

PHASE EQUILIBRIA AT LIQUIDUS TEMPERATURES IN THE
SYSTEM IRON OXIDE-TITANIUM OXIDE
AT LOW OXYGEN PRESSURES*

J. B. MACCHESNEY† AND ARNULF MUAN, *The Pennsylvania State
University, University Park, Pa.*

ABSTRACT

Phase relations in the system iron oxide-titanium oxide were determined by heating oxide mixtures at oxygen pressures defined by the iron-wüstite equilibrium. The mixtures were either heated in iron crucibles in a nitrogen atmosphere, or enclosed in sealed vitreous-silica tubes together with an iron-wüstite buffer. Compositions of mixtures prepared under these conditions were found to deviate somewhat from those of the join FeO-TiO₂. Mixtures of high iron content contained some Fe³⁺, whereas mixtures of high titanium oxide content contained some titanium of valence states below +4.

INTRODUCTION

The experimental study at high temperatures of phase relations in iron oxide containing systems is difficult, and only after the major breakthrough in 1932 by Bowen and Schairer could systematic progress on such systems be achieved. By equilibrating oxide phases in iron crucibles in a purified nitrogen atmosphere, practically all iron of the oxide sample is present as Fe²⁺. Later it has become practical also to study phase relations in iron oxide containing systems by other techniques which permit controlled variations of oxygen partial pressures over wide ranges (see for instance a review paper by Muan, 1958).

The work to be described in the following represents one unit of study of the complicated ternary system Fe—Ti—O. The authors have previously reported on their investigation of this system in air (MacChesney and Muan, 1959). The present paper deals with phase relations in an atmosphere of very low oxygen partial pressure, that at which iron and its lowest oxide, wüstite (Fe_{1-x}O), coexist in equilibrium. The experimental procedures adopted for realizing this situation are described in a later section.

PREVIOUS WORK

Several studies of phase relations in systems containing the oxides of iron and titanium have been reported in the literature. Investigations of the bounding binary systems Fe—O and Ti—O in particular have been extensive.

Discussions of equilibria in the system Fe—O are found in papers by Greig, Posnjak, Merwin and Sosman (1934), by Darken and Gurry (1945, 1946), and recently by Phillips and Muan (1960).

* Contribution No. 59-113 from College of Mineral Industries, The Pennsylvania State University, University Park, Pennsylvania.

† Present address: Bell Telephone Laboratories, Murray Hill, New Jersey.

The Ti—O system has attracted considerable interest in recent years. Magneli *et al.* (1958), as well as Andersson *et al.* (1957), have made very comprehensive studies of the phases present in this system. The data obtained by those groups will serve to refine the approximate diagram for Ti—O which was inferred by DeVries and Roy (1954) on the basis of scattered data available in the literature.

Some of the general features of the ternary system $\text{FeO—Fe}_2\text{O}_3\text{—TiO}_2$ are fairly well established. Three solid solution series are known to exist in the system: cubic magnetite-ulvospinel ($\text{FeO} \cdot \text{Fe}_2\text{O}_3\text{—}2\text{FeO} \cdot \text{TiO}_2$),* hexagonal hematite-ilmenite ($\text{Fe}_2\text{O}_3\text{—FeO} \cdot \text{TiO}_2$), and orthorhombic pseudobrookites ($\text{Fe}_2\text{O}_3 \cdot \text{TiO}_2\text{—FeO} \cdot 2\text{TiO}_2$). In the first of these, magnetite-ulvospinel, a continuous solid solution exists at high temperatures, with exsolution taking place below 600°C . (Kawai, Kume and Sasajima, 1954; Vincent and Wright, 1957). Controversies exist in the literature with respect to the continuity of the hematite-ilmenite solid solution series. Ramdohr (1926, 1950, 1953) reported that hematite and ilmenite form a continuous solid solution series above 600°C ., whereas Pouillard (1950) found that two solid solution phases exist together in equilibrium at 950°C ., the miscibility gap extending approximately from 33 to 67 mole %. Basta (1953) showed that complete miscibility exists between the two end members at 1050°C ., and Nicholls (1955) in a recent review refers to the work of Ramdohr (1926) and of Posnjak and Barth (1934) as indicating that complete solid solubility exists between ilmenite and hematite above 1050°C .

