. In comparison with the classical methods of studying high temperature equilibria this method is dynamic in that identification of the phases present depends on observing the growth and melting of crystals.

Cavalier ⁽²⁷⁾ alleges that errors as large as 30°C are possible due



Fig. 2. General view of high temperature microscope.

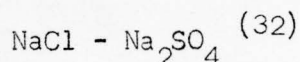
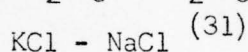
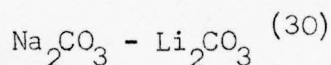
to thermal gradients, and in consequence advocates the use of an M-shaped heating wire, the sample being placed in the V-shaped depression. The temperature is measured by means of an extremely thin thermocouple inserted into the melt by means of a micromanipulator. At the International Congress at Brussels in 1961, Gutt (28), in defence of the more usual high temperature microscope using the triple function thermocouple discounted these objections. He showed that accuracy of the order of 5°C was obtainable with correctly shaped thermocouples made from 5 per cent Rh-Pt/20 per cent Rh-Pt wires. Apparently, Cavalier had not, in effect, manufactured his thermocouples so as to obtain a parallel portion with no thermal gradients. Molloy et al (29) also reported accuracy of the order of 5°C using triple function thermocouples. At the Building Research Station, England, during the seven years of constant use of the equipment, repeated determinations were made of melting points of standard substances such as diopside and pseudowollastonite, all these experiments indicating reproducibility of the order of 5°C .

3. Testing of the high temperature microscope.

Once the high temperature microscope had been constructed and the circuit tested for performance and stability, it was necessary to acquire experience in the preparation and mounting of samples, operation of the equipment and the interpretation of the visual phenomena occurring.

To ensure that the small weights of sample used are representative, sample homogeneity is clearly important. Repeated fusion, quenching, and grinding of the components will achieve this uniformity.

Equilibrium diagrams were constructed for the following systems:-



and the diagrams so obtained were compared with the published data. It was found that there was good agreement with the published equilibrium data and that the accuracy of the high temperature microscope was as good as claimed by other research workers, namely $\pm 5^\circ\text{C}$ - this value applying both to accuracy and precision. Also, the errors alleged by Cavalier ⁽²⁷⁾ of the order of 30°C were found to be absent when due care was taken to shape the thermocouple as described above.

For periodic calibration of the high temperature microscope in the temperature region in which it was to be used, three standard samples were employed. Dr. Steyn ⁽³³⁾ at the South African Iron and Steel Industrial Corporation had determined the liquidus temperatures on a high temperature microscope constructed in accordance with Cavalier's ⁽²⁷⁾ design while Dr. Sehlke at the Council for Scientific and Industrial Research had checked two of these using the classical quench method. The results are presented in Table I.

• Phase equilibria in the slag system (CaO + MgO) = 30.00 per cent, SiO₂ = 19.69 per cent, Al₂O₃ = 13.12 per cent, and TiO₂ = 37.19 per cent.

The slag samples were prepared by weighing and mixing the high purity constituents. These mixtures were then placed in platinum foil

TABLE I.

Comparison of liquidus temperatures of three different materials obtained using three different methods.

Sample	Dr. Steyn (i)	Dr. Sehlke (ii)	Author (iii)
A	1392°C	-	1385°C
B	1478°C	1480°C	1473°C
C	1484°C	1481°C	1483°C

- (i) By high temperature microscope designed to Cavalier's principle.
- (ii) By classical quench method.
- (iii) By high temperature microscope as used in this work.

containers and repeatedly fused, quenched, and ground. To check the homogeneity of the samples so produced, one sample was split into ten portions and the liquidus temperature of each portion was accurately determined in duplicate. The precision was better than $\pm 5^{\circ}\text{C}$. During these experiments, tests were also conducted to determine whether any poisoning of the thermocouples took place and whether appreciable volatilisation of the specimen occurred. These aspects are discussed in Appendix iii. As this procedure for the sample preparation had been proved to be completely effective in producing homogeneous samples, it was adopted for the production of all subsequent slag samples.

Specimens of each slag composition were then examined on the high temperature microscope to determine the liquidus temperature. These determinations were carried out in quadruplicate - a new sample being used for each determination and only two determinations being carried out on the same thermocouple.

The phase equilibria were plotted in the following manner. The liquidus temperature of a particular slag was determined. If this agreed to within $\pm 5^{\circ}\text{C}$ with the value previously determined when plotting the liquidus curve, then the specimen was accepted as a representative sample. This specimen was then cooled at a rate of 10°C per minute from 50°C above the liquidus temperature to a predetermined temperature and allowed to equilibrate at this temperature for 60 minutes. It was then either air- or water-quenched using whichever method was found necessary to prevent further transformation on quenching to ambient temperature. In this respect, the high temperature

microscope proved particularly useful in that every slag could be quenched at a sufficiently high rate to prevent any crystallization during cooling from the equilibrating temperature to ambient temperature. This prevents the formation of phases occasionally produced under conditions of rapid cooling which may make construction of phase equilibria extremely difficult. Water-quenching was found necessary only for slags with high MgO contents. This could be judged from observation of the slag bead while it was being quenched. The cooling rate of 10°C per minute was obtained by means of a motor-driven variac connected into the power supply of the high temperature microscope circuit.

This fully treated slag specimen at the thermal junction of the thermocouple was then separated from the thermocouple by lightly tapping it in a small agate mortar. It was then ground to a fine powder suitable for X-ray powder photography. To obtain the specimen for the X-ray camera, a bristle mounted in a collet was covered with rubber solution at one end and rolled into the powder, giving a small pellet. The collet holding the bristle and sample was then mounted in a 114.83 mm. diameter Debye-Scherrer X-ray diffraction camera and subjected to copper K α radiation with nickel filter for three hours at 40 KV x 20 mA.

The phases present were identified from the X-ray powder patterns in the normal manner. The Numerical (Hannawalt) Index and the Fink Index were used to obtain the data card numbers of the Powder Diffraction File. After initial identification, the phases were synthesised to facilitate repeated identification of the phases by direct comparison of the powder patterns. A graph was prepared showing the phases identified versus the equilibrating

temperatures. This process of plotting the phase equilibria was assisted visually by following the course of crystallization through the microscope. When the amount of crystalline material already present was still small enough to permit accurate observation of the appearance of a subsequent phase, the temperature of this subsequent appearance, determined in this manner, correlated with that determined by the X-ray method.

The temperature of appearance of a subsequent phase was bracketed to within a temperature range of 25°C . This means that a temperature quoted for the appearance of a particular phase is on an average, correct to within $\pm 12\frac{1}{2}^{\circ}\text{C}$, provided that very small quantities of the new phase are already detectable on the X-ray film. The estimation of the temperature of first appearance of a particular phase was facilitated by placing all the films of a particular slag composition obtained at the various equilibrating temperatures onto a high-intensity viewing box. It was then possible by comparison, having established the powder pattern for the new phase, to examine the film taken of the specimen treated at a higher temperature to establish whether traces of the major lines of this new phase were already visible. This technique, together with the visual observations, permitted the presence of a subsequent phase to be noticed at quite low concentrations of that new phase. In this manner the transverse section of the phase equilibria was established and this is depicted in Fig. 3. Table II shows the phases identified at the various equilibrating temperatures for the different slag compositions.

An example of a series of X-ray films obtained at the various equilibrating temperatures (for the slag with the $\text{CaO} = 14.00\%$ and $\text{MgO} = 16.00\%$

Fig. 3. Phase equilibrium diagram.

Slag system: $(\text{CaO} + \text{MgO}) = 30.00\%$, $\text{SiO}_2 = 19.69\%$,
 $\text{Al}_2\text{O}_3 = 13.12\%$, and $\text{TiO}_2 = 37.19\%$.

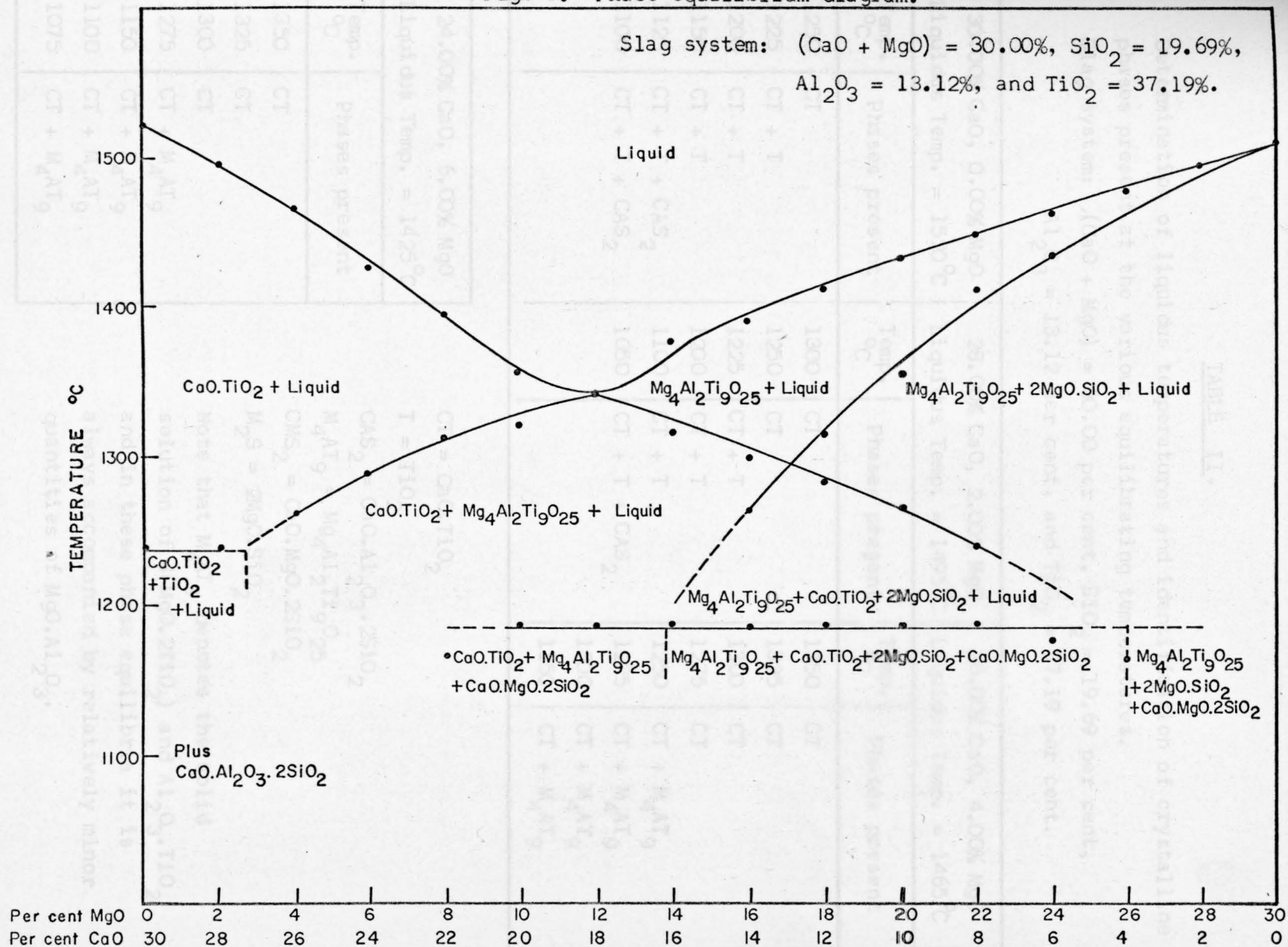


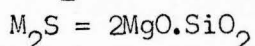
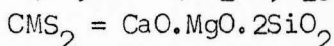
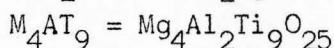
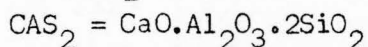
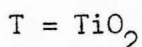
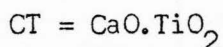
TABLE II.

Determination of liquidus temperatures and identification of crystalline phases present at the various equilibrating temperatures.

Slag system: (CaO + MgO) = 30.00 per cent, SiO₂ = 19.69 per cent, Al₂O₃ = 13.12 per cent, and TiO₂ = 37.19 per cent.

30.00% CaO, 0.00% MgO Liquidus Temp. = 1520°C		28.00% CaO, 2.00% MgO Liquidus Temp. = 1495°C		26.00% CaO, 4.00% MgO Liquidus Temp. = 1465°C	
Temp. °C	Phases present	Temp. °C	Phases present	Temp. °C	Phases present
1250	CT	1300	CT	1350	CT
1225	CT + T	1250	CT	1325	CT
1200	CT + T	1225	CT + T	1300	CT
1150	CT + T	1200	CT + T	1275	CT
1125	CT + T + CAS ₂	1100	CT + T	1250	CT + M ₄ AT ₉
1100	CT + T + CAS ₂	1050	CT + T + CAS ₂	1225	CT + M ₄ AT ₉
				1200	CT + M ₄ AT ₉
				1150	CT + M ₄ AT ₉

24.00% CaO, 6.00% MgO Liquidus Temp. = 1425°C	
Temp. °C	Phases present
1350	CT
1325	CT
1300	CT
1275	CT + M ₄ AT ₉
1150	CT + M ₄ AT ₉
1100	CT + M ₄ AT ₉
1075	CT + M ₄ AT ₉



Note that M₄AT₉ denotes the solid solution of 4(MgO · 2TiO₂) and Al₂O₃ · TiO₂ and in these phase equilibria it is always accompanied by relatively minor quantities of MgO · Al₂O₃.

TABLE II (CONTINUED).

22.00% CaO, 8.00% MgO Liquidus Temp. = 1395°C		20.00% CaO, 10.00% MgO Liquidus Temp. = 1355°C		18.00% CaO, 12.00% MgO Liquidus Temp. = 1340°C	
Temp. °C	Phases present	Temp. °C	Phases present	Temp. °C	Phases present
1325	CT	1320	CT + M_4AT_9	1330	M_4AT_9 + CT
1300	CT + M_4AT_9	1300	CT + M_4AT_9	1310	M_4AT_9 + CT
1200	CT + M_4AT_9	1200	CT + M_4AT_9	1300	M_4AT_9 + CT
1175	CT + M_4AT_9	1175	CT + M_4AT_9	1200	M_4AT_9 + CT
1150	CT + M_4AT_9 + CMS_2			1175	M_4AT_9 + CT + CMS_2
1100	CT + M_4AT_9 + CMS_2			1100	M_4AT_9 + CT + CMS_2
1000	CT + M_4AT_9 + CMS_2			900	M_4AT_9 + CT + CMS_2
900	CT + M_4AT_9 + CMS_2				

16.00% CaO, 14.00% MgO Liquidus Temp. = 1375°C		14.00% CaO, 16.00% MgO Liquidus Temp. = 1390°C	
Temp. °C	Phases present	Temp. °C	Phases present
1325	M_4AT_9	1370	M_4AT_9
1300	M_4AT_9 + CT	1325	M_4AT_9
1200	M_4AT_9 + CT	1300	M_4AT_9
1175	M_4AT_9 + CT + CMS_2	1275	M_4AT_9 + CT
1150	M_4AT_9 + CT + CMS_2	1250	M_4AT_9 + CT + M_2S
		1200	M_4AT_9 + CT + M_2S
		1175	M_4AT_9 + CT + M_2S + CMS_2
		1100	M_4AT_9 + CT + M_2S + CMS_2
		1000	M_4AT_9 + CT + M_2S + CMS_2
		900	M_4AT_9 + CT + M_2S + CMS_2

TABLE II (CONTINUED).

12.00% CaO, 18.00% MgO Liquidus Temp. = 1410°C		10.00% CaO, 20.00% MgO Liquidus Temp. = 1430°C	
Temp. °C	Phases present	Temp. °C	Phases present
1325	M_4AT_9	1400	M_4AT_9
1300	$M_4AT_9 + M_2S$	1350	$M_4AT_9 + M_2S$
1275	$M_4AT_9 + M_2S + CT$	1325	$M_4AT_9 + M_2S$
1200	$M_4AT_9 + M_2S + CT$	1300	$M_4AT_9 + M_2S$
1175	$M_4AT_9 + M_2S + CT + CMS_2$	1275	$M_4AT_9 + M_2S$
		1250	$M_4AT_9 + M_2S + CT$
		1225	$M_4AT_9 + M_2S + CT$
		1200	$M_4AT_9 + M_2S + CT$
		1175	$M_4AT_9 + M_2S + CT + CMS_2$
		1150	$M_4AT_9 + M_2S + CT + CMS_2$

8.00% CaO, 22.00% MgO Liquidus Temp. = 1445°C		6.00% CaO, 24.00% MgO Liquidus Temp. = 1460°C	
Temp. °C	Phases present	Temp. °C	Phases present
1425	M_4AT_9	1430	$M_4AT_9 + M_2S$
1400	$M_4AT_9 + M_2S$	1400	$M_4AT_9 + M_2S$
1300	$M_4AT_9 + M_2S$	1300	$M_4AT_9 + M_2S$
1250	$M_4AT_9 + M_2S$	1200	$M_4AT_9 + M_2S$
1225	$M_4AT_9 + M_2S + CT$	1175	$M_4AT_9 + M_2S + CMS_2$
1200	$M_4AT_9 + M_2S + CT$	1150	$M_4AT_9 + M_2S + CMS_2$
1175	$M_4AT_9 + M_2S + CT + CMS_2$	1100	$M_4AT_9 + M_2S + CMS_2$
1100	$M_4AT_9 + M_2S + CT + CMS_2$	950	$M_4AT_9 + M_2S + CMS_2$
900	$M_4AT_9 + M_2S + CT + CMS_2$		

TABLE II (CONTINUED).

4.00% CaO, 26.00% MgO Liquidus Temp. = 1475°C		2.00% CaO, 28.00% MgO Liquidus Temp. = 1490°C		0.00% CaO, 30.00% MgO Liquidus Temp. = 1505°C	
Temp. °C	Phases present	Temp. °C	Phases present	Temp. °C	Phases present
1440	$M_4AT_9 + M_2S$	1450	$M_4AT_9 + M_2S$	1480	M_4AT_9
1400	$M_4AT_9 + M_2S$	1150	$M_4AT_9 + M_2S$	1470	$M_4AT_9 + M_2S$
1300	$M_4AT_9 + M_2S$	1100	$M_4AT_9 + M_2S$	1400	$M_4AT_9 + M_2S$
1175	$M_4AT_9 + M_2S$	900	$M_4AT_9 + M_2S$	1300	$M_4AT_9 + M_2S$
1150	$M_4AT_9 + M_2S + CMS_2$			1200	$M_4AT_9 + M_2S$
1100	$M_4AT_9 + M_2S + CMS_2$			900	$M_4AT_9 + M_2S$
900	$M_4AT_9 + M_2S + CMS_2$				

content) is shown in Fig. 4. Photomicrographs of the primary phases occurring in the slags are shown in Fig. 5.

It must be appreciated that a 60 minute duration for the equilibrating soaking period subsequent to a cooling rate of 10°C per minute is not necessarily sufficient to establish absolute equilibrium conditions. This point becomes of importance at temperatures below 1150°C where the phase changes, when they exist, are no longer able to be delineated accurately. However, when the slag specimens were removed from the thermocouple and thin-sections made from them, the following conclusion could be arrived at. If the specimen was cooled at 10°C per minute to below the solidus (1190°C) and soaked for the normal period of 60 minutes, then no glass could be identified under the polarising microscope. This means that crystallization had at least occurred throughout the specimen as opposed to some of the slags investigated later.

The horizontal line representing the appearance of diopside ($\text{CaO.MgO}.2\text{SiO}_2$) is also the solidus line. This was ascertained by cooling the slag specimens at 10°C per minute and observing at which temperature the last liquid solidifies. This occurred at a temperature just below this straight line and with lower rates of cooling the observed solidus temperature more closely approached the solidus line. Also, all the other subsequent phases appear gradually in that the pattern of the new phase becomes progressively more intense with decrease in equilibrating temperature. But the crystallization of the diopside occurs at constant temperature at the solidus since the X-ray films just above the solidus exhibit no trace of diopside

Fig. 4. Series of X-ray films illustrating progressive order of crystallization of phases in a titaniferous slag.

