

Fig. 7. Cross-sectional view of polishing lines on glass surface treated with nitric acid.

the existence of polishing lines filled with flowed glass, according to Rawstron's theory.

After the color changes produced by successive mild attacks on a specimen were determined, the maximum depth of attack was measured in the lines. The succession of colors in the lines proceeded more quickly than in the film; an upper limit was attained, however, where ionic exchange stopped (lead glasses) or degenerated to a superficial corrosion process and the corroded glass surface impeded the observations. The maximum depth attained was 5000 Å.

Greater attack occurred in certain glasses, and exchange films as thick as  $1\mu$  and faintly colored were obtained, which cracked slowly (Fig. 8). Lines without color showed a weak contrast. Even if a faint difference in the refractive index of lines is accepted to explain the greater optical path which made the observation possible, the linear zones of different nature must also have had a depth of about  $1\mu$ ; too much, indeed, if the origin of the lines is to be explained as tracks of different composition produced by the polishing grains or as lines filled with flowed glass.

As a better explanation of the observed facts the writers propose the existence of deeply disturbed zones produced by compression from the polishing grains, following the ideas of Brüche, Peter, and Poppa. Such zones would be more easily

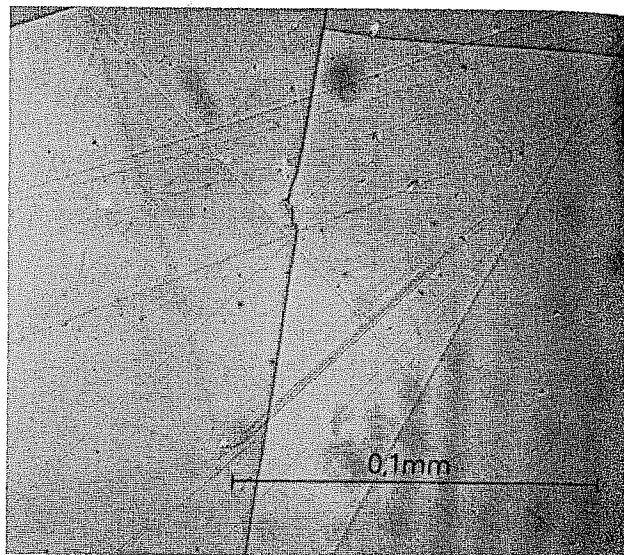


Fig. 8. Glass BaSF1 after leaching with 10%  $\text{HNO}_3$  at  $90^\circ$  for 3 hours

attacked by leaching than the surrounding glass. The same explanation also might be given for the lines developed by etching. These disturbed linear zones would be the origin of the mechanical weakness of the polished surfaces.

#### IV. Conclusions

Fine crossed lines that appear on polished optical glass surfaces after leaching in nitric acid are linear zones where the attack progresses faster than in the surrounding glass because their structure has been modified by the action of the polishing grains.

Such action may be attributed to strong vertical compressions which produce permanent distortions in glass to a depth of at least  $1\mu$ . The existence of such disturbed zones may explain the mechanical weakness of the polished surfaces.

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## Liquidus Temperatures in the System $\text{FeO}-\text{Fe}_2\text{O}_3-\text{TiO}_2$

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Liquidus temperatures in the system  $\text{FeO}-\text{Fe}_2\text{O}_3-\text{TiO}_2$  have been estimated from data in the literature supplemented with experimental determinations of the liquidus temperature for about fifty different compositions within the system using the quenching method.

