

Correction to the Phase Equilibria in the Fe-Mn-Ti-O System

RICHARD R. MERRITT

*CSIRO Division of Mineral Chemistry, P.O. Box 124, Port Melbourne,
Victoria 3207, Australia*

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The reported phase relations for the Fe-Mn-Ti-O system (R. R. Merritt, *J. Solid State Chem.*, **43**, 267, 1982) have been redetermined because they were found to be affected by the presence of 1.34 wt% Al_2O_3 in the TiO_2 used. This impurity lowers the temperature at which the pseudobrookite phase is stable. The results of the new work reaffirm the changes to the phase diagram that result from the replacement by manganese of part of the iron in the Fe-Ti-O system. On the basis of the earlier results, a phase diagram is proposed for an aluminum-containing five-component system. © 1985 Academic Press, Inc.

Introduction

Subsequent to the publication of the equilibrium phase relations for part of the Fe-Mn-Ti-O system (1), it was found that the TiO_2 used to prepare the samples contained 1.34 wt% Al_2O_3 . In this note, the correct phase relations are given for the compositions $\text{Fe}_{0.297}\text{-Mn}_{0.097}\text{-Ti}_{0.606}\text{-O}$, and the earlier results are interpreted in terms of an aluminum-containing five-component system.

Experimental Methods

In the new work, the previously described equilibration-and-quench method (1) was used to determine the phase equilibria as a function of both oxygen fugacity and temperature for the compositions $\text{Fe}_{0.297}\text{-Mn}_{0.097}\text{-Ti}_{0.606}\text{-O}$. However, a second batch of reagent TiO_2 was used to prepare the samples. The compositions of this and the previous batch are given in Table I. An energy-dispersive X-ray analyzer fitted

to an SEM was used to show that impurity elements were not incorporated into the samples during the equilibration process.

Results

The phase found in the quenched samples and the conditions under which the samples were heated have been tabulated.¹ The temperature and oxygen fugacity of heating, the number of phases found in the quenched samples, and a set of phase boundaries that is consistent with the ob-

¹ See NAPS document No. 04286 for 3 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance \$4.00 for microfiche copy or, for photocopy, \$7.75 for up to 20 pages plus \$.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of \$15. Foreign orders add \$4.50 for postage and handling for the first 20 pages, and \$1.00 for each additional 10 pages, or \$1.50 for postage of microfiche orders.

TABLE I
COMPOSITION (wt%) OF REAGENT TiO₂^a

	Lot used in Ref. (1)	Lot used in current work
TiO ₂	97.18	99.17
Al ₂ O ₃	1.34	0.10
P ₂ O ₅	0.24	0.09
SiO ₂	0.21	0.04
K ₂ O	0.09	0.07
CaO	0.06	<0.01
Na ₂ O	0.03	0.02
Loss on ignition	0.89	0.34

^a Determined by atomic absorption spectroscopy and wet chemical methods.

served phases are shown in Fig. 1. To simplify discussion, the boundaries in this and later figures are labeled A through G.²

Discussion

The experimental conditions used allow equilibrium divariant three-solid-phase assemblages to form. In all but five runs, two- or three-phase assemblages were produced and so it is likely that equilibrium was usually achieved. In the five exceptions, X-ray microanalysis did not show, in any phase, the even distribution of an impurity element that would indicate impurity stabilization. It is therefore suggested that the lack of equilibrium resulted from slow reaction rates.

Three of the samples that did not achieve equilibrium were heated at conditions near boundary A. Nevertheless, the equilibrium assemblage for these could be determined because repeated heating consistently lowered the concentration of one of the con-

² The labels for the phase boundaries in Figs. 1, 2, and 3 were chosen so that particular phase assemblages are defined by boundaries that have the same labels in all three figures. For example, the high-temperature limit of the assemblage $M_2O_3 + MO_{2-x} + Fe_m$ is boundary A in every case.

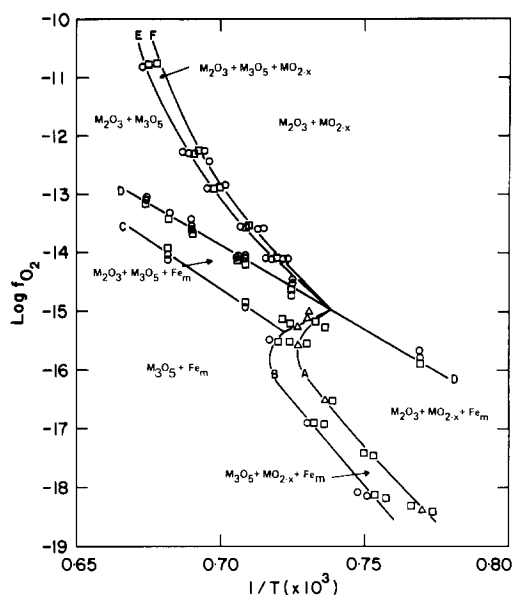


FIG. 1. Revised equilibrium-phase relations for the compositions $Fe_{0.297}-Mn_{0.097}-Ti_{0.606}-O$. The circles indicate the presence of two phases in the quenched samples, the squares indicate three phases, and the triangles indicate four phases.