The only systematic work on phase equilibria in the system iron oxide-titanium oxide at liquidus temperatures under strongly reducing conditions seems to be that of Grieve and White (1939). They used differential thermal analysis techniques, measuring temperatures with tungsten-molybdenum thermocouples and containing the oxide mixtures in molybdenum crucibles in vacuo or in an inert atmosphere. Phase relations as determined in their study are illustrated in Fig. 1. The diagram shows only two compounds, $2\text{FeO} \cdot \text{TiO}_2$ (ulvospinel, which they incorrectly named pseudobrookite) and $\text{FeO} \cdot \text{TiO}_2$ (ilmenite), in addition to "FeO" (wüstite) and TiO_2 (rutile). It is difficult to understand their results in light of those obtained in the present investigation.

EXPERIMENTAL METHOD

General Procedure

Phase relations were determined by the quenching technique. Pre-heated mixtures of iron oxide and titanium oxide were held in iron crucibles in carefully controlled atmospheres and at accurately meas-

* This phase as well as others appearing in the system may have oxygen contents deviating somewhat from the stoichiometric values listed here for sake of simplicity.

ured temperatures until equilibrium was established. The samples were then quenched rapidly to room temperature and the phases present identified by microscopic and x -ray examination. Compositions of mixtures at equilibration temperatures were determined by chemical analysis of quenched samples.

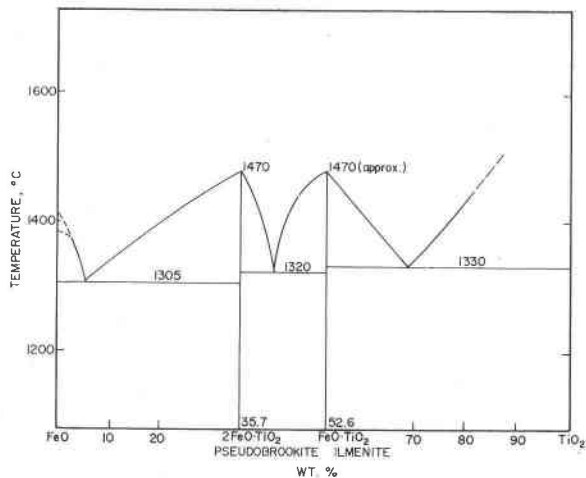


FIG. 1. Diagram illustrating phase relations at liquidus temperatures in the system FeO—TiO₂, after Grieve and White (1939).

Starting Materials

“Baker Analyzed” reagents, Fe₂O₃ and TiO₂, were used as starting materials in most of the experiments. The oxides were dried at approximately 400° C. for 12 hours, mixed in desired proportions, ground under alcohol and heated to melting or sintering in a gas-air combustion furnace. Prior to their use in the equilibration runs these mixtures (prepared during our previous investigation of the system iron oxide-titanium oxide in air) were brought close to equilibrium with the oxygen partial pressure prevailing when iron and wüstite coexist in equilibrium. This was accomplished by containing the samples in iron crucibles in a nitrogen atmosphere at approximately 1300° C.

As the work advanced, the above mixtures were supplemented with a new set of mixtures prepared from TiO₂ and iron oxide which was obtained by high-temperature (~1300° C.) oxidation of pure metallic iron in nitrogen gas containing a small amount of oxygen as an impurity.

