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Phase Equilibria for the System Mn$_{0.394}$–Ti$_{0.606}$–O–S at 1380 and 1485°K

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This paper reports equilibrium phase data for the manganese-containing system Mn$_{0.394}$–Ti$_{0.606}$–O–S. The system was studied at 1380 and 1485°K by an equilibration and quench technique. The oxygen and sulfur fugacities of the equilibrating gas atmosphere were independently controlled using mixtures of the three gases hydrogen, carbon dioxide, and hydrogen sulfide. The results are presented on $\log f_{S_2}$ vs $\log f_{O_2}$ phase diagrams which are discussed in terms of the equilibria between manganese in the oxide phases and manganese in the α-MnS sulfide phase. The results are shown to be consistent with previously published data for the subsystems Mn–Ti–O, Mn–O–S, Mn–S, and Ti–O–S.

1. Introduction

In a companion paper (*1*) which reported a phase study for the system Fe–Ti–O–S, it was shown that equilibrium data for the Fe–Mn–Ti–O–S system were needed to understand the chemistry of the coal reduction process for upgrading ilmenite. The present paper reports another part of the study of this five-component system, that is, the subsystem Mn–Ti–O–S at 1485 and 1380°K. The system was restricted to a titanium to total metal ratio of 0.606, which approximated that of the altered ilmenite feed used by Western Titanium Limited at its ilmenite upgrading plant at Capel in Western Australia. The experimental temperatures were chosen to give data applicable to the maximum and minimum temperature at which reduction occurs in the coal reduction kiln.

The equilibration and quench method was used with independent control of the sulfur and oxygen fugacities. The range of fugacities studied at 1485°K was for sulfur, $10^{-5.7}$ to $10^{-3.8}$ atm, and for oxygen, $10^{-16.1}$ to $10^{-12.6}$ atm. At 1380°K the sulfur fugacity ranged from $16^{-6.3}$ to $10^{-4.9}$ atm, and the oxygen fugacities from $10^{-17.1}$ to $10^{-14.0}$ atm.

2. Previous Work

There are no published phase data on the Mn–Ti–O–S system which are relevant to the present work. However, useful information is available from studies of some of the ternary and binary subsystems. The most relevant of these is an investigation of the MnO–TiO$_2$–Ti$_2$O$_3$ system at 1473°K by Grey *et al.* (*2*). They established the phase equilibria as a function of composition for oxygen fugacities in the range 10^{-18} to $10^{-13.5}$ atm. Their results showed that manganese was incorporated into the reduced rutile phases, MO_{2-x}, with the ratio [Mn]/[Mn + Ti] equal to 0.022 for $x = 0.25$; but this ratio fell to 0.015 as the value of x decreased. At oxygen fugacities greater than $10^{-13.95}$, an M_2O_3 phase with the α-Al$_2$O$_3$ structure and with the ratio [Mn]/[Mn + Ti] approximately equal to 0.5 was found to be in equilibrium with the MO_{2-x} phases. An

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oxide with the pseudobrookite structure and of composition M_3O_5 was stable at oxygen fugacities less than $10^{-13.95}$ atm. The M_3O_5 phase is a solid solution between Ti_3O_5 and the hypothetical compound $MnTi_2O_5$, and it has [Mn]/[Mn+Ti] ratios intermediate between those of the M_2O_3 and the MO_{2-x} phases. The present study used the ratio [Mn]/[Mn+Ti] = 0.394 for which Grey *et al.* (*2*) showed that the oxides M_2O_3 and M_3O_5 were in equilibrium for oxygen fugacities in the range $10^{-17.0}$ to $10^{-13.95}$ atm, and for those above $10^{-13.95}$ atm the equilibrium oxides were M_2O_3 and MO_{2-x}.

The data of Mills (*3*) may be used to show that for conditions applicable to the present study only the α-MnS phase would be stable in the binary system Mn–S. In a recent publication Turkdogan *et al.* (*4*) showed that the MnO/MnS equilibrium lay at oxygen fugacities just above, or at sulfur fugacities just below, those of the present experimental conditions.

