

## LIQUIDUS TEMPERATURES IN THE $\text{TiO}_2$ -RICH SIDE OF THE $\text{FeO-TiO}_2$ SYSTEM

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(Received 22 February 1979; in revised form 28 May 1979)

**Abstract**—Liquidus temperatures of  $\text{FeO-TiO}_2$  slags in the composition region between 52.4 wt.%  $\text{TiO}_2$  and 80%  $\text{TiO}_2$  have been determined by means of the cooling curve technique. The results agree reasonably well with previously published data for slags containing up to about 68%  $\text{TiO}_2$ . However, the liquidus temperatures of  $\text{TiO}_2$ -richer slags have been found to differ markedly from those reported in previous works. On the basis of these results, a modification of the  $\text{TiO}_2$ -rich side of the  $\text{FeO-TiO}_2$  phase diagram is proposed.

**Résumé**—Des températures de liquidus ont été déterminées par analyse thermique directe sur des laitiers  $\text{FeO-TiO}_2$  dans le domaine de composition s'étendant de 52.4% en poids à 80% en poids de  $\text{TiO}_2$ . Les résultats sont en bon accord avec les données publiées antérieurement pour les laitiers contenant jusqu'à 68 pds % de  $\text{TiO}_2$  environ. Cependant, les températures de liquidus obtenues pour les laitiers les plus riches en  $\text{TiO}_2$  diffèrent nettement de celles rapportées dans des travaux antérieurs. Une modification de la zone riche en  $\text{TiO}_2$  du diagramme de phase du système  $\text{FeO-TiO}_2$  est proposée en fonction de ces nouveaux résultats.

### INTRODUCTION

Titania-rich slag is a co-product of the smelting of ilmenite ore which is used as a raw material for the rutile pigment industry. Basically, these slags contain  $\text{FeO}$ ,  $\text{TiO}_2$ ,  $\text{Ti}_2\text{O}_3$  and some other oxides which are present in the ore as impurities. These three oxides account for 81–82% of the slag produced in Sorel, Quebec, and for about 93% of the slag produced in Richards Bay, South Africa. Thus, the region of the  $\text{Fe-Ti-O}$  system corresponding to low oxygen pressures and low values of the ratio  $\text{Fe/Ti}$ , is of fundamental importance for the better understanding of the nature of industrial titania slags. Previous investigations in this region have concentrated on the identification of phases present at sub-solidus temperatures [1,2]. However, other aspects such as liquidus temperatures or relations involving the equilibrium of solid, liquid and vapour phases, remain largely unknown.

A basic building unit of the  $\text{Fe-Ti-O}$  system is the  $\text{FeO-TiO}_2$  binary system. Phase diagrams for such system have been proposed by Grieve and White [3] and also by MacChesney and Muan [4]. The diagram of the latter authors is the one generally accepted and is reproduced in Fig. 1. It may be seen in the Figure that the  $\text{TiO}_2$ -rich side of this diagram is characterized by the existence of two congruently melting compounds, namely ilmenite ( $\text{FeO} \cdot \text{TiO}_2$ ) and ferrous dititanate ( $\text{FeO} \cdot 2\text{TiO}_2$ ) the latter having a pseudo-brookite type structure. In this region, there would be two eutectic points, the first marking the coexistence of the solid phases ilmenite and pseudo-brookite with a liquid of

approximately 58%  $\text{TiO}_2$ , and the second corresponding to the equilibrium between pseudo-brookite, rutile ( $\text{TiO}_2$ ) and a molten phase containing about 80%  $\text{TiO}_2$ .

According to the diagram of Fig. 1, slags containing up to 85%  $\text{TiO}_2$  would melt at temperatures below 1500° C. However, attempts made in our laboratory to melt  $\text{FeO-TiO}_2$  mixtures held in molybdenum crucibles by heating them to 1500° C under purified Ar were unsuccessful. Similar results have been previously reported by Smith and Bell [5] who found that a temperature of 1475° C was insufficient to melt  $\text{FeO-TiO}_2$  slags (contained in iron crucibles) in the 79–85%  $\text{TiO}_2$  composition range. Since this evidence pointed out to some inconsistency in the  $\text{TiO}_2$ -rich side of the proposed phase diagram, a series of experiments was carried out to redetermine the liquidus temperature of  $\text{FeO-TiO}_2$  slags in the range between 52.7%  $\text{TiO}_2$  (ilmenite composition) and 80%  $\text{TiO}_2$ .