Control of Atmosphere

A few introductory runs were carried out in iron crucibles in nitrogen atmosphere, following the procedure developed by Bowen and Schairer

(1932). However, FeO contamination of the sample by oxidation of the iron crucible, as well as loss of liquids by creep on crucible walls caused difficulties in the present investigation. More reliable results were obtained in experiments carried out by a technique illustrated in Fig. 2. An iron-wüstite buffer* is sealed together with the oxide sample into a vitreous silica tube to maintain a fixed oxygen partial pressure at any chosen temperature. Oxidation of the crucible and accompanying contamination of the sample could be minimized by placing the tube in the furnace in such a manner that the crucible and its contents were at the hot zone while the buffer was at a slightly ($\sim 20^\circ$ C.) lower temperature.

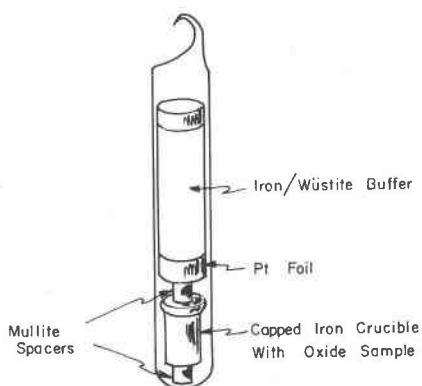


FIG. 2. Sealed vitreous silica tube assembly used for studying the system iron oxide-titanium oxide in the present investigation. The iron crucible and iron-wüstite buffer were held away from the silica wall by means of mullite spacers and platinum foil which was wrapped around the ends of the buffer. This precaution prevented attack on the tube by iron oxide liquid formed at temperatures in excess of 1369° C.

Furnaces, and Temperature Measurement

Equilibration runs were carried out in vertical tube furnaces with resistance windings of platinum or an 80% platinum 20% rhodium alloy. Temperatures were kept constant to approximately $\pm 3^\circ$ C. by means of a commercial Tagliabue Celectray Controller connected to a platinum-90% platinum 10% rhodium thermocouple inserted close to the hot spot of the furnace.

Temperatures were measured before and after each run with a platinum-90% platinum 10% rhodium thermocouple calibrated against

* This buffer consisted of an iron slug coated with a layer of wüstite formed by oxidation of the iron in air at approximately 1200° C. When sealed in a vitreous silica tube, the buffer maintained within the tube an oxygen partial pressure corresponding to the equilibrium coexistence of metallic iron and wüstite at any specific temperature.

standards with melting points defined as follows: Gold (Au), 1063° C.; diopside ($\text{CaMgSi}_2\text{O}_6$), 1391.5° C.; pseudowollastonite (CaSiO_3), 1544° C. Temperatures thus defined are according to the Geophysical Laboratory Scale, which is almost identical to the 1948 International Scale up to 1550° C. Temperatures above 1550° C. reported in the present paper are on the 1948 International Scale.

Examination of Quenched Samples

Phases present in quenched samples were determined by α -ray and microscopic examination. Examination of polished samples in reflected light was found more informative than observations under the petrographic microscope because of the opacity of the samples. The recognition of dendrites as opposed to primary crystals was at times very difficult. In some cases, dendritic growth was so rapid that the quench specimen was honeycombed with large euhedral crystals. Therefore, the use of crystal size and shape as criteria for identification of primary crystals was not entirely satisfactory. The accumulation of primary crystals at the bottom of the specimen, however, was quite useful in this regard. It was often possible to observe a distinct boundary between the liquid and the accumulated primary crystals. A second reliable guide was the presence of characteristic dendritic patterns or textures. For instance, liquids with pseudobrookite as primary crystalline phase were found to produce a characteristic quench pattern which resembled a coarsely woven cloth.

