

PHASE EQUILIBRIUM STUDIES IN THE SYSTEM $MgO-TiO_2$ BY HOT STAGE MICROSCOPIC TECHNIQUE*

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Phase equilibria relations in the system $MgO-TiO_2$ were studied by means of hot stage microscope and X-ray techniques. The existence of three binary compounds in the system was confirmed. From the liquidus and solidus temperatures of compositions in the system an equilibrium diagram for the system was constructed.

A study of the phase equilibrium relations in the system $CaO-MgO-TiO_2$ ¹ was made considering the importance of titanate ceramics as dielectrics. A survey of the literature pertinent to the problems revealed several discrepancies in the published data on the subordinate binary systems. It was therefore, considered essential that a preliminary study of the binary systems be made.

An equilibrium diagram for the system $MgO-TiO_2$ was first published in 1932 by Van Wartenberg and Prophet.² Two compounds $2MgO.TiO_2$ and $MgO.2TiO_2$ were proposed but the subsequent work of other investigators³⁻⁷ showed that there are three binary compounds in the system. These are the two listed by Van Wartenberg and also $MgO.TiO_2$.

The existence of three compounds in the system was also confirmed by Conghanour and Depresse⁸ in an investigation of solid state reaction between components MgO and TiO_2 . They studied the completeness of the reaction and compound formation petrographically and by means of X-ray diffraction patterns of the fired samples. All these workers⁸ reported that the three compounds $2MgO.TiO_2$, $MgO.TiO_2$ and $MgO.2TiO_2$ are congruently melting with m.ps of 1732°C, 1630°C and 1625°C, respectively

In 1956, Cocoo and Massaza⁹ and later in 1958 Massaza and Sirchia¹⁰ studied the binary system $MgO-TiO_2$ in the course of work on the ternary system $MgO-SiO_2-TiO_2$ but their findings on the nature of the compounds and on their m.ps differed from those of previous workers.^{2,8}

According to Coughanour and Depresse⁸ the eutectic temperatures between the respective compounds are as follows:—

$MgO.TiO_2$ and $MgO.2TiO_2$, 1592°C at 56 mol% TiO_2

$MgO.2TiO_2$ and TiO_2 , 16060°C at 86 mol% TiO_2

MgO and $2MgO.TiO_2$, 1707°C at 21 mol% TiO_2

$2MgO.TiO_2$ and $MgO.TiO_2$, 1583°C at 44 mol% TiO_2

But Van Wartenberg² determined the m.ps of $2MgO.TiO_2$ and $MgO.2TiO_2$ as 1840°C and 1680°C respectively and the respective eutectic temperature as follows:

MgO and $2MgO.TiO_2$, 1800°C

$2MgO.TiO_2$ and $MgO.2TiO_2$, 1625°C

$MgO.2TiO_2$ and TiO_2 , 1645°C

All these determinations were made using optical pyrometers under black body conditions. Coughanour and Depresse explained the difference in their measurements from those of Van Wartenberg by simply saying that they used more refined method of study. The investigations of Cocoo and Massaza, and Massaza and Sirchia revealed that the compounds $MgO.TiO_2$ and $2MgO.TiO_2$ are incongruently melting compounds. The m.ps obtained for these compounds were different from those of earlier workers. They showed that the compound $MgO.2TiO_2$ melts congruently at $1690 \pm 20^\circ C$ and that there are peritectic reactions involving $MgO.TiO_2$ and $MgO.TiO_2$ as follows:

$MgO.TiO_2 \rightarrow 2MgO.TiO_2 + \text{liquid}$ at $1680 \pm 20^\circ C$

$2MgO.TiO_2 \rightarrow MgO + \text{liquid}$ at $1740 \pm 20^\circ C$

The eutectic temperature between $MgO.TiO_2$ and $MgO.2TiO_2$ was found to be $1600 \pm 20^\circ C$ at 56 mol% of TiO_2 and between $MgO.2TiO_2$ and TiO_2 as $1610 \pm 20^\circ C$ at 80 mol% of TiO_2 .

Experimental

Sample Preparation

The components used in preparing different compositions were TiO_2 and MgO (B.D.H. Analar).

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The MgO contained about 5.7% moisture, so it was calcined at 700–800°C in a muffle furnace and kept in a desiccator. The desired amounts of the two constituents were weighed, pelletised and melted in a molybdenum crucible by means of a high frequency induction generator. The melted slags were then crushed in a percussion mortar and remelted. The slags after grinding were ready for determination of liquidus and solidus temperatures using a hot stage microscope.

The slags which melted below 1500°C were melted in a platinum-wound furnace in air using a platinum cup as a small crucible.