### EXPERIMENTAL

Liquidus temperatures of  $\text{FeO-TiO}_2$  slags were determined using the cooling curve technique. This method has already been used with satisfactory results for the determination of melting temperatures of industrial titania slags [6]. In this technique, the slag temperature is continuously recorded during a cooling cycle and the liquidus point is determined from the arrest in the time-temperature curve which indicates the beginning of the crystallization. Besides the

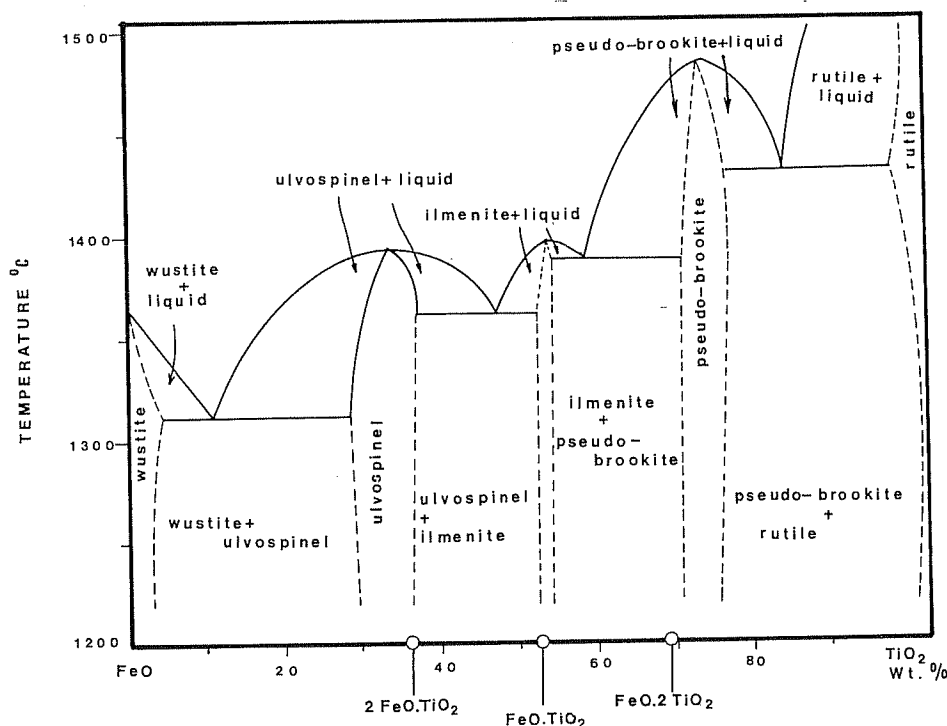
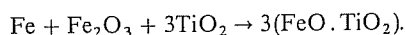


Fig. 1. Phase diagram for the  $\text{FeO}$ - $\text{TiO}_2$  system proposed by MacChesney and Muan [4].

simplicity of this technique, there are two other factors which make it attractive for the study of  $\text{FeO}$ - $\text{TiO}_2$  slags:

- (a) the slags crystallize rapidly and only occasionally show a weak tendency to supercool, and;
- (b) the relatively high heats of fusion of titania and titanates ( $16 \text{ kcal mol}^{-1}$  for rutile [7],  $21.7 \text{ kcal mol}^{-1}$  for ilmenite [8]) should result in clear changes in the cooling curve patterns at the beginning of the solidification.

The method used for the sample preparation consisted in thoroughly mixing synthetic ilmenite with reagent grade  $\text{TiO}_2$  (in the form of anatase) in the proportions corresponding to the desired slag composition. The synthetic ilmenite was prepared in batches of about 220 g by mixing together pure iron powder and reagent grades  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  in the amounts required to satisfy the stoichiometry of the reaction



The mixture of Fe,  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  was then pressed to form briquettes and heated under Ar to  $1200$ – $1300^{\circ}\text{C}$  for periods of approximately 12 h. The X-ray diffraction patterns of every batch thus prepared corresponded to essentially pure ilmenite.

A schematic representation of the experimental apparatus used for the liquidus point determinations is shown in Fig. 2. In this apparatus, all parts in contact with the slag were made of molybdenum. This metal behaves extremely well at high temperatures and is only slightly attacked by the highly corrosive titania