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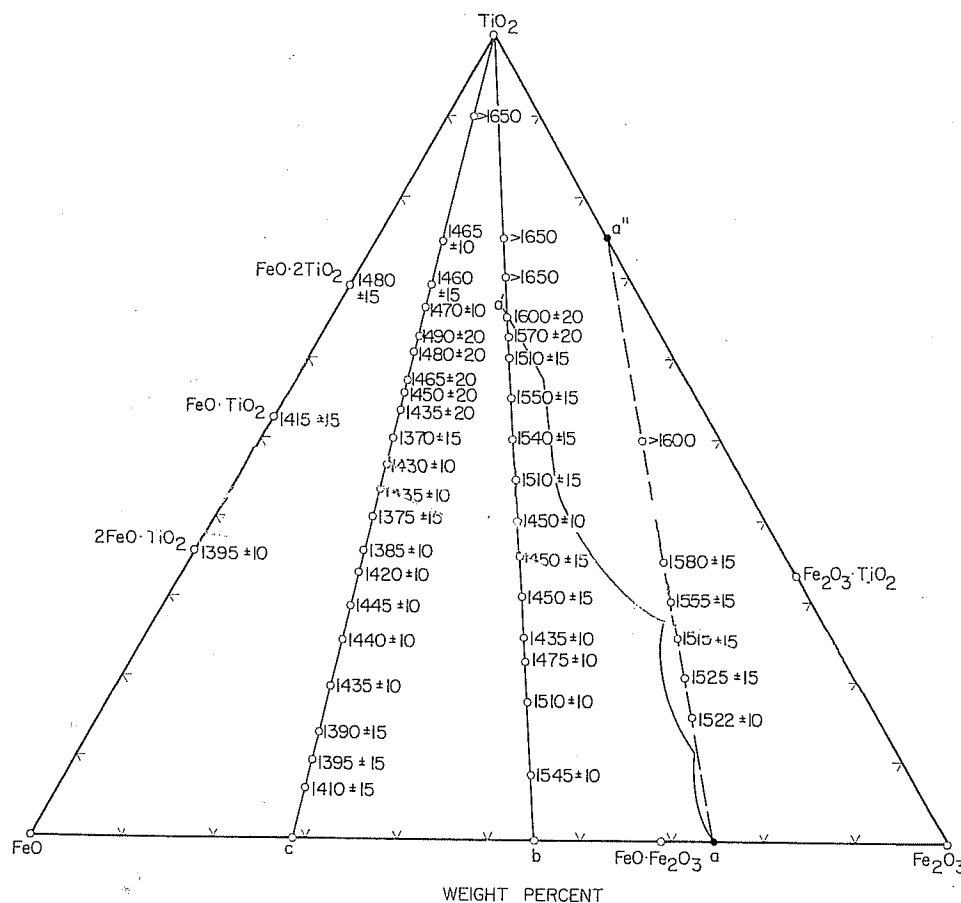


Fig. 1. Compositions and liquidus temperatures ( $^{\circ}\text{C}$ ) for samples used to estimate liquidus temperatures in the system  $\text{FeO}-\text{Fe}_2\text{O}_3-\text{TiO}_2$ . Curved line  $a-a'$  locates compositions which samples assume when heated to liquidus temperatures in equilibrium with air, according to MacChesney and Muan (footnote 4). Circles along lines  $a-a'$ ,  $b-\text{TiO}_2$ , and  $c-\text{TiO}_2$  represent compositions of samples used in the present study. The temperature of total melting for each of these compositions is indicated, including an estimate of the errors involved. The melting points of ulvöspinel ( $2\text{FeO}\cdot\text{TiO}_2$ ), ilmenite ( $\text{FeO}\cdot\text{TiO}_2$ ), and  $\text{FeO}\cdot 2\text{TiO}_2$  also were measured.

## I. Introduction

LIQUIDUS temperatures in the system  $\text{FeO}-\text{Fe}_2\text{O}_3$  are well known (see for example Darken and Gurry<sup>1</sup> and Phillips and Muan<sup>2</sup>). Ernst<sup>3</sup> outlined compositions in the ternary system  $\text{FeO}-\text{Fe}_2\text{O}_3-\text{TiO}_2$  within which various phases crystallized. MacChesney and Muan measured the temperatures at which mixtures of  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  were totally melted when heated in air<sup>4</sup> and in equilibrium with metallic iron.<sup>5</sup> The compositions of samples when totally melted in air are shown by the solid scalloped line  $a-a'$  in Fig. 1. This line represents the intersection of the liquidus surface and the surface defined by all compositions in the system  $\text{Fe}-\text{Ti}-\text{O}$  which are in equilibrium with air. The compositions of samples in equilibrium with metallic iron at liquidus temperatures are close to the join  $\text{FeO}-\text{TiO}_2$ , according to MacChesney and Muan.<sup>5</sup>