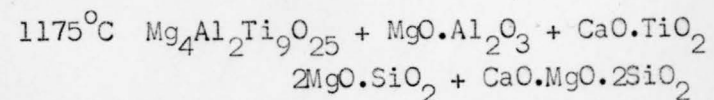
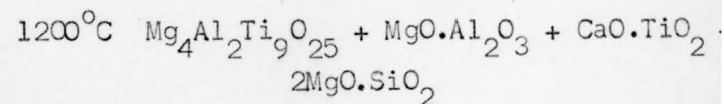
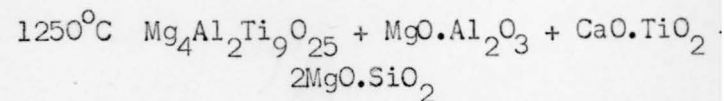
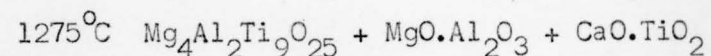
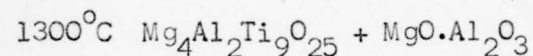
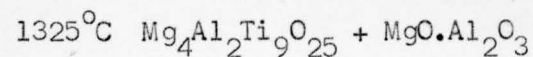
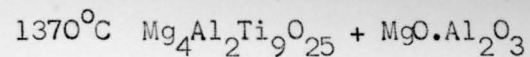
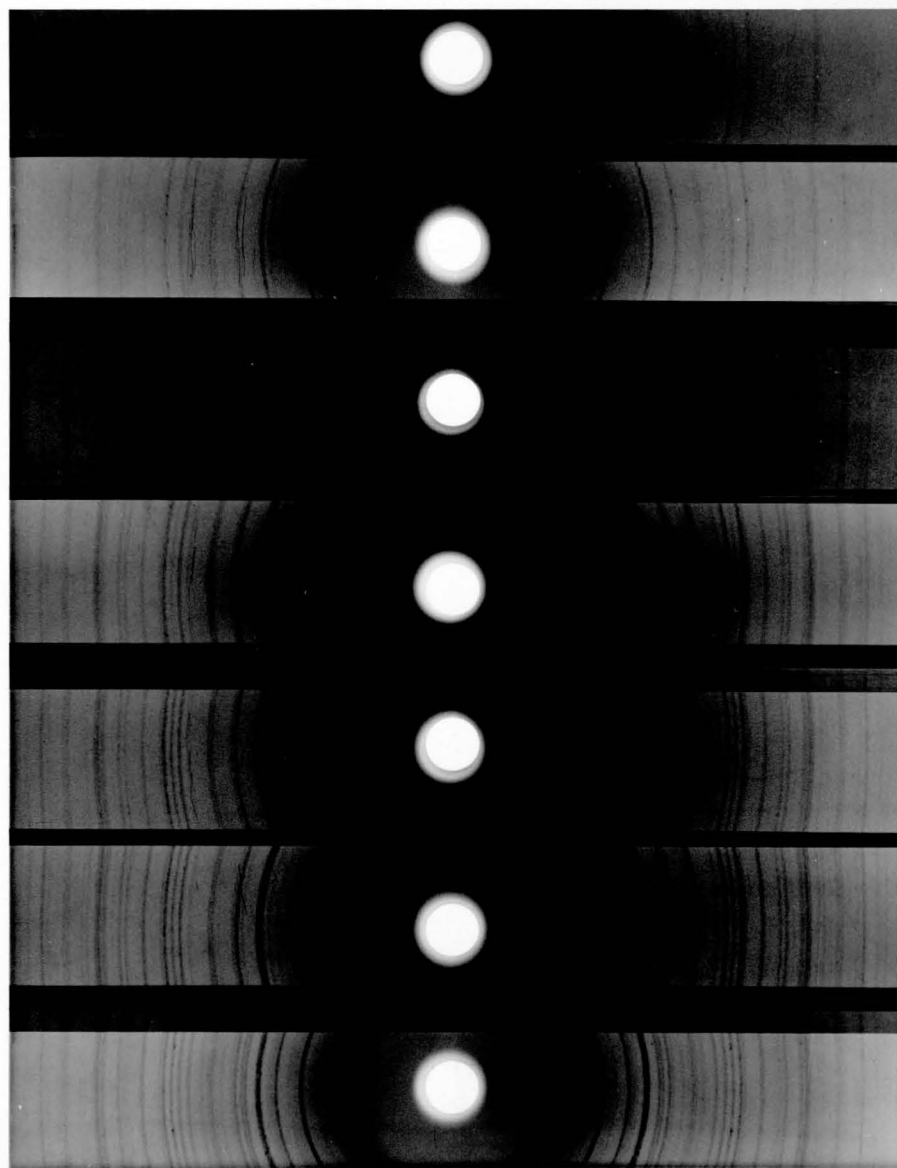


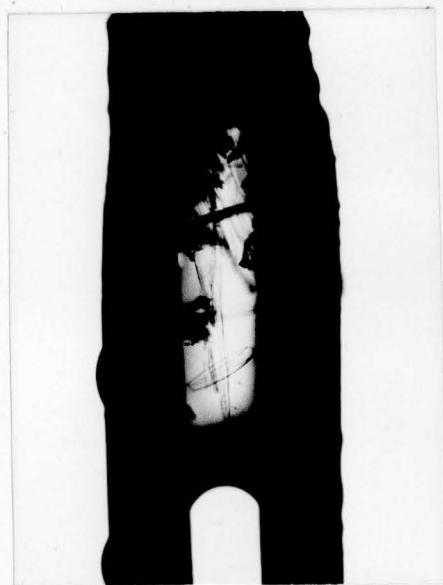
Fig. 5. Photomicrographs showing primary phases in titaniferous slags (slags were photographed while in position on the thermocouple/heating element).



Dendrites of perovskite



Lath-like crystals of
 $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$



Co-precipitation of perovskite
 and $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$

whereas just below the solidus, diopside lines are clearly present and do not become more intense with decrease in equilibrating temperature. In the composition range of high CaO content, the solidus temperature is lower by about 60°C.

When this phase equilibrium diagram is considered in relation to published work, the following confirmatory points emerge : Considering the composition $\text{CaO} = 30.00$ per cent, $\text{SiO}_2 = 19.69$ per cent, $\text{Al}_2\text{O}_3 = 13.12$ per cent, and $\text{TiO}_2 = 37.19$ per cent, i.e., the L.H.S. end with no MgO present, then this composition can be roughly expressed as 40 per cent $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ and 60 per cent $\text{CaO} \cdot \text{TiO}_2$ with relatively smaller percentages of SiO_2 and TiO_2 remaining. According to Nisioka ⁽³⁴⁾ such a composition would lead to the primary crystallization of $\text{CaO} \cdot \text{TiO}_2$ followed by $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. In Fig. 3 it can be seen that this is the case and that the surplus TiO_2 has crystallized as rutile. Considering the composition $\text{MgO} = 30.00$ per cent, $\text{SiO}_2 = 19.69$ per cent, $\text{Al}_2\text{O}_3 = 13.12$ per cent, and $\text{TiO}_2 = 37.19$ per cent, i.e., the R.H.S. end with no CaO present, it is found that, if in consideration of the primary phase the SiO_2 is neglected (in Fig. 3. SiO_2 does not appear in the primary phase) then according to Berezhnoi and Gul'ko ⁽³⁵⁾ the primary phases are likely to be a solid solution of $\text{MgO} \cdot 2\text{TiO}_2$ and $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ with a smaller proportion of $\text{MgO} \cdot \text{Al}_2\text{O}_3$. This is confirmed in Fig. 3 in that the primary phase is $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$ with traces of $\text{MgO} \cdot \text{Al}_2\text{O}_3$. This $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$ is a solid solution corresponding to 80 mol. per cent $\text{MgO} \cdot 2\text{TiO}_2$ and 20 mol. per cent $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$. The identification was made by comparison of the powder patterns with the published data of Sigurdson and Cole ⁽³⁶⁾ whereby very good correlation was established with that of the 80/20 solid solution, i.e., $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$.

As mentioned above, the $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$ phase is accompanied by some weak lines corresponding to the phase $\text{MgO}.\text{Al}_2\text{O}_3$ which would be expected to be present. Visually, the $\text{MgO}.\text{Al}_2\text{O}_3$ cannot be resolved from the $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$.

The perovskite ($\text{CaO}.\text{TiO}_2$) always crystallizes in the form of dendrites irrespective of the cooling rate. Ohno (37), while examining the physical properties of titaniferous slags, also found that the perovskite crystals grow dendritically. None of the other phases ever exhibit dendritic growth. The perovskite structure in its idealized form is cubic with the titanium atoms occupying the corners of the cell, a calcium atom is at its centre and the oxygen atoms lie at the mid-points of its edges. The perovskite structure is inclined to exhibit pseudosymmetric variations of this ideal arrangement as a result of small displacements of the atoms and it is possibly this fact which produces the strain, imperfections or irregularities associated with the formation of dendrites. It is also indicated that the initial rate of growth of the perovskite must be high under continuous cooling conditions. During the soaking period at the equilibrating temperature, the early dendritic superstructure is filled in as growth continues.

From Fig. 3 it can be seen that the liquidus temperatures of these slags change from 1520°C at 30 per cent CaO and 0 per cent MgO to 1505°C at 0 per cent CaO and 30 per cent MgO , passing through a minimum of 1340°C at 12 per cent MgO and 18 per cent CaO . It is indicated that the slags must have both CaO and MgO present to obtain sufficiently low liquidus temperatures of the order required for arc smelting of the Bushveld titaniferous magnetite ores. Changing the basic oxide components of the flux from a limestone/

dolomite mixture ($\text{CaO} = 22$ per cent, $\text{MgO} = 8$ per cent in the slag) to dolomite ($\text{CaO} = 16$ per cent, $\text{MgO} = 14$ per cent in the slag) as envisaged, would result in the liquidus temperature of the slag changing from 1395°C to 1375°C . By the progressive replacement of the limestone in the limestone/dolomite mixture by dolomite, the liquidus temperature can be varied between 1340°C and 1395°C within the limits of composition contemplated. Also, by this replacement of the limestone by dolomite, the phase equilibria of the slags will change. In the slag as used on the pilot plant, the primary phase to crystallize is perovskite ($\text{CaO}.\text{TiO}_2$) followed by ($\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$ plus $\text{MgO}.\text{Al}_2\text{O}_3$) while in the proposed dolomitic slag this order of crystallization is reversed. In addition, forsterite ($2\text{MgO}.\text{SiO}_2$) crystallizes as the tertiary phase in the proposed slag. The crystallization of diopside occurs at the solidus temperature and it appears that this temperature is constant over this range of slag compositions.

5. Liquidus curves of slags with a ($\text{CaO} + \text{MgO}$) content of 25.00 per cent and 35.00 per cent respectively.

The phase equilibria presented in Fig. 3 are for slags with a ($\text{CaO} + \text{MgO}$) content = 30.00 per cent, which it is thought approach most closely to those which are likely to be produced on the plant. Thus, the effect on the phase equilibria of any variations in the relative amounts of limestone and dolomite, provided that the total ($\text{CaO} + \text{MgO}$) = 30.00 per cent, are depicted in this phase equilibrium diagram.

Interest was, however, also attached to knowledge of the behaviour of the liquidus temperatures for slags where the total ($\text{CaO} + \text{MgO}$) contents

are more and less than 30 per cent. Consequently, two series of slags were prepared - one having a total of 25.00 per cent ($\text{CaO} + \text{MgO}$), the other having a total of 35.00 per cent ($\text{CaO} + \text{MgO}$). The other three components, namely SiO_2 , Al_2O_3 , and TiO_2 are increased and decreased respectively but their proportions within the slag remain constant. These slag samples were prepared not by the lengthy fusion and quench method but merely by mechanically mixing the oxide components in an oscillatory mechanical mixer. It had previously been shown that this more rapid method of sample preparation was accompanied by the expected loss in precision (precision = $\pm 15^\circ\text{C}$), which can be attributed to incomplete mixing mainly due to the disparity in density of the various oxide components.

The liquidus temperatures and primary phases were determined in the same manner as detailed in Section 2.4. The results are presented in Table III and graphically illustrated in Fig. 6. together with the liquidus curve for the ($\text{CaO} + \text{MgO}$) content = 30.00 per cent from Section 2.4.

From Fig. 6 it can be seen that the titaniferous slags with various ($\text{CaO} + \text{MgO}$) contents exhibit large changes in liquidus temperatures with comparatively minor changes in ($\text{CaO} + \text{MgO}$) contents. The liquidus temperatures for the slags with 25 per cent CaO and 0 per cent MgO , 30 per cent CaO and 0 per cent MgO , and 35 per cent CaO and 0 per cent MgO are 1370°C , 1520°C , and 1650°C respectively. As the MgO content relative to the CaO content is increased in each of these curves, the liquidus temperatures are decreased to minima of 1295°C , 1340°C , and 1440°C respectively. The trough of minimum liquidus temperatures extends from the lime-rich side for the lower ($\text{CaO} + \text{MgO}$)

TABLE III.

Determination of liquidus temperatures and identification of primary phases in titaniferous slags with (CaO + MgO) contents of: 25.00 per cent and 35.00 per cent respectively.

(a) Slag system: (CaO + MgO) = 25.00%, SiO₂ = 21.10%, Al₂O₃ = 14.06%, and TiO₂ = 39.84%.

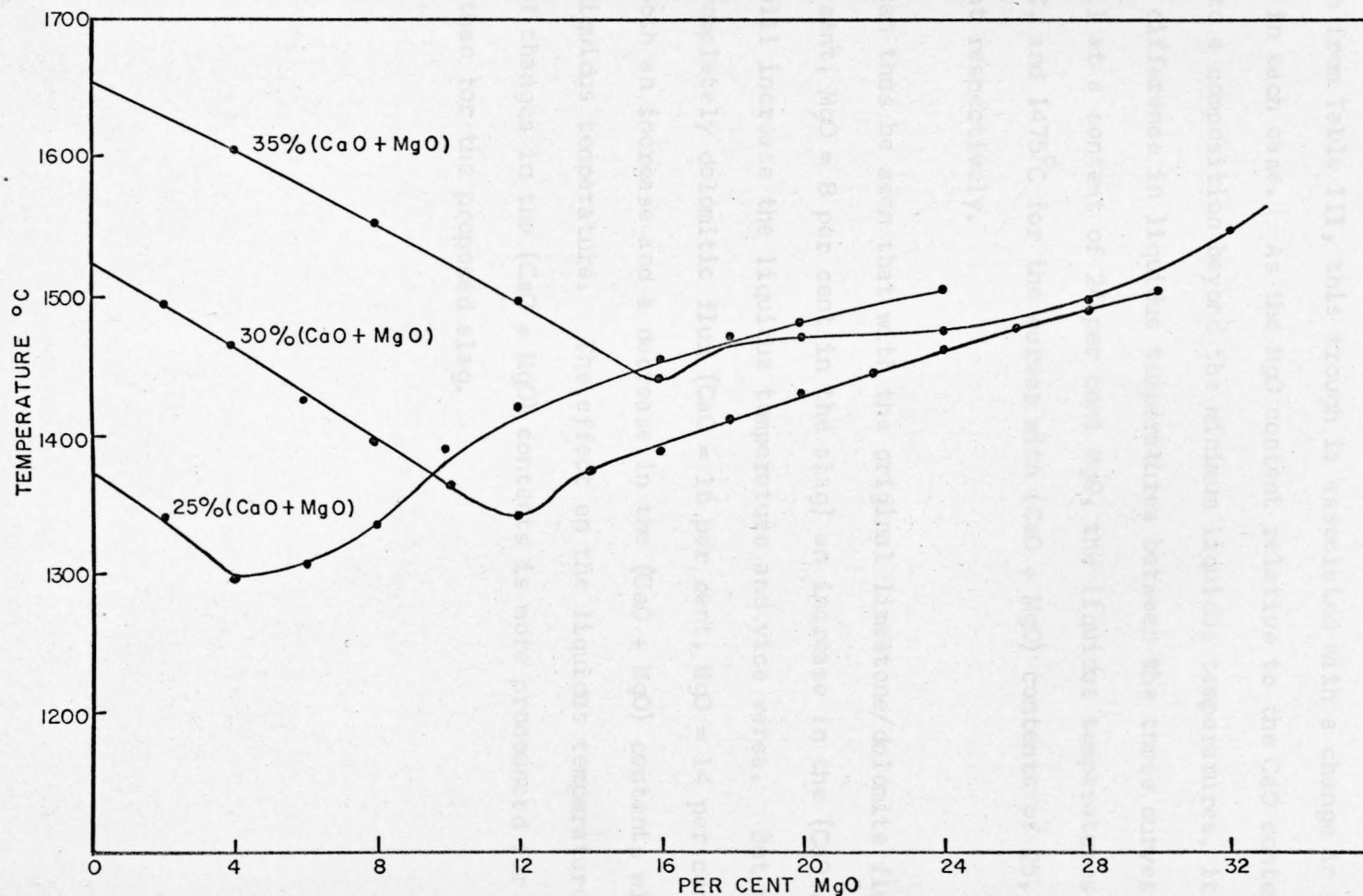
CaO %	MgO %	Liquidus Temp. °C	Primary phase
25	0	1370	CaO.TiO ₂
23	2	1340	CaO.TiO ₂
21	4	1295	CaO.TiO ₂ + Mg ₄ Al ₂ Ti ₉ O ₂₅
19	6	1305	Mg ₄ Al ₂ Ti ₉ O ₂₅
17	8	1335	Mg ₄ Al ₂ Ti ₉ O ₂₅
15	10	1390	Mg ₄ Al ₂ Ti ₉ O ₂₅
13	12	1420	Mg ₄ Al ₂ Ti ₉ O ₂₅
9	16	1455	Mg ₄ Al ₂ Ti ₉ O ₂₅
5	20	1480	Mg ₄ Al ₂ Ti ₉ O ₂₅
1	24	1505	Mg ₄ Al ₂ Ti ₉ O ₂₅

TABLE III (CONTINUED).

(b) Slag system: $(\text{CaO} + \text{MgO}) = 35.00\%$, $\text{SiO}_2 = 18.29\%$, $\text{Al}_2\text{O}_3 = 12.19\%$,
and $\text{TiO}_2 = 34.52\%$.

CaO %	MgO %	Liquidus Temp. °C	Primary phase
35	0	1650	$\text{CaO} \cdot \text{TiO}_2$
31	4	1605	$\text{CaO} \cdot \text{TiO}_2$
27	8	1550	$\text{CaO} \cdot \text{TiO}_2$
23	12	1495	$\text{CaO} \cdot \text{TiO}_2$
19	16	1440	$\text{CaO} \cdot \text{TiO}_2$ + not indexed in the Powder Diffraction File
17	18	1470	Not indexed in the Powder Diffraction File
15	20	1470	"
11	24	1475	"
7	28	1495	"
3	32	1545	"

Fig. 6. Liquidus curves for titaniferous slags with (CaO + MgO) contents of 25.00%, 30.00%, and 35.00% respectively.



content to the magnesia-rich side for the higher (CaO + MgO) content curve. As can be seen from Table III, this trough is associated with a change in the primary phase in each case. As the MgO content relative to the CaO content is increased to a composition beyond the minimum liquidus temperatures, it is seen that the difference in liquidus temperatures between the three curves is decreased until at a content of 24 per cent MgO, the liquidus temperatures are 1505°C, 1460°C, and 1475°C for the curves with (CaO + MgO) contents of 25, 30, and 35 per cent respectively.

It can thus be seen that with the original limestone/dolomite flux (CaO = 22 per cent, MgO = 8 per cent in the slag) an increase in the (CaO + MgO) content will increase the liquidus temperature and vice versa. But with the proposed completely dolomitic flux (CaO = 16 per cent, MgO = 14 per cent in the slag) both an increase and a decrease in the (CaO + MgO) contents will increase the liquidus temperature. The effect on the liquidus temperatures of the slags of changes in the (CaO + MgO) contents is more pronounced for the original slag than for the proposed slag.

CHAPTER III.

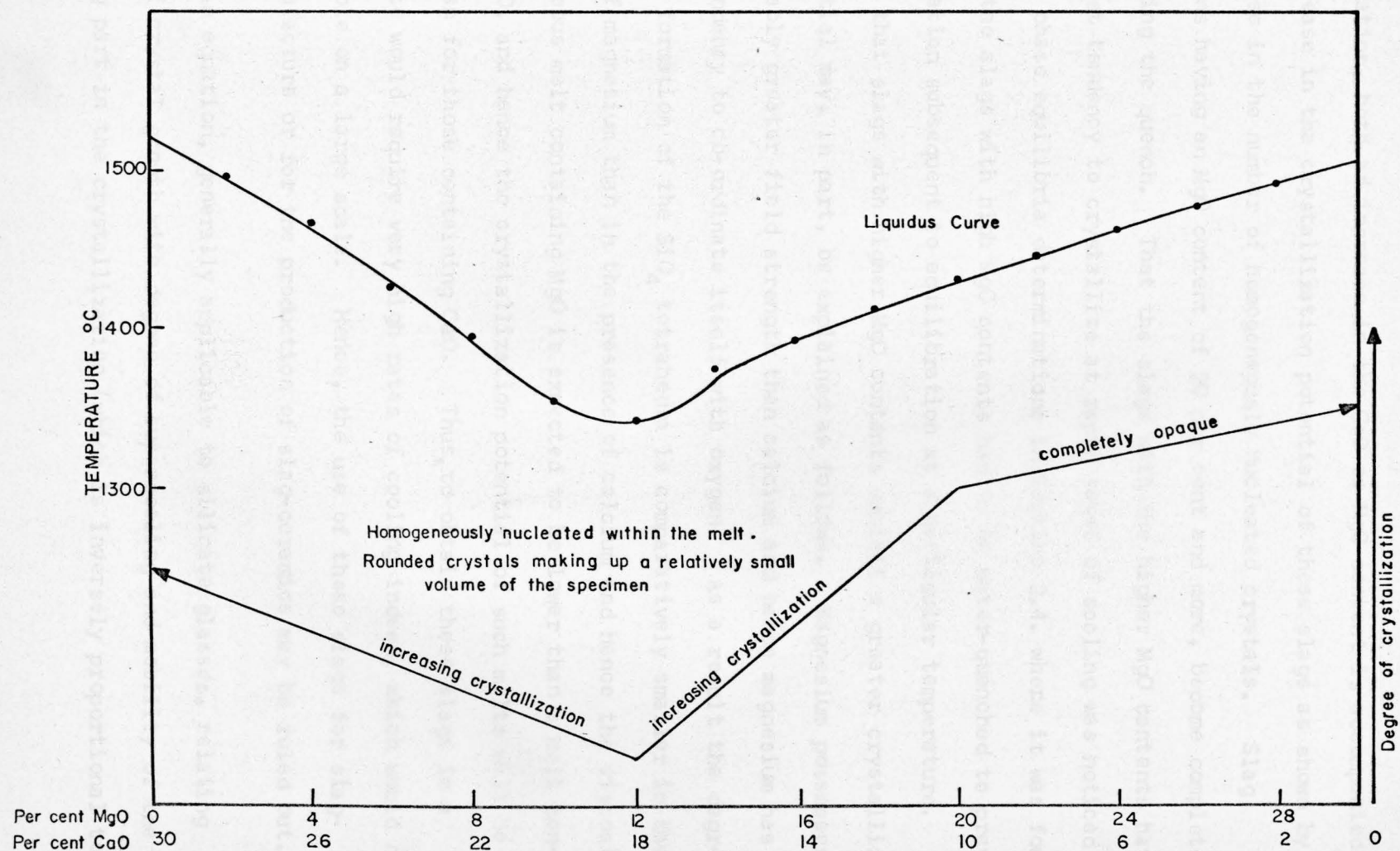
PHASE EQUILIBRIA OF A TITANIFEROUS SLAG WITH INCREASING CONTENTS OF SiO_2 .

Reasons for increasing the SiO_2 content.

From Fig. 3 it can be seen that the TiO_2 crystallizes either as perovskite ($\text{CaO} \cdot \text{TiO}_2$) or as a solid solution between $\text{MgO} \cdot 2\text{TiO}_2$ and $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ namely, $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$ with minor quantities of $\text{MgO} \cdot \text{Al}_2\text{O}_3$, depending on the lime and magnesia contents. Only at very high CaO contents does TiO_2 crystallize as a separate phase and then only as a comparatively small amount of secondary phase. These phase equilibria would make extraction of the TiO_2 difficult.

Also, during the establishment of these phase equilibria, it was noticed that the crystallization potential of these slags, i.e., their readiness to crystallize even at high rates of cooling, was very marked. This is shown in Fig. 7 which is a pictorial representation of the degree of crystallization obtained at cooling rates of 400°C per second from 50°C above the liquidus. This rate of cooling is obtained by switching off the power supply to the thermocouple. From this diagram it can be seen that minimum crystallization occurs in the slag with a 12 per cent MgO and 18 per cent CaO content. In the glass industry, the measure taken to prevent crystallization is to change the composition of the melt so that it corresponds to a phase boundary. Hence, in these titaniferous slags the minimum crystallization potential can be expected at the minimum temperature which is associated with a change in phase constitution. From this composition of minimum

Fig. 7. Graphical representation of the crystallization potential of titaniferous slags when cooled at a rate of $400^{\circ}\text{C}/\text{second}$.



crystallization, both an increase in the CaO or MgO content is accompanied by an increase in the crystallization potential of these slags as shown by the increase in the number of homogeneously nucleated crystals. Slag compositions having an MgO content of 20 per cent and more, become completely opaque during the quench. That the slags with the higher MgO contents have the greatest tendency to crystallize at rapid rates of cooling was noticed during the phase equilibria determinations in Section 2.4, where it was found that only the slags with high MgO contents had to be water-quenched to prevent crystallization subsequent to equilibration at a particular temperature. The reason that slags with higher MgO contents exhibit a greater crystallization potential may, in part, be explained as follows. Magnesium possesses a considerably greater field strength than calcium and hence magnesium has a greater tendency to co-ordinate itself with oxygen. As a result the degree of network formation of the SiO_4 tetrahedra is comparatively smaller in the presence of magnesium than in the presence of calcium and hence the viscosity of a siliceous melt containing MgO is expected to be lower than a melt containing CaO, and hence the crystallization potential of such melts will be greater than for those containing CaO. Thus, to obtain these slags in a glassy state would require very high rates of cooling indeed, which would not be attainable on a large scale. Hence, the use of these slags for slag-cement manufacture or for the production of slag-ceramics may be ruled out.