slags [6]. The very high temperatures required in some experiments were rapidly attained by means of the graphite resistance type furnace incorporated in the design. In each experiment, about 100 g of a mixture of ilmenite and  $\text{TiO}_2$  corresponding to the desired slag composition were placed in a molybdenum crucible (38 mm dia.  $\times$  69 mm high) which was held in the hot zone of the graphite resistance furnace. Super-purified Ar was passed by a drying column, deoxidized in copper turnings at  $400^{\circ}\text{C}$  and flowed in the furnace during the experiments. The oxygen pressure in this gas was sufficiently low to prevent the oxidation of the molybdenum parts incorporated in the apparatus. A Pt-6% Rh/Pt-30% Rh thermocouple placed outside the crucible was used to monitor the hot zone temperature. When this temperature was about  $50$ – $100^{\circ}\text{C}$  above the estimated slag melting temperature, a second thermocouple made of the same Pt-Rh alloys and provided with a molybdenum protection tube (6.3 mm I.D., 9.5 mm O.D., one closed end) was immersed in the center of the melt. This thermocouple could be moved from the outside so as to provide a stirring action in the slag. The stirring operation was performed previous to every determination to assure the homogeneity of the melts. The slags were maintained above melting temperatures for periods of about 15 min after which the power to the furnace was shut-off and the EMF output of the immersed thermocouple continuously registered by means of a chart recorder. To improve the sensitivity of the recorder, the full scale was adjusted to a 2 mV span. For every slag composition, the liquidus temperature was determined at least twice during the same

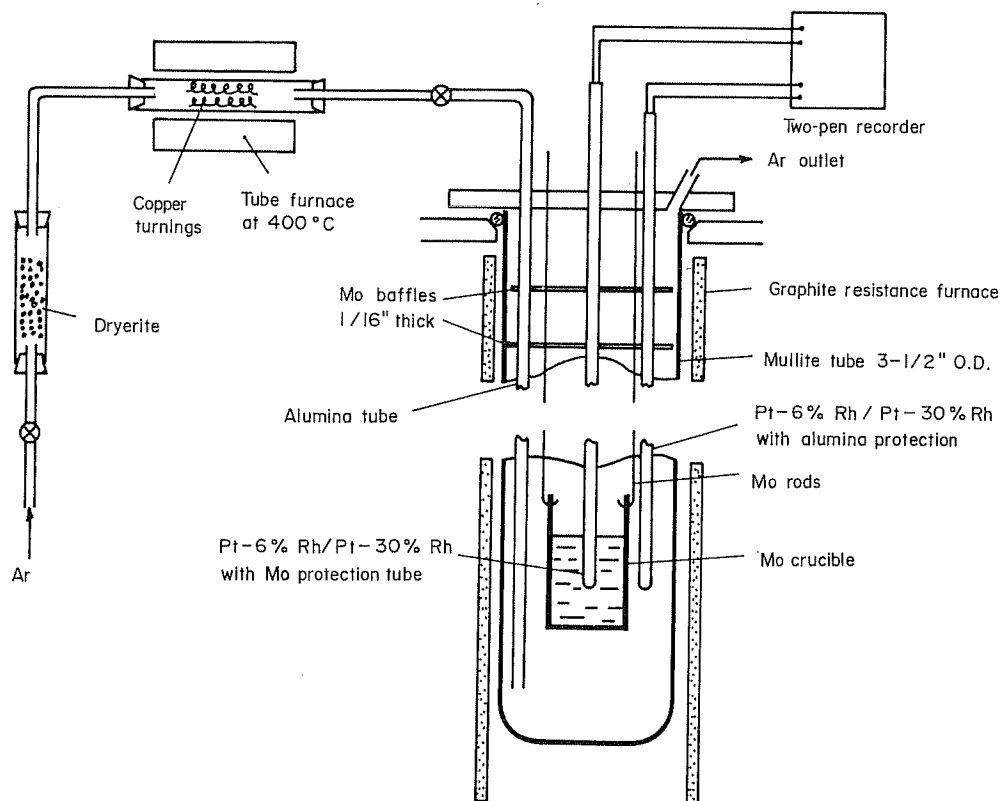


Fig. 2. Experimental apparatus.

experiment. Following these determinations, the crucible was broken to recover the whole mass of slag which was crushed and subsequently analysed.

## RESULTS

The nominal composition (calculated from the weight of  $\text{TiO}_2$  and  $\text{FeO}$  added to the crucible) of the 12 samples used in this study is shown in Table 1. The results of the chemical analysis of slag samples taken after the experiments are also included in Table 1. As it will be discussed in detail in a later section, the analytical results shown in the table have been corrected for the presence of metallic molybdenum which was found in the slags in proportions varying between 0.6 and 2.2% depending on the  $\text{TiO}_2$  content of the samples. In general, the analyses indicate a certain  $\text{TiO}_2$  loss during the experiments which may have been caused by the volatilization of this component from the slag. The  $\text{TiO}_2$  losses are seen to increase in the direction of increasing  $\text{TiO}_2$  contents, which may be explained by the higher thermodynamic activity of  $\text{TiO}_2$  and also by the higher temperature required to melt the slags.

In view of the composition changes noted above, attempts were made to sample the slag immediately before a cooling curve was to be obtained. The sampling method consisted in immersing in the slag a molybdenum tube in which a negative pressure was

created by means of a hand bulb; the slag would rise in the tube and would solidify rapidly in the upper part. This method, however, was often unsuccessful and even in those cases when some slag was collected, its removal from the tube was an extremely difficult and tedious operation. Ceramic tubes were not tried since it was felt that they would produce contaminated samples.

