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Phase Equilibria in the Fe–Mn–Ti–O System for the Compositions $Fe_{0.297}$–$Mn_{0.097}$–$Ti_{0.606}$–O

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This paper reports equilibrium-phase data for the Fe–Mn–Ti–O system at oxygen fugacities between $10^{-18.2}$ and $10^{-10.0}$ atm and at temperatures between 1249 and 1514K. An equilibration-and-quench method was used, and the oxygen fugacities were controlled with mixtures of hydrogen and carbon dioxide. The phase relations are presented on a $\log f_{O_2}$ vs $1/T$ diagram and are discussed in terms of the phase relations in the two systems Fe–Ti–O and Mn–Ti–O.

Introduction

Mineral phases from the quaternary system Fe–*M*–Ti–O, where *M* is Mn, Mg, Cr, or Al, have commercial interest as sources of titanium (e.g., ilmenite, which is nominally $FeTiO_3$). They are also of scientific interest as possible indicators of both geological temperature and oxygen fugacity (*1*). The equilibrium-phase data that are needed to determine the latter information and to improve the performance of ilmenite-upgrading plants have recently become available for the systems that contain magnesium, chromium, or aluminum (*2–4*). The study reported here gives detailed information on part of the least studied of these quaternary systems, namely, Fe–Mn–Ti–O.

A previous study of this system (*5*) defined the composition limits for the solid solutions M_2O_3 and M_3O_5 at 1473K.[1] Ilmenite and its analog $MnTiO_3$ formed a continuous solid solution that could incorporate some excess Ti_2O_3. A stability gap was shown to occur between the compositions Fe_2TiO_5 and Ti_3O_5, but it closed at sufficiently high concentrations of manganese.

The temperature/oxygen-fugacity/composition relations for the stability of the M_3O_5 phase in the Fe–Ti–O system were recently established (*6*). This study confirmed an earlier suggestion (*7*) that two stability gaps could occur, and from the experimentally determined phase relations for the composition $Fe_{0.394}$–$Ti_{0.606}$–O estimates were given for the invariant temperature

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[1] For consistency with previous terminology (*6*), 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/or titanium. For MO_{2-x}, the value of *x* varies from 0.25 to 0.00. The composition range from $MO_{1.75}$ to $MO_{1.90}$ 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.

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and oxygen fugacity at the minimum between the two gaps.

The present paper reports a study of the equilibria in the Fe–Mn–Ti–O system for the compositions $Fe_{0.297}$–$Mn_{0.097}$–$Ti_{0.606}$–O. These compositions were studied in order to allow the measured equilibrium-phase relations, which are given in a $\log f_{O_2}$ vs $1/T$ phase diagram, to be compared with those published for the ternary compositions $Fe_{0.394}$–$Ti_{0.606}$–O (*6*). Such a comparison illustrates the effect of substituting manganese for part of the iron in the ternary system, and it shows that although the manganese stabilizes the M_3O_5 solution to lower temperatures, two stability gaps remain in it.

Results

The phase equilibria were determined by the equilibration-and-quench method. The experimental procedures were the same as those described previously (*6*), but the lower temperatures used in the present study required a correction to be made to the oxygen fugacity ($\log f_{O_2}$) as calculated from the H_2/CO_2 ratio in the equilibrating atmosphere. The value of this correction, as determined from the metallic iron/wustite equilibrium and the data of Spencer and Kubaschewski (*8*), changed linearly from −0.21 at 1250K to zero at 1375K.

The phases found in the quenched samples and the conditions under which the samples were heated are tabulated.[2] 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 observed phases are shown on the $\log f_{O_2}$ vs $1/T$ plot in Fig. 1. To simplify discussion, the boundaries in this figure are labeled A to G.