Arrangement for Melting of Slags by High Frequency Induction Generator

The melting chamber consisted of a vitreous silica tube 24 in long and 3½ in i.d. Two concentric alumina tubes were used as radiation shields. Both ends of the silica tube were sealed tightly by rubber bungs. Gas inlet and outlet arrangements were made through the rubber bungs. The bung was fitted with a small glass

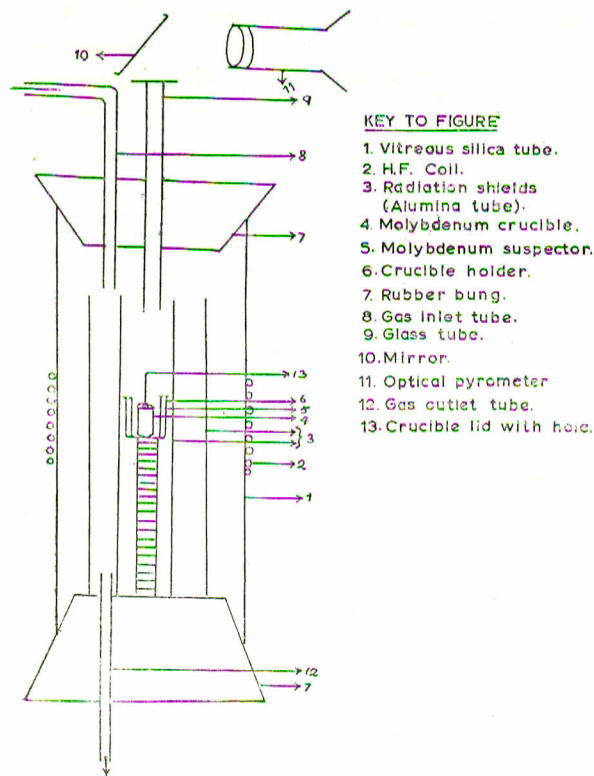


Fig. 1.—Melting chamber for the slags using a high frequency induction furnace.

window to allow temperature measurement by an optical pyrometer. At high temperatures in air, molybdenum oxidises to give a volatile oxide thus argon was passed for a while before starting a melt to expel the air from inside the reaction chamber. At very high temperature a small amount of hydrogen was also passed to protect the crucible. The crucible holder was an alumina tube which rested on the lower rubber bung of the silica tube. On the top of this tube was an alumina crucible in which a molybdenum susceptor was placed. Inside this susceptor a small molybdenum crucible containing the slag was placed for melting purposes. The crucible was covered with a molybdenum lid which has a hole in the centre. This allowed a rough measurement of the melting temperature of the slags under black body conditions by means of a Leeds Northrup optical pyrometer. The arrangement of the melting chamber is shown Fig. 1.

The Hot Stage Microscope

Power Unit.—Welch¹¹⁻¹⁹ overcame the electrical problem of isolating the voltage which supplies the heating current, from the thermoelectric electromotive force by the use of silicon rectifiers. These pass only the positive half cycle of the applied voltage to heat the couple while a phased switch (a synchronous converter or chopper) allows the thermoelectric e.m.f. to be measured during the part of the intermediate half cycles (Fig. 2). The e.m.f. is measured on a 5-in scale meter calibrated in degrees centigrade for use with 20% Rh–Pt vs. 5% Rh–Pt thermocouples. For higher accuracy a potentiometer was used in the circuit.

The Microscope.—This is a Beck petrological binocular type microscope mounted horizontally

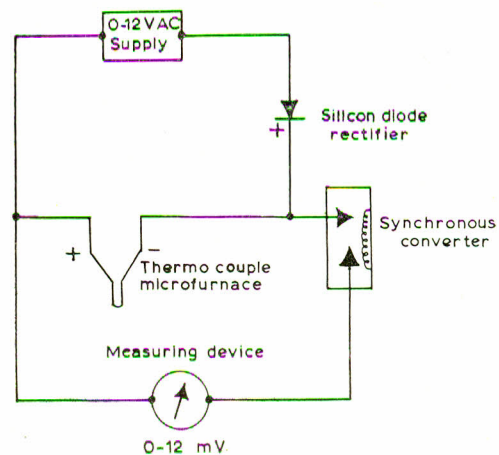


Fig. 2.—Microfurnace power supply and measuring circuit of hot stage microscope.

on cast base. The optics include paired eye pieces 25 mm \times 10, one objective 25 mm NA 0.15 and a substage condenser 0.625 in focus (Fig 3).