In view of the difficulties discussed above, the slag sampling efforts were discontinued and the compositions of the melts were taken to be those given by the chemical analyses reported in Table 1. This decision naturally affects the total error associated with the results of this work.

Table 1 shows the result of the various liquidus temperature determinations together with the average value corresponding to each of the slag compositions investigated. For all slags, with the exception perhaps of slag no. 8, the determinations showed an acceptable degree of reproducibility. Four typical examples of cooling curves obtained in the course of this investigation are shown in Fig. 3. In these curves, the rate of cooling decreases abruptly when a liquidus point is reached, thus marking the beginning of the exothermal crystallization process. The marked changes in cooling rate seen in Fig. 3 for slags no. 1 and no. 3, are indicative of a high rate of crystallization. For slags no. 5 and no. 8 however, the relatively mild change in the cooling curves at the liquidus point, indicate a slow crystallization rate in the initial stages

Table 1. Experimental results

Slag no.	Composition on weighing		Analyses after the experiments		Liquidus temperatures ( $^{\circ}\text{C}$ )	
	% $\text{TiO}_2$	% $\text{FeO}$	% $\text{TiO}_2$	% $\text{FeO}$	determinations	average
1	52.6	47.4	52.4	47.3	1378 1378	1378
2	58.0	42.0	56.7	42.7	1384 1384 1386	1385
3	62.0	38.0	60.9	39.5	1439 1434	1437
4	66.0	34.0	65.4	34.8	1465 1468	1467
5	78.0	22.0	75.4	24.3	1591 1593	1592
6	82.0	18.0	79.5	20.1	1638 1624	1631
7	74.0	26.0	71.5	27.9	1551 1548 1561	1553
8	70.0	30.0	68.8	31.4	1521 1501 1502	1508
9	72.0	28.0	71.0	28.8	1542 1549	1545
10	82.0	18.0	80.3	19.7	1626 1628	1627
11	52.6	47.4	52.4	47.4	1394 1394	1394
12	69.0	31.0	68.3	31.8	1497 1503	1500

of the solidification process. In some cases, a second temperature arrest was observed in the portion of the cooling curve which was recorded. These second changes were much less pronounced than those indicating the liquidus temperature and could not be clearly identified for all the slags investigated.

The average liquidus temperatures reported in Table 1 are also shown in Fig. 4 on a temperature-composition diagram. The dotted lines in this figure represent the  $\text{TiO}_2$ -rich side of the phase diagram due to MacChesney and Muan [4] previously shown in Fig. 1. It may be seen that the liquidus

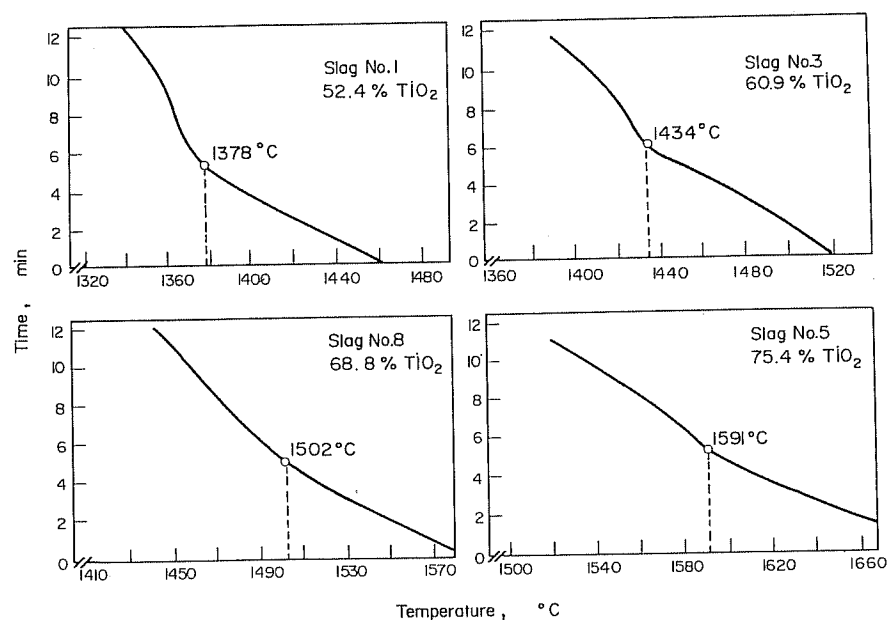


Fig. 3. Typical examples of cooling curves obtained in this work.