Total iron oxide content as well as $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios of mixtures before and after equilibration were determined by wet chemical analysis. The following analytical methods were used:

For determination of total iron oxide, samples containing less than 60 wt. % TiO_2 were dissolved by boiling them in a mixture of 20 ml. 1:3 H_2SO_4 and five ml. HF. The resulting solution was then diluted to 100 ml. with five % (by volume) H_2SO_4 and passed through a Jones Reductor. The emerging solution contained all iron as Fe^{2+} and all titanium as Ti^{3+} . Following the procedure of Grimaldi, Stevens and Carron (1943), three ml. of a 0.0001 molar cupric sulfate solution was added as catalyst and the solution aerated for 10 to 15 minutes to quantitatively oxidize titanium to the tetravalent state while leaving the iron in the divalent state.* The solution was then titrated with a 0.01 N potassium permanganate solution.

Samples containing more than 60 wt. % TiO_2 required fusion with potassium pyrosulfate ($\text{K}_2\text{S}_2\text{O}_7$) to put them into a soluble form. A weighed amount of the reagent (two to five grams) was added to the 50 mg. sample and heated to a temperature at which melting occurred without rapid dissociation to the pyrosulfate. The fusion generally required between 30 and 45 minutes to completely dissolve the sample. After cooling, the

* Grimaldi *et al.* (1943) reported that no oxidation of divalent iron occurred during 20-minute aeration by this method. A check run made in the present study on a sample of known composition confirmed this.

salt cake was dissolved by boiling in five % (by volume) H_2SO_4 . The solution was then reduced, aerated and titrated as described above. It was found that the reagents used in this technique made a small but significant contribution to the total number of milliequivalents needed for titration of the ferrous iron concentration. This quantity was determined and the analysis corrected accordingly.

Samples for determination of divalent iron were placed in a covered platinum crucible and brought to boiling in 20 ml. of 1:3 H_2SO_4 . When steam was evolved, five ml. of HF was added and the solution allowed to boil for five to 10 minutes. The crucible was then plunged into a 600 ml. beaker containing five % H_2SO_4 saturated with boric acid. Copper sulfate was added, the solution aerated for 10 to 15 minutes and titrated with 0.05 N potassium permanganate. This method of course was applicable only to samples which were soluble by acid treatment (<60 wt. % TiO_2).

Another analysis was carried out in order to determine the sum of Fe^{2+} and Ti^{3+} . Samples for this purpose were mixed with 10 ml. of a ferric sulfate solution (two mg. $\text{Fe}_2(\text{SO}_4)_3$ per ml.) prior to acid treatment, and the solution was titrated with 0.05 N permanganate without addition of copper sulfate and aeration of the solution beforehand. According to Hillebrand *et al.* (1953), this procedure prevents Ti^{3+} from decomposing water in the presence of platinum. From the quantity of permanganate required to titrate this solution, the total milliequivalents of reduced oxides could be calculated. Subtraction of the number of milliequivalents of potassium permanganate required to titrate the ferrous iron from the value for the total reduced oxides left a remainder which could be calculated as trivalent titanium. The assumption is made that all iron in these crystalline samples is in the divalent state when trivalent titanium is detected. This assumption seems justified in view of the far greater stability of Ti^{4+} than of Fe^{3+} in oxide structures, as discussed in a previous paper (MacChesney and Muan, 1959).

RESULTS AND DISCUSSION

Results of equilibration runs are illustrated graphically in Fig. 3. A similar procedure has been used in the construction of this diagram as has been described in previous papers from our laboratories (see for instance Muan, 1958). Points representing compositions of condensed phases in the ternary system (Fe—Ti—O) have been projected onto the join FeO-TiO_2 to give a diagram with the appearance of a binary system.

The essential features of the diagram at oxygen pressures dealt with in the present study are as follows: Liquidus temperatures first decrease as TiO_2 is added to iron oxide, from 1369° C. for wüstite to approximately 1312° C. at the "eutectic" temperature where wüstite,* ulvospinel, liquid with approximately 10 wt.% TiO_2 and gas coexist in equilibrium. Further addition of TiO_2 results in a rise in liquidus temperature, with ulvospinel as primary phase. A maximum is reached at 1395° C. and approximately 33 wt.% TiO_2 . Temperatures then decrease toward a second "eutectic" located at approximately 47 wt.% TiO_2 and 1363° C., where the phases present are ulvospinel, ilmenite, liquid and gas. Ilmenite is the next phase to appear in order of increasing TiO_2 con-

* This phase, as well as others appearing in the present system, are solid solutions in which the iron to titanium ratios vary.