In general, the uncertainties in the locations of the phase boundaries are similar to those that occur in the heating conditions (i.e., ±8K and ±0.08 in $\log f_{O_2}$). In two areas of Fig. 1, repeated heating did not always remove a fourth phase, so equilibrium was not always attained. These areas are (1) at the left of boundary A and (2) near boundary G. In the former area, the reproducible appearance and disappearance of the M_3O_5 phase when boundary A is crossed suggest that its position is also defined within the above limits, despite the continued existence of the M_2O_3 phase at its left. On moving the heating conditions from boundary A to the region where the

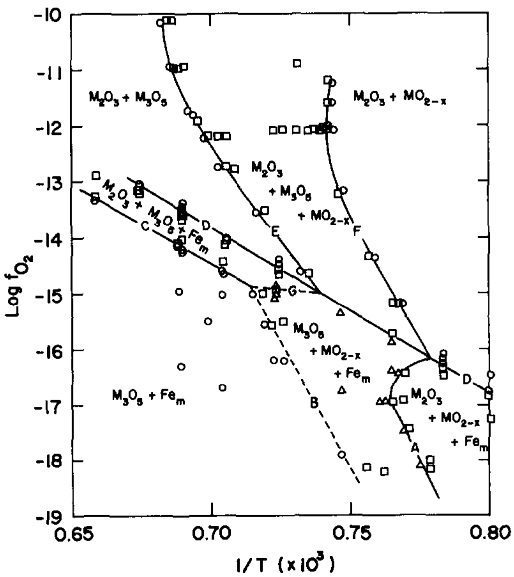

FIG. 1. Experimentally determined equilibrium-phase relations for the compositions $Fe_{0.297}$–$Mn_{0.097}$–$Ti_{0.606}$–O. The circles indicate the presence of two phases in the quenched samples, the squares indicate three phases, and the triangles indicate four phases.

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[2] See NAPS document No. 03952 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 additional 10 pages of material. Remit $1.50 for postage of any microfiche orders.

assemblage $M_3O_5 + Fe_m$ is stable, there is a steady reduction in the concentration of first the M_2O_3 phase and then the MO_{2-x} phases. The gradual loss of the MO_{2-x} phases in combination with their relatively diffuse X-ray diffraction patterns makes it difficult to locate boundary B precisely. The uncertainties in this boundary's location may exceed the numbers given above, and so the boundary is indicated by a broken line in Fig. 1.

Boundary G is also indicated by a broken line since the nearby nonequilibrium does not allow it to be experimentally defined, although such a boundary is required to complete a plausible phase diagram. Nonequilibrium in this part of the phase diagram may result from the close proximity of several stable-phase assemblages. To construct a sensible phase diagram, the high-temperature end of boundary G must be at the intersection of boundaries B and C, while its low-temperature end is most likely to be at the intersection of boundaries D and E (i.e., at the minimum temperature for stability of the oxide assemblage $M_2O_3 + M_3O_5$).

The phase boundaries in Fig. 1 intersect at three points, the temperatures and oxygen fugacities of which are given in Table I.

Discussion

The Phase Diagram

The phase relations shown in Fig. 1 relate primarily to those of the Fe–Ti–O system at the higher oxygen fugacities, but the influence of the Mn–Ti–O system becomes apparent as the fugacity is lowered. The extra degree of freedom that is introduced by the fourth component allows the univariant three-phase boundaries that occur in the Fe–Ti–O system (*6*) to become divariant three-phase assemblages in the quaternary system. Thus a single-phase boundary in the Fe–Ti–O system is replaced by two boundaries that contain a three-phase assemblage. Two examples of this change are the assemblages $M_2O_3 + M_3O_5 + MO_{2-x}$ (top center, Fig. 1) and $M_2O_3 + M_3O_5 + Fe_m$ (left center). They correspond to the two boundaries in the Fe–Ti–O system that lie between the two-phase assemblages $M_2O_3 + MO_{2-x}$, $M_2O_3 + M_3O_5$, and $M_3O_5 + Fe_m$.