An equation, generally applicable to silicate glasses, relating the rate of crystal growth with degree of supercooling and mobility of the ions taking part in the crystallization (which is inversely proportional to

the viscosity of the liquid) is :

$$R = k(T_{\text{liq.}} - T) \left[\frac{1}{\eta} \right]^2 \quad (38)$$

where R = rate of crystal growth.

η = viscosity, which is a complex function of T and composition

$T_{\text{liq.}}$ = liquidus temperature of the system.

T = temperature at which rate of growth is measured.

k = constant.

Therefore, there are two different methods of preventing crystallization. Either the initial cooling rate or the viscosity must be high. Now, it has been shown that the rates of cooling required to prevent crystallization in these slags are very high and as expected the viscosity is low. (The viscosity is lower than normal blast furnace slags as judged on the high temperature microscope). Therefore, to enable these slags to be cooled at slower rates and yet be in the glassy state, the viscosity of the slags must be increased. This increase in viscosity can be most readily obtained by the addition of SiO_2 . With an increase in the proportion of network-forming oxide, the slag will tend progressively to change from the Frenkel model of a "fissured liquid" of low viscosity towards the Bernal model of a "flawless liquid" with an accompanying increase in viscosity.

The addition of SiO_2 to these titaniferous slags, apart from increasing the viscosity, may have another very desirable effect. According to Dietzel (39) Si and Ti have field strengths of 1.57 and 1.04 respectively; where field strength = $\frac{Z}{a^2}$, Z = valency and a = ionic distance with respect to

oxygen for the correct co-ordination number of the cation. Since the field strengths of both Si and Ti are extremely high there will be a strong tendency for both the Si and Ti to co-ordinate themselves completely. This is shown in the TiO_2 - SiO_2 system which exhibits complete immiscibility in the solid state (i.e., eutectic system with the eutectic point close to the SiO_2 -rich side) and even very extensive immiscibility in the liquid state ⁽⁴⁰⁾. Thus, by increasing the SiO_2 content of the slags, it may be possible to cause considerable changes in the phase relationships with the possibility of producing the TiO_2 in a more readily extractable form.

Phase equilibria in the slag system CaO = 18 per cent, MgO = 12.00 per cent SiO_2 = 19.69 per cent, Al_2O_3 = 13.12 per cent, and TiO_2 = 37.19 per cent with increasing contents of SiO_2 .

The SiO_2 content of the following slag was progressively increased.

CaO = 18.00 per cent

MgO = 12.00 per cent

SiO_2 = 19.69 per cent

Al_2O_3 = 13.12 per cent

TiO_2 = 37.19 per cent

This slag has a composition intermediate between that of the present slag (limestone/dolomite flux) and the proposed slag (dolomite flux).

These slags were made up as before, i.e., by the melting, quenching, and grinding technique. They were then examined on the high temperature microscope to determine the liquidus temperatures and subsequently the phase equilibria were established in the manner previously outlined in Section 2.4.

The results are presented in Table IV and plotted in Fig. 8. A series of X-ray films obtained at the various equilibrating temperatures for the slag with a 38.23 per cent SiO_2 content is shown in Fig. 9. In Fig. 10 photomicrographs are shown of the primary phases occurring in these slags.

Below 1200°C , phase equilibria are difficult to determine both because of the number of phases present and because of the slow rate of establishment of equilibrium at these temperatures. With increased contents of SiO_2 , the phase equilibria even below the solidus exhibit no phase containing Al_2O_3 . This is suggestive of glass formation and thin-sections made from specimens cooled at 10°C per minute and equilibrated for 60 minutes at temperatures below the solidus were examined to determine the presence of glass. It was found that traces of glass were present when the SiO_2 content was 38.23 per cent or more and that the glass content increased with increase in SiO_2 content. Hence in the phase diagram, glass is recorded as a phase below the solidus for slags with contents of SiO_2 in excess of 38.23 per cent. Also as expected from earlier reasoning, the viscosity increased rapidly with increase in SiO_2 as judged by the thermal movement in the melt when viewed microscopically.

This glass probably contains Al_2O_3 and SiO_2 as well as CaO and/or MgO . The Al ions when in four-fold co-ordination give rise to tetrahedral AlO_4 groups and these can replace SiO_4 tetrahedra in silicate lattices. Since each Al ion has a charge of 3+ as compared with a charge of 4+ for each Si ion, an additional positive charge must be present to ensure electro-neutrality. One alkaline earth metal ion (from CaO and/or MgO) per two AlO_4

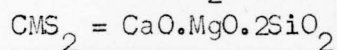
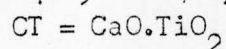
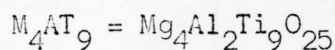
TABLE IV.

Determination of liquidus temperatures and identification of crystalline phases present at the various equilibrating temperatures.

Slag system: CaO = 18.00 per cent, MgO = 12.00 per cent, SiO₂ = 19.69 per cent, Al₂O₃ = 13.12 per cent, and TiO₂ = 37.19 per cent with increasing contents of SiO₂.

SiO ₂ addition = 0.00% SiO ₂ content = 19.69% Liquidus Temp. = 1340°C		SiO ₂ addition = 4.00% SiO ₂ content = 22.78% Liquidus Temp. = 1355°C		SiO ₂ addition = 8.00% SiO ₂ content = 25.64% Liquidus Temp. = 1355°C	
Temp. °C	Phases present	Temp. °C	Phases present	Temp. °C	Phases present
1330	M ₄ AT ₉ + CT	1300	M ₄ AT ₉	1300	M ₄ AT ₉
1310	M ₄ AT ₉ + CT	1275	M ₄ AT ₉ + CT	1250	M ₄ AT ₉
1300	M ₄ AT ₉ + CT	1250	M ₄ AT ₉ + CT	1225	M ₄ AT ₉ + CT
1200	M ₄ AT ₉ + CT	1200	M ₄ AT ₉ + CT	1200	M ₄ AT ₉ + CT
1175	M ₄ AT ₉ + CT + CMS ₂	1175	M ₄ AT ₉ + CT + CMS ₂	1175	M ₄ AT ₉ + CT
1100	M ₄ AT ₉ + CT + CMS ₂	1150	M ₄ AT ₉ + CT + CMS ₂	1150	M ₄ AT ₉ + CT + CMS ₂
900	M ₄ AT ₉ + CT + CMS ₂			1100	M ₄ AT ₉ + CT + CMS ₂

SiO ₂ addition = 12.00% SiO ₂ content = 28.30% Liquidus Temp. = 1345°C	
Temp. °C	Phases present
1250	M ₄ AT ₉
1200	M ₄ AT ₉
1175	M ₄ AT ₉
1150	M ₄ AT ₉ + CT
1125	M ₄ AT ₉ + CT
1100	M ₄ AT ₉ + CT + CMS ₂



S = Alpha-cristobalite

TABLE IV (CONTINUED).

SiO_2 addition = 16.00% SiO_2 content = 30.76% Liquidus Temp. = 1340°C		SiO_2 addition = 20.00% SiO_2 content = 33.08% Liquidus Temp. = 1335°C	
Temp. °C	Phases present	Temp. °C	Phases present
1200	M_4AT_9	1250	$\text{T} + \text{M}_4\text{AT}_9$
1150	M_4AT_9	1200	$\text{T} + \text{M}_4\text{AT}_9$
1125	M_4AT_9	1150	$\text{T} + \text{M}_4\text{AT}_9$
1100	$\text{M}_4\text{AT}_9 + \text{T} + \text{CMS}_2$	1125	$\text{T} + \text{M}_4\text{AT}_9$
1050	$\text{M}_4\text{AT}_9 + \text{T} + \text{CMS}_2 + \text{CT}$	1100	$\text{T} + \text{M}_4\text{AT}_9 + \text{CMS}_2$

SiO_2 addition = 25.00% SiO_2 content = 35.75% Liquidus Temp. = 1330°C		SiO_2 addition = 30.00% SiO_2 content = 38.23% Liquidus Temp. = 1350°C		SiO_2 addition = 35.00% SiO_2 content = 40.51% Liquidus Temp. = 1360°C	
Temp. °C	Phases present	Temp. °C	Phases present	Temp. °C	Phases present
1300	T	1250	T	1100	T
1275	$\text{T} + \text{M}_4\text{AT}_9$	1225	T	1075	$\text{T} + \text{M}_4\text{AT}_9$
1225	$\text{T} + \text{M}_4\text{AT}_9$	1200	$\text{T} + \text{M}_4\text{AT}_9$	1050	$\text{T} + \text{M}_4\text{AT}_9 + \text{CMS}_2$
1200	$\text{T} + \text{M}_4\text{AT}_9$	1100	$\text{T} + \text{M}_4\text{AT}_9$	1000	$\text{T} + \text{M}_4\text{AT}_9 + \text{CMS}_2$
1100	$\text{T} + \text{M}_4\text{AT}_9$	1075	$\text{T} + \text{M}_4\text{AT}_9 + \text{CMS}_2$		
1075	$\text{T} + \text{M}_4\text{AT}_9 + \text{CMS}_2$	1050	$\text{T} + \text{M}_4\text{AT}_9 + \text{CMS}_2$		
1050	$\text{T} + \text{M}_4\text{AT}_9 + \text{CMS}_2$	1000	$\text{T} + \text{M}_4\text{AT}_9 + \text{CMS}_2$		
1025	$\text{T} + \text{M}_4\text{AT}_9 + \text{CMS}_2$				

TABLE IV (CONTINUED).

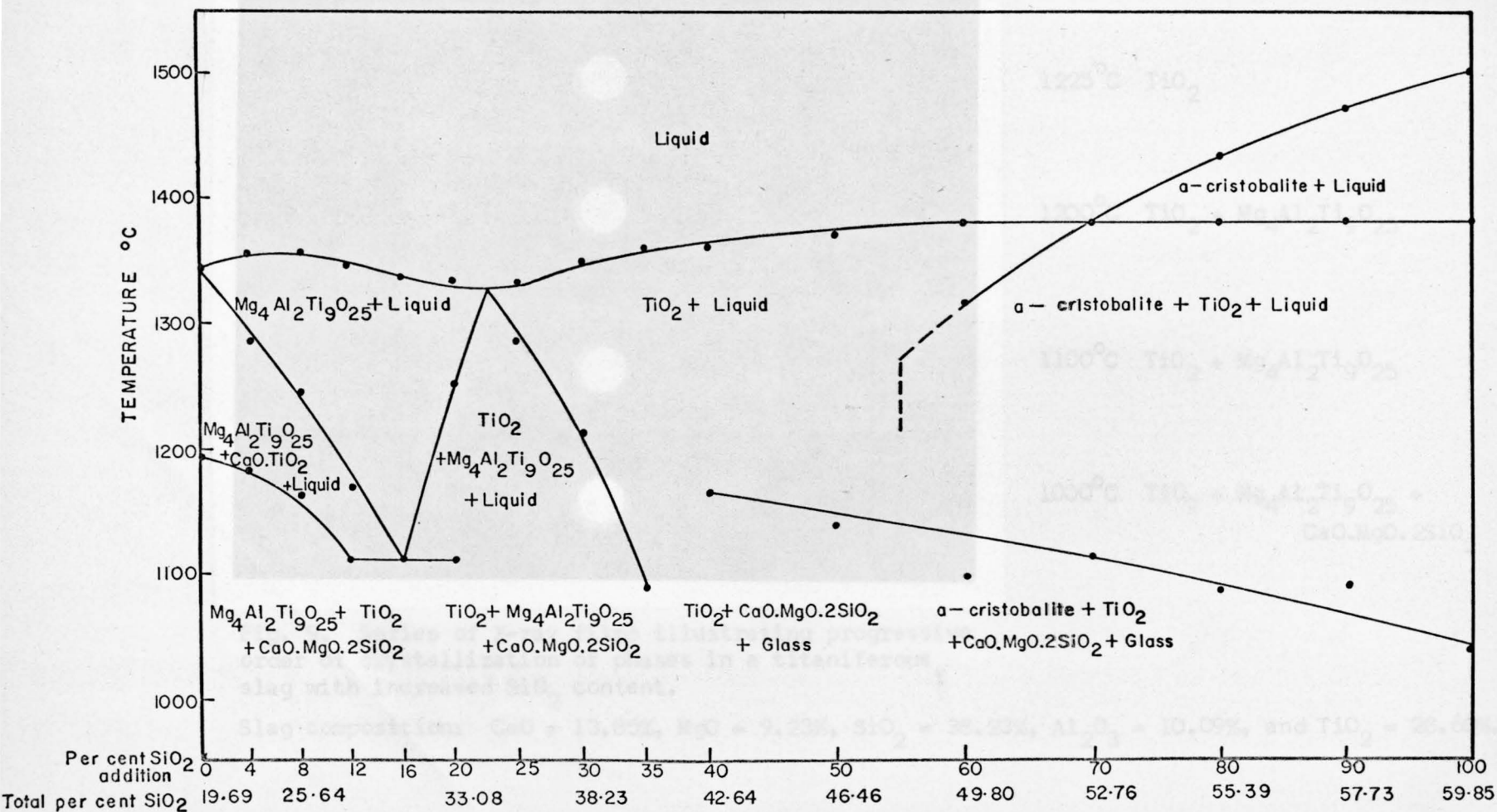
SiO ₂ addition = 40.00% SiO ₂ content = 42.64% Liquidus Temp. = 1360°C		SiO ₂ addition = 50.00% SiO ₂ content = 46.46% Liquidus Temp. = 1370°C		SiO ₂ addition = 60.00% SiO ₂ content = 49.80% Liquidus Temp. = 1380°C	
Temp. °C	Phases present	Temp. °C	Phases present	Temp. °C	Phases present
1200	T	1200	T	1325	T
1175	T	1150	T	1300	T + S
1150	T + CMS ₂	1125	T + CMS ₂	1250	T + S
1100	T + CMS ₂	1100	T + CMS ₂	1175	T + S
1075	T + CMS ₂ + M ₄ AT ₉	1000	T + CMS ₂	1100	T + S
1050	T + CMS ₂ + M ₄ AT ₉			1075	T + S + CMS ₂
1000	T + CMS ₂ + M ₄ AT ₉			1050	T + S + CMS ₂
				1000	T + S + CMS ₂

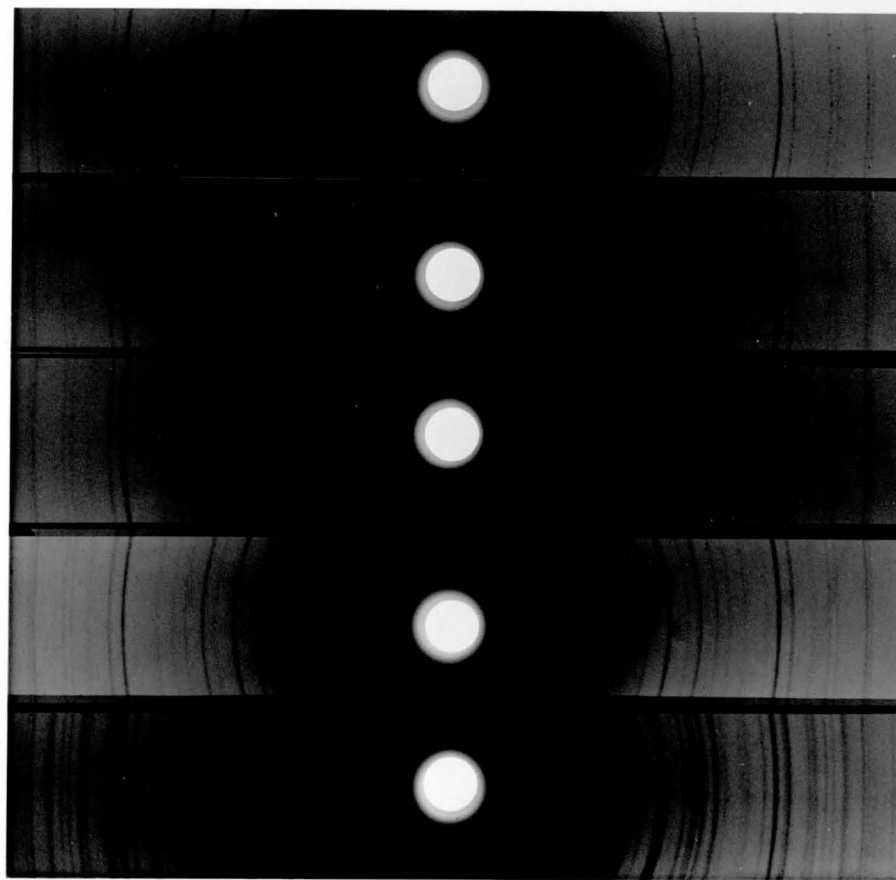
SiO ₂ addition = 70.00% SiO ₂ content = 52.76% Liquidus Temp. = 1380°C		SiO ₂ addition = 80.00% SiO ₂ content = 55.39% Liquidus Temp. = 1435°C		SiO ₂ addition = 90.00% SiO ₂ content = 57.73% Liquidus Temp. = 1470°C	
Temp. °C	Phases present	Temp. °C	Phases present	Temp. °C	Phases present
1360	S + T	1400	S	1400	S
1250	S + T	1360	S + T	1360	S + T
1150	S + T	1300	S + T	1150	S + T
1125	S + T	1125	S + T	1100	S + T
1100	S + T + CMS ₂	1100	S + T	1075	S + T + CMS ₂
1050	S + T + CMS ₂	1075	S + T + CMS ₂	1050	S + T + CMS ₂
1000	S + T + CMS ₂	1050	S + T + CMS ₂	1000	S + T + CMS ₂
		1000	S + T + CMS ₂		

TABLE IV (CONTINUED).

SiO_2 addition = 100.00% SiO_2 content = 59.85% Liquidus Temp. = 1500°C	
Temp. °C	Phases present
1400	S
1360	S + T
1200	S + T
1050	S + T
1025	S + T + CMS_2
1000	S + T + CMS_2

Fig. 8. Phase equilibrium diagram for the slag system $\text{CaO} = 18.00\%$, $\text{MgO} = 12.00\%$, $\text{SiO}_2 = 19.69\%$, $\text{Al}_2\text{O}_3 = 13.12\%$, and $\text{TiO}_2 = 37.19\%$ with increasing contents of SiO_2 .





1250°C TiO_2

1225°C TiO_2

1200°C $\text{TiO}_2 + \text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$

1100°C $\text{TiO}_2 + \text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$

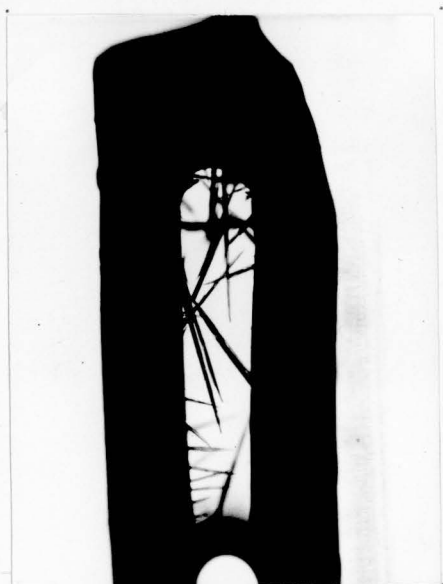
1000°C $\text{TiO}_2 + \text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25} +$
 $\text{CaO.MgO}.2\text{SiO}_2$

Fig. 9. Series of X-ray films illustrating progressive order of crystallization of phases in a titaniferous slag with increased SiO_2 content.

Slag composition: $\text{CaO} = 13.85\%$, $\text{MgO} = 9.23\%$, $\text{SiO}_2 = 38.23\%$, $\text{Al}_2\text{O}_3 = 10.09\%$, and $\text{TiO}_2 = 28.60\%$.

Fig. 10. Photomicrographs showing primary phases in titaniferous slags with increasing contents of SiO_2 .

(Slags were photographed while in position on the thermocouple/heating element).



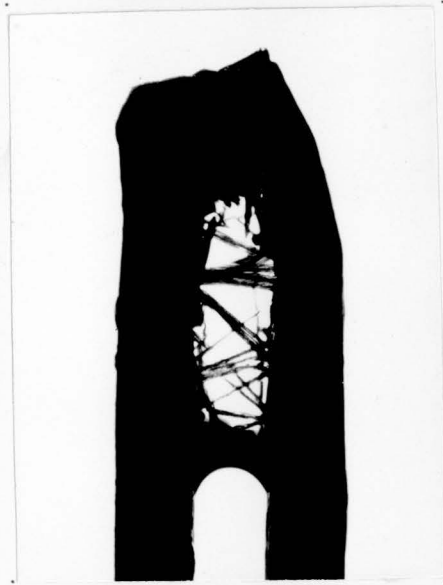
Needle-like crystals of rutile



Alpha-cristobalite



Primary alpha-cristobalite
and secondary rutile



Primary rutile and secondary
 $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$

tetrahedra would satisfy this requirement - hence the description of the glass as an alumina - silicate containing CaO and/or MgO. It is thought that very little TiO_2 is present in the glass. Although titanium has a cation field strength such as to make TiO_2 an intermediate oxide, it can only take part in the silicate network if its normal co-ordination number of six is decreased to four. Titanium can transfer from six-fold to four-fold co-ordination in glasses with a high alkalinity but in glasses containing MgO the titanium preferentially remains in hexenary co-ordination with the result that it does not to any large extent take part in the silicate network (41).

From the phase diagram it can be seen that with even small increases in SiO_2 content, CaO.TiO_2 is the second phase to crystallize after $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$. This would be expected from the liquidus curves and primary phases presented in Fig. 6 and Table III. In these it is seen that the trough of minimum liquidus temperatures is associated with a change in primary phases. Thus, the addition of SiO_2 to the original slag with the $\text{CaO} = 18.00$ per cent and $\text{MgO} = 12.00$ per cent, results in a decrease of the $(\text{CaO} + \text{MgO})$ content to a level at which the primary phase is $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$ as exhibited in the curve for the $(\text{CaO} + \text{MgO}) = 25.00$ per cent.