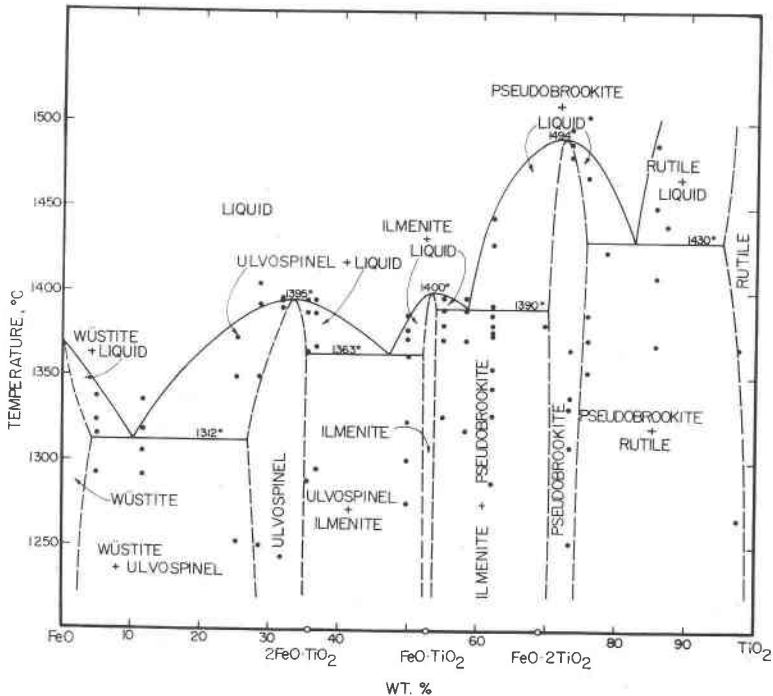


FIG. 3. Phase diagram for the system iron oxide-titanium oxide at oxygen pressures defined by the iron-wüstite equilibrium. For sake of simplicity the phase relations are shown in a projection onto the join FeO-TiO₂. Solid dots represent equilibration runs, and heavy lines are boundary curves separating the various phase areas, as labeled on the diagram. Dash curves represent boundary curves whose location is uncertain.

tent, and a maximum exists on the liquidus curve at approximately 1400° C. and 53 wt. % TiO₂. After a slight drop in liquidus temperatures to 1390° C., the third "eutectic" point at approximately 58 wt. % TiO₂ marks the coexistence of the phases ilmenite, pseudobrookite, liquid and gas. Further increase in TiO₂ content causes liquidus temperatures to increase to approximately 1494° C., the maximum melting temperature of the pseudobrookite phase. This point, located at approximately 69 wt. % TiO₂, is followed by a decline in liquidus temperature to the fourth "eutectic" at 1430° C. and approximately 80 wt. % TiO₂. Finally, liquidus temperatures increase toward the melting point of what is believed to be an oxygen-deficient rutile phase (probably ~1800° C.).

The partial pressure of oxygen in the gas phase, as calculated from the iron-wüstite equilibrium (Darken and Gurry, 1945), varies from approximately 10^{-10.7} atm. at 1312° C. to approximately 10^{-9.1} atm. at 1494° C.

The diagram in Fig. 4 is presented in order to show compositions of mixtures heated at temperatures ranging from 1250 to 1350° C. The composition area bounded by the points FeO, Fe₂O₃, and TiO₂ is shown as an equilateral triangle, and arrows indicate directions to the apices of the triangle Fe-Ti-O, of which the area in Fig. 4 is a part. Light dash-dot lines represent the solid solution joins magnetite-ulvospinel, hematite-ilmenite and pseudobrookites. The dash curve connects points (solid dots) representing analytically determined compositions of various mixtures. Projection of spinel composition points onto the joint FeO-TiO₂ results in points located on the FeO side of the stoichiometric composition (see Fig. 3), whereas the opposite situation prevails for the pseudobrookite phase.