TABLE I

TEMPERATURES AND OXYGEN FUGACITIES FOR THE INTERSECTION POINTS OF THE PHASE BOUNDARIES SHOWN IN FIG. 1

Intersecting boundaries	Reciprocal temperature ($K^{-1} \times 10^3$)	Temperature (K)	Oxygen fugacity (atm)
B, C, G	0.7144	1400	$10^{-14.86}$
D, E, G	0.7398	1352	$10^{-15.00}$
A, F, D	0.7789	1284	$10^{-16.16}$

A less obvious example of this principle is the low-temperature end of boundary D, which can be considered as one of a hypothetical pair having an analog in the ternary system, namely, a boundary between the assemblages $M_2O_3 + MO_{2-x}$ and $MO_{2-x} + Fe_m$. Similarly, the decomposition of the M_3O_5 phase into the assemblage $MO_{2-x} + Fe_m$, which takes place at two univariant boundaries in the Fe–Ti–O system, occurs in a divariant assemblage at the right of boundary B. On crossing the hypothetical pairs to either boundary B or boundary D, the assemblage $MO_{2-x} + Fe_m$ would be stabilized. Since no more than 2.2% Mn can be accommodated in the MO_{2-x} phases (*9*), the assemblage $MO_{2-x} + Fe_m$ could occur only at very low oxygen fugacities where there may be an appreciable concentration of manganese in the metal phase. Thus boundary A, which has no analog in the Fe–Ti–O system, is needed to separate the two three-phase assemblages $M_2O_3 + MO_{2-x} + Fe_m$ and $M_3O_5 + MO_{2-x} + Fe_m$.

There is a reaction in the Mn–Ti–O system that is analogous to the one that occurs at boundary A. As metallic iron is formed by the lowering of the oxygen fugacity, the oxide part of the quaternary system tends to an Mn–Ti–O subsystem in which the ratio of manganese to total metal (in the oxide phases) is 0.138. For the ternary system with this composition, the oxides M_3O_5 + MO_{2-x} become stable relative to M_2O_3 + MO_{2-x} at a low enough oxygen fugacity (*9, 10*). This is the reaction that occurs at boundary A. Thus it is when iron is metallized that the reactions in the four-component system begin to reflect those that occur in the Mn–Ti–O system.

Stability of the M_3O_5 Solution

The shape of boundaries A and F show that in the four-component system, as in the Fe–Ti–O system, there are two stability gaps in the M_3O_5 solution. The minimum temperature between these gaps is 1284K, compared to 1339K for the invariant point in the ternary system. Similarly, the temperatures at which the gaps close in the quaternary system are lower than the corresponding temperatures in the ternary system. For boundary F, although the oxygen fugacity could not be raised sufficiently to clearly show the maximum temperature, its changing slope indicates that the experimental limits lie just beyond the fugacity at which the gap closes, and so it is suggested that the gap closes at 1348K and $10^{-12.0}$ atm. The corresponding gap in the ternary system closes near 1416K and $10^{-11.8}$ atm (*6*).

For boundary A, the maximum occurs at 1308 ± 8K and $10^{-16.9 \pm 0.2}$ atm, compared to 1619 ± 8K and $10^{-12.9 \pm 0.2}$ atm for the ternary system (*6*). The larger than usual uncertainty in the former oxygen fugacity is because of the difficulty in estimating the position of the peak in boundary A. Thus the presence of manganese lowers the temperature at which the M_3O_5 solution becomes unstable, which is consistent with the earlier observation that "the effect of incorporation of manganese into the $FeTi_2O_5$–Ti_3O_5 solid solution is to close the miscibility gap" (*5*). Both effects are in accord with Navrotsky's suggestion (*11*) that compounds with a pseudobrookite structure are stabilized by a large positive entropy that results from the disordering of different cations on the two crystallographically independent cation sites. For the four-component system, the third cation, manganese, should increase the disorder entropy relative to that of the ternary system.

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