There are no published data for the Ti–O–S system relevant for our work. However, the results of Abendroth and Schlechten (*5*) for the titanium–sulfur system suggest that a phase of composition near Ti_2S_3 would exist at the H_2/H_2S ratios used in this study. Thermodynamic data for this phase combined with those for the oxides in the titanium–oxygen system (*6–9*) have been used to calculate the sulfide–oxide equilibrium constants which show that titanium oxides, not titanium sulfides, would be stable at the experimental conditions.

The results summarized above suggest that under the present experimental conditions the phase relations will be controlled by the distribution of manganese between the ternary oxides and the sulfide phase, α-MnS. The formation of α-MnS would remove manganese from the oxide phases and so would stabilize the more titanium-rich oxides. Thus α-MnS would only be found in two-phase equilibrium with M_3O_5 or MO_{2-x} phases. When α-MnS is not stable the phase relations appropriate to the Mn–Ti–O system should occur, and so there would be a boundary between the two-phase assemblages $M_2O_3+MO_{2-x}$ and $M_2O_3+M_3O_5$.

3. Experimental

The phase equilibria in the system $Mn_{0.394}$–$Ti_{0.606}$–O–S were determined by the quenching technique. A mixture of the oxides Mn_2O_3 and TiO_2 was heated at the appropriate temperature under an atmosphere with controlled oxygen and sulfur fugacities and then quenched under liquid nitrogen. The phases present in the quenched samples were determined by X-ray diffraction. The Mn_2O_3 was prepared by decomposing A.R. $MnCl_2 \cdot 6H_2O$ in air at 923°K. The TiO_2 was Fischer certified reagent titanium dioxide (anatase) which was dried at 1073°K prior to use.

Some additional data were measured for the $Mn_{0.394}$–$Ti_{0.606}$–O system. For these experiments sulfur was excluded from the equilibrating atmosphere and only the oxygen fugacity was controlled.

3.1. *Control of the Gas Fugacities*

The oxygen and sulfur fugacities were controlled by mixing the three gases hydrogen, carbon dioxide, and hydrogen sulfide in ratios established by metering the gases through calibrated flowmeters. Calculation of the established fugacities was achieved using the computer program CHEMIX (*10*). The uncertainty in the value of $\log f_{X_2}$, $X_2 = S_2$ or O_2, was estimated to be ±0.05.

3.2. *X-Ray Diffraction*

X-Ray powder diffraction patterns were obtained with a Philips diffractometer fitted with a graphite monochromator and using Cu$K\alpha$ radiation.

3.3. *Sample Equilibrium*

An important finding in the study was that mixtures heated under conditions where the

α-MnS phase was stable usually resulted in more phases than were thermodynamically allowed. A scanning electron microscope study of such samples showed that the sulfide formed rims around the exposed surfaces of the pellet and lumps up to 100 μm across formed near the surface (see Fig. 1A). There was an obvious sulfur gradient from the edge of the pellet to its center. The oxide phases found near the center were those found by Grey *et al.* (*2*) at the same oxygen fugacities in the Mn–Ti–O system, namely, M_2O_3 and M_3O_5. A procedure of grinding the sample, repelleting, and reheating usually gave reasonable phase assemblages. Figure 1B shows a micrograph of a sample which had been reheated. It is clear that the sulfide is more evenly distributed and there is no rim on the surface of the pellet. Thus to avoid nonequilibrium the samples were routinely heated at least twice.

For some samples, particularly those from the study at 1380°K, heating four times did not remove the extra phase. In this situation the equilibrium phase assemblage was deduced from the change which occurred in the X-ray diffraction patterns of the quenched samples taken after each heating.

4. Results and Discussion

4.1. *The Phase Diagram at 1485°K*

The phases found in the quenched samples at 1485°K are shown in Table I, and the log f_{S_2} vs log f_{O_2} phase diagram derived from these results is given in Fig. 2. The phase diagram is consistent with the data for the subsystems discussed in Sect. 2 in that the only sulfide phase formed is α-MnS. The manganese-rich oxides are sulfidized to α-MnS and an oxide less rich in manganese, and when the α-MnS phase is not stable there is a boundary between the two-phase oxide assemblages $M_2O_3+MO_{2-x}$ and $M_2O_3+M_3O_5$.