Between the compositions corresponding to contents of SiO_2 of 19.69 per cent and 30.76 per cent the primary phase is therefore $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$ followed by the secondary phase CaO.TiO_2 while CaO.MgO.2SiO_2 crystallizes at the solidus temperatures. The $\text{MgO.Al}_2\text{O}_3$ lines normally accompanying the $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$ pattern become very weak with an increase in the SiO_2 content. Between SiO_2 contents of 30.76 per cent and 34.70 per cent the primary phase

is still $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$ but the secondary phase is now the most stable polymorphous structure of TiO_2 , namely, rutile. SiO_2 contents in excess of 34.70 per cent lead to the formation of TiO_2 as primary phase with $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$ as secondary phase and at SiO_2 additions between 42.64 per cent and 48.18 per cent rutile is the primary phase over a long temperature interval followed by crystallization of diopside. With contents of SiO_2 in excess of 52.76 per cent the primary phase becomes alpha-cristobalite and the liquidus temperatures increase rapidly with increase in SiO_2 content.

From a consideration of existing phase diagrams relating some of the component oxides, it was thought that sphene ($\text{CaO} \cdot \text{TiO}_2 \cdot \text{SiO}_2$) might have crystallized over a certain range of SiO_2 contents, but this did not prove to be the case.

Therefore, to provide for the crystallization of TiO_2 , contents of SiO_2 between 42.64 per cent and 48.18 per cent are required. It was actually found that if the slags in this region were cooled at 10°C per minute from above the liquidus to room temperature, the secondary crystalline phase (diopside) would not form since the viscosity of the remaining silica-rich liquid is sufficiently high to make subsequent crystallization difficult. The diopside requires the equilibrating period of 60 minutes to crystallize.

This implies that these slags (SiO_2 contents between 42.64 and 48.18 per cent) can be cooled at rates required to produce suitable crystallization of the TiO_2 , and provided the cooling rate is in excess of 10°C per minute below temperatures of about 1200°C down to say 500°C then the product will be

crystals of rutile in a glassy matrix. Experiments on larger quantities, i.e., 20 gms. have confirmed this for various rates of cooling. X-ray diffraction patterns and thin-section work revealed only rutile in a glassy matrix. TiO_2 may thus be made to crystallize in a form more readily extractable. This is evident in Fig. 11, which shows the top of the slag in a platinum crucible. The large needle-like crystals of rutile can be readily seen. However, under the microscope, these rutile crystals appear as fibrous agglomerations with entrained glassy material. This would render difficult complete extraction of the rutile.

Certainly, a large proportion of the rutile should be extractable. Theoretically, if all the rutile could be extracted from the slag with an original composition of $\text{CaO} = 12.86$ per cent, $\text{MgO} = 8.57$ per cent, $\text{SiO}_2 = 42.64$ per cent, $\text{Al}_2\text{O}_3 = 9.37$ per cent, and $\text{TiO}_2 = 26.56$ per cent (40 per cent SiO_2 addition) then the composition of the residual material would be $\text{CaO} = 17.52$ per cent, $\text{MgO} = 11.67$ per cent, $\text{SiO}_2 = 58.05$ per cent, and $\text{Al}_2\text{O}_3 = 12.76$ per cent. This composition appears suitable for the production of slag-ceramics and this aspect will be discussed in Chapter V.

These titaniferous slags with the increased SiO_2 contents definitely become more viscous with increase in SiO_2 content and this is reflected in a decrease in the tendency to crystallize. This point will be dealt with in Section 4.3.



Fig. 11. Macrograph of rutile
crystals in a glassy matrix.

CHAPTER IV.

NON-EQUILIBRIUM PHASE RELATIONSHIPS OF THE TITANIFEROUS SLAGS.

Construction of micro differential thermal analyser.

The existing high temperature microscope incorporating an oscilloscope had been successfully used in monitoring thermal effects during a study of the rate-dependent crystallization of beryllium-containing melts (21), (42). These experiments were successful because the beryl melts display large exothermic effects during rapid cooling which can be observed on a curve of temperature of the specimen versus time. The titaniferous slags exhibited no such exothermic effects on the cooling curves although they did crystallize. An obvious refinement therefore, would be the conversion of the high temperature microscope to differential thermal analysis with correspondingly enhanced sensitivity.

In order to achieve this incorporation of the principle of differential thermal analysis into the high temperature microscope, the following requirements had to be met :

- (i) Retention of the facility continuously to observe the specimen.
- (ii) The ability to control separately the upper and lower pre-set temperatures of both thermocouples in order to annul temperature differences.
- (iii) Simultaneous temperature programming, measurement of the sample temperature and measurement of the differential temperature between the sample junction and the inert junction.

- (iv) Means of recording simultaneously the cooling or heating curve and the differential curve.

Although considerable research had been undertaken, no circuitry was available for such an instrument until the publications by Sommer and co-workers in 1964 (43), (44), (45), (46). This circuitry was based on that of the high temperature microscope as described in Section 2.2. During 1966, Sommer (47) described a modified circuit for a micro differential thermal analyser based on the silicon controlled rectifier (S.C.R.) instead of the conventional silicon rectifier. The S.C.R. differs from the conventional silicon rectifier in that it is possible to control the amount of current that passes through the rectifier during the positive half-cycle by means of an electrical gate that requires a triggering pulse to start the conduction. An auxiliary circuit, in which the resistor-capacitor combination determines the time constant and a unijunction transistor supplies the triggering pulse to the S.C.R., makes it possible to control the S.C.R. over nearly 180° of phase. This latter circuit apart from obvious sophistication, has several inherent advantages: the temperature program control can now be based on electronic circuitry since it is now no longer necessary to control the heating current but merely the triggering pulse to the S.C.R., while the transient switching pulses associated with the normal high temperature microscope circuit are eliminated.

A micro differential thermal analyser (micro-D.T.A.) based on this circuitry was constructed. The circuit for the micro-D.T.A. is presented in Fig. 12. Supply voltage enters transformer T1 and the output is controlled by an S.C.R. The angle of ignition of this S.C.R. is controlled by the

- T.1 step-down transformer
 T.2 step-down transformer
 T.3 variable transformer
 MR silicon diode
 S.C.R silicon controlled rectifier
 U.J.T unijunction transistor
 TC thermocouple

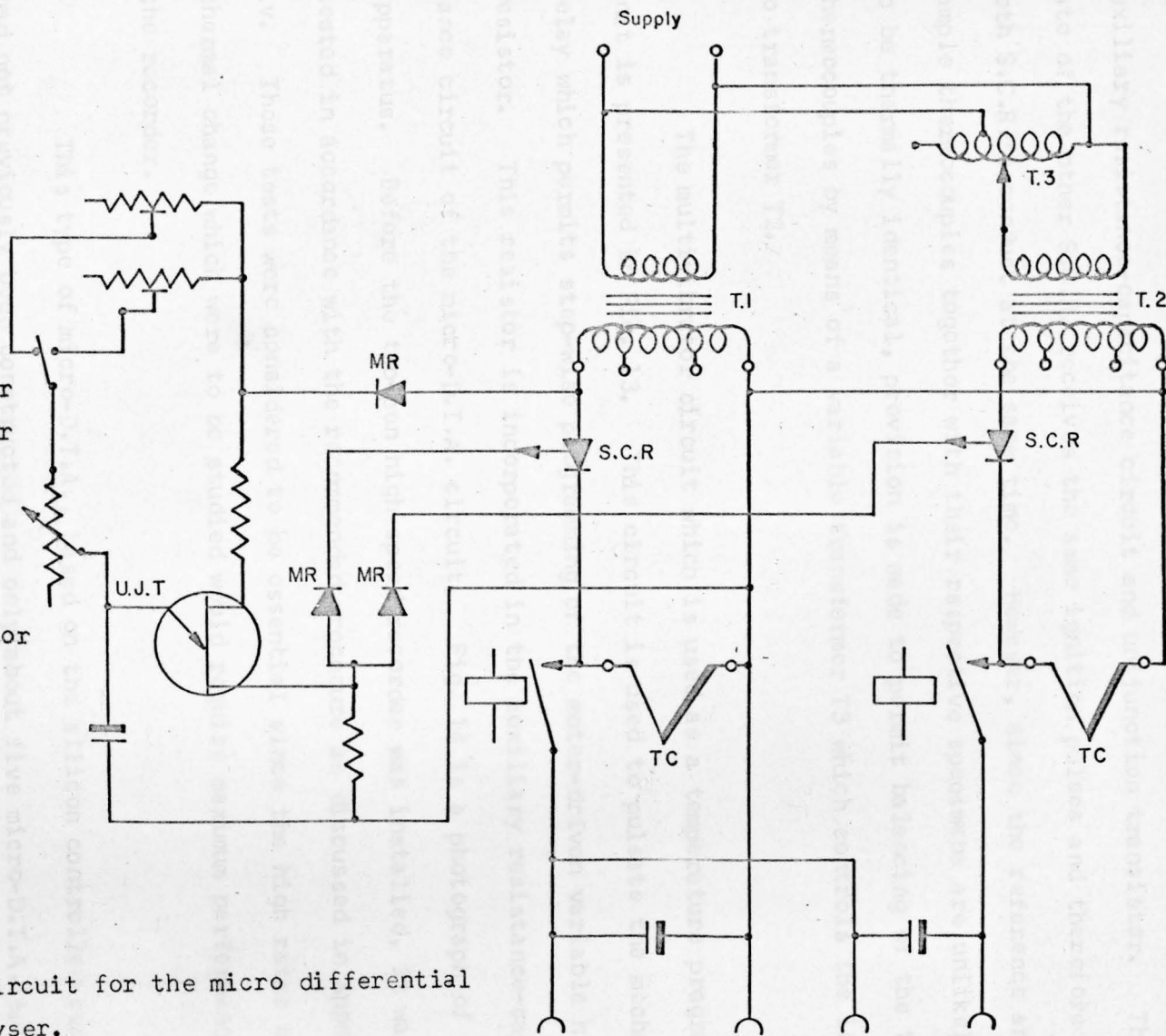


Fig. 12. Electronic circuit for the micro differential thermal analyser.

auxiliary resistance-capacitance circuit and unijunction transistor. The gate of the other S.C.R. receives the same ignition pulses and therefore both S.C.R.'s conduct at the same time. However, since the reference and sample thermocouples together with their respective specimens are unlikely to be thermally identical, provision is made to permit balancing of the two thermocouples by means of a variable transformer T3 which controls the input to transformer T2.

The multivibrator circuit which is used as a temperature program unit is presented in Fig. 13. This circuit is used to pulsate the mechanical relay which permits step-wise programming of the motor-driven variable helical resistor. This resistor is incorporated in the auxiliary resistance-capacitance circuit of the micro-D.T.A. circuit. Fig. 14 is a photograph of the apparatus. Before the two-pen high-speed recorder was installed, it was tested in accordance with the recommended procedure as discussed in Appendix iv. These tests were considered to be essential since the high rates of thermal change which were to be studied would require maximum performance from the recorder.

This type of micro-D.T.A., based on the silicon controlled rectifier, had not previously been constructed and only about five micro-D.T.A.'s, based on the original circuit, had been constructed during the period 1964-1965. It is thus to be expected that considerable development work was required in the actual assembly of the micro-D.T.A. Some of the points which emerged are :

The diameter of the thermocouple wires was increased to 0.35 mm. as

T step-down transformer
 MR silicon diode
 VT transistor
 M motor

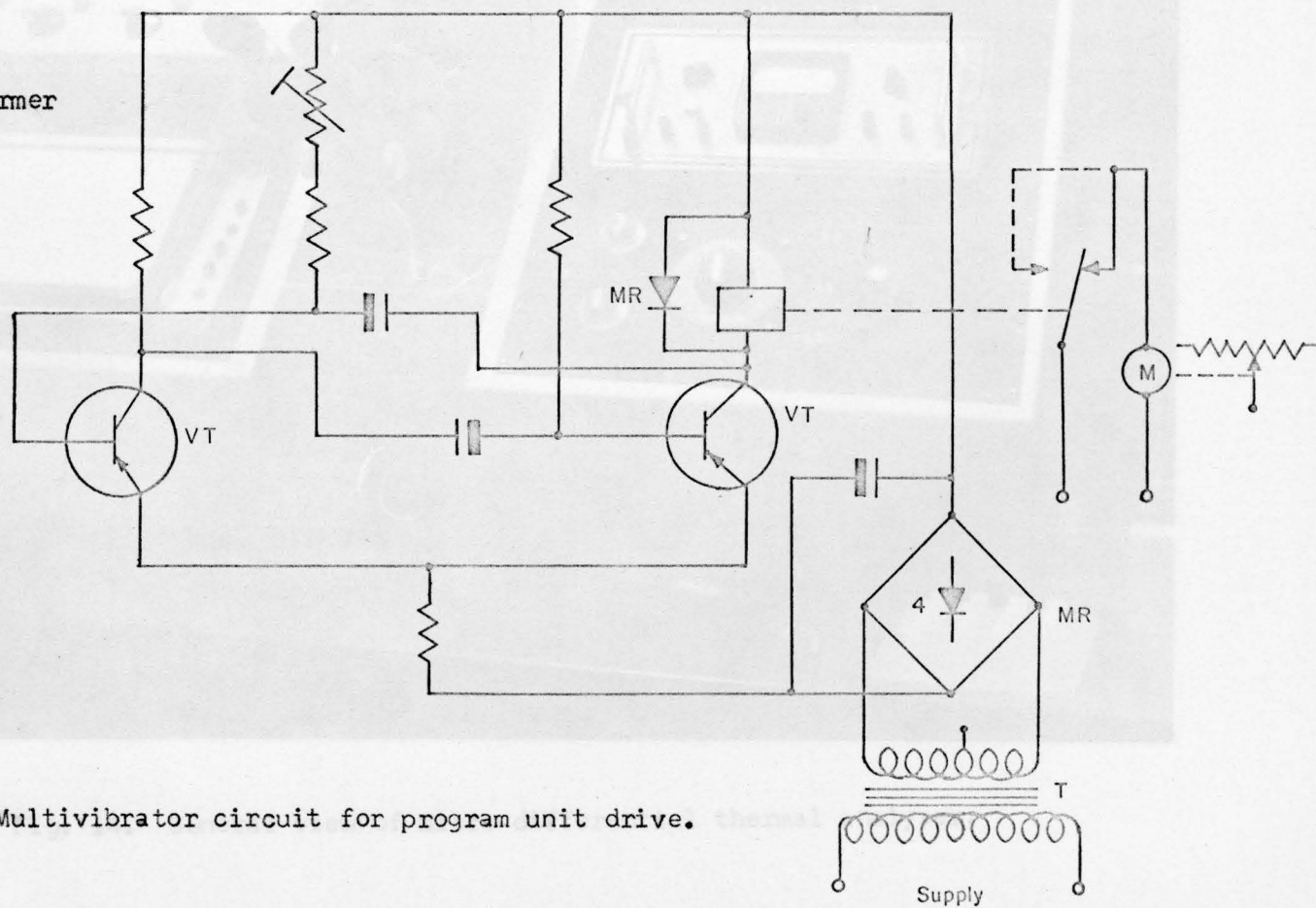


Fig. 13. Multivibrator circuit for program unit drive.



Fig. 14. General view of micro differential thermal analyser.

this facilitated balancing of the sample and reference temperatures.

The two thermocouples were housed in separate cells as shown in Fig. 14. This permitted better observation of the sample by reducing the thickness of the cell and made it unnecessary to subject the reference thermocouple to quenching by water when the sample was subjected to water-quenching for subsequent X-ray analysis.

It was found necessary to apply water cooling to the thermocouple holders as the sensitivity, with which the differential temperature was recorded through the amplifier, was seriously affected by cold-junction errors which, as mentioned previously, could be neglected on the high temperature microscope.

For temperatures up to 1000°C , the thermocouple known as "Pallaplat" (Hereaus) is recommended as this has a very high e.m.f. output per degree Centigrade. For higher temperatures, the 6 per cent Rh-Pt/30 per cent Rh-Pt thermocouple is employed.

Various inert reference materials were selected; such as borax for lower temperatures and albite feldspar for elevated temperatures. A larger thermojunction on the reference thermocouple was employed for high rates of thermal change.

From theoretical considerations, it would be expected that this apparatus could be more accurately considered as a differential calorimeter since there is no heat flow between the sample and reference. However, the associated lack in response to thermal changes occurring over a narrow temperature range characteristic of a differential calorimeter is not encountered in this instrument because the micro-D.T.A. inherently permits

rapid decay of the temperature difference and is hence capable of detecting a subsequent thermal effect with a high degree of sensitivity.

Testing of the micro differential thermal analyser.

The micro-D.T.A. was tested in a similar manner to that employed for the high temperature microscope and an attempt was made to assess its advantages and disadvantages since very little was known about its capabilities generally. Up to temperatures of 400°C , the micro-D.T.A. has a sensitivity and precision comparable with that claimed by Mazieres ⁽⁴⁹⁾ for his micro differential thermal analyser; this was also confirmed by Sommer ⁽⁴⁶⁾ when investigating the solid-state changes in the Na_2SO_4 system. However, at higher temperatures (especially above 1000°C) there appears to be a loss in sensitivity in the micro-D.T.A. at the normal rates of thermal change ($\pm 10^{\circ}\text{C}$ per minute), probably mainly due to increasing radiation losses. This loss in sensitivity at high temperatures can to some considerable extent be alleviated by passing through the two thermocouple cells a gas of low thermal conductivity such as argon, xenon or krypton and by placing platinum radiation shields around the thermocouple junctions.

Contrary to all expectations, when the titaniferous slags were cooled at the conventional rate of 10°C per minute, the first thermal change recorded at the liquidus was a strong endothermic deviation. This represents an anomaly for which at present no entirely satisfactory explanation can be offered. The same slags, when tested at the same cooling rate on the conventional Leeds and Northrup D.T.A. equipment, produced the normal exotherm. The term deviation is used in preference to peak because after the initial

deviation of the differential temperature accompanying the liquidus, the differential temperature does not return to the zero base line, as shown in Fig. 15 (a). However, the start of this endothermic deviation exactly corresponds with the observed first appearance of crystals within the specimen. The liquidus temperatures and phases obtained when the titaniferous slags with the increasing SiO_2 contents were subjected to a 10°C per minute cooling rate on the micro-D.T.A. are presented in Table V. It can readily be seen that the degree of undercooling increases and that crystallization of the various phases departs to an increasing degree from equilibrium conditions with increase in the SiO_2 content. This illustrates one of the major disadvantages of differential thermal analysis when applied to equilibrium studies of systems with sluggish crystallization characteristics.

Other selected cooling rates were also investigated and it was found that at cooling rates of 200°C per minute, especially with occasional relatively high degrees of supercooling, the endothermic deviation of the liquidus was sometimes preceded by a rapid exothermic peak which corresponds to the observed liquidus temperature. See Fig. 15 (b). At higher rates of cooling than 200°C per minute, the liquidus was accompanied by the usual exothermic peak, as shown in Fig. 15 (c). This leads to the conclusion, that although heat is liberated at the liquidus temperature, this amount of heat is negligible (due to radiation losses) in comparison with thermal differences (thermal conductivity or diffusivity, specific heat or differences in radiation) of the slag immediately prior to and after the recorded liquidus temperature at comparatively low rates of thermal change. At high rates of thermal change, the amount of heat liberated per unit time is increased and

Fig. 15. Thermograms illustrating differences in morphology of the liquidus peak at various cooling rates.

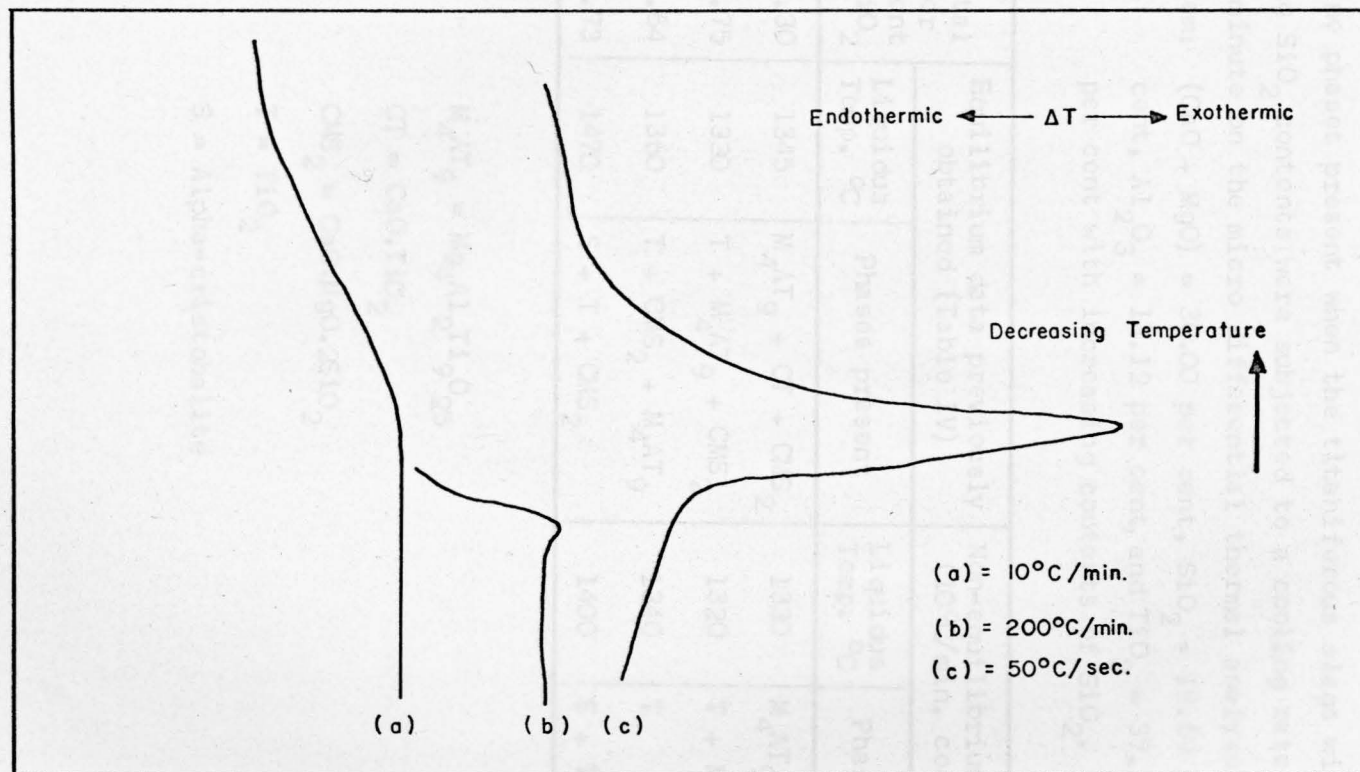
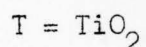
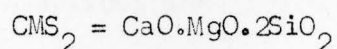
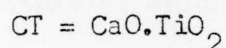
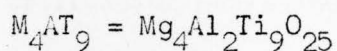


TABLE V.