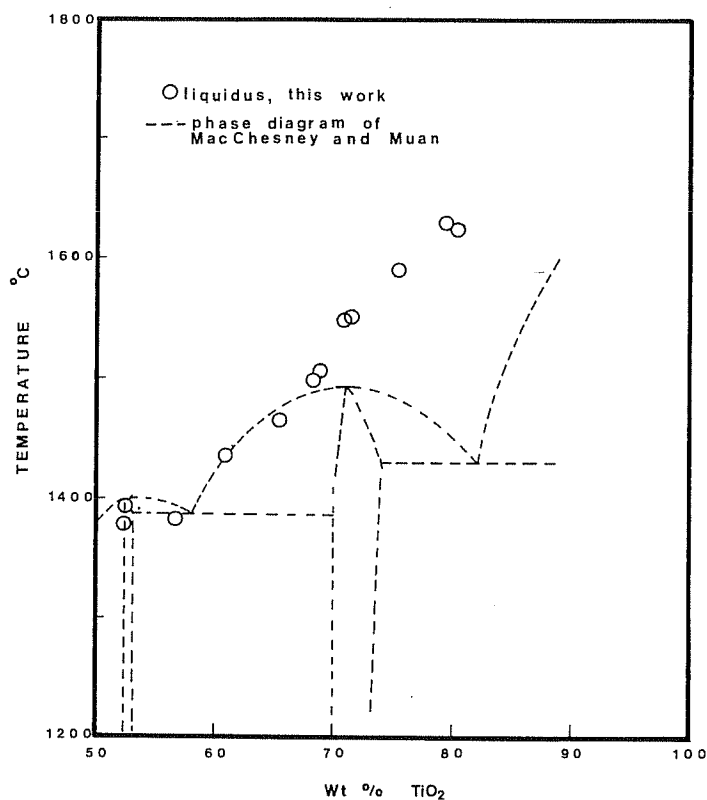


Fig. 4. Comparison between the liquidus temperatures determined in this work and those proposed by MacChesney and Muan.

temperatures proposed by these authors are in reasonable agreement with the results of this work for slags containing less than about 70%  $\text{TiO}_2$ . However, for slags richer in  $\text{TiO}_2$ , the two sets of data are seen to be in complete disagreement.

Figure 5 presents a proposed modification of the  $\text{TiO}_2$ -rich side of the phase diagram which is compatible with the results of this work. The circles in the diagram are the liquidus points and the triangles are the temperatures at which a second transformation was observed in the cooling curves of slags 4, 5, 6, 7 and 8. (As previously noted, a temperature indicated for a second transformation should be less accurate than one given for a liquidus point.) The proposed diagram involves the following modifications to that due to MacChesney and Muan:

- pseudo-brookite is considered to melt incongruently at about 1475°C producing a rutile phase and a liquid containing approximately 67 or 68%  $\text{TiO}_2$ , and;
- the eutectic point which MacChesney and Muan located at about 80%  $\text{TiO}_2$  is eliminated.

The proposed diagram is consistent with a previous suggestion of Smith and Bell [5] in the sense that rutile should be the primary phase to appear upon solidification of  $\text{FeO-TiO}_2$  slags containing more than 67-68%  $\text{TiO}_2$ .

## DISCUSSION

The discrepancies between the results of this work and those of MacChesney and Muan cannot be easily explained. These authors employed the "quenching" method which they had already used to investigate a number of oxide systems. In that method,  $\text{FeO-TiO}_2$  mixtures contained in iron crucibles were equilibrated at pre-established temperatures under a nitrogen atmosphere or under oxygen pressures defined by the iron-wustite equilibrium. The samples were then quenched and the phases present at equilibrium identified by X-ray and microscopic examination. The application of this technique to  $\text{FeO-TiO}_2$  mixtures may encounter difficulties in the rapid transitions which seem to take place even under quenching conditions. Confirmation of this is the rapid dendritic growth reported by MacChesney and Muan which in some cases made their microscopic observations very difficult. A second problem reported by these authors was the presence of metallic iron globules in the quenched samples, the formation of which was attributed to interactions between the iron crucibles and the  $\text{FeO-TiO}_2$  mixtures. It is obviously very difficult for anyone foreign to the work of these authors to ascertain the extent to which these problems may have influenced their results.