To melt  $\text{Fe}_2\text{O}_3$  or  $\text{TiO}_2$  congruently (into liquids which have precisely the compositions  $\text{Fe}_2\text{O}_3$  or  $\text{TiO}_2$ ) oxygen pressures greater than the oxygen partial pressure of air are necessary. Although no one yet claims to have melted  $\text{Fe}_2\text{O}_3$  congruently, Brauer and Littke<sup>6</sup> have melted  $\text{TiO}_2$  congruently at  $1870^{\circ}\text{C}$  by raising the oxygen pressure about the sample to 1.5 atm. The melting point of both  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3\cdot\text{TiO}_2$  are estimated by extrapolation from the ternary system.

## II. Experiments

To complete the liquidus surface, liquidus temperatures were measured for samples whose compositions are represented by points along lines  $a-a'$ ,  $b-\text{TiO}_2$ , and  $c-\text{TiO}_2$ , shown

in Fig. 1. The melting points of the compounds ulvöspinel ( $2\text{FeO}\cdot\text{TiO}_2$ ), ilmenite ( $\text{FeO}\cdot\text{TiO}_2$ ), and  $\text{FeO}\cdot 2\text{TiO}_2$  also were measured.

Samples were prepared in two ways. In one case  $\text{TiO}_2$  was mixed with wüstite ( $71.3 \pm 0.5$  wt%  $\text{FeO}$ ); in the other case  $\text{TiO}_2$  was mixed with both  $\text{Fe}_2\text{O}_3$  and metallic iron. Sections of 80Pt20Rh tubing 0.2 cm in inside diameter and about 1.5 cm long were packed nearly full of sample and then welded

<sup>1</sup> L. S. Darken and R. W. Gurry, "The System Iron-Oxygen: II, Equilibrium and Thermodynamics of Liquid Oxide and Other Phases," *J. Am. Chem. Soc.*, 68 [5] 798-816 (1946); *Ceram. Abstr.*, 1947, February, p. 50g.

<sup>2</sup> Bert Phillips and Arnulf Muan, "Stability Relations of Iron Oxides: Phase Equilibria in the System  $\text{Fe}_3\text{O}_4-\text{Fe}_2\text{O}_3$  at Oxygen Pressures up to 45 Atmospheres," *J. Phys. Chem.*, 64 [10] 1451-53 (1960).

<sup>3</sup> Th. Ernst, "Über Schmelzgleichgewichte im System  $\text{Fe}_2\text{O}_3-\text{FeO}-\text{TiO}_2$  und Bemerkungen über die Minerale Pseudobrookit und Arizonit" (Fusion Equilibria in the System  $\text{Fe}_2\text{O}_3-\text{FeO}-\text{TiO}_2$  and Remarks on the Minerals Pseudobrookite and Arizonite), *Z. Angew. Mineral.*, 4 [4] 394-409 (1943).

<sup>4</sup> J. B. MacChesney and Arnulf Muan, "Studies in the System Iron Oxide-Titanium Oxide," *Am. Mineralogist*, 44 [9-10] 926-45 (1959); *Ceram. Abstr.*, 1961, January, p. 24i.

<sup>5</sup> J. B. MacChesney and Arnulf Muan, "Phase Equilibria at Liquidus Temperatures in the System Iron Oxide-Titanium Oxide at Low Oxygen Pressures," *Am. Mineralogist*, 46 [5-6] 572-82 (1961).

<sup>6</sup> G. Brauer and W. Littke, "Über den Schmelzpunkt und die thermische Dissoziation von Titandioxyde" (Melting Point and Thermal Dissociation of Titanium Dioxide), *J. Inorg. Nucl. Chem.*, 16 [1-2] 67-76 (1960).