Gas Tight Cell with Thermocouple.—The cell provides a draught-free enclosure and at the same time permits the use of any desired atmosphere. The thermocouple may be heated in an atmosphere of air but heating in air for an hour or two at high temperatures causes a heavy deposition on the cell windows due to the oxidation and volatilisation of the platinum alloys. For this reason an inert gas such as argon or nitrogen is passed with a slight positive pressure. The thermocouple units are provided with neoprene gaskets which provide an efficient seal when the retaining nuts on the guide rods are tightened. Standard microscopic slide cover glass 7/8 in dia. is used for observation windows and are sealed to the window opening by polyethylene washers (Fig 4).

Determination of Liquidus and Solidus Temperature by Hot Stage Microscope

The sample was ground finer than 200 mesh for determining the liquidus temperature and other properties. To load the sample on the thermocouple, the tip of the thermocouple is dipped into the powder sample and is withdrawn. The excess quantity of powder is then gently tapped off. Alternatively, the tip of the thermocouple is moistened with an inert liquid to reduce the chances of the slag falling off during the mounting of the thermocouple.

After loading with the sample the thermocouple is carefully inserted into the cell casing and screwed up with the knurled retaining nuts to a good finger tightness. The cell is then purged with an inert gas (argon) for few minutes.

The ease of determining the liquidus and solidus temperature depends to some extent on the mobility of the melt and relative ease of crystallization of the primary phase. To obtain liquidus temperatures for simple systems having mobile melts, the temperature is raised to melt the slag and lowered after melting until near the thermojunction a very small crystal remains in the melt without showing sign of any growth or decay. At this point the liquidus temperature of the melt is determined. The solidus temperature is determined by observing the behaviour of the liquid formed by melting the powder sample on the limb of the thermocouple. Crystallization from viscous melts is very sluggish and more patience has to be exercised in determination of the liquidus temperature. Experience of crystal habits, crystal growth characteristics, birefringence

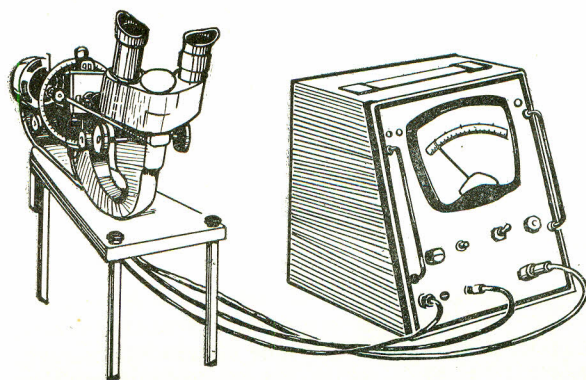


Fig. 3.—Hot stage microscope with heating panel.

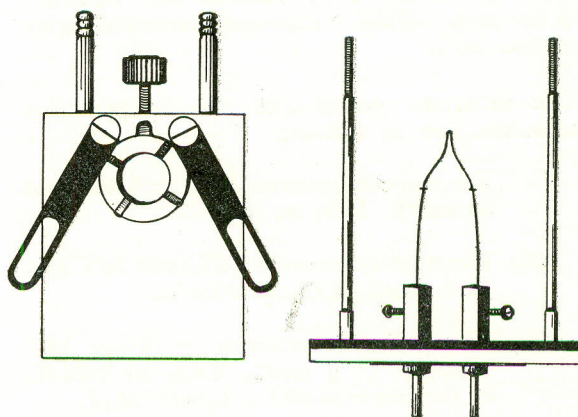


Fig. 4.—Sketch of the thermocouple cell with the thermocouple.

and general behaviour is also helpful in recognising crystals in the melt. Such evidence of crystal identity is not available in other methods employed in studying phase equilibria. Naturally when initial identification is required the material is subjected to X-ray analysis. In comparison with classical methods of studying high temperature phase equilibria, this method is dynamic in that identification of phases present depends on observing the growth and melting of the crystals.

Results and Discussion of the System MgO-TiO_2

The MgO-TiO_2 system was studied very carefully because of the contradictory publications by Conghanour and Deprosse,⁸ and Massaza and Sirchia.¹⁰ Three binary compounds have been reported, namely the cubic orthotitanate ($2\text{MgO} \cdot \text{TiO}_2$) M_2T , the uniaxial metatitanate ($\text{MgO} \cdot \text{TiO}_2$) MT and the biaxial dititanate ($\text{MgO} \cdot 2\text{TiO}_2$) MT_2 . But there are a great number of

discrepancies concerning the nature of the compounds and melting behaviour. In the present study the existence of the three binary compounds was confirmed by their X-ray powdered diffraction patterns. Twenty-one compositions in the system $\text{MgO}\cdot\text{TiO}_2$ were prepared. The liquidus and solidus temperature are given in Table I and were determined by the hot stage microscope technique described earlier.