The sulfur-fugacity-independent boundary between the assemblages $M_2O_3+MO_{2-x}$ and $M_2O_3+M_3O_5$ occurs at an oxygen fugacity of $10^{-13.63}$ atm. For oxygen fugacities greater than $10^{-13.63}$ atm, M_2O_3 is sulfidized directly to α-MnS and MO_{2-x}, but below $10^{-13.63}$ atm M_2O_3 disappears first and then the M_3O_5 phase is sulfidized. The final oxide product is again MO_{2-x}. The removal of manganese from the oxide system on sulfidization lowers the [Mn]/[Mn + Ti] ratio in the oxide, and so the loss first of M_2O_3 and then of M_3O_5 is consistent with the phase diagram of Grey *et al.* (*2*) (their Fig. 2).

Grey *et al.* established that at oxygen fugacities where M_2O_3 is sulfidized directly to MO_{2-x}, the ternary oxide is essentially $MnTiO_3$ and the reduced rutile, TiO_2. Thus sulfidation at the boundary may be represented by Eq. (1), which predicts that the boundary should be straight, as observed, with a slope of 1:

$$MnTiO_3+\tfrac{1}{2}S_2=\alpha\text{-}MnS+TiO_2+\tfrac{1}{2}O_2. \quad (1)$$

Similarly, the boundary where the phases M_2O_3, M_3O_5, and α-MnS are in equilibrium is straight, which is consistent with the data of Grey *et al.* (*2*), who showed that the change of composition of the oxides is small over the appropriate range of oxygen fugacities. The slope of approximately 0.8 also agrees with the published data (*2*). In contrast, the boundary where the phases M_3O_5, MO_{2-x}, and α-MnS are in equilibrium shows a continuously varying slope from close to unity at high oxygen fugacities to an asymptotic approach to a line parallel to the log f_{O_2} axis at low oxygen fugacities. The slope change results from significant changes in the ratios [Mn]/[Mn + Ti] in the M_3O_5 phase and [O]/[Mn + Ti + O] in the reduced rutiles, as the oxygen fugacity is varied.

4.2. *The Phase Diagram at 1380°K*

The phases found in the quenched samples at 1380°K are shown in Table II and the phase diagram derived from the results is given in Fig. 3. The data define only one