tained phases. This probably indicates a high activation energy for the structural rearrangement needed to form hexagonal M_2O_3 from orthorhombic M_3O_5 , or vice versa.³

The remaining samples (all containing four phases) were heated at conditions near boundary G. In these, the relative concentrations of the four phases did not change significantly after the third heating. The

³ For consistency with previous terminology (1), a solid solution with a pseudobrookite structure is represented by M_3O_5 , a solid solution with an ilmenite structure is represented by M_2O_3 , a reduced rutile phase is represented by MO_{2-x} , and metallic iron is represented by Fe_m . In this terminology, M indicates iron, manganese, and titanium. For MO_{2-x} , the value of x varies from 0.25 to 0.00. The composition range from $MO_{1.75}$ to $MO_{1.99}$ is spanned by a series of discrete phases whose structures may be considered to derive from the rutile type by crystallographic shear. Between $MO_{1.75}$ and $MO_{1.889}$, the six discrete phases that occur, with the general formula M_nO_{2n-1} , where $n = 4-9$, are known as Andersson-Magneli phases.

close proximity of boundary G to other boundaries indicates that only small energy differences separate the stable phase assemblage from one or more metastable phase assemblages. The consequent minimal energy gain that would follow the formation of the stable assemblage from one of the metastable assemblages, in combination with the high activation energy for the hexagonal-to-orthorhombic rearrangement, is the probable cause of the almost zero reaction rates seen near boundary G.

Relationships to Phase Equilibria in the Fe-Ti-O System

The phase equilibria reported here are related to those defined previously in the Fe-Ti-O system for the compositions $\text{Fe}_{0.394}\text{-Ti}_{0.606}\text{-O}$ (2). Similar sets of two-phase assemblages exist in both systems, but the result of replacing approximately a quarter of the iron by manganese is to separate these by divariant three-phase assemblages instead of univariant boundaries, as in the ternary system. Clear examples of this are the assemblages $M_2O_3 + M_3O_5 + \text{Fe}_m$ and $M_2O_3 + M_3O_5 + \text{MO}_{2-x}$. However, the remaining three-phase assemblages in Fig. 1 also replace other boundaries in the ternary system, namely those that define the assemblage $\text{MO}_{2-x} + \text{Fe}_m$. This two-phase assemblage does not appear in Fig. 1 because of the limited solubility of manganese in the MO_{2-x} phases (3), but it may occur at low oxygen fugacities where there could be appreciable solubility of manganese in the metal phase.

The two miscibility gaps that occur in the ternary M_3O_5 solid solution remain when manganese is present. Although the position of the minimum between the two gaps is not greatly affected by the manganese (see Table II), the fourth component significantly changes both the temperature and the oxygen fugacity at the points where the two gaps close. At high oxygen fugacities,

TABLE II
EFFECT OF MANGANESE ON THE MISCIBILITY GAPS
IN THE M_3O_5 SOLID SOLUTION

	$\text{Fe}_{0.394}\text{-Ti}_{0.606}\text{-O}$ (Ref. (2))		$\text{Fe}_{0.297}\text{-Mn}_{0.097}\text{-Ti}_{0.606}\text{-O}$ (this work)	
	Temperature (K)	Oxygen fugacity (atom)	Temperature (K)	Oxygen fugacity (atm)
Conditions at closing of miscibility gap with only oxide phases present	1416	$10^{-11.8}$	>1480	$>10^{-10.8}$
Conditions at closing of miscibility gap with both oxide and metal phases present	1619	$10^{-12.9}$	1377	$10^{-15.7}$
Conditions at the minimum between the two miscibility gaps	1339	$10^{-14.95}$	1354	$10^{-15.0}$

manganese stabilizes the M_2O_3 phase, thus raising the temperature at which the miscibility gap closes. In contrast, when metallic iron is present, the M_3O_5 phase is stabilized and the closing temperature is lowered. This relative stability of the M_2O_3 and M_3O_5 phases accords with that in the Mn-Ti-O system (3), where higher oxygen fugacities favor the formation of the M_2O_3 phase.