In addition to the phases mentioned in the previous text and illustrated in the diagram of Fig. 3, globules of metallic iron were observed in all quenched samples obtained in this investigation. Evidence presented in the following suggests that iron is not an equilibrium phase under the experimental conditions used, but that its presence is caused instead by complicated kinetic characteristics of the reactions. Inasmuch as the sample is kept at a temperature slightly higher than that of the iron-wüstite buffer, the oxygen partial pressure of the gas phase is slightly lower than that corresponding to the wüstite-iron equilibrium at the temperature of the sample. Hence wüstite, if present as a pure phase in the sample, would tend to be reduced to metallic iron, causing a transport of oxygen from the sample to the buffer. However, when iron oxide is combined with TiO₂ to form the phases ulvospinel, ilmenite or pseudobrookite, the FeO activity of the sample is reduced enough to prevent deposi-

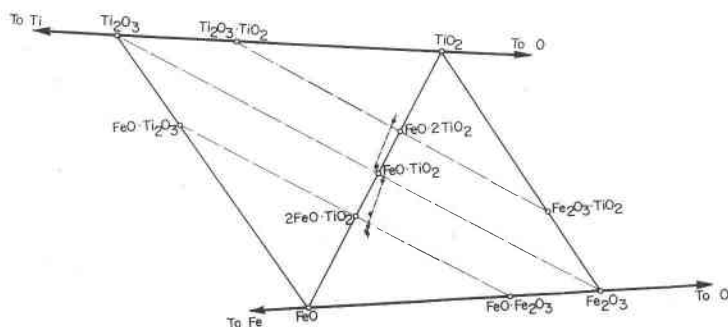
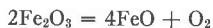


FIG. 4. Diagram of a part of the system Fe—Ti—O to show approximate compositions of oxide mixtures equilibrated at the oxygen partial pressures of the iron-wüstite equilibrium in the temperature interval 1250–1350° C. Solid dots represent compositions determined by chemical analysis, and the dash curve has been drawn to pass approximately through these points. Light dash-dot lines represent solid solution joins (magnetite-ulvospinel, hematite-ilmenite, and pseudobrookites).

tion of metallic iron under equilibrium conditions in spite of the temperature difference between sample and buffer. (See data on free energies of formation of these phases from the oxide components, as listed for instance by Michaud and Pidgeon (1954).)

The following mechanism is suggested for explaining the occurrence of globules of metallic iron in all quenched samples in the present investigation: The starting materials for the equilibration runs, prepared by pre-heating at lower temperatures, have higher $\text{Fe}_2\text{O}_3/\text{FeO}$ ratios than those corresponding to the final equilibrium state. The samples, when put into the quench furnace at the equilibration temperature, try to establish the "correct" oxidation state by reducing the amount of Fe_2O_3 and increasing the amount of FeO present. There are two possible ways in which this can be accomplished. One is for the sample to give off oxygen to the gas phase according to the equation



The other is a reaction of Fe_2O_3 of the oxide sample with metallic iron of the crucible according to the equation



The FeO formed by the latter process may be reduced partially to metallic iron by the prevailing atmosphere before FeO reacts with TiO_2 to form phases in which the divalent iron is stabilized. This inferred mechanism is supported by the following observations made on the quenched samples: Ridges and other relief features on the inside surface of the crucibles appeared to have been leveled by contact with the sample. Microscopic examination of the crucible surface showed embayment of areas where contact with the sample was maintained. Globules of metallic iron were localized near contact with the crucible. The latter observation is particularly significant, for if the initial sample was homogeneous and the oxygen pressure was constant throughout the volume of the sealed-silica tube, then the distribution of metallic iron should have been uniform within the volume of the sample upon reduction *in situ*. On the other hand, iron emplaced as a result of reaction with the crucible material would be concentrated near the contact with the container.