Determination of liquidus temperatures and identification of crystalline phases present when the titaniferous slags with the increasing SiO_2 contents were subjected to a cooling rate of 10°C per minute on the micro differential thermal analyser.

Slag system: $(\text{CaO} + \text{MgO}) = 30.00$ per cent, $\text{SiO}_2 = 19.69$ per cent, $\text{Al}_2\text{O}_3 = 13.12$ per cent, and $\text{TiO}_2 = 37.19$ per cent with increasing contents of SiO_2 .

Per cent SiO_2 addition	Total per cent SiO_2	Equilibrium data previously obtained (Table IV)		Non-equilibrium conditions ($10^\circ\text{C}/\text{min.}$ cooling rate)	
		Liquidus Temp. $^\circ\text{C}$	Phases present	Liquidus Temp. $^\circ\text{C}$	Phases present
12	28.30	1345	$\text{M}_4\text{AT}_9 + \text{CT} + \text{CMS}_2$	1330	$\text{M}_4\text{AT}_9 + \text{CT}$
25	35.75	1330	$\text{T} + \text{M}_4\text{AT}_9 + \text{CMS}_2$	1320	$\text{T} + \text{M}_4\text{AT}_9 + \text{CMS}_2$
40	42.64	1360	$\text{T} + \text{CMS}_2 + \text{M}_4\text{AT}_9$	1340	T
90	57.73	1470	$\text{S} + \text{T} + \text{CMS}_2$	1400	$\text{S} + \text{T}$



S = Alpha-cristobalite

this permits the normal exotherm to be recorded.

The precision of the micro differential thermal analyser as regards reproducibility of peaks was checked by conducting devitrification tests on a titaniferous slag having the following composition : $\text{CaO} = 18.00$ per cent, $\text{MgO} = 12.00$ per cent, $\text{SiO}_2 = 19.69$ per cent, $\text{Al}_2\text{O}_3 = 13.12$ per cent, and $\text{TiO}_2 = 37.19$ per cent. This slag was water-quenched from 50°C above the liquidus temperature and then heated at a rate of 150°C per minute. These titaniferous slags have such a strong tendency to devitrify (they require a water-quench to obtain them in the glassy state initially) that even at rates of heating of 150°C per minute they could be expected to undergo the devitrification process reproducibly. Because devitrification proceeds by a homogeneous nucleation step, the surface characteristics of the thermocouple and specimen itself are less likely to affect reproducibility. The results are presented in Table VI; each result was obtained on a new thermocouple and a new specimen. An example of these thermograms is presented in Fig. 16. This slag exhibited four devitrification peaks and the temperature of the start of each peak and the temperature at which the peak amplitude was at a maximum are recorded, as are also the solidus and liquidus temperatures.

For reactions occurring at high rates of thermal change, this micro-D.T.A. has proved capable of achieving results hitherto considered extremely difficult. Conventional differential thermal analysers incorporate a furnace which heats the sample and reference specimens. Hence, the maximum rate of heating possible is limited by the rate at which the furnace temperature can be increased and by the rate of heat transfer from the furnace to the specimens.

TABLE VI.

Indicated limits of precision as shown by the thermograms for devitrification, solidus and liquidus reactions in a titaniferous slag.

Heating rate = 150°C per minute.

Slag composition: CaO = 18.00 per cent, MgO = 12 per cent, SiO₂ = 19.69 per cent, Al₂O₃ = 13.12 per cent, and TiO₂ = 37.19 per cent.

1st Devitrifica- tion peak		2nd Devitrifica- tion peak		3rd Devitrifica- tion peak		4th Devitrifica- tion peak		Solidus Temp. °C	Liquidus Temp. °C
Start °C	Max °C	Start °C	Max °C	Start °C	Max °C	Start °C	Max °C		
780	800	840	860	890	910	925	950	1195	1345
780	805	850	870	885	910	930	950	1200	1350
770	800	840	855	890	910	920	940	1190	1350
770	790	840	855	880	900	920	940	1190	1350
780	805	840	850	890	910	930	950	1195	1345
780	810	855	865	885	915	930	940	1190	1350

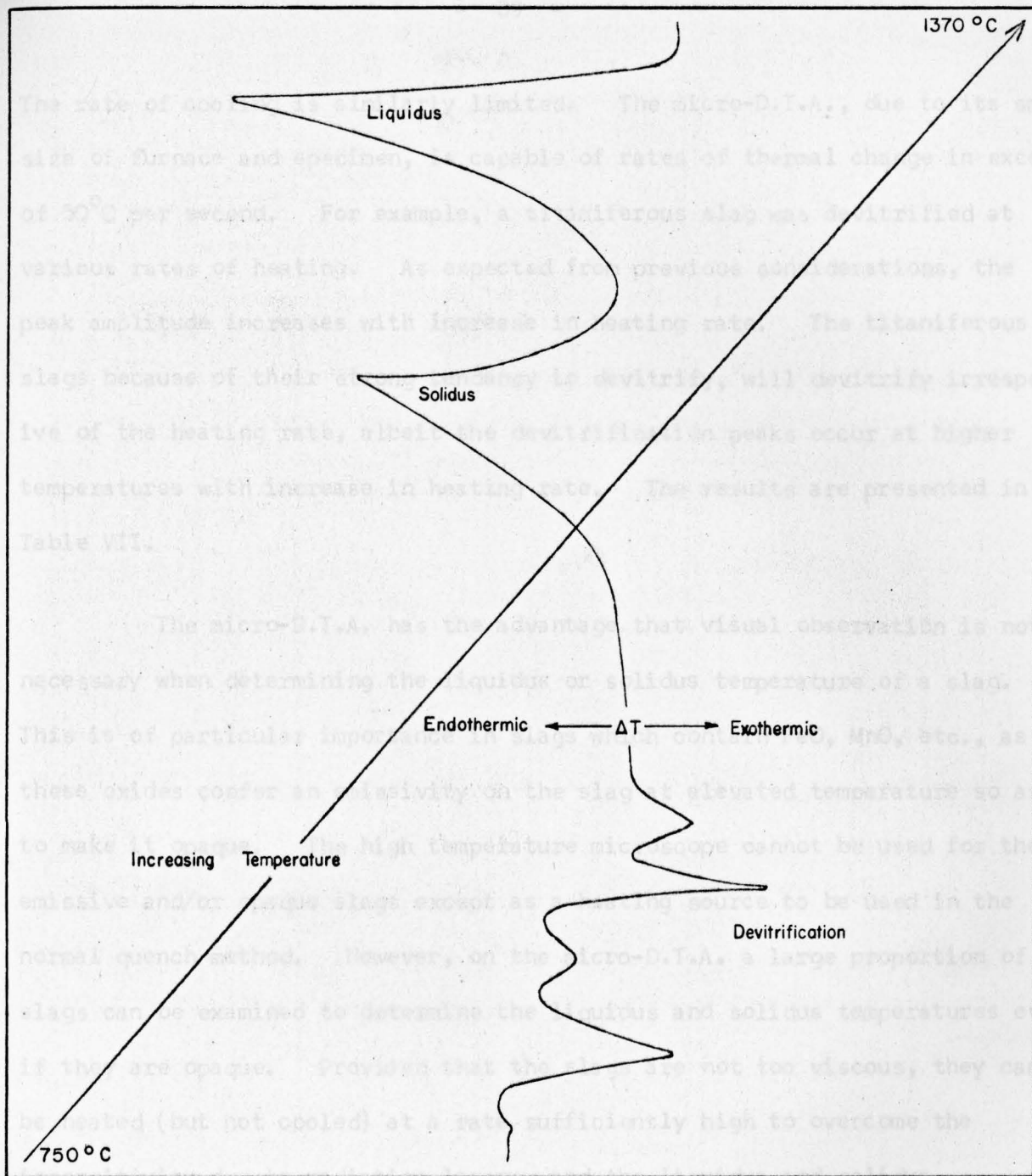


Fig. 16. Thermogram of a water-quenched titaniferous slag heated at a rate of 150°C/minute on the micro differential thermal analyser.

3. Simulation of granulillar plant conditions.

The micro-D.T.A. appears most suitable for rapid non-equilibrium phase studies, namely to determine the behaviour of these titaniferous slags

The rate of cooling is similarly limited. The micro-D.T.A., due to its small size of furnace and specimen, is capable of rates of thermal change in excess of 50°C per second. For example, a titaniferous slag was devitrified at various rates of heating. As expected from previous considerations, the peak amplitude increases with increase in heating rate. The titaniferous slags because of their strong tendency to devitrify, will devitrify irrespective of the heating rate, albeit the devitrification peaks occur at higher temperatures with increase in heating rate. The results are presented in Table VII.

The micro-D.T.A. has the advantage that visual observation is not necessary when determining the liquidus or solidus temperature of a slag. This is of particular importance in slags which contain FeO , MnO , etc., as these oxides confer an emissivity on the slag at elevated temperature so as to make it opaque. The high temperature microscope cannot be used for these emissive and/or opaque slags except as a heating source to be used in the normal quench method. However, on the micro-D.T.A. a large proportion of the slags can be examined to determine the liquidus and solidus temperatures even if they are opaque. Provided that the slags are not too viscous, they can be heated (but not cooled) at a rate sufficiently high to overcome the insensitivity due to radiation losses, and the liquidus and solidus temperatures can be measured with an accuracy of $\pm 10^{\circ}\text{C}$.

.3. Simulation of granulation plant conditions.

The micro-D.T.A. appears most suitable for rapid non-equilibrium phase studies, namely to determine the behaviour of these titaniferous slags

TABLE VII.

Various rates of heating which can be monitored on the micro differential thermal analyser.

Devitrification thermograms of a titaniferous slag having the following composition: CaO = 14.00 per cent, MgO = 16.00 per cent, SiO₂ = 19.69 per cent, Al₂O₃ = 13.12 per cent, and TiO₂ = 37.19 per cent.

Heating Rate °C/Min.	1st Devitrification peak		2nd Devitrification peak		3rd Devitrification peak	
	Start °C	Max °C	Start °C	Max °C	Start °C	Max °C
49	740	755	870	875	880	890
160	760	780	870	885	900	915
194	760	780	880	890	910	925
330	765	785	880	895	910	930
4000	820	860	980	985	985	1020
30000	920	955	TRACE		1020	1080

with and without increased SiO_2 contents when subjected to the thermal conditions prevailing on a granulation plant.

Various blast furnace slags which had been successfully water-quenched on granulation plants to produce a granulate of low crystalline content were examined to gain information relating to the quenching rates which had to be achieved to obtain such slags in the glassy state.

These blast furnace slags were placed on the thermocouple and the liquidus temperature was established. They were then heated to 50°C above the liquidus and cooled at various preselected rates. The quenched slags were visually examined to establish at what rate of cooling crystallization could just be prevented. Reproducibility is not good but a considerable improvement can be achieved by treating each slag on a new/smooth thermocouple, which technique was adopted for these experiments.

Table VIII indicates the range of quenching rates which had to be obtained on the micro-D.T.A. to obtain these slags in the same glassy condition as that in which they had previously been produced on the granulation plant.

Crystallization always occurred heterogeneously on the thermocouple limbs and this explains the difficulty of obtaining reproducible results. However, by conducting each test on a new/smooth thermocouple, as mentioned earlier, more definite conclusions could be drawn. It is thus seen that to simulate the effect of the rapid quench of the granulation plant treatment, these blast furnace slags have to be subjected to cooling rates between 40°C

TABLE VIII.

Rates of cooling required to produce blast furnace slags in the same glassy condition that they had obtained on the granulation plant.

Blast furnace slag	Cooling rate °C/sec.	Observation on degree of crystallinity	Cooling rate °C/sec.	Observation on degree of crystallinity
Slag No. 1 (South Africa)	40°C/sec.	Slight crystallization	55°C/sec.	No crystallization
Slag No. 2 (South Africa)	40°C/sec.	No crystallization	55°C/sec.	No crystallization
Slag No. 3 (South Africa)	40°C/sec.	Slight crystallization	55°C/sec.	Slight crystallization
Slag No. 4 (Switzerland)	40°C/sec.	No crystallization	55°C/sec.	No crystallization

and 55°C per second on the micro-D.T.A. Hence, by subjecting other slags to this treatment on the micro-D.T.A. information can be gained relating to the amount of crystallization that can be expected if these slags were to be treated on a granulation plant.

The titaniferous slags were subjected to cooling rates of 50°C per second and then examined for their crystalline content. The pseudo liquidus temperatures and the phases which have crystallized are presented in Table IX.

The titaniferous slags with the increasing contents of SiO_2 were examined in a similar manner and the results are presented in Table X.

From Table IX it can be seen that considerable crystallization occurs in the titaniferous slags even at these rapid quenching rates. The primary phase always crystallizes and so does the secondary phase if this contains TiO_2 . With the very high MgO content, the forsterite crystallizes as secondary phase. The difference in liquidus temperatures for the equilibrium condition and the 50°C per second quenching rate, decreases with increase in the MgO content, i.e., from a difference of 140°C to 95°C . This confirms the previously mentioned fact that the slags with high MgO contents display a greater tendency to crystallize than the slags with high CaO contents when subjected to high rates of quenching.

Although the primary and often the secondary phases do crystallize, no tertiary and subsequent phases crystallize. Hence, these slags must contain considerable proportions of glass. This glass content was verified by thin-section work. However, the crystalline material content is higher than

TABLE IX.

Determination of pseudo liquidus temperatures and identification of crystalline phases present when the titaniferous slags are cooled at a rate of 50°C per second.

Slag system: (CaO + MgO) = 30.00 per cent, SiO₂ = 19.69 per cent, Al₂O₃ = 13.12 per cent, and TiO₂ = 37.19 per cent.

(CaO + MgO) = 30%		Equilibrium data previously obtained (Table II)		Non-equilibrium conditions 50°C/sec. cooling rate	
CaO %	MgO %	Liquidus °C	Phases present	Liquidus °C	Phases present
28	2	1495	CT + T + CAS ₂	1365	CT
22	8	1395	CT + M ₄ AT ₉ + CMS ₂	1240	CT + M ₄ AT ₉
18	12	1340	M ₄ AT ₉ + CT + CMS ₂	1200	CT + M ₄ AT ₉
12	18	1410	M ₄ AT ₉ + M ₂ S + CT + CMS ₂	1270	M ₄ AT ₉
8	22	1445	M ₄ AT ₉ + M ₂ S + CT + CMS ₂	1330	M ₄ AT ₉
2	28	1490	M ₄ AT ₉ + M ₂ S	1395	M ₄ AT ₉ + M ₂ S

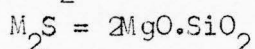
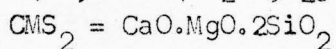
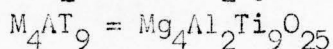
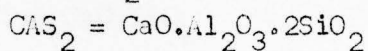
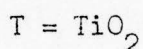
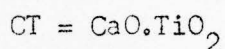
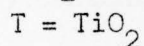
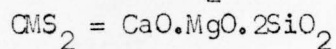
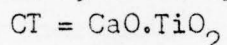
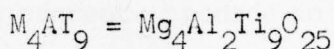


TABLE X.

Determination of pseudo liquidus temperatures and identification of crystalline phases present when the titaniferous slags with increasing contents of SiO_2 are cooled at a rate of 50°C per second.

Slag system: $\text{CaO} = 18.00$ per cent, $\text{MgO} = 12.00$ per cent, $\text{SiO}_2 = 19.69$ per cent, $\text{Al}_2\text{O}_3 = 13.12$ per cent, and $\text{TiO}_2 = 37.19$ per cent with increasing contents of SiO_2 .

Per cent SiO_2 addition	Per cent SiO_2 content	Equilibrium data previously obtained (Table IV)		Non-equilibrium conditions $50^\circ\text{C}/\text{sec.}$ cooling rate	
		Liquidus $^\circ\text{C}$	Phases Present	Liquidus $^\circ\text{C}$	Phases present
12	28.30	1345	$\text{M}_4\text{AT}_9 + \text{CT} + \text{CMS}_2$	1180	M_4AT_9
25	35.75	1330	$\text{T} + \text{M}_4\text{AT}_9 + \text{CMS}_2$	1200	T
40	42.64	1360	$\text{T} + \text{CMS}_2 + \text{M}_4\text{AT}_9$	1260	T
90	57.73	1470	$\text{S} + \text{T} + \text{CMS}_2$	1340	T



S = Alpha-cristobalite

the maximum 20 per cent normally specified for slag-cement manufacture.

As in the case of the blast furnace slags tested, these titaniferous slags all crystallize heterogeneously from the thermocouple limbs. A comparison between these results and those obtained from the blast furnace slags indicates that the titaniferous slags would not be suitable for granulation plant treatment.

The slags with the increasing SiO_2 contents exhibit a lower crystalline content after being subjected to this 50°C per second quench. Here, only the primary phase crystallizes with one notable exception. In that part of the phase equilibrium diagram where alpha-cristobalite is the primary phase with rutile as the secondary phase, at high quenching rates rutile crystallizes as the primary and only phase. But the rutile again crystallizes heterogeneously from the thermocouple limbs. This crystallization of the rutile accounts for the fact that the degree of undercooling of these slags does not increase with an increase in the SiO_2 content as had been expected. The slags with the higher SiO_2 contents produce an amount of crystalline material sufficiently small to make them suitable for a granulate, at least from a consideration of the glassy content.

High-speed continuous cooling behaviour.

The titaniferous slags have now been shown to have a substantial crystalline content at cooling rates of 50°C per second and yet it has also been shown that at very much higher rates of cooling they can be quenched into glass (during phase equilibria determinations). It appears that there

must be some type of transitional behaviour at rates of cooling above 50°C per second which will eventually permit the formation of glass.

A method was devised whereby such an investigation could be conducted. The slag selected for these experiments had the following composition: $\text{CaO} = 12.00$ per cent, $\text{MgO} = 18.00$ per cent, $\text{SiO}_2 = 19.69$ per cent, $\text{Al}_2\text{O}_3 = 13.12$ per cent, and $\text{TiO}_2 = 37.19$ per cent. The equilibrium phase relationships of this slag were presented in Table II.

From the previous experiments on granulation plant simulation, it had been shown that when conducting experiments at these very high rates of quenching, reproducibility was very poor indeed. This is to be expected and the chief source of error is the thermocouple - NOT as a measuring device but as the specimen holder, i.e., the containing walls for the specimen. Heterogeneous crystallization predominates because of the surface condition of the thermocouple and this dominates the actual crystallization temperature. This factor was alleviated by conducting the various tests on the same specimen mounted onto the same new/smooth thermocouple.

The slag specimen was quenched at various rates from 50°C above the liquidus temperature by switching the heating current from this temperature to some preselected lower temperature - the lower this preselected temperature, the higher the rate of cooling. Reproducibility was fair when the same specimen was examined on the same thermocouple at the various rates of cooling. But even another new thermocouple with the same specimen would produce different pseudo liquidus temperatures because of slight changes in geometry

and surface defects on the wire (especially at the weld of the thermojunction). However, the very rapid onset of crystallization could be recorded on the micro-D.T.A. quite readily if extreme care was taken to balance the sample and reference since it can be readily envisaged that any thermal differences in the two would be magnified excessively at these high rates of cooling. This balancing was aided by the fact that the high rate of crystallization produced relatively large peak amplitudes thus permitting the use of low amplification in recording the differential temperature. It should be pointed out that these slags did not exhibit heat effects large enough to influence the temperature curve of the specimen.

These tests were repeated with a used/rough thermocouple. It was during these tests that the samples on cooling were water-quenched immediately the crystallization peak had been completed. The X-ray powder patterns of these specimens were then obtained. The results are presented in Table XI and graphically illustrated in Fig. 17.

For the specimen quenched at a rate of 250°C per second, the X-ray powder pattern is no longer that of exactly $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$ nor is it that of $\text{MgO} \cdot 2\text{TiO}_2$ but rather some intermediate value. Since $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$ is a solid solution of 80 mol. per cent $\text{MgO} \cdot 2\text{TiO}_2$ and 20 mol. per cent $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ the X-ray powder pattern for $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$ has d spacing values and intensities lying between these two components. The d spacing values for $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ are smaller than those for $\text{MgO} \cdot 2\text{TiO}_2$ so that it may be inferred that when the d spacing values increase to larger values than those for $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$ then the $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ content has been decreased. Hence the description

TABLE XI.

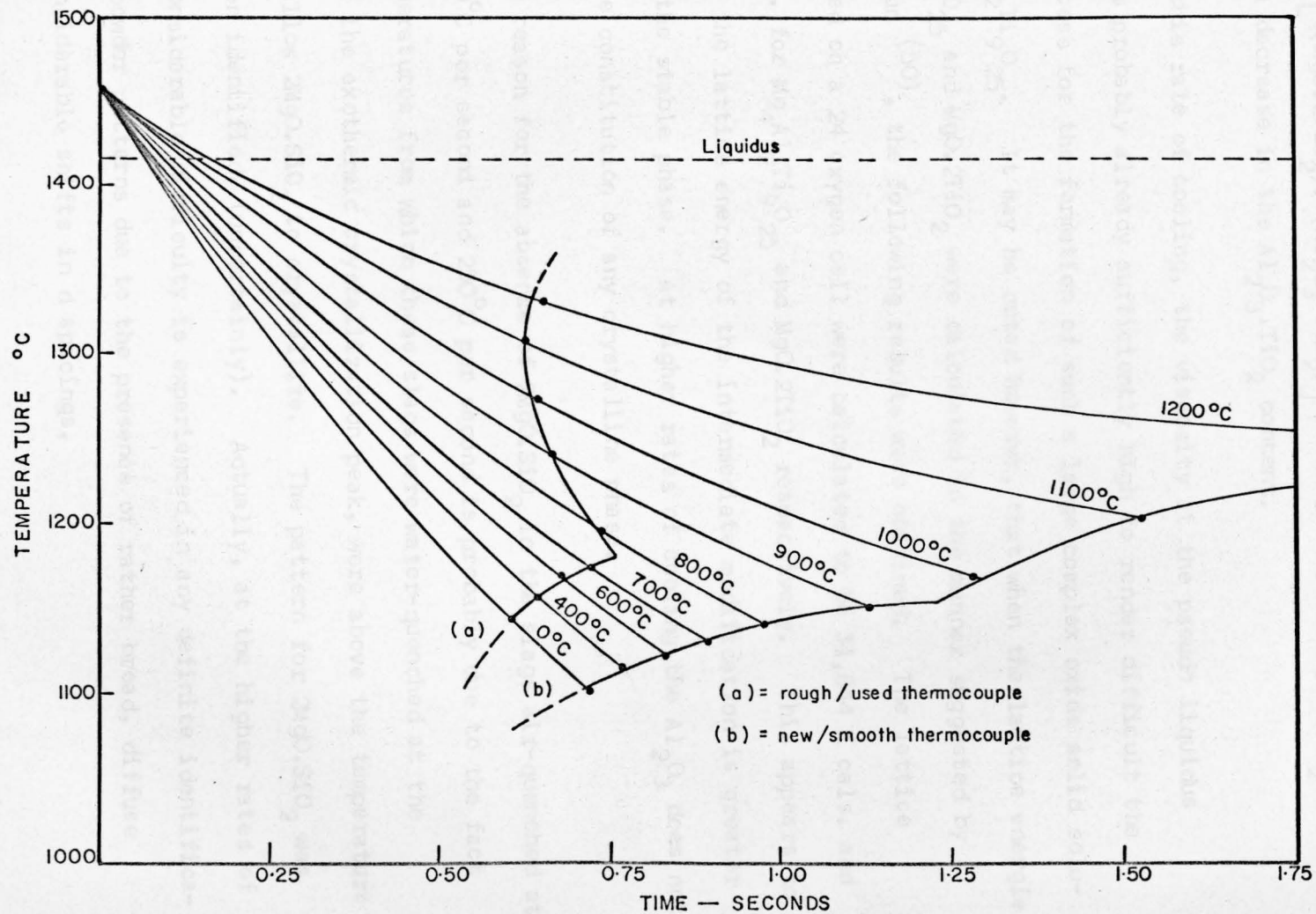
Determination of pseudo liquidus temperatures and identification of crystalline phases present when a titaniferous slag is subjected to various high-speed continuous cooling rates.