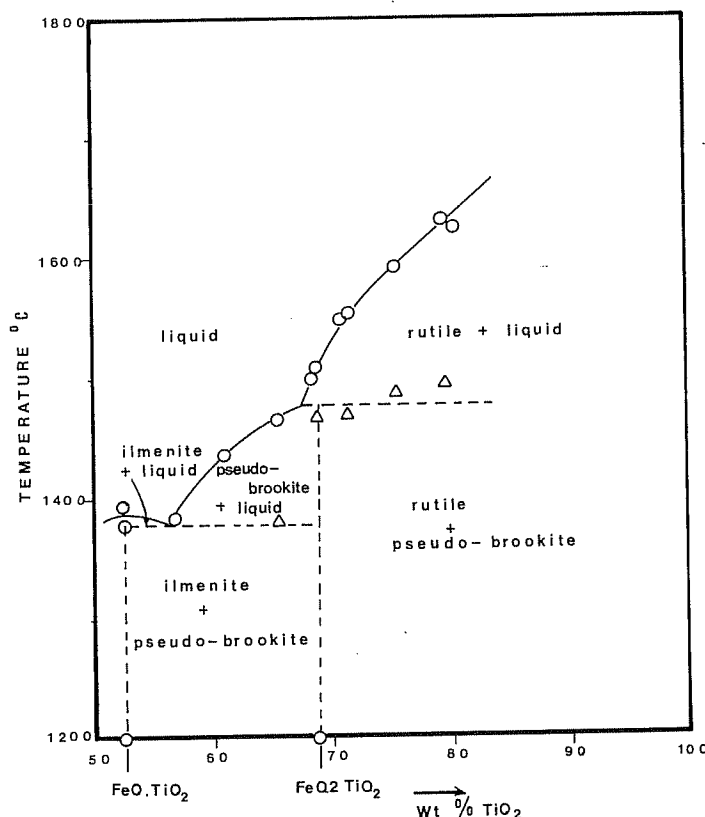


Fig. 5. Proposed modification of the  $\text{TiO}_2$ -rich side of the  $\text{FeO-TiO}_2$  phase diagram.

In view of the "dynamic" nature of the technique employed in the present work, no attempts were made to equilibrate the melts with the oxygen pressure existing in the argon gas. On the contrary, steps were taken to prevent the melts from approaching equilibrium, since this could have implied perhaps large changes in composition. These steps consisted in using rather large amounts of slag (the depth of the melt in the crucible was always of the order of 2.5 cm or more) and in restricting as much as possible the time during which the slags had to be maintained at elevated temperatures. In addition, the slags recovered after the experiments were carefully checked to determine possible changes in composition. These checks concentrated on:

- (a) extent of  $\text{FeO}$  reduction, and;
- (b) extent of formation of reduced titanium oxide.

It should be noted that these are the only possible composition changes which could be expected for the type of atmosphere used in this work and for the range of compositions covered by the experiments. For all the compositions investigated, the analyses gave no indication of  $\text{FeO}$  reduction; on the contrary, a certain increase in  $\text{FeO}$  was found which appears to have resulted from the volatilization of  $\text{TiO}_2$ . Reduced titanium oxide ( $\text{Ti}_2\text{O}_3$ ) was found in small proportions varying between 0.2% for a 52.4%  $\text{TiO}_2$  slag and 1.9% or less for a 79.5%  $\text{TiO}_2$  slag. (In the analyses of Table I, the reduced titanium oxide is reported together with

$\text{TiO}_2$ .) It can be maintained, therefore, that the slags investigated corresponded essentially to binary  $\text{FeO-TiO}_2$  melts.

In spite of the fact that the crucibles used in the determinations were always found in very good condition and completely free of oxidation, the chemical analysis of the slags recovered after the experiments indicated in all cases the presence of molybdenum. The concentration of this element showed a relation approximately linear with the  $\text{TiO}_2$  contents, varying between 0.6% for a 52.4%  $\text{TiO}_2$  slag and 2.2% for a 79.5%  $\text{TiO}_2$  slag. Since molybdenum oxidation could be discounted, it was suspected that the presence of this element was due to the erosion of the crucible by the molten slag and, to a lesser extent, to the solubility of molybdenum metal in the melts. To verify this, pieces of several slag samples were polished and examined in the microscope, revealing in all cases the presence of a metallic phase finely dispersed in the slag. The examination of pieces taken from the top and bottom of the solidified slags also showed the tendency of these metallic particles to settle through the liquid slags. The metallic phase was identified with the aid of a microprobe and it was found to consist almost entirely of molybdenum with very minor proportions of zirconium and titanium, the last two elements being impurities commonly present in the crucible material. Thus, it was concluded that the molybdenum detected by the chemical analysis was present as fine metallic particles forming a separate phase from the slag. This

conclusion allowed the correction of the analytical results so as to report the slag composition purely in terms of TiO<sub>2</sub> and FeO as it has been done in Table 1.

The presence of a separate metallic phase should not affect the liquidus temperatures reported in this work. However, a small effect may result from the possible solubility of molybdenum in the liquid slag at the high temperatures used in the experiments. The latter effect, if any, should be inherent to the use of metallic containers for the investigation of molten slags.