The data obtained in the present investigation show that the pseudobrookite structure is stable under the reducing conditions prevailing when FeO is in equilibrium with metallic iron. This observation confirms the findings of Akimoto and Nagata (1957) who reported that a complete solid solution series exists between $\text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$ and $\text{FeO} \cdot 2\text{TiO}_2$ at 1200°C . In contrast to this, Grieve and White (1939) presented a phase diagram for the system " $\text{FeO}-\text{TiO}_2$ " which does not incorporate

pseudobrookite as a phase, and in addition shows other disagreements with results obtained in the present study. It is believed that their use of molybdenum crucibles in poorly defined atmospheres may be the reason for the deviating results.

SUMMARY

Phase relations in the system iron oxide-titanium oxide have been determined at oxygen partial pressures defined by the equilibrium between wüstite and metallic iron. Equilibration runs were made by keeping oxide mixtures in iron crucibles in nitrogen atmosphere or by sealing the mixtures together with an iron-wüstite buffer into tubes of vitreous silica. Compositions of mixtures prepared under these conditions were found to deviate somewhat from those of the join FeO-TiO₂. Mixtures containing large percentages of iron oxide showed excess Fe³⁺ whereas Ti³⁺ was inferred (from chemical analysis) to be present in samples of high titanium oxide content.

Four "eutectic" points have been determined in the system "FeO-TiO₂." The phase assemblage, approximate liquid composition and temperature of each are as follows: At approximately 1312° C. wüstite, ulvospinel, liquid (approximately 90 wt. % FeO,* 10 wt. % TiO₂) and gas are in equilibrium. The phases ulvospinel, ilmenite, liquid of composition 53 wt. % FeO, 47 wt. % TiO₂ and gas coexist in equilibrium at 1363° C. The third point at 1390° C. marks the existence of ilmenite, pseudobrookite, liquid of composition 42 wt. % FeO, 58 wt. % TiO₂ and gas in equilibrium. At 1430° C. pseudobrookite, rutile, liquid of approximate composition 20 wt. % FeO, 80 wt. % TiO₂ are in equilibrium with a gas phase.

In addition to the phases mentioned above, globules of metallic iron were observed in quenched samples. Phase rule consideration shows that metallic iron cannot be an equilibrium phase. It is proposed that the metal is incorporated into the sample from the crucible. This reaction, being more rapid than the exchange of oxygen between sample and buffer, results in the precipitation of an amount of metallic iron equivalent to that incorporated from the crucible.

ACKNOWLEDGMENTS

This work was carried out as part of a research project on oxide systems sponsored by the American Iron and Steel Institute. The authors are indebted to E. F. Obsorn for his critical reading of the manuscript.

* Total iron oxide content calculated as FeO.