Slag composition: CaO = 12.00 per cent, MgO = 18.00 per cent,
 SiO_2 = 19.69 per cent, Al_2O_3 = 13.12 per cent,
 and TiO_2 = 37.19 per cent.

Temperature to which air-quenched from 1460°C °C	New/Smooth Thermocouple		Used/Rough Thermocouple		Phases identified after water-quenching of slag specimens on used/rough thermocouple at completion of exothermic peak
	Start of Peak °C	Rate of Cooling °C/sec.*	Start of Peak °C	Rate of Cooling °C/sec.*	
1200	1230	-	1340	190	$\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$
1100	1205	165	1310	250	$(\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25} \rightarrow \text{MgO} \cdot 2\text{TiO}_2)$
1000	1170	225	1275	285	$(\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25} \rightarrow \text{MgO} \cdot 2\text{TiO}_2) +$ $\text{MgO} \cdot \text{TiO}_2 + 2\text{MgO} \cdot \text{SiO}_2$
900	1150	270	1240	325	$\text{MgO} \cdot 2\text{TiO}_2 + \text{MgO} \cdot \text{TiO}_2 +$ $2\text{MgO} \cdot \text{SiO}_2$
800	1140	330	1195	355	$\text{MgO} \cdot 2\text{TiO}_2 + \text{MgO} \cdot \text{TiO}_2 +$ $2\text{MgO} \cdot \text{SiO}_2$
700	1130	360	1175	395	$\text{MgO} \cdot 2\text{TiO}_2 + \text{MgO} \cdot \text{TiO}_2 +$ $2\text{MgO} \cdot \text{SiO}_2$
600	1120	395	1170	430	$\text{MgO} \cdot 2\text{TiO}_2 + \text{MgO} \cdot \text{TiO}_2$
400	1115	450	1155	455	$\text{MgO} \cdot 2\text{TiO}_2 + \text{MgO} \cdot \text{TiO}_2$
0	1095	495	1145	525	$\text{MgO} \cdot 2\text{TiO}_2 + \text{MgO} \cdot \text{TiO}_2$

* The rate of cooling is not constant as can be seen on the graph. As expected from the laws of radiation and conduction, the rate of cooling is most rapid initially and decreases in rate as the lower preset temperature is approached.

Fig. 17. High-speed continuous cooling curves for a titaniferous slag.
The lines (a) and (b) indicate the start of crystallization.



$\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$, $[4(\text{MgO} \cdot 2\text{TiO}_2) \cdot (\text{Al}_2\text{O}_3 \cdot \text{TiO}_2)]$ tending to ($\rightarrow$) $\text{MgO} \cdot 2\text{TiO}_2$ is given, i.e., a decrease in the $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ content.

At this rate of cooling, the viscosity at the pseudo liquidus temperature is probably already sufficiently high to render difficult the diffusion process for the formation of such a large complex oxide solid solution as $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$. It may be noted however, that when the lattice energies for $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$ and $\text{MgO} \cdot 2\text{TiO}_2$ were calculated in the manner suggested by Huggins and Sun ⁽⁵⁰⁾, the following results were obtained. The lattice energies, based on a 24 oxygen cell were calculated to be 31,844 K cal. and 32,045 K cal. for $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$ and $\text{MgO} \cdot 2\text{TiO}_2$ respectively. This appears to indicate that the lattice energy of the intermediate modification is greater than that of the stable phase. At higher rates of cooling the Al_2O_3 does not enter into the constitution of any crystalline phase.

The reason for the absence of $2\text{MgO} \cdot \text{SiO}_2$ in the slags air-quenched at a rate of 190°C per second and 250°C per second is probably due to the fact that the temperatures from which these slags were water-quenched at the completion of the exothermic crystallization peak, were above the temperature required to allow $2\text{MgO} \cdot \text{SiO}_2$ to crystallize. The pattern for $2\text{MgO} \cdot \text{SiO}_2$ was very weak when identified, (uncertainly). Actually, at the higher rates of quenching, considerable difficulty is experienced in any definite identification of the powder patterns due to the presence of rather broad, diffuse lines and considerable shifts in d spacings.

As will be evident from Table XI, the forsterite ($2\text{MgO} \cdot \text{SiO}_2$) crystallizes at intermediate rates of cooling but the diopside does not form

at any of the rates of cooling investigated. Apart from the fact that in the equilibrium order of phase generation, forsterite precedes diopside, this could also be attributed to the fact that the forsterite is an orthosilicate which consists simply of isolated SiO_4^{4-} groups linked only through the medium of the Mg ions as opposed to diopside which possesses a more complex chain structure.

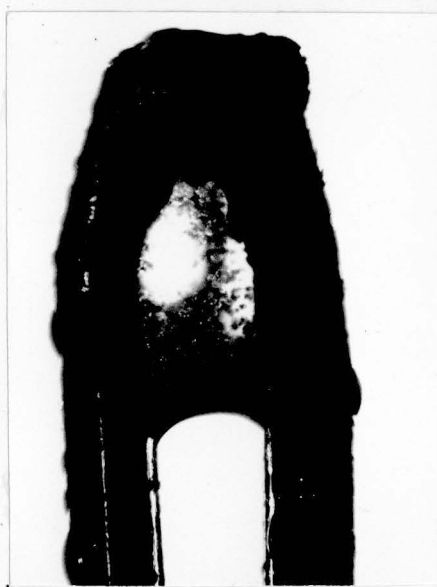
From the curves representing the pseudo liquidus temperatures for various rates of cooling for specimens mounted on new/smooth and used/rough thermocouples, it can be seen that the onset of crystallization occurs at higher temperatures for the used/rough thermocouple because, as expected, this will more readily permit heterogeneous nucleation. Visual microscopic examination revealed that heterogeneously nucleated crystallization is accompanied by increasing amounts of homogeneously nucleated crystallization within the melt at cooling rates of 300°C per second and higher. When the rate of cooling is increased to 400°C per second and higher then homogeneously nucleated crystallization is the predominant mechanism. Thus at these increased rates of cooling, the effect of the nature of the surface of the thermocouple plays an ever-decreasing role and this explains why the two curves tend to approach one another at these higher rates of cooling. The point of inflexion in these curves appears to be associated with this change in crystallization mechanism. Fig. 18 shows photomicrographs illustrating heterogeneously and homogeneously nucleated crystallization.

This progressive change from heterogeneously nucleated to homogeneously nucleated crystallization with increase in the rate of cooling is

Fig. 18. Photomicrographs illustrating heterogeneously nucleated and homogeneously nucleated crystallization in titaniferous slags.



Heterogeneously nucleated crystallization



Homogeneously nucleated crystallization

characteristic of siliceous melts. The amount of crystalline phase decreases at each successively higher rate of cooling. A stage is eventually reached where the nuclei undergo only very limited growth and at still higher rates of cooling it is possible to prevent growth and possibly even nucleation. Experimentally, higher CONTROLLED rates of cooling than those shown in Fig. 17 could not be obtained but various degrees of water-quenching showed that the crystals which are homogeneously nucleated, decrease in size with increase in cooling rate until a point is reached where only isolated small dots can be seen at X200 magnification. At even higher cooling rates, visually-clear glasses were produced. At these high rates of quenching, the viscosity of the melt increases so rapidly that the structural units are unable to arrange themselves into the appropriate crystalline order before solidification.

Phase identification was assisted by obtaining X-ray powder patterns from prepared samples of all the above phases. During these tests it was also established that when the prepared samples of $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$, $\text{MgO} \cdot 2\text{TiO}_2$ and $\text{MgO} \cdot \text{TiO}_2$ were subjected to very high rates of quenching (400°C per second) the X-ray powder pattern characteristics were the same as those obtained under equilibrium conditions.

It is probable that these titaniferous slags, when in the molten state, do not contain a large proportion of network since the content of network-former (SiO_2) is comparatively low although the content of intermediate oxides (Al_2O_3 and TiO_2) is high. This is in agreement with the relatively low viscosity values. During rapid cooling, the larger $\text{Mg}_4\text{Al}_2\text{Ti}_9\text{O}_{25}$ solid solution complex oxide has not time to form and the simpler

structures of $\text{MgO} \cdot 2\text{TiO}_2$ and $\text{MgO} \cdot \text{TiO}_2$ crystallize. Now, according to Ostwald this crystallization of a transient stable modification is an expression of the tendency of a melt in an unstable state to change not into the most stable form, but into the form the stability of which most nearly resembles its own. This indicates that in the liquid, the major proportions of MgO and TiO_2 are not present in complex structural units and can therefore crystallize even at high rates of cooling.

CHAPTER V.

DEVITRIFICATION STUDIES.

Introduction.

Recently, the production and properties of slag-ceramics are being studied as a means of finding a suitable outlet for iron-making slags. They are perhaps a natural development of glass-ceramics which are at present being intensively investigated. Slag-ceramics are polycrystalline solids prepared from suitable slags as follows : A melting operation, which, if possible, should be integrated with the original slag forming process to save fuel, a pouring and forming step to obtain the desired shape or form and a final two-stage heat-treatment. The first heat-treatment stage is to produce the nuclei and the second stage is to permit these nuclei to grow into micro-crystals. It is known that various research organisations such as the British Iron and Steel Research Association are investigating the production of these slag-ceramics and their possible applications. Not much literature is available on slag-ceramics but considerable literature is obtainable concerning glass-ceramics which are essentially the same. The only difference being a compositional difference in that in glass-ceramics it is possible to select the composition of the glass to produce the required glass-ceramic while for the production of slag-ceramics, a particular slag has to be employed, albeit there exists the possibility for additions to be made to the slag.

The properties and possible uses of these slag-ceramics can be gauged by the provisional list of properties of slag-ceramics reproduced in

Appendix v. To-date it has been possible to establish that if slags in the composition range 45 to 65 per cent SiO_2 , 15 to 45 per cent CaO , 5 to 30 per cent Al_2O_3 , and up to 10 per cent MgO have their silica content adjusted (sand addition) to a composition which yields wollastonite and/or diopside as primary phases, and TiO_2 in quantities up to about 10 per cent is added as a nucleation agent then very acceptable slag-ceramics can be produced.

Now, as discussed in Section 3.2., the slag to which 40 per cent SiO_2 has been added has a final composition of : CaO = 12.86 per cent, MgO = 8.57 per cent, SiO_2 = 42.64 per cent, Al_2O_3 = 9.37 per cent, and TiO_2 = 26.56 per cent. With all the TiO_2 extracted it would have a composition of :

CaO	=	17.52 per cent
MgO	=	11.67 per cent
SiO_2	=	58.05 per cent
Al_2O_3	=	12.76 per cent
		<u>100.00 per cent</u>

As can be seen, this composition is not unlike that being used in the experiments for the production of slag-ceramics. Furthermore, it is most probable that not all the TiO_2 could be extracted and since this TiO_2 is the most common nucleation agent used in the slag-ceramic process, it would be advantageous not to let the extraction go to completion but to allow the amount of TiO_2 required for optimum nucleation to remain in the slag.

Also, the composition approaches closely to that of a diopsidic

glass and it has been shown by Nikandrov ⁽⁵¹⁾ that this type of glass is much less likely to crystallize during casting when additions of alumina were made to it. This action of the alumina on glass formation in diopsidic glasses is apparently associated with the part played by the transformation of the Al^{3+} ion into four-fold co-ordination.

Since separation into two liquid or glass phases is the precursor to highly disperse and uniform devitrification, it would be expected that the optimum phase separation in the glass is micro-separation in which the separation gives rise to very small regions or drops. Furthermore, these minute regions should be incapable of further growth with formation of large regions isolated from each other, as occurs in macro-separation ⁽⁵²⁾. Hence, the SiO_2 content is of prime importance in these slag-ceramics. At intermediate SiO_2 contents, only rings $Si_3O_9^{6-}$ or threadlike groupings SiO_3^{2-} of silicon-oxygen tetrahedra exist in the melt. These are incapable of forming sufficiently stable aggregates and therefore do not form regions which can undergo subsequent growth. However, they do form micro-regions in the melt resembling colloidal particles consisting of a large number of atoms with negative charge, which retain the surrounding cations. At higher SiO_2 contents, however, bands $Si_4O_{11}^{6-}$ or sheets $Si_2O_5^{2-}$ composed of silicon-oxygen tetrahedra can form in the melt. Such anions lead to union of regions with similar composition into regions reaching the critical size at which they are capable of further growth, which is observed as macro-separation.

Hence the above slag composition appears eminently suitable for the production of slag-ceramics if the correct content of TiO_2 can be determined

to cause devitrification.

Theory of the mechanism of TiO_2 as nucleation catalyst in devitrification of glasses.

Devitrification is the transformation from the glassy state (which is thermodynamically unstable because it has a higher internal energy than the crystalline state) to the crystalline state (which is the thermodynamically stable state) by the addition of energy in the form of heat.

The technical development of glass-ceramics was started in the Corning Glass Works in New York. A large number of patents and reports, especially those of S.D. Stookey (53) demonstrates the different kinds, and varied possibilities for the application of, such products, particularly those nucleated by TiO_2 . However, satisfying explanations of the structural processes have for a long time not been possible, and even at present, studies in this field are not completed.

Glass-ceramics have such a fine and randomly oriented structure that the pre-requisite for the formation of these glass-ceramics catalytically nucleated by TiO_2 is that the first step must occur homogeneously. This first step is believed to be associated with the prior separation into two liquid phases, which process is thought to proceed homogeneously because only small interfacial free energies are involved (53), (54). The separation of the drop-let microphase may be, and frequently is, initiated during the cooling of the glass and is naturally revived and more intensely developed during the nucleation step (54).

It has been shown that when TiO_2 is added to various glass systems it acts as nucleation catalyst by promoting the formation of droplet micro-phases (55), (56). These are described by Roy (57) as isotropic regions or an emulsion in which the glass is taken into the metastable liquation region. This action of the TiO_2 in producing imperfect liquid behaviour, such as evidenced by an immiscibility gap or by a flattening of the liquidus curves, is in accordance with the conclusions advanced by Dietzel.

The degree of freedom in a liquid suggests that the interfacial energy between two liquids is usually small compared to the interfacial energy between a crystal and a liquid. Since this comprises the barrier to nucleation, assuming the system tends to separate into two phases in bulk, droplet formation should nucleate readily. Roy (57) pictures the nucleation of the second glass phase, which he terms a short-range order phase, as follows: In the original liquid "nuclei" of sub-critical radius exist in large numbers - conceivably making up nearly half the volume. These nuclei are simply regions of different compositions, still having only short-range order, and in dynamic equilibrium with each other and with no surfaces separating the areas. On cooling and reheating, such nuclei can grow as a result of a very low activation energy process, since the structural demands of the glass phase are minimal and since the number of the "nuclei" is so large that diffusion only over very short distances is required. Obviously the viscosity at the temperature concerned will influence whether this phase separation step occurs at a finite rate. When separation phenomena occur, it is believed that one phase will be rich in network-modifiers while the other tends to have a higher proportion of network-formers. According to

Dietzel's postulates, in the case of conventional silicate glasses, all those ions catalyzing a crystallization process will preferably be found in a droplet phase. This droplet phase, because it contains the larger proportion of the network-modifying cations, will tend preferentially to crystallize (55).

Once this phase separation has occurred, there would appear to be a reasonable free energy gradient for further reaction since the two phases are metastable. Moreover, the enormous internal surface area and resulting strain all tend to increase the rate of crystallization (57).

A somewhat different more detailed mechanism is proposed by several authors - Bobovich (58), McMillan (59), and Weyl (60). The size of the titanium ion is such that its normal co-ordination number with oxygen is 6. However, at the glass melting temperature the co-ordination number may decrease to 4 thus allowing the Ti^{4+} ion to take part in the silica network. During cooling of the melt the tendency will be for the titanium ions to reassume the equilibrium co-ordination number of 6. Thus they will no longer be able to occupy network-forming positions and TiO_2 will be displaced from the network and will appear as a separate phase, possibly in combination with another oxide of the RO type. Bobovich (58) and Vertsner and Degteva (61) maintain that at this stage the specimen is still in the glassy state, i.e., crystallites, defined as geometrically ordered regions of definite composition, are not present at this stage of the heat-treatment.

For the subsequent course of the process Bobovich (58) advanced the following hypothesis : The precrystallization period of the process

culminates in the separation of a glassy component consisting of linked TiO_6 octahedra and certain structural alterations in the main phase. Further heating may result in the removal of aluminium-oxygen and lithium-oxygen radicals from the titanium-containing network, and as a result the TiO_6 octahedra become joined partly by the edges, i.e., forming crystallites fully analogous to rutile, or of a more complex composition. These crystallites or the liberated aluminium-oxygen and lithium-oxygen radicals (most probably joined into crystals of submicroscopic dimensions) may become crystallization centres. It is also possible that heat-treatment is accompanied by the formation of crystallites of the composition $m\text{Al}_2\text{O}_3 \cdot n\text{TiO}_2$ and that these become the crystallization centres (62).

Ohlberg and co-workers (63) found that once the glass in glass separation had occurred either the droplet phase or the matrix phase, depending on composition, could undergo a glass-crystal transformation initiated at the droplet-matrix interface, which crystalline phase thereby nucleated the bulk of the original glass.

There are two schools of thought when deciding whether epitaxy (oriented substance segregation on produced nuclei) must be considered as the starting process of controlled crystallization in glass-ceramics. Vogel and Gerth (54) postulate that the start of any controlled crystallization from the interior or from glass surfaces proceeds via epitactic overgrowth and prove this by citing that in many glass-ceramic types it is possible to trace crystalline TiO_2 radiographically. They state that TiO_2 has a two-fold function, namely, on the one hand it affects the separation process positively,

and on the other hand TiO_2 itself separates in the form of crystalline TiO_2 . This viewpoint is also adhered to by Bobovich (58) and Kind (62). Weyl (64) offers an alternative explanation on the basis that the Ti^{4+} ions, due to their greater polarizability, may take the place of Si^{4+} ions in the surface of the nuclei and it has been shown that the temporary participation of a polarizable ion accelerates nucleation.

However, Podushko and Kozlova (65) and Alekseev and Fedorova (66) maintain that glasses catalyzed by TiO_2 contain neither rutile nor any titanate in the crystalline state. They consider that crystallization centres arising at the liquid-liquid interface correspond to the composition of the main crystalline phase.

Critical cooling rates, liquidus temperatures, and primary phases.

To establish whether the titaniferous slags with increased SiO_2 contents, after the extraction of the rutile, could in fact be used for the production of slag-ceramics and what the optimum content of TiO_2 is, the following slag samples were prepared: the slag composition as stated above with the rutile extracted ($\text{CaO} = 17.52$ per cent, $\text{MgO} = 11.67$ per cent, $\text{SiO}_2 = 58.05$ per cent, and $\text{Al}_2\text{O}_3 = 12.76$ per cent), and with 4, 6, 8, 10, 12, and 14 per cent TiO_2 additions. The oxide components were mixed in the required proportions to give a weight of 20 gms., placed in a platinum crucible and suspended for 30 minutes in a furnace at $1350 - 1400^\circ\text{C}$. (It had previously been established that the melting points were well below this temperature). The crucible was then withdrawn from the furnace and placed on a metal block to cool. Visual examination indicated that all the slags were thus produced in

the glassy state. It was noticed that with an increase in TiO_2 the slags became increasingly more yellow in colour.

The first series of experiments conducted on these slag-ceramics was to establish the rate at which each had to be cooled to obtain them in the glassy state. Knowledge of this critical rate of cooling is important on two counts. Firstly, the slag must be cooled at a rate which prevents the formation of crystals as these would cause undesirable effects due to their relatively large size as compared with those produced during the subsequent devitrification step. Secondly, this critical cooling rate must not be so high as to make the pouring and shaping processes difficult or impossible.

Experimentally, each slag composition was subjected to various cooling rates on the micro-D.T.A. and then optically examined to determine the degree of crystallization, if any. In this manner, the actual cooling rate required to produce each slag in the glassy state was determined. The results were as follows : The slag containing no TiO_2 and slags with 4 and 6 per cent TiO_2 could be cooled at $12 - 15^\circ\text{C}$ per minute to obtain them in the completely glassy state. At rates of cooling below 10°C per minute, very slight crystallization occurred on the thermocouple limbs. With higher additions of TiO_2 there is a sudden change in the crystallization characteristics. At a cooling rate of 30°C per minute the slag with 8 per cent TiO_2 still exhibits a very small amount of crystallization on the thermocouple limbs while the slag with 14 per cent TiO_2 exhibits the same small degree of crystallization even at rates of cooling in excess of 100°C per minute.

However, it has also been found that the slags with 8 per cent and 10 per cent TiO_2 , if cooled at only 10°C per minute still only exhibit very limited crystallization. Tiny crystals form on the thermocouple limbs at isolated points and to a depth of only about 0.1 mm. maximum. Under these conditions the slags would still be suitable for the production of slag-ceramics since a successful slag-ceramic supplied by an overseas laboratory also exhibited isolated crystallization on the thermocouple limbs at a cooling rate of 15°C per minute. From these results, it is evident that the crystallization potential of these slags increases with increase in TiO_2 addition and that there exists a discontinuity of this effect between a 6 per cent and 8 per cent TiO_2 content.

While these tests were being conducted, it was also possible to determine the liquidus temperature for each of the slags and to identify the primary phase crystallizing on cooling. The results are shown in Table XII.

These results, show that the liquidus temperature is lowered with TiO_2 additions up to 12 per cent and then is raised again. The primary phase for TiO_2 additions from 0 to 10 per cent is diopside whereas for higher TiO_2 additions the primary phase is TiO_2 . On cooling the slag containing 10 per cent TiO_2 , the first crystals appearing are TiO_2 followed by diopside but on heating, the rutile melts first.