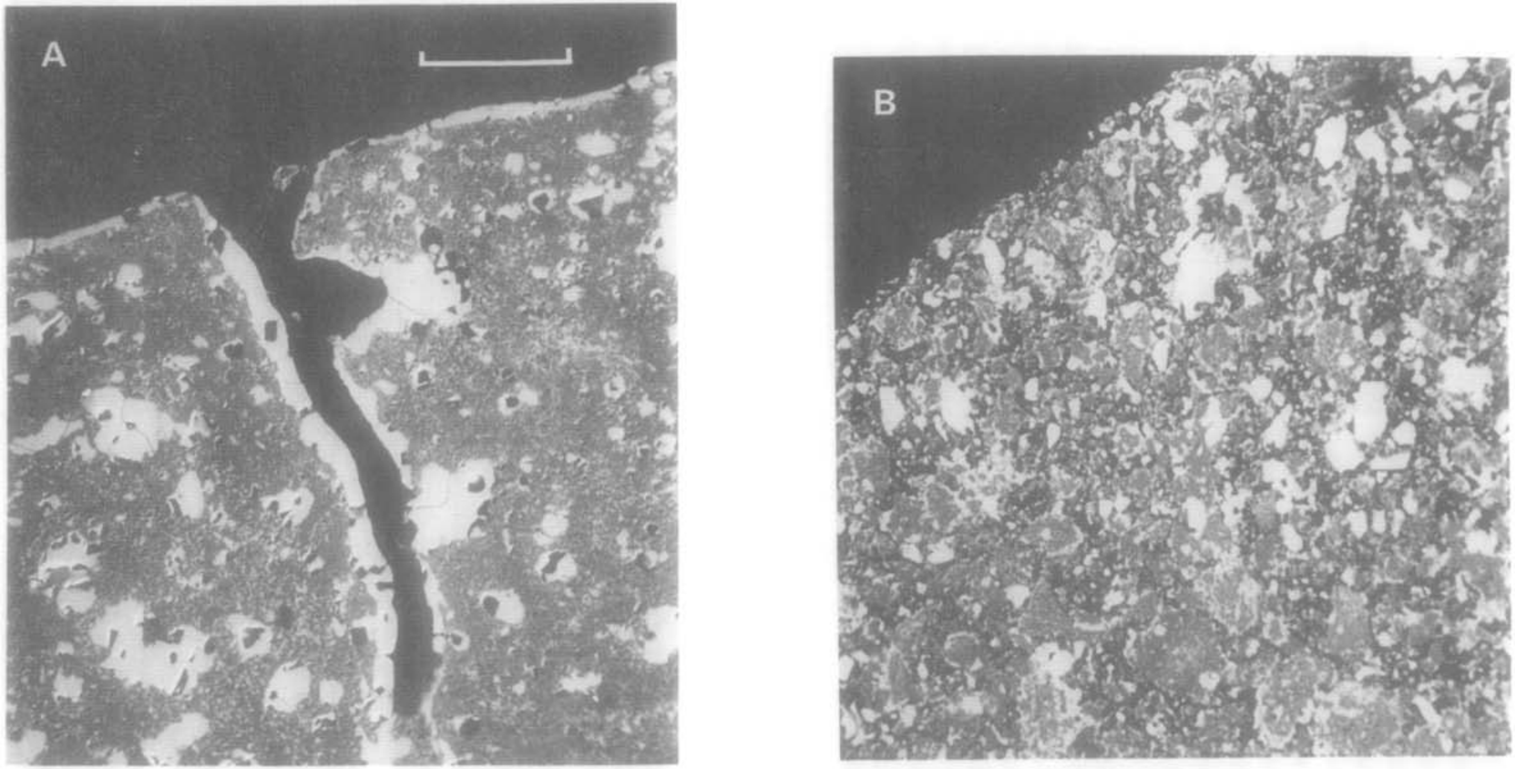

FIG. 1. *Scanning electron micrographs of samples heated under conditions where* α*-MnS is stable.* (A) Part of the surface of a pellet which had been heated only once; the α-MnS (light gray) occurs in large and unevenly distributed lumps and there are rims of sulfide on the exposed surfaces. (B) Sample which had been heated twice; the α-MnS (light gray) is shown to be more evenly distributed throughout the sample than is the case in (A), and there is no sulfide rim on the pellet surface. (Scale bar = 200 μm.)

TABLE I

PHASES FOUND IN SAMPLES FROM THE $Mn_{0.394}$-$Ti_{0.606}$-O-S SYSTEM AT 1485°K

$\log f_{S_2}$	$\log f_{O_2}$	M_2O_3	M_3O_5	MO_{2-x}	α-MS
−4.133	−12.646	P[a]		P	?
−3.946	−12.654	P		P	P
−3.829	−12.679			P	P
−4.429	−13.034	P		P	
−4.292	−13.059	P		P	P
−4.103	−13.034			P	P
−3.872	−13.038			P	P
−4.437	−13.288	P		P	
−4.443	−13.445			P	P
−5.322	−13.560	P		P	
−5.051	−13.616	P	P	P	
−4.988	−13.621	P		P	
−4.887	−13.601	P	T	P	
−4.749	−13.598	P	P		
−4.640	−13.612			P	P
−4.546	−13.618			P	P
−4.469	−13.601			P	P
−4.877	−13.738	P	P		
−5.638	−13.856	P	P		
−5.450	−13.849	P	P		
−5.272	−13.907	P	P		
−5.081	−13.906	P	P		
−4.967	−13.886		P		P
−4.883	−13.910		P	P	P
−4.777	−13.924			P	P
−5.423	−14.139	P	P		
−5.343	−14.121	P	P		
−5.218	−14.127		P		P
−5.430	−14.216	P	P		T
−5.718	−14.342	P	P		
−5.577	−14.325	P	P		T
−5.473	−14.287		P		P
−5.402	−14.379		P		P
−5.202	−14.319		P		P
−5.125	−14.365			P	P
−5.710	−14.647		P		P
−5.502	−14.596		P		P
−5.427	−14.657		P		P
−5.341	−14.649		P	P	P
−5.528	−14.925		P		P
−5.409	−14.926		P	P	P
−5.326	−14.934			P	P
−5.224	−14.937			P	P
−4.998	−14.885			P	P
−5.722	−15.066		P		P
−5.712	−15.347		P		P
−5.609	−15.330		P	P	P
−5.517	−15.347			P	P
−5.422	−15.352			P	P
−5.748	−16.055		P		P
−5.658	−15.960		P	P	P
−5.524	−15.954		P	P	P
−5.434	−16.000		T	P	P