Probably more important contributions to the total error associated with the results of this work, are those originating in the following sources:

- temperature measurement system;
- variations in slag chemical composition during the experiments;
- inherent error in the analytical determinations;
- location of the liquidus temperatures in the cooling curves;
- averaging of individual determinations.

Considering all the above contributions, the maximum error in the determinations of this work may be estimated at about  $\pm 20^\circ\text{C}$ .

#### SOLID PHASES IN THE FeO-TiO<sub>2</sub> SYSTEM

In spite of the fact that this work was mostly concerned with liquidus temperatures, it seems pertinent to comment briefly on the phases produced upon solidification of FeO-TiO<sub>2</sub> slags. Figure 5 suggests that in the TiO<sub>2</sub>-rich side of the phase diagram there exist three compounds, namely,

ilmenite, ferrous pseudo-brookite and rutile. The existence of ferrous pseudo-brookite is recognized in the diagram due to MacChesney and Muan [4] but it was ignored in the previous work by Grieve and White [3]. Occasional differences of opinion may still arise concerning the existence of this compound, perhaps because it is generally unknown as a natural mineral.

The earliest determination of the crystallographic properties of FeO.2TiO<sub>2</sub> seems to be that of Akimoto *et al.* [9]. These authors synthesized the compound by heating for 2 h a stoichiometric mixture of Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and metallic Fe (sealed in an evacuated quartz tube) followed by quenching from 1150°C. The specimen thus produced was composed of a single phase having the same orthorhombic crystal structure of ferric pseudo-brookite Fe<sub>2</sub>O<sub>3</sub>.TiO<sub>2</sub>. As shown in Table 2, the crystal parameters proposed by Akimoto *et al.* for ferric and ferrous pseudo-brookite are very similar being only slightly larger for the latter compound. The table also shows a comparison between the *d*-spacings for Fe<sub>2</sub>O<sub>3</sub>.TiO<sub>2</sub> [10] and those for FeO.2TiO<sub>2</sub> calculated from the corresponding crystal parameters. The similitude between these values is apparent.

FeO.2TiO<sub>2</sub> has also been synthesized in this laboratory and the diffractograms have shown very good agreement with the *d*-spacings of Table 2 [11]. In addition, FeO.2TiO<sub>2</sub> is a compound usually found in industrial titania slags forming a solid solution with Ti<sub>3</sub>O<sub>5</sub> (anosovite). It is also found as one of the products of the solid-state reduction of ilmenite ores at temperatures of the order of 1200°C [12].

Table 2. Crystal parameters and *d*-spacings for ferric and ferrous pseudo-brookite

Fe <sub>2</sub> O <sub>3</sub> .TiO <sub>2</sub>			FeO.2TiO <sub>2</sub>	
<i>a</i> = 9.767 Å <i>b</i> = 9.947 <i>c</i> = 3.717 Vol. of unit cell = 361.1 Å <sup>3</sup>			<i>a</i> = 9.798 Å <i>b</i> = 10.041 <i>c</i> = 3.741 Vol. of unit cell = 368.0 Å <sup>3</sup>	
( <i>hkl</i> )	<i>d</i> (Å)	<i>I</i> / <i>I</i> <sub>1</sub>	( <i>hkl</i> )	<i>d</i> (Å)
200	4.902	45	020	5.020
220, 101	3.483	100	200	4.899
230	2.748	80	220, 101	3.500
301	2.454	20	230	2.763
131	2.402	25	301	2.460
240	2.221	11	131	2.417
321	2.198	15	240	2.234
331	1.971	25	321	2.209
002	1.862	30	331	1.982
022	1.744	15	002	1.870
060	1.663	15	022	1.753
600	1.632	20	060	1.673
232	1.54	35	600	1.633
			232	1.549

*d*-spacings for Fe<sub>2</sub>O<sub>3</sub>.TiO<sub>2</sub> are from X-ray powder data file [10].

*d*-spacings for FeO.2TiO<sub>2</sub> are calculated from data of Akimoto *et al.* [9].

Crystal parameters are from Akimoto *et al.* [9].