In the slags with the high TiO_2 additions, rutile could be readily nucleated on cooling but subsequently the slags could be further undercooled without heterogeneous nucleation of the diopside occurring on the rutile. This demonstrates that this phase is not itself a strong nucleating agent and

TABLE XII.

Determination of liquidus temperatures and identification of primary phases in slags with progressive additions of TiO_2 .

Slag composition: CaO = 17.52 per cent, MgO = 11.67 per cent, SiO_2 = 58.05 per cent, and Al_2O_3 = 12.76 per cent.

Percent TiO_2 addition	Liquidus Temperature $^{\circ}\text{C}$	Primary Phase
0	1290	CaO.MgO.2SiO_2
4	1260	CaO.MgO.2SiO_2
6	1245	CaO.MgO.2SiO_2
8	1240	CaO.MgO.2SiO_2
10	1220	CaO.MgO.2SiO_2 (TiO_2 is secondary phase)
12	1180	TiO_2
14	1210	TiO_2

in fact the rutile itself never nucleated homogeneously but only on the thermocouple limbs. Hence, Hillig ⁽⁶⁷⁾ states that the mechanism of nucleation whereby TiO_2 is a precursor phase appears unlikely.

Devitrification tests at a rate of heating of 10°C per minute could not be conducted on the micro-D.T.A. since as explained earlier, at these slow rates of heating, this instrument is very insensitive. However, for the determination of the critical cooling rates, the micro-D.T.A. was simply used as a high temperature microscope whereby the variable speeds obtainable due to its different and modified circuitry make it more useful than the high temperature microscope.

Differential thermal analysis applied to the study of devitrification of slags in powder form.

Several investigators have shown the usefulness of D.T.A. ⁽⁶⁸⁾, ⁽⁶⁹⁾, ⁽⁷⁰⁾, ⁽⁷¹⁾, ⁽⁷²⁾, ⁽⁷³⁾, ⁽⁷⁴⁾, ⁽⁷⁵⁾ for devitrification studies. The peak morphology has been very successfully related to surface and volume devitrification by Tudorovskaya and Sherstyuk ⁽⁶⁸⁾ and these authors have been able to differentiate between these two devitrification processes with the use of D.T.A. Unfortunately, no reference is made to sample condition or to the method of measurement of temperature and differential temperature. Krüger ⁽⁷⁶⁾, ⁽⁷⁷⁾ used finely divided slags when determining the devitrification characteristics of blast furnace slags and also for estimating the slag content of mixtures of unhydrated Portland cement and ground granulated blast furnace slag.

When the slags with the TiO_2 additions were subjected to differential

thermal analysis treatment on a Leeds & Northrup D.T.A. they were placed as a -200 mesh powder into the platinum crucibles. The temperature of the sample, (T), was measured in the slag sample and the differential temperature (ΔT), was measured between the slag sample and calcined alumina powder of the same mesh as the slag.

The assembly of the D.T.A. sample-holder in the shape of a cylindrical block is shown in Fig. 19. The two platinum crucibles were loaded with weighed quantities of sample and calcined alumina respectively and the lid, bearing the thermocouples, was lowered so that the thermocouples were located along the axes of the cylinders. Exact positioning of the thermocouples was ensured by the mechanical sliding device to which the inner tube, holding the thermocouple wires and lid, was attached. This prevented any lateral movement. A jig attachment was used to ensure that the depth to which the thermocouples were immersed in the powders was kept constant. The furnace could be moved vertically within a framework which enabled the hot zone to be accurately positioned around the sample-holder assembly. During the design and construction of the furnace and the sample-holder, continuous reference was made to the textbooks by Garn ⁽⁷⁸⁾ and Wendlandt ⁽⁷⁹⁾ and the references quoted therein although the sample-holder assembly is of rather novel design.

Apart from the normal calibration of the measuring instruments on the Leeds & Northrup D.T.A., the complete apparatus was tested by carrying out devitrification experiments on the same slags examined by Krüger ⁽⁷⁶⁾, ⁽⁷⁷⁾. Very good agreement was obtained for the devitrification peaks.

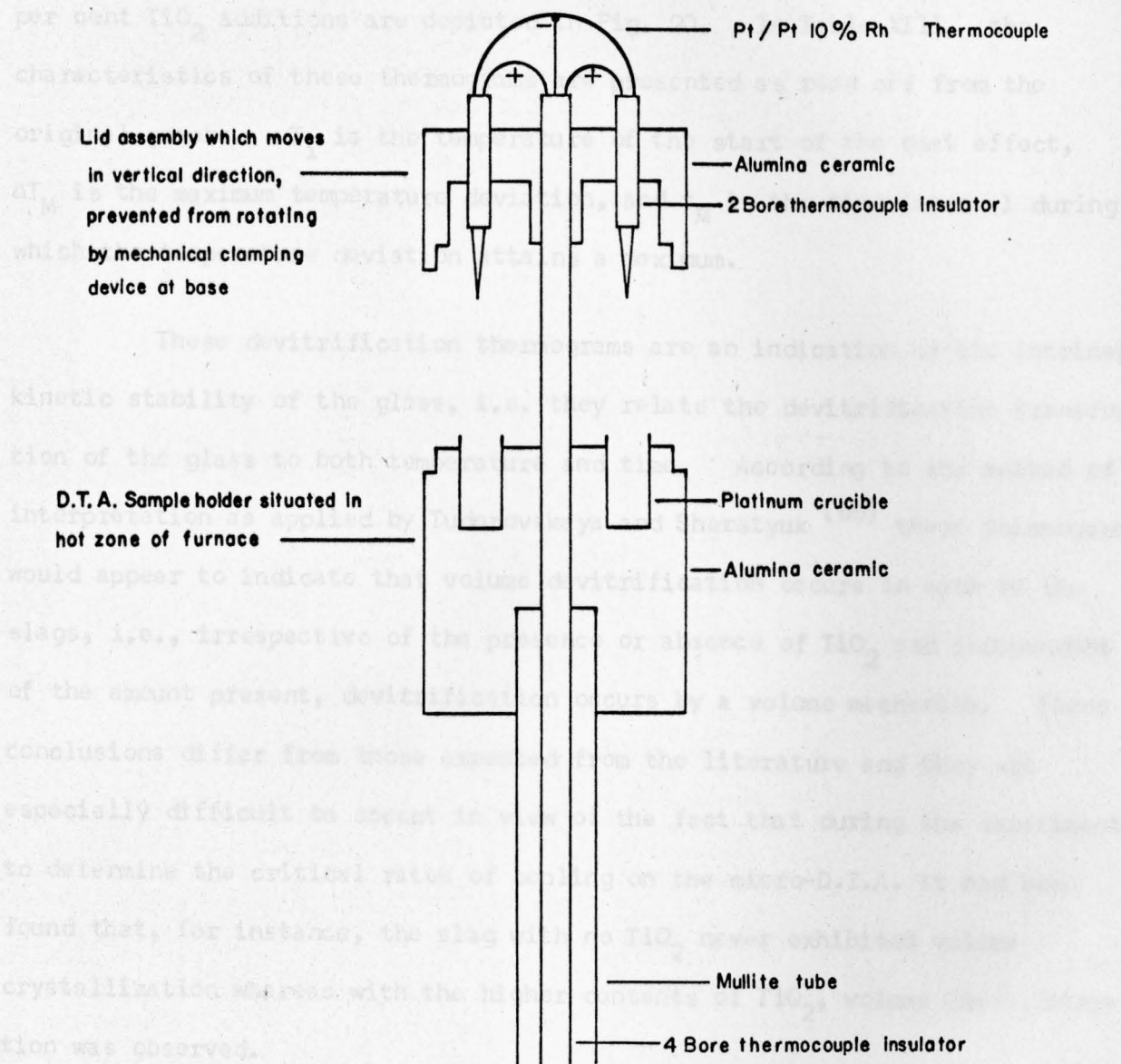


Fig. 19. Differential thermal analyser sample-holder assembly.

It was thought that these thermograms might not be suitable for

differentiating between surface and volume crystallization. The use of the sample in the finely divided form. On the other hand, the powder

The three thermograms for the slags with no TiO_2 and with 6 and 10 per cent TiO_2 additions are depicted in Fig. 20. In Table XIII, the characteristics of these thermograms are presented as read off from the original graphs. T_i is the temperature of the start of the heat effect, ΔT_M is the maximum temperature deviation, and t_M is the time interval during which the temperature deviation attains a maximum.

These devitrification thermograms are an indication of the intrinsic kinetic stability of the glass, i.e. they relate the devitrification transformation of the glass to both temperature and time. According to the method of interpretation as applied by Tudorovskaya and Sherstyuk (68) these thermograms would appear to indicate that volume devitrification occurs in each of the slags, i.e., irrespective of the presence or absence of TiO_2 and independent of the amount present, devitrification occurs by a volume mechanism. These conclusions differ from those expected from the literature and they are especially difficult to accept in view of the fact that during the experiments to determine the critical rates of cooling on the micro-D.T.A. it had been found that, for instance, the slag with no TiO_2 never exhibited volume crystallization whereas with the higher contents of TiO_2 , volume crystallization was observed.

Observed devitrification characteristics on the micro differential thermal analyser.

It was thought that these thermograms might not be capable of differentiating between surface and volume devitrification due to the use of the sample in the finely divided form. On the micro-D.T.A. when the powder

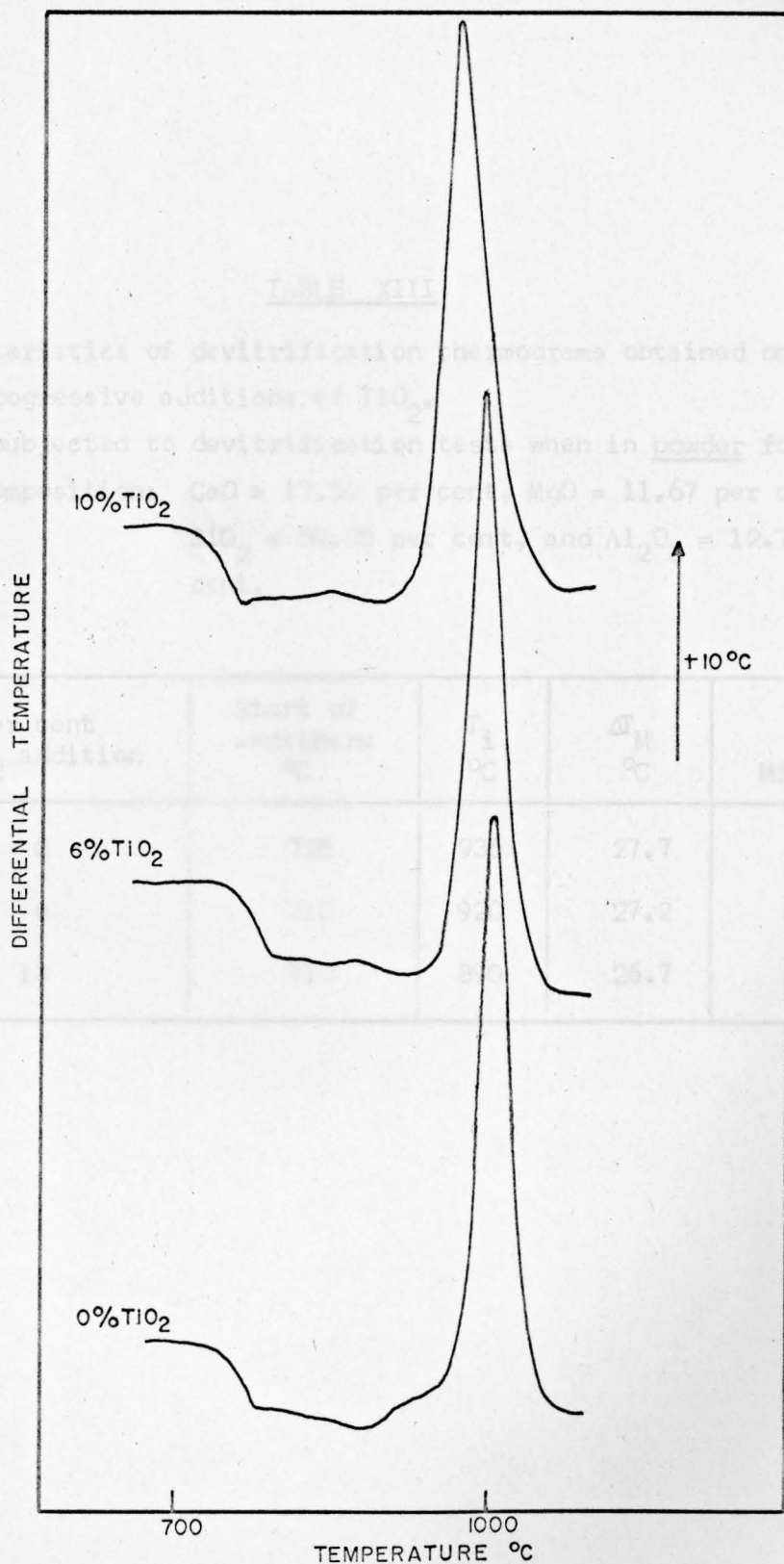


Fig. 20. Devitrification thermograms of slags in powder form with progressive additions of TiO_2 .

TABLE XIII.

Characteristics of devitrification thermograms obtained on slags with progressive additions of TiO_2 .

Slags subjected to devitrification tests when in powder form.

Slag composition: CaO = 17.52 per cent, MgO = 11.67 per cent, SiO_2 = 58.05 per cent, and Al_2O_3 = 12.76 per cent.

Per cent TiO_2 addition	Start of endotherm $^{\circ}\text{C}$	T_i $^{\circ}\text{C}$	ΔT_M $^{\circ}\text{C}$	t_M Minutes
0	725	935	27.7	6.1
6	710	920	27.2	5.9
10	710	890	26.7	6.6

was slowly heated, it was found that softening and coalescence occurred at temperatures below the formation of the exothermic devitrification peak. This means that at the devitrification stage, every "surface" of the coalesced particles initiates surface crystallization and due to the smallness of the particles this would produce thermograms characteristic of volume devitrification. This would to a large extent explain the inability to differentiate between surface and volume devitrification in the above experiments.

When the slag samples were completely melted onto the thermocouple and then allowed to cool to give a glass bead of 0.3 mm. in diameter by 0.6 mm. long, it was observed that volume crystallization could not be produced in slags with 0, 4, and 6 per cent TiO_2 . No volume crystallization occurred irrespective of the cooling rate used to obtain the glass and the subsequent heating rate and equilibrating period during devitrification - only crystallization from the thermocouple limbs occurred, i.e. heterogeneous crystallization. Slags with 8 per cent and higher contents of TiO_2 did exhibit volume devitrification.

The high temperature microscope and similar types of apparatus (59), (67) have been successfully used for determining optimum nucleation temperatures. An important point to note in connection with the nucleation process is that to achieve a glass-ceramic of optimum strength, the glass must be cooled below the maximum nucleation temperature before the glass is subjected to the nucleation heat-treatment (59). A series of experiments was conducted on the slag with 10 per cent TiO_2 . Specimens of this slag were cooled at a rate of 150°C per minute from above the liquidus to 400°C and then heated at

the same rate of 150°C per minute to 600, 650, 700, 750, 800, 850, and 950°C respectively. The specimens were allowed to equilibrate at these temperatures for 60 minutes and then heated at the same rate to 1000°C and soaked for one minute to permit the nuclei to grow sufficiently to make them visible under the microscope. They were then air-quenched and the following optical observations were made: Apart from the fact that the temperature of 950°C brought about simultaneous nucleation and growth (i.e. both the rate of nucleation and rate of crystal growth curves deviate from zero) all the other temperatures produced roughly the same number of nuclei. This would appear to indicate that the number of nuclei is independent of the equilibrating period at any nucleation temperature. This was confirmed by cooling the slag at 200°C per second and heating at 100°C per second to 1000°C . Nucleation as shown by the crystal growth at 1000°C was comparable with that produced by cooling at 50°C per minute and heating at 10°C per minute to 1000°C . This also shows that the rate of cooling from above the liquidus to the lower temperature has no significant effect provided the cooling rate is sufficient to prevent primary crystallization. This applies to all slags containing 10 per cent or more of TiO_2 . The slag with 8 per cent TiO_2 does undergo volume devitrification but the heating rate and equilibrating period at the optimum nucleation temperature are of importance. This finding that in slags with higher contents of TiO_2 nucleation occurs even on direct heating through the nucleation temperature has also been described by Podushko and Kozlova (65).

Thin-sections made of these slag-ceramics revealed that crystallization occurred in the form of spherulitic crystals, where each spherulite was made up of radiating needles.

Differential thermal analysis applied to the study of devitrification of slags in massive form.

To be able to differentiate between surface and volume crystallization in the manner used by Tudorovskaya and Sherstyuk ⁽⁶⁸⁾ it was thought that the slag must be placed into a crucible, melted, cooled and then subjected to devitrification on the Leeds & Northrup D.T.A. This procedure would produce a cylinder of glass of $\frac{1}{4}$ in. diameter with a height of $\frac{7}{16}$ in. It had been observed on the micro-D.T.A. that volume devitrification occurred much more rapidly than heterogeneous crystallization from the thermocouple limbs. Therefore, using the solid cylinder of glass, there should now be a difference in the morphology of the devitrification peaks for the various TiO_2 contents. The assembly of the D.T.A. sample-holder was again as shown in Fig. 18. The procedure adopted was as follows: A weighed amount of slag was melted in the crucible. This crucible together with that containing the inert material were then placed in the D.T.A. sample-holder assembly with the lid in the upper position and heated to above the liquidus temperature of the slag. When this temperature was reached the lid with the thermocouples was lowered into position and the furnace allowed to cool at a rate of 40°C per minute. This ensured that the sample was in the form of a solid glassy cylinder with the thermocouple embedded in it. Devitrification was then brought about by heating at the normal rate of 10°C per minute. The thermograms are depicted in Fig. 21 and the thermogram characteristics are presented in Table XIV.

From these results it can be seen that in this manner it has been possible to distinguish between surface and volume crystallization. The temperature of the initiation of the peak (T_i) is lowered with increase in

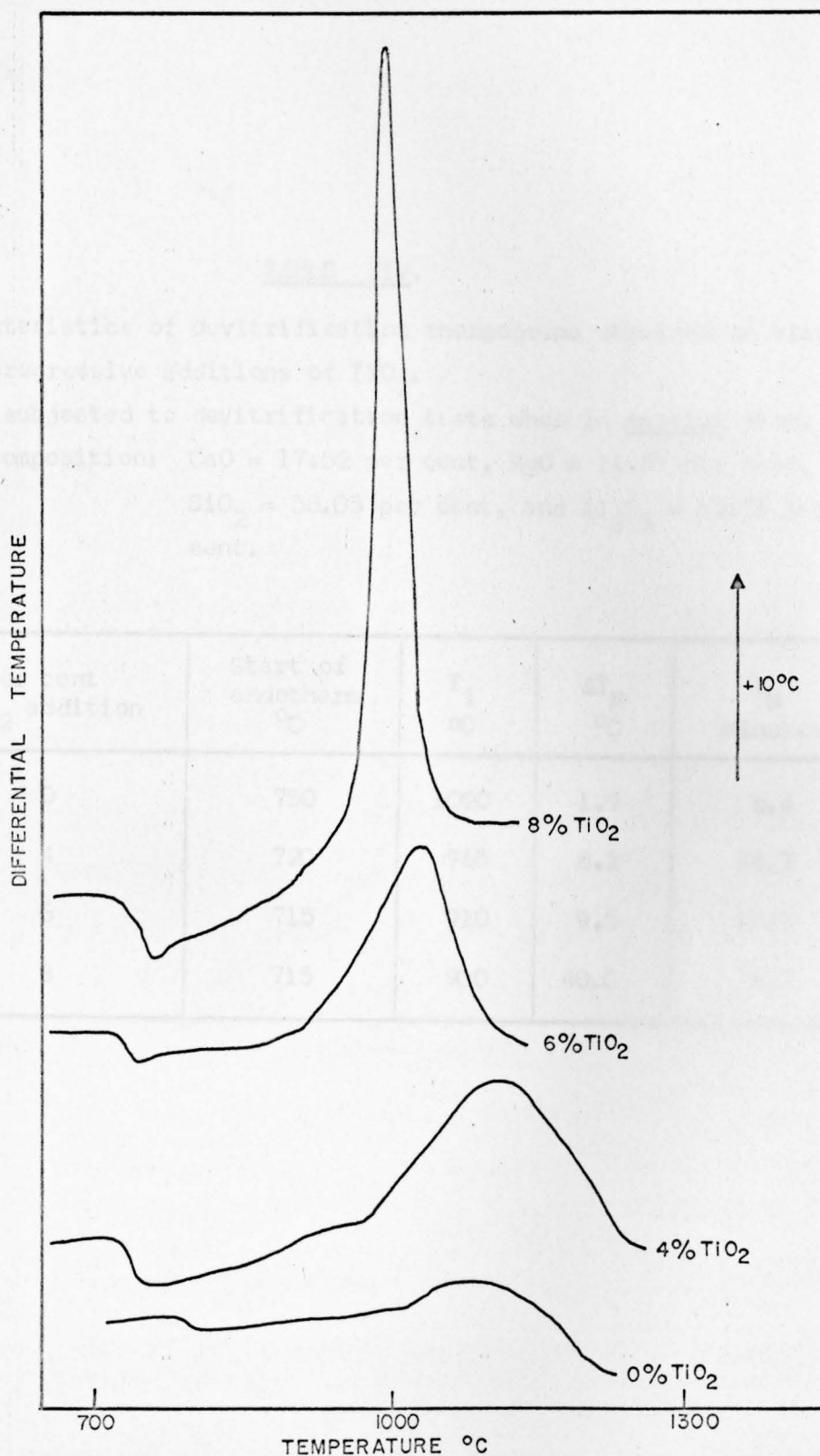


Fig. 21. Devitrification thermograms of slags in massive form with progressive additions of TiO_2 .

TABLE XIV.

Characteristics of devitrification thermograms obtained on slags with progressive additions of TiO_2 .

Slags subjected to devitrification tests when in massive form.

Slag composition: CaO = 17.52 per cent, MgO = 11.67 per cent, SiO_2 = 58.05 per cent, and Al_2O_3 = 12.76 per cent.

Per cent TiO_2 addition	Start of endotherm $^{\circ}\text{C}$	T_i $^{\circ}\text{C}$	ΔT_M $^{\circ}\text{C}$	t_M Minutes
0	750	1020	1.9	8.4
4	720	965	8.2	18.7
6	715	910	9.5	14.1
8	715	900	40.0	8.4

TiO_2 , the height of the peak (ΔT_M) is increased with increase in TiO_2 while the time interval between the initiation of the peak and the maximum temperature (t_M) is decreased with increase in TiO_2 . An anomaly exists in the case of the slag containing no TiO_2 , in which case t_M is 8.4 minutes, which is a much shorter time than would be expected in the light of the other results. This is probably due to the fact that this surface devitrification thermogram is accompanied by such small quantities of heat that accurate recording of the peak is difficult. As the TiO_2 content is increased, devitrification changes from a surface to a volume process. The TiO_2 content corresponding to this change is between 6 and 8 per cent. These results agree with the visual observations of devitrification made on the micro-D.T.A.