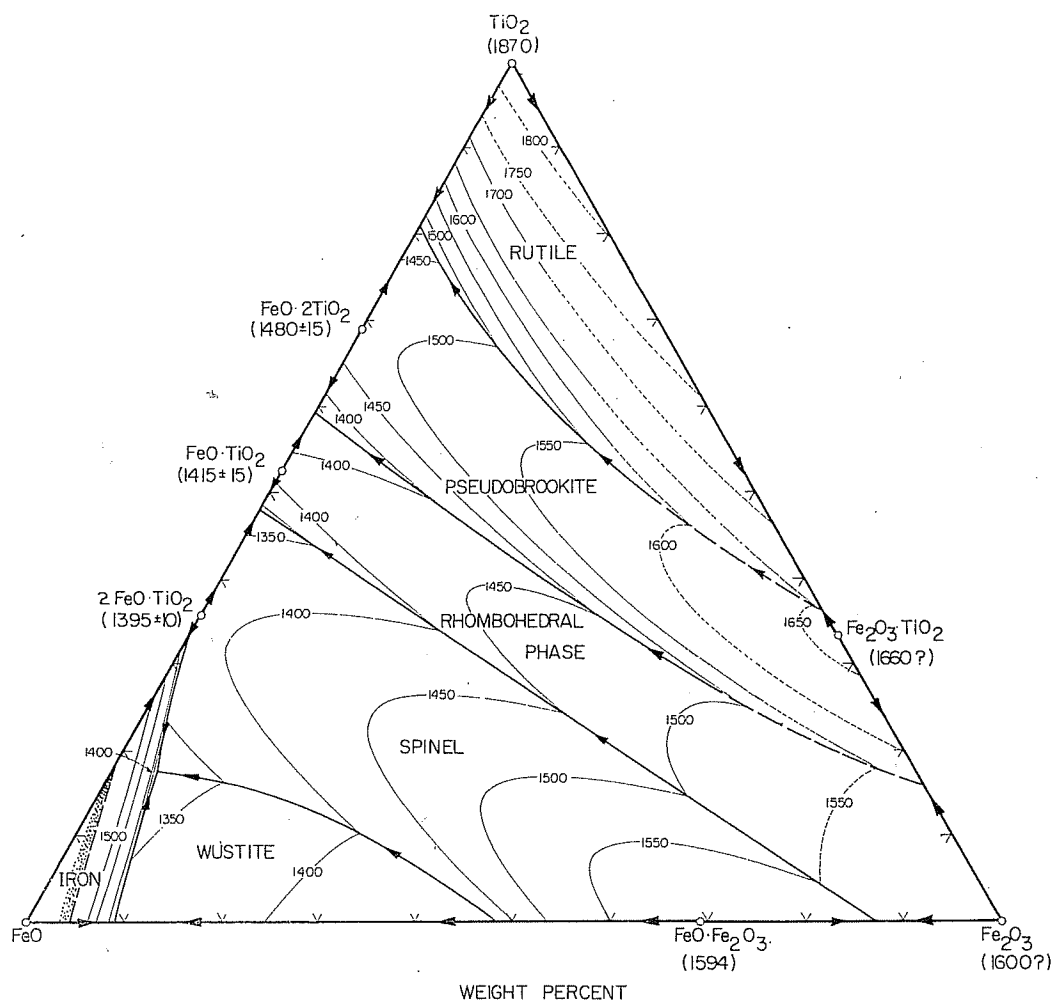


Fig. 2. Approximate liquidus temperatures ( $^{\circ}\text{C}$ ) for the system  $\text{FeO}-\text{Fe}_2\text{O}_3-\text{TiO}_2$ . Heavy solid lines are phase boundaries. Arrows point to decreasing temperatures. The heavy dashed line with stippling on one side, located in the phase field of iron, represents the limit of a two-liquid region (liquid oxide and liquid metal).

shut. After being heated at temperature for about 5 minutes in a Pt-wound resistance furnace, samples were quenched by dropping them directly from the furnace through water onto mercury. Quenched samples, as well as the tube which contained them, were mounted on glass slides with Lakeside cement, ground open with coarse abrasive, and then polished. Investigation was carried out with a microscope and by X-ray diffraction.