REFERENCES

- AKIMOTO, S. AND NAGATA, T. (1957), The TiFe_2O_5 - Ti_2FeO_3 Solid Solution Series: *Nature*, **179**, 37-38.
- ANDERSSON, S., COLLEN, B., KUYLENSTIERNA, U. AND MAGNELI, A. (1957), Phase Analysis Studies on the Titanium-Oxygen System: *Acta Chem. Scand.*, **11**, 1641-1652.
- BASTA, E. Z. (1953), Ph.D. Thesis, Bristol.
- BOWEN, N. L. AND SCHAIRER, J. F. (1932), The System FeO-SiO_2 : *Am. J. Sci.*, **224**, 177-213.
- DARKEN, L. S. AND GURRY, R. W. (1945), The System Iron-Oxygen: I, The Wüstite Field and Related Equilibria: *J. Am. Chem. Soc.*, **67**, 1398-1412.
- DARKEN, L. S. AND GURRY, R. W. (1946), The System Iron-Oxygen: II, Equilibrium and Thermodynamics of Liquid Oxide and Other Phases: *J. Am. Chem. Soc.*, **68**, 798-816.
- DEVRIES, R. C. AND ROY, R. (1954), A Phase Diagram for the System Ti-TiO_2 Constructed from Data in the Literature: *Bull. Am. Ceram. Soc.*, **33**, 370-372.
- GREIG, J. W., POSNJAK, E., MERWIN, H. E. AND SOSMAN, R. B. (1935), Equilibrium Relationships of Fe_3O_4 , Fe_2O_3 and Oxygen: *Am. J. Sci.*, **30** (5th Series), 239-316.
- GRIEVE, J. AND WHITE, J. (1939), The System FeO-TiO_2 : *Journ. Roy. Techn. Coll.*, **4**, 441-448.
- GRIMALDI, F. S., STEVENS, R. E. AND CARRON, M. K. (1943), Determination of Iron in the Presence of Chromium and Titanium with the Jones Reductor: *Ind. and Eng. Chem.*, **15**, 387-388.
- HILLEBRAND, W. F., LUNDELL, G. E. F., BRIGHT, H. A. AND HOFFMAN, J. I. (1953), Applied Chemical Analysis: John Wiley and Sons, New York.
- KAWAI, N., KUME, S. AND SASJIMA, S. (1954), Magnetism of Rocks and Solid Phase Transformation in Ferromagnetic Minerals: *Proc. Japan. Acad.*, **30**, 588-593.
- MAGNELI, A., ANDERSSON, S., WESTMAN, S., ASBRINK, S. AND HOMBERG, B. (1958), Studies on the Crystal Chemistry of Titanium, Vanadium and Zirconium Oxides at Elevated Temperatures: Final Tech. Rept. No. 1, Dept. of Army Contracts No. Da-91-508-NUC-254.
- MICHAUD, G. G. AND PIDGEON, L. M. (1954), The Selective Reduction of Iron in Ilmenite and the Oxygen Pressure of TiO_2 -y Rutile: *Can. Mining and Metal. Bull.*, **47**, 307-309.
- MUAN, A. (1958), Phase Equilibria at High Temperatures in Oxide Systems Involving Changes in Oxidation States: *Am. J. Sci.*, **256**, 171-207.
- NICHOLLS, G. P. (1955), The Mineralogy of Rock Magnetism: *Advanc. Physics*, **4**, 113-190.
- PHILLIPS, B. AND MUAN, A. (1960), Stability Relations of Iron Oxides: Phase Equilibria in the System Fe_3O_4 - Fe_2O_3 at Oxygen Pressures up to 45 Atmospheres: *J. Phys. Chem.*, **64**, 1451-1453.
- POSNJAK, E. AND BARTH, T. F. W. (1934), Notes on Some Structures of the Ilmenite Type: *Zeit. Krist.*, **88**, 271-280.
- POUILLARD, E. (1950), Sur le Comportement de l'Alumine et l'Oxyde de Titane vis-à-vis des Oxydes de Fer: *Ann. de Chim.*, **5**, 164-214.
- RAMDOHR, P. (1926), Beobachtungen an Magnetit, Ilmenit, Eisenglanz und Ueberlengungen über das System FeO , Fe_2O_3 , TiO_2 : *Neues Jahrb. Min., Abt. A, Beil.-Bd.*, **54**, 320-379.
- RAMDOHR, P. (1960), Die Erzminerale und ihre Verwachsungen: Akademie Verlag, Berlin.
- RAMDOHR, P. (1953), Ulvospinel and its Significance in Titaniferous Iron Ores: *Econ. Geol.*, **48**, 677-687.
- SIDGWICK, N. V. (1950), The Chemical Elements and Their Compounds: Oxford University Press, London.
- VINCENT, E. A. AND WRIGHT, J. B. (1957), Heating Experiments on Some Natural Titaniferous Magnetites: *Min. Mag.*, **31**, 624-688.