Effect of Aluminum on the Phase Relations

By comparing Fig. 1 with the phase diagram in the earlier paper (1), reproduced here as Fig. 2, it can be seen that aluminum causes the phase boundaries to shift to lower temperatures. The magnitude of the displacement varies with the change in concentration of the M_3O_5 phase upon crossing a boundary. Thus, the largest changes occur at the boundaries associated with the miscibility gap in the M_3O_5 solid solution (i.e., boundaries A, E, and F), while almost no change occurs at boundary D, which defines the conditions at the start of the destabilizing of the M_2O_3 phase. This behavior is consistent with the phase diagram for the

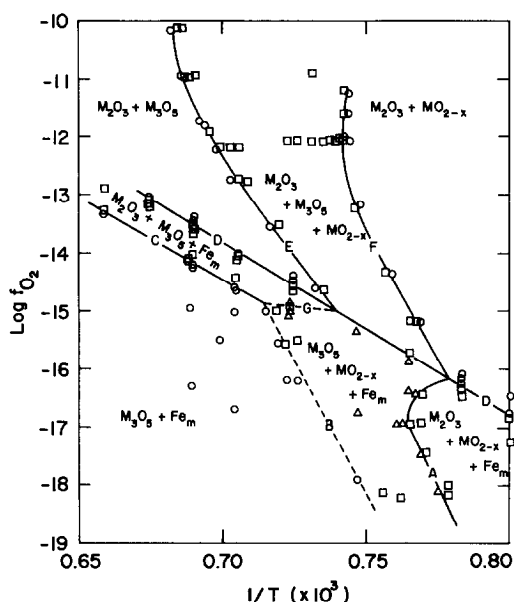


FIG. 2. Previous equilibrium-phase relations for the compositions $\text{Fe}_{0.297}\text{-Mn}_{0.097}\text{-Ti}_{0.606}\text{-O}$. Aluminum-containing TiO_2 was used to prepare the samples used in this work. The circles indicate the presence of two phases in the quenched samples, the squares indicate three phases, and the triangles indicate four phases.

Fe-Al-Ti-O system (4), which shows that aluminum can exist in an extensive M_3O_5 solid solution but is practically insoluble in the M_2O_3 phase.

The second consequence of the aluminum impurity is an increased number of samples containing four phases in the vicinity of boundary A. While in Fig. 1 the samples containing four phases lie virtually on the boundary, the four-phase region in Fig. 2 extends at least 30 K to the right of boundary A. The kinetic explanation given above would not hold for such a large field of four-phase coexistence. A more likely explanation is that this field shows four-phase equilibrium in the aluminum-containing five-component system. From the data in Table I, the compositions previously used can be shown to be $\text{Al}_{0.013}\text{-Fe}_{0.297}\text{-Mn}_{0.097}\text{-Ti}_{0.593}\text{-O}$.

Although four-phase equilibrium could occur in samples containing aluminum and

heated near boundary G, it is more likely that they are nonequilibrium assemblages. The reasons for this are the same as were outlined in the case of the four-component system.

Assuming that there is four-phase equilibrium in the five-component system, a plausible set of phase boundaries can be fitted to the published data (see Fig. 3). Figure 3 differs from Fig. 2 in that boundary A' has been added to define the upper limit of the four-phase equilibrium, and that boundary B has been redrawn. For the reasons given before (1), the experimental data do not accurately locate these boundaries, but their positions can be estimated from the results of the present work. In Fig. 3, boundaries A' and B are drawn with shapes similar to those of boundaries A and B in Fig. 1, and, consistently with the above discussion, they are displaced toward lower temperatures. The displacement for bound-

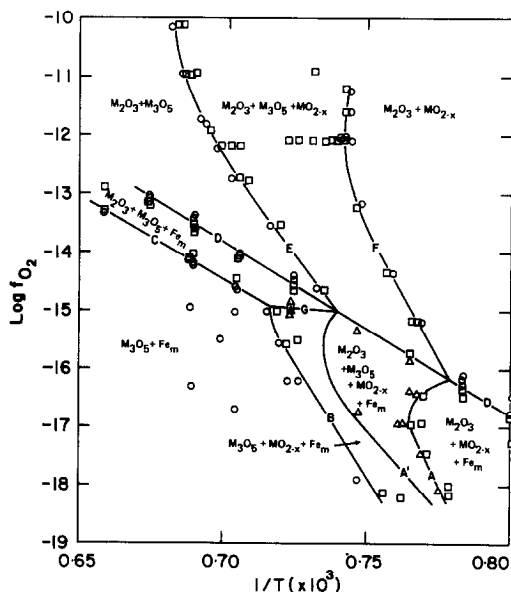


FIG. 3. Equilibrium-phase relations for the compositions $\text{Al}_{0.013}\text{-Fe}_{0.297}\text{-Mn}_{0.097}\text{-Ti}_{0.593}\text{-O}$. The experimental data are the same as in Fig. 2. The circles indicate the presence of two phases in the quenched samples, the squares indicate three phases, and the triangles indicate four phases.

ary B was chosen to comply with the experimental data. For boundary A', where there are insufficient data to make a reliable choice, the displacement was estimated to be between 5 and 10 K. This range is consistent with that found for other compositions in a continuing investigation of the equilibria in the Fe-Mn-Ti-O and Al-Fe-Mn-Ti-O systems.

Acknowledgments

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