Generally, the temperature at which liquid first formed on heating a sample (the solidus temperature) could be recognized when a sample changed from a friable porous mass to a compact welded mass. The temperature of total melting (the liquidus temperature) was much more difficult to determine. Many times samples were heated as much as  $100^{\circ}\text{C}$  above and below the liquidus temperature in the hope of finding criteria upon which to characterize the liquidus. Even a sample which was all liquid quenched to dendritic crystals and never formed a glass. In many cases it was impossible to tell the difference between crystals formed during the quenching and crystals which had been present at the temperature from which the sample was quenched. When crystals were arranged coaxially with the sample tube, and increased in size toward the center, they were assumed to have formed during the rapid cooling to room temperature. Repeated determinations of the liquidus temperatures for a given composition differed as much as  $20^{\circ}\text{C}$ ; hence the probable error in the temperature of the liquidus surface was at least  $\pm 15^{\circ}\text{C}$ .

Crystalline phases were identified in reflected light as follows. Rutile appeared as circular blebs which were only very slightly different in color from the matrix or from pseudobrookite, but under plane-polarized light rutile was honey-colored. Pseudobrookite was characterized by large euhedral laths and was not as bright as the rhombohedral phase. The rhombohedral phase was the brightest phase except for metallic iron and was also strongly anisotropic. Crystals of the iron-titanium spinels were isotropic in polarized light and generally were euhedral in outline.

The length of time that a sample was held near liquidus temperatures was kept at a minimum in an attempt to keep iron from diffusing into and through the 80Pt20Rh containers. The containers also were filled as full as possible, so that when a sample did lose iron to the container the change in composition of the sample was not large. This nevertheless was a serious problem. The sample weight in an average experiment was about the same as the weight of the container (about 0.3 g). When wüstite, having the composition 71.3 wt% FeO, was melted and kept at  $1450^{\circ}\text{C}$  for 5 minutes in one of these containers, it lost iron to the container, so that after the experiment the wüstite contained only 65% FeO. When  $\text{TiO}_2$  was added to wüstite, the loss of iron was less. For example, when 24 wt%  $\text{TiO}_2$  was added, the FeO content decreased only 2 wt% in 5 minutes at  $1450^{\circ}\text{C}$ . As the  $\text{Fe}_2\text{O}_3$  content of the sample increased, and the oxygen pressure within the sample container increased, the amount of iron lost by the sample to the container decreased. It is

possible to estimate the maximum amount of iron which alloys with Pt containers under these experimental conditions from data on the system Pt-Fe-O by Taylor and Muan.<sup>7</sup> This estimate does not take into account iron which will, in time, diffuse completely through the containers to react with oxygen in the air on the outside of the sealed container. Except for compositions near FeO, errors in the determination of liquidus temperatures because of loss of iron were probably less than errors arising from poor criteria for recognizing liquidus temperatures.

<sup>7</sup> R. W. Taylor and Arnulf Muan, "Activities of Iron in Iron-Platinum Alloys at 1300°," *Trans. AIME*, 224 [3] 500-502 (1962).

### III. Results

Figure 2 shows approximate liquidus temperatures for the system FeO-Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>. The primary-phase fields, outlined by heavy lines, are iron, wüstite, spinel (FeO·Fe<sub>2</sub>O<sub>3</sub>·2FeO·TiO<sub>2</sub>), rhombohedral phase (Fe<sub>2</sub>O<sub>3</sub>·FeO·TiO<sub>2</sub>), pseudobrookite (Fe<sub>2</sub>O<sub>3</sub>·TiO<sub>2</sub>·FeO·2TiO<sub>2</sub>), and rutile. Isothermal contours are spaced every 50°C, and arrows point to decreasing temperatures. Phase boundaries between rutile and pseudobrookite and between pseudobrookite and the rhombohedral phase are in doubt where they are dashed because the oxygen pressure developed when trying to melt samples of these compositions burst the sample tubes.