On all thermograms, whether obtained when the slag was in the ground form or in the massive form, a reversible endotherm occurs **before** the irreversible exothermic peak corresponding to devitrification. This endotherm has been reproduced with high precision. From evidence in the literature (80), (81), (82) it appears that this endotherm is associated with precrystallizational increase of the heat capacity of the glass due to increased mobility of the structural elements in the glass and to intensified fluctuations of concentration and structure which precede the formation of crystal nuclei of critical size. The endotherm is also due to relaxation processes in establishment of the meta-equilibrium "liquid" structure of the slag. As mentioned above, if the sample is in powder form, then it sinters at the temperature indicated by this endotherm prior to devitrification.

During both series of devitrification tests on the Leeds &

Northrup D.T.A. and on tests conducted on the micro-D.T.A. the devitrification product was always identified as diopside. In the available information on slag-ceramics it is stated that diopside and/or wollastonite are the crystalline species which should be obtained in slag-ceramics to produce the most suitable properties. In these thermograms, devitrification is accompanied by a single peak corresponding to the crystallization of diopside.

The titaniferous slags, on devitrification, exhibited up to four peaks as indicated in Table VI. Often, in the titaniferous slags, the primary devitrification peak had no visual effect on the glass although X-ray powder patterns confirmed crystalline phase appearance. This "invisible devitrification" has been reported by a number of investigators (66) (71). The subsequent devitrification peak was accompanied by opacity of the specimen which opacity increased with increase in temperature. X-ray patterns obtained from specimens heated to various temperatures along the devitrification thermograms indicated the following. The X-ray powder patterns associated with the primary peak were diffuse and weak but it could be occasionally established that crystallization of the quaternary or tertiary phase had occurred, and that subsequent peaks were associated with the crystallization of secondary and primary phases (where the phases have been named according to the order of crystallization during slow cooling). At lower devitrification temperatures, the lattice constants of the phases were distorted but at temperatures approaching the solidus, the X-ray patterns were sharp and consisted of the phases which would have crystallized under normal conditions of slow cooling. Some devitrification peaks were associated with the crystallization of more than one phase and occasionally, an intermediate metastable phase such as

MgO.TiO₂ would crystallize.

It is thought that the number of devitrification peaks is related to the number of phases which crystallize at normal cooling rates. Hence, these devitrification tests on the slag-ceramics, by virtue of the fact that only one devitrification peak is recorded, indicate that the devitrification process is a relatively simple one consisting of the crystallization of diopside. However, the slags with TiO₂ contents of 10 per cent and more, on slow cooling, deposit both diopside and rutile. The rutile either does not crystallize during devitrification or it acts as nucleation agent for the diopside but its presence cannot be identified by X-ray means.

An interesting point in these devitrification studies is the inability to differentiate between surface and volume devitrification when the slags were devitrified in the finely divided form. Each blast furnace slag examined by Krüger (which were used to calibrate the Leeds & Northrup D.T.A.) exhibited its own characteristic thermogram. Thus, different slags can be identified and even quantitatively estimated in slag-Portland cement mixtures by testing the samples in the powder form on a differential thermal analyser. But it appears that a study of devitrification in relation to the amounts of nucleation catalyst, optimum thermal treatment, etc. requires that the slag be in the massive form.

CHAPTER VI.

CONCLUSION.

The phase equilibria in the slag system $(\text{CaO} + \text{MgO}) = 30.00$ per cent, $\text{SiO}_2 = 19.69$ per cent, $\text{Al}_2\text{O}_3 = 13.12$ per cent, and $\text{TiO}_2 = 37.19$ per cent are presented in Fig. 3. This composition range was chosen because of its industrial significance in the process to be adopted by the Highveld Steel and Vanadium Corporation. From this phase diagram it is possible to determine the changes in liquidus and solidus temperatures, and in constitution of the slags with changes in the CaO and MgO contents of the flux, provided that the total $(\text{CaO} + \text{MgO})$ content of the slag remains constant at 30 per cent. Judging from this diagram there would appear to be no reason to suggest that the replacement of limestone in the limestone/dolomite flux by dolomite would have deleterious effects.

Further, no indications of significant differences in viscosity between the two slags could be observed on the high temperature microscope although, as mentioned in Section 3.1., it is indicated that the viscosities of the slags with high MgO contents are slightly lower. The viscosities of the titaniferous slags appeared to be somewhat lower than normal blast furnace slags. It has been reported ⁽⁸³⁾ that an increase in viscosity occurs when slags with TiO_2 contents in excess of 15 per cent are maintained for prolonged periods at temperatures above the liquidus under strongly reducing conditions. This increase in viscosity is due to the heterogeneity of the system brought about by the reduction of TiO_2 to lower oxides and the formation of carbides. As these new phases have very high melting points they probably exist in the

molten slag as finely dispersed phases.

An effect of importance, which could be brought about by the replacement of the limestone by dolomite, is a change in the desulphurization potential of the slag. Because of the low basicity of the titaniferous slags, the sulphur capacity of the original slag is expected to be low and by replacing the limestone by dolomite, the CaO content is decreased in favour of MgO, which would probably result in a further decrease in the already low sulphur capacity.

In connection with the viscosity and sulphur capacity of slags, it has been shown by Baldwin ⁽²²⁾ that slags of similar basicity may vary considerably in viscosity below the liquidus temperature. For instance, the one may not become very viscous while the other may exhibit a sharp increase in viscosity directly the temperature is decreased below the liquidus temperature. These differences in behaviour are probably due to differences in the temperature interval between the liquidus and solidus temperatures. However, even if the viscosity of the slag does not increase rapidly at temperatures below the liquidus, crystal formation will occur with the result that a decreased quantity of liquid remains to effect the desulphurization of the molten metal.

The liquidus curves and primary phases for titaniferous slags with combined (CaO + MgO) contents of 25, 30, and 35 per cent respectively are presented in Fig. 6 and Table III. From these curves it is possible to predict the changes in liquidus temperatures with changes in the total

(CaO + MgO) content and also with changes in the relative CaO and MgO contents for each particular (CaO + MgO) content. An important feature of these curves is the trough of minimum liquidus temperatures and the fact that even small changes in the (CaO + MgO) content or in the proportions of CaO and MgO for a particular (CaO + MgO) content of the slags are accompanied by large changes in the liquidus temperature. This is more marked for the slag derived from a limestone/dolomite flux than for the slag which is to be derived from an entirely dolomitic flux. An interesting point is that to obtain low liquidus temperatures, both CaO and MgO have to be present in the slag.

The silica content of these slags was increased in order to increase the viscosity and also in the hope of changing the phase constitution to permit extraction of the TiO_2 . The phase equilibria for progressive additions of silica to the slag having the composition CaO = 18.00 per cent, MgO = 12.00 per cent, SiO_2 = 19.69 per cent, Al_2O_3 = 13.12 per cent, and TiO_2 = 37.19 per cent are presented in Fig. 8. It can be seen that rutile is the primary phase to crystallize and does so over a long temperature interval with SiO_2 contents between 42.64 and 48.18 per cent. Larger quantities of slag of this composition were cooled at suitable rates and crystals of rutile in a glassy matrix were obtained. It should be possible to extract the larger proportion of the rutile either by flotation or by heavy-medium separation. If this suggested procedure proved feasible then the silica additions could be made to the hot slag in a separate slag-treatment section of the plant.

The testing of the micro differential thermal analyser showed that this apparatus is very useful for the monitoring of rapid thermal changes as

for example in the simulation of granulation plant conditions. Amounts of crystalline material in excess of that specified for the production of slag-cement were exhibited by the titaniferous slags after being subjected to simulated granulation plant cooling rates of 50°C per second. The slags with the SiO_2 content increased to 33 per cent and upward would be suitable for slag-cement production as less than the maximum permissible crystalline material is formed. If the rutile was previously extracted, then the slags would certainly be produced entirely in the glassy state - though even in this case the hydraulicity index would be poor.

The high-speed continuous cooling curves for a titaniferous slag emphasize once again the importance of heterogeneously nucleated crystallization. These tests clearly illustrated the characteristic of siliceous melts to undergo a change from heterogeneously nucleated to homogeneously nucleated crystallization with increasing cooling rates.

A synthetic slag was made up containing all the oxides in the proportions already noted but containing no TiO_2 . Definite quantities of TiO_2 were then added to this slag to enable devitrification studies to be carried out to determine the effect of TiO_2 as a nucleation agent. These studies showed that volume devitrification could be obtained when the TiO_2 content was in excess of 6 per cent but below this quantity of TiO_2 only surface devitrification took place. For determining the correct amount of TiO_2 to produce volume devitrification, it was indicated that the slag sample had to be in the massive form to differentiate between surface and volume devitrification.

Therefore, the titaniferous slags with contents of SiO_2 of 43 per cent and more can be cooled in such a manner that a large proportion of the rutile should be extractable. Further, the material remaining after extraction of the rutile would be suitable either for the production of granulate or for the production of slag-ceramics. In the latter case, the correct amount of TiO_2 can be left in the slag during the extraction of the rutile to act as nucleation catalyst.

APPENDIX (i).

Previous applications of the high temperature microscope to phase constitution studies.

The phase equilibrium relationships along the join anorthite-spinel in the system $\text{CaO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ are not readily susceptible to investigation by the conventional quenching technique because of the sluggishness of crystallization. Welch ⁽¹¹⁾ found that the liquidus temperatures could be readily determined using the high temperature microscope; he also conducted research on the behaviour of anorthite at subsolidus temperatures ⁽¹²⁾.

Baldwin ⁽²²⁾ was successful in determining the liquidus temperatures and high temperature properties of blast furnace slags.

The application of the technique of high temperature microscopy to a study of the $\text{Al}_2\text{O}_3 - \text{SiO}_2$ system appears to have resolved some of the outstanding questions surrounding the melting behaviour and constitution of mullite ⁽¹⁵⁾, ⁽¹⁶⁾.

Mercer and Miller ⁽²⁰⁾ conducted work on the spontaneous phase changes which occur during rapid cooling of beryl melts.

High temperature phase equilibria studies were conducted in the following systems : dicalcium silicate - tricalcium phosphate ⁽¹⁴⁾, calcium oxide - phosphorus pentoxide ⁽¹⁷⁾, $2\text{CaO} \cdot \text{SiO}_2 - 3\text{CaO} \cdot \text{P}_2\text{O}_5 - \text{CaO}$ ⁽²³⁾, $2\text{CaO} \cdot \text{SiO}_2 - 2\text{MgO} \cdot \text{SiO}_2 - \text{Al}_2\text{O}_3$ in the quaternary system $\text{CaO} - \text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{MgO}$ ⁽²⁴⁾ and $\text{Gd}_2\text{O}_3 - \text{Al}_2\text{O}_3$ and $\text{Sm}_2\text{O}_3 - \text{Al}_2\text{O}_3$ ⁽²⁵⁾.

A new form of calcium magnesiosilicate ⁽²⁶⁾ and a new form of tricalcium phosphate ⁽¹³⁾ were discovered.

APPENDIX (ii).

Temperature fluctuations due to half-cycle heating.

One of the major advantages of the principle used in these high temperature microscopes, whether normal high temperature microscope or with the modified circuitry in the micro differential thermal analyser, is the high rate of cooling possible merely by switching off the heating current. At temperatures in the region of 1500°C this cooling rate can be of the order of 600°C per second initially.

However, this advantage leads to the following deduction :

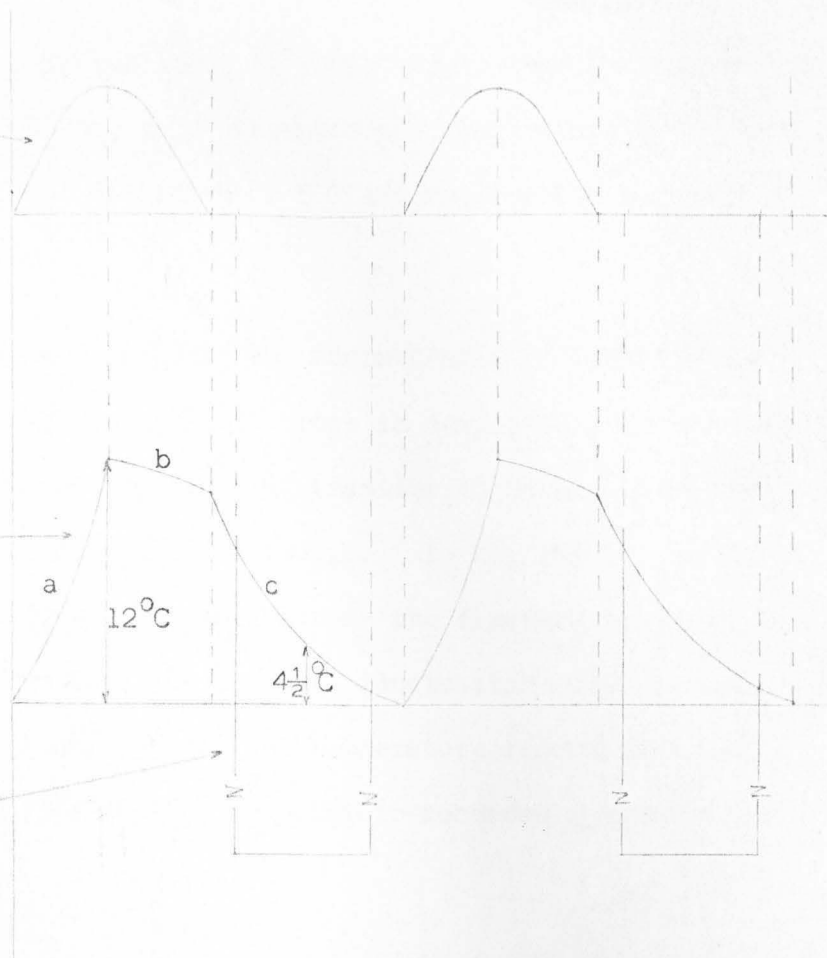
The temperature of the thermocouple must be continuously fluctuating by $\frac{600^{\circ}\text{C}/\text{second}}{50 \text{ cycles/second}}$ i.e., 12°C per cycle. The questions thus arising are : what temperature is actually being measured, at what temperature is the specimen being visually observed, and how does this affect the accuracy of the equipment? This point of the temperature fluctuations has apparently not been investigated as the publications on this type of equipment make no mention of it. In order to justify any results quoted to within an accuracy of $\pm 5^{\circ}\text{C}$ (some authors using this equipment quote $\pm 3^{\circ}\text{C}$) it is necessary to analyse this problem of the temperature fluctuations.

In the accompanying sketch the usual diagram to represent the d.c. positive half-cycle heating and the measurement of the e.m.f. generated in the thermocouple, which is measured over $66\frac{2}{3}$ per cent of the negative half-cycles, is shown. Beneath this, the theoretical fluctuations in the temperature of the thermocouple due to this half-cycle heating are drawn.

Heating current, d.c.
positive half-cycles only.

Fluctuations in temperature
of thermocouple above some
minimum datum level.

The temperature is measured
over this interval.
After the smoothing circuit,
virtually only the average
temperature over this
measuring period is recorded.



- (a) Increase in temperature due to start of heating cycle.
- (b) Decrease in temperature as the heating current is now diminishing.
- (c) Natural cooling of the thermocouple as no heat is being supplied.

From this graphical presentation it would appear that the temperature recorded is lower than the "average" thermocouple temperature by $(\frac{12}{2} = 6) - 4\frac{1}{2} = 1\frac{1}{2}^{\circ}\text{C}$, i.e., well within the $\pm 5^{\circ}\text{C}$ accuracy quoted by the author.

Also, when a sample is placed in the thermocouple apex this would have the tendency to smooth out these fluctuations in temperature because of the additional mass and the necessity for heat transfer to occur within the sample and between the sample and the thermocouple. In the sample itself, it can be expected that there will be a phase shift in the fluctuation curve due to this lag in heat transfer so that the original fluctuation curve is both smoothed and shifted to the right. Hence the temperature fluctuation is decreased to a value less than 12°C and the temperature recorded approaches more closely the average temperature of the system.

A temperature gradient is also to be expected from the centre of the thermocouple wire to its surface. The maximum temperature difference within the wire may be calculated approximately by the formula

$$\Delta T = \frac{qr^2}{4k}$$

where q = rate of heat generation per unit volume of wire

r = radius of wire

k = heat conductivity of wire.

The maximum difference in temperature is calculated as 2.2°C (9).

It would thus appear that the experimentally proven accuracy and precision of $\pm 5^{\circ}\text{C}$ are within the apparatus limitations.

APPENDIX (iii).

Poisoning of thermocouples and volatilisation of specimen.

It has been shown that some slags can poison thermocouples so that with increasing time, repeated determinations of the liquidus temperature will produce decreasing results. The correct value for the liquidus temperature can then only be achieved by extrapolation to zero time on a graph of temperature reading versus lapse of time (33). However, these slags were blast furnace slags and it is thought that the iron oxide and sulphur contents were mainly responsible for this poisoning effect.

To check the titaniferous slags for their effect on the thermocouples, one slag as investigated in Chapter II and one slag as investigated in Chapter III were examined. The slag was molten onto a new thermocouple and the liquidus was determined every 2 minutes for 50 minutes. No changes in the liquidus temperature could be observed within the usual precision of $\pm 5^{\circ}\text{C}$. This indicates that slag attack on the thermocouple (unless instantaneous) is negligible. That there is no instantaneous attack was proved by determining the liquidus temperature of a test-substance on the same thermocouple before and after the above tests.

However, if volatilisation of the specimen occurred then the liquidus temperature would increase with time. Seeing that it was proved that no attack occurred on the thermocouple and that the liquidus temperature remained constant, it can also be said that the volatilisation of these slags is negligible at the liquidus temperature.

APPENDIX (iv).

Analysis of recorder performance (48).

The recorder built into the micro differential thermal analyser is a Rika-Denki two-pen recorder, model B-24SS. The two independent channels each have their own attenuator. The channel measuring the temperature T of the sample has voltage dividers of 2.5, 5, 10, 20, 50, 100, 500 mV, 1, 5, 10 V, while the channel measuring the differential temperature ΔT has voltage dividers of 10, 20, 50, 100, 500 mV, 1, 5, 10, 50, 100 V. This latter channel is fed via a pre-amplifier, Rika-Denki model A10, with input sensitivity between 50 μV - 2000 μV .

The millivolt recorder (potentiometric recorder) is of prime importance since it is the only measuring device in the micro differential thermal analyser. Accurate analysis is dependent upon the ability of the recorder to monitor the detector output accurately, rapidly, and reliably. "Full-span response time" is the value which determines whether or not the instrument is capable of monitoring a given signal at its original speed. The full-span response time quoted for the recorder is less than 0.5 seconds. This quoted value was checked by feeding both channels from an audible frequency generator. A square wave extending over 100% span was fed into each channel and the chart drive was set at the maximum speed of 1200 mm. per minute. The vertical limbs of the square wave have an infinite speed relative to the recorder so that a measurement of the speed of this part of the wave on the chart paper will allow an evaluation of the maximum response time of the recorder. This maximum mechanical speed was determined as 0.35 seconds

for 100% span. When a sine-wave signal was fed into either channel it was evaluated that 0.4 seconds was sufficient time to record 90° of a sine-wave over 100% span. At higher sine-wave frequencies, the height of the wave diminishes; this decrease increasing with increase in frequency. This is a measure of the frequency response of the recorder, and it thus shows that as long as the frequency is such that the full-span travel of the sine-wave for one limb is ≥ 0.4 seconds, it can be recorded efficiently. At higher frequencies, the recordings become less than full-span. If a smaller amplitude were considered then the fall-off with increase in frequency would be less marked.

Recorder dynamic performance is critical at points of maximum trace curvature where acceleration demands are greatest. The dynamic limitation can cause distortion in the trace shape, particularly so in smaller peaks.

It should be pointed out that if the magnitude of deflection is decreased to say 10% full-span, the time required to record this signal might be expected to be 0.04 seconds. The actual time when compared with 0.04 seconds becomes a finite measure of the ability of the instrument to approach the ideal velocity limited system. The actual time will be from 0.07 to well over 0.1 seconds, depending upon the exact span step.

Deadband is defined by the American Standard Association C39.4 as "the range through which the measured quantity can vary, without initiating response". Deadband can be measured by adjusting the gain and damping to optimum conditions and then either shorting the input terminals or connecting to them a steady d.c. signal input. The servomotor is offset manually by a

few increments and allowed to return to balance and this procedure is then repeated in the opposite direction. The difference between the rebalancing positions is a measure of the deadband. The recorder showed no measurable deadband when subjected to this test. When the recorder's deadband was tested electrically by feeding both channels with the same sine-wave and then decreasing the amplitude of the wave on the one channel, it was found that the amplitude of the sine-wave could be decreased to an amplitude approaching pen-line thickness and yet be a true reflection of the sine-wave as fed into the other channel.

APPENDIX (v).

Provisional list of properties of slagceram.

Specific gravity (bulk)	3.00.
Specific heat	0.17 cals per gram per °C.
Coefficient of expansion	5×10^{-6} per °C at room temperature.
Crushing strength	30,000 lbs. per square inch, for a standard three-inch cube.
Porosity	4.4% maximum water absorption. Sizes of pores in the ranges 0.2 microns to 0.3 microns, and 50 microns to 1000 microns.
Scratch hardness	Mohs scale 8-9.
Abrasion resistance	Much better than good ceramic tiles, and basalt.
Thermal stability	No measurable dimensional changes after heating up to 900°C and subsequent cooling (B.S. 1902).
Impact Resistance (falling weights)	Similar properties to good ceramic floor tiles.
Coefficient of friction	Slagceram tiles, as cast, are rougher than polished worn ceramic floor tiles, but nearly as rough as new ceramic tiles.
Effects of concentrated loads	No measurable indentations after several weeks. Durability much better than ceramic floor tiles.
Long-term constant temperature expansion	Negligible.
Test-floor	A test panel has been inserted in a busy corridor at BISRA, Battersea. No noticeable wear, chipping or cracking has occurred after several months.
Exposure tests	Tiles exposed on test sites show only slight surface discoloration effects after periods up to two years.

Resistance to mould growth	No harmful effects by common moulds.
Adhesion to cements	Slagceram can be mounted in conventional cements, as well as more expensive epoxy adhesives.
Accelerated weathering	No measurable changes after 800 hours.
Volume resistivity	10^8 ohm.cm.
Modulus of rupture	20,000 p.s.i.
Resistance to chemical attack	Resists sulphates, alkalis and many acids.

The British Iron and Steel Research Association.

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