A phase diagram was constructed and is shown in Fig. 5. The form of the liquidus in this system suggests that there is only one compound, namely $(\text{MgO}\cdot\text{TiO}_2)\text{MT}_2$, which is a congruently melting compound, the other two $(\text{MgO}\cdot\text{TiO}_2)\text{MT}$, $(2\text{MgO}\cdot\text{TiO}_2)\text{M}_2\text{T}$ are incongruently melting compounds. The phase diagram constructed is similar to that given by Massaza and Sirchia¹⁰ and the m.ps of the compounds recorded agree with that work.

The invariant points and the temperatures determined are as follows:

- (i) The eutectic between TiO_2 and MT is at 80 mol% TiO_2 at 1630°C.
- (ii) The eutectic between MT_2 and MT is at 56.6 mol% TiO_2 at 1620°C.
- (iii) The peritectic reaction involving MT starts at 51.5 mol% TiO_2 at 1680°C by the reaction $\text{MT} + \text{liquid} = \text{M}_2\text{T}$.

All these results confirm the phase diagram of Massaza and Sirchia.¹⁰ In the present investiga-

tions the determination of liquidus and solidus temperatures up to 1700°C are more accurate than the previous reports because of the observation during the time of measurement. The incongruent melting of the compounds MT and M_2T was later confirmed while studying the ternary system $\text{CaO}\text{--}\text{MgO}\text{--}\text{TiO}_2$.

TABLE I.—LIQUIDUS AND SOLIDUS TEMPERATURES OF THE SLAGS ON THE SYSTEM $\text{MgO}\text{--}\text{TiO}_2$

Slag No.	Composition mol%		Solidus temp by observation °C	Liquidus temp by observation °C
	MgO	TiO ₂		
1	12.50	87.50	1630	1750
2	15	85	1630	1670
3	20	80	1630	1630
4	25	75	1630	1640
5	28.50	71.50	1630	1660
6	33.33	66.66	1630	1690
7	34.50	65.50	1630	1680
8	35.71	64.29	1620	1675
9	37.03	62.97	1620	1670
10	37.50	62.50	1620	1670
11	38.50	61.50	1620	1660
12	40	60	1620	1650
13	41.70	58.30	1620	1645
14	43.47	56.53	1620	1630
15	45.45	54.55	1620	1660
16	47.14	52.86	1620	1665
17	50	50	1620	1680
18	54.54	45.45	1620	1720
19	56.52	43.48	1620	1750
20	58.35	41.67	1620	1750
21	66.66	33.33	1620	1750

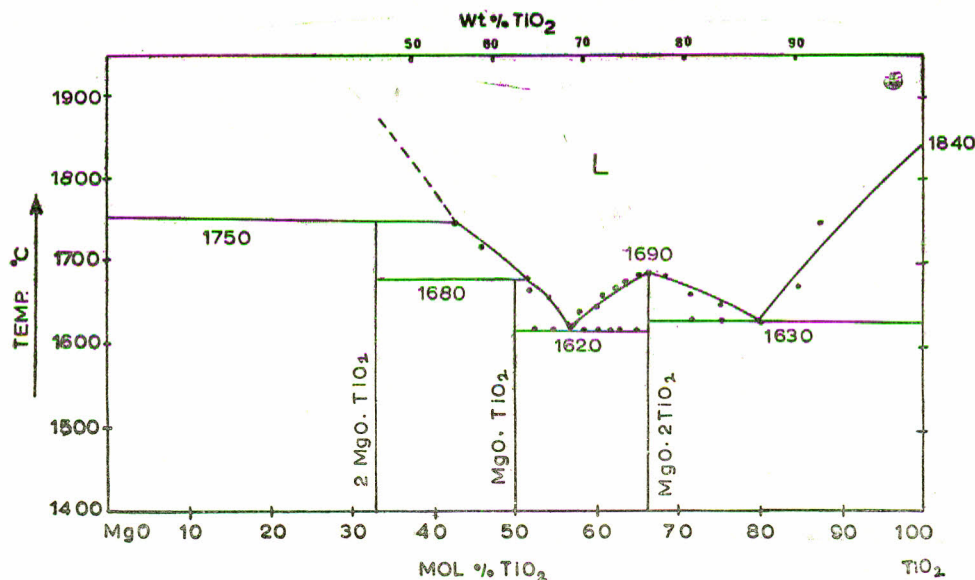


Fig. 5.—Constructed phase diagram of the system $\text{MgO}\text{--}\text{TiO}_2$.

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