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## Phase Equilibria for the Ternary Fused-Salt System NaF-BeF<sub>2</sub>-UF<sub>4</sub>

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The phase equilibrium diagram for the ternary fused-salt system NaF-BeF<sub>2</sub>-UF<sub>4</sub> was based on evidence from differential thermal analysis, polarized light microscopy, and X-ray examination of samples obtained from thermal-gradient quenching studies and from high-temperature filtration experiments. All the stable compounds in the binary systems NaF-BeF<sub>2</sub> and NaF-UF<sub>4</sub> displayed primary-phase fields in the ternary system, including a new subsolidus compound which was observed and tentatively assigned the formula NaF·4UF<sub>4</sub>. No ternary compounds or solid solutions were observed. The following three eutectics were found in the ternary system: (1) 72.5 NaF, 17.0 BeF<sub>2</sub>, and 0.5 mole % UF<sub>4</sub> at 486°C, (2) 56.0 NaF, 43.5 BeF<sub>2</sub>, and 10.5 mole % UF<sub>4</sub> at 339°C, and (3) 43.5 NaF, 56.0 BeF<sub>2</sub>, and 0.5 mole % UF<sub>4</sub> at 345°C.

### I. Introduction

THE utilization of fused salts as nuclear reactor components has been demonstrated.<sup>1</sup> Mound Laboratory, at the suggestion of Oak Ridge National Laboratory, developed further information on molten-salt mixtures for use as circulating fuels, coolants, and breeder systems in nuclear power reactors.

Mixtures of alkali metal fluorides which dissolve a fluoride of uranium are of interest as nuclear fuel systems. Uranium tetrafluoride and sodium fluoride yield a eutectic mixture of 21.5 mole % uranium tetrafluoride which melts at 620°C.<sup>2</sup> The addition of beryllium fluoride to the system NaF-UF<sub>4</sub> yields fused salts with lower liquidus temperatures.

The study of the equilibria for the system NaF-BeF<sub>2</sub>-UF<sub>4</sub> is discussed in this report. The phase diagram has been presented.<sup>3</sup> The NaF-UF<sub>4</sub> binary phase diagram (Fig. 1) is

the same as that reported by Barton *et al.*,<sup>2</sup> except for the inclusion of the compound NaF·4UF<sub>4</sub>, which will be discussed later. The BeF<sub>2</sub>-UF<sub>4</sub> binary phase diagram by Rhinehammer, Tucker, and Joy has been presented.<sup>4</sup> The phase

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<sup>1</sup>(a) A. M. Weinberg and R. C. Briant, "Molten Fluoride as a Power Reactor Fuel," *Nucl. Sci. Eng.*, 2, 797-803 (1957).

(b) A. M. Weinberg, "Some Aspects of Fluid Fuel Reactor Development," *ibid.*, 8 [4] 346-60 (1960).

<sup>2</sup>C. J. Barton, H. A. Friedman, W. R. Grimes, H. Insley, R. E. Moore, and R. E. Thoma, "Phase Equilibria in the Alkali Fluoride-Uranium Tetrafluoride Fused Salt Systems: I, The Systems LiF-UF<sub>4</sub> and NaF-UF<sub>4</sub>," *J. Am. Ceram. Soc.*, 41 [2] 63-69 (1958).

<sup>3</sup>(a) W. R. Grimes and D. R. Cuneo, "Molten Salts as Reactor Fuels," p. 437 in *Reactor Handbook: Vol. 1, Materials*. 2d ed. (C. R. Tipton, Jr., editor). Interscience Publishers, Inc., New York, 1960. 1207 pp.; *Ceram. Abstr.*, 1961, March, p. 79i.

(b) R. E. Thoma (editor), "Phase Diagrams of Nuclear Reactor Materials," *Oak Ridge National Laboratory Rept.*, ORNL-2548, 205 pp. (November 20, 1959).

(c) J. E. Ricci, "Guide to Phase Diagrams of the Fluoride Systems," *ibid.*, ORNL-2396, 106 pp. (1958).

(d) E. M. Levin and H. F. McMurdie, *Phase Diagrams for Ceramists*, Part II, p. 105. The American Ceramic Society, Inc., Columbus, Ohio, 1959. 153 pp.

<sup>4</sup>L. V. Jones, D. E. Etter, C. R. Hudgens, A. A. Huffman, T. B. Rhinehammer, N. E. Rogers, P. A. Tucker, and L. J. Wittenberg, "Phase Equilibria in the Ternary Fused-Salt System: LiF-BeF<sub>2</sub>-UF<sub>4</sub>," *J. Am. Ceram. Soc.*, 45 [2] 79-83 (1962).