Table 3. X-ray identification of slags cooled in the furnace

<i>d</i> , Å	Intensity estimation		Identification†	Relative intensity‡ <i>I</i> / <i>I</i> <sub>1</sub> in pure compound
	Slag AO.3 (60.9% TiO <sub>2</sub> )	Slag AO.5 (75.4% TiO <sub>2</sub> )		
5.030	v. weak	v. weak	<i>p</i> -brookite	—
4.892	weak	weak	<i>p</i> -brookite	45
3.740	strong	weak	ilmenite	50
3.507	strong	strong	<i>p</i> -brookite	100
3.251	weak	v. strong	rutile	100
2.770	medium	medium	<i>p</i> -brookite	80
2.754	v. strong	medium	ilmenite	100
2.544	v. strong	medium	ilmenite	85
2.487	weak	medium	rutile	50
2.461	weak	weak	<i>p</i> -brookite	20
2.422	v. weak	v. weak	<i>p</i> -brookite	25
2.237	medium	weak	ilmenite	70
2.221		v. weak	<i>p</i> -brookite	11
2.197	v. weak	v. weak	<i>p</i> -brookite	15
2.187	v. weak	medium	rutile	25
1.976	weak	weak	<i>p</i> -brookite	25
1.879	v. weak	v. weak	<i>p</i> -brookite	30
1.870	medium	v. weak	ilmenite	85
1.727	medium	weak	ilmenite	100
1.689	weak	medium	rutile	60
1.682	v. weak		<i>p</i> -brookite	15
1.626		v. weak	rutile	20
1.555	v. weak	v. v. weak	<i>p</i> -brookite	35
1.507	medium	weak	ilmenite	85
1.479		v. weak	?	—
1.470	medium	weak	ilmenite	85

† *p*-brookite: ferrous pseudo-brookite.‡ *I*/*I*<sub>1</sub> values for ferrous pseudo-brookite assumed to be equal to those of ferric pseudo-brookite shown in Table 2.

The absence of natural occurrences of ferrous pseudo-brookite has been satisfactorily explained by Lindsley [13]. This author found that at temperatures below  $1140 \pm 10^\circ\text{C}$ , the compound becomes unstable and decomposes into rutile and ilmenite according to the reaction



It is because of this reaction that the phase diagram in Fig. 5 has been restricted to temperatures above  $1200^\circ\text{C}$ .

According to the above reaction, it is to be expected that slowly cooled FeO-TiO<sub>2</sub> slags whose overall composition lie between those of ilmenite and pseudo-brookite, will contain, in addition to these, a rutile-phase. The quantity of this phase will naturally depend on the cooling rate. Similarly, an ilmenite phase should be found in slowly cooled slags with composition richer in TiO<sub>2</sub> than pseudo-brookite.

This situation was confirmed by X-ray examination of the samples used in this investigation. These samples were cooled in the furnace by shutting-off the power once the liquidus temperature determinations were concluded. Typical X-ray data for 2 of these samples containing respectively 60.9 and 75.4% TiO<sub>2</sub> are shown in Table 3. This table shows that the first of these slags contains ilmenite and ferrous pseudo-

brookite as the major phases, but also shows the presence of a minor rutile phase. The second slag shows rutile and ferrous pseudo-brookite as the major phases with ilmenite as a minor phase. Thus, the data in Table 3 not only lends further support to the existence of ferrous pseudo-brookite as a distinct phase in the FeO-TiO<sub>2</sub> system, but also confirms the unstability of it at lower temperatures, as previously reported in the work by Lindsley [13].

*Acknowledgements*—The author acknowledges the helpful comments on the manuscript of Dr A. D. Pelton and Dr D. Poggi. The technical assistance of Mr G. Matte and Mr C. Gagnon is appreciated.

## REFERENCES

1. T. Yoshida and T. Takei, *J. Electrochem. Soc. Japan* (Overseas suppl. ed.) **28**, E 105 (1960).
2. A. H. Webster and N. F. H. Bright, *J. Am. ceram. Soc.* **44**, 112 (1961).
3. J. Grieve and J. White, *J. Roy. Tech. Coll. (Glasgow)* **4**, 444 (1939).
4. J. B. MacChesney and A. Muan, *Am. mineral.* **46**, 572 (1961).
5. I. C. Smith and H. B. Bell, *Trans. Inst. Min. Metall. (C)* **79**, C 253 (1970).
6. A. E. Grau and D. Poggi, 1978 Annual Volume of the Metallurgical Society of the Canadian Inst. of Mining and Metallurgy.



7. Janaf Thermochemical Tables, NSRDS-NBS 37, U.S. Dept of Commerce, 2nd edn (1971).
8. K. K. Kelley, S. S. Todd and E. G. King, Heat and free energy data for titanates of iron and of the alkaline-earth metals. Bureau of Mines RI 5059, U.S. Dept of the Interior (1954).
9. S. Akimoto, T. Nagata and T. Katsura, *Nature* **179**, 37 (1957).
10. *Powder Diffraction File*. Joint Committee on Powder Diffraction Standards, PA (1972).
11. M. Bergeron and D. Poggi, Private communication.
12. D. G. Jones, *Trans. Inst. Min. Metall. (C)* **82**, C186 (1973).
13. D. H. Lindsley, Year Book, Carnegie Institution **64**, 144 (1965).