[a] Major phases are indicated by the letter P; phases that occur in trace amounts but show sufficient lines to enable positive identification are indicated by the letter T. Where there are not enough lines to identify a phase without doubt, a question mark is used.

boundary, between the assemblages $M_2O_3 + MO_{2-x}$ and $MO_{2-x} + \alpha$-MnS, and there were no fugacities at which the M_3O_5 was an equilibrium phase. However, the X-ray pattern of samples heated once at low sulfur fugacities and with oxygen fugacities less than 10^{-16} atm showed M_3O_5 to be present

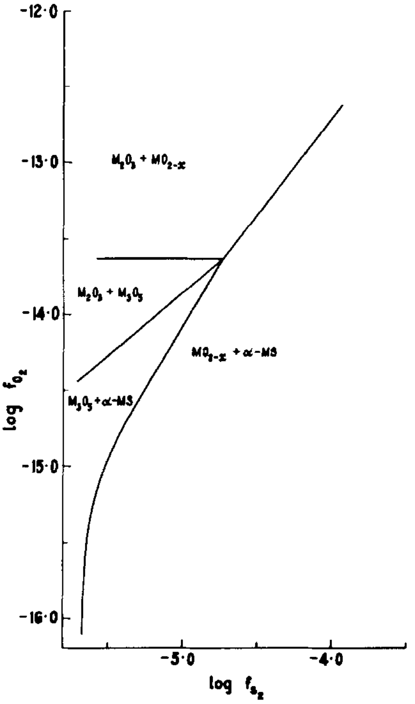

FIG. 2. The equilibrium phase assemblages and phase boundaries for the system $Mn_{0.394}$-$Ti_{0.606}$-O-S at 1485°K on a plot of log f_{S_2} vs log f_{O_2}.

TABLE II

PHASES FOUND IN SAMPLES FROM THE $Mn_{0.394}$–$Ti_{0.606}$–O–S SYSTEM AT 1380°K

$\log f_{S_2}$	$\log f_{O_2}$	M_2O_3	MO_{2-x}	α-MS
−6.248	−15.380	P	P	
−6.225	−15.568	P	P	
−6.270	−15.790	P	P	
−6.208	−15.894	P	P	P
−6.203	−16.023	T	P	P
−6.218	−16.205		P	P
−6.310	−17.145		P	P
−5.778	−14.233	P	P	
−5.800	−15.034	P	P	
−5.809	−15.213	P	P	
−5.827	−15.384	P	P	T
−5.978	−15.388	P	P	
−5.830	−15.538	P	P	P
−5.854	−15.616	P	P	P
−5.822	−15.906		P	P
−5.822	−16.210		P	P
−6.012	−17.128		P	P
−5.367	−14.483	P	P	
−5.402	−14.812	P	P	
−5.404	−15.012	P	P	P
−5.419	−15.211	P	P	P
−4.884	−14.020	P	P	
−4.935	−14.262	P	P	
−4.982	−14.478	P	P	P
−4.983	−14.583	P	P	P
−4.986	−14.696		P	P

with the phases MO_{2-x} and α-MnS. From this and the discussion of nonequilibrium (Sect. 3.3) it can be concluded that at the sulfur fugacities below those experimentally achieved there would be an equilibrium phase assemblage M_3O_5 + α-MnS. A plausible set of boundaries to accommodate this assemblage is shown by the broken lines in Fig. 3. The location of the boundary where the phases $M_3O_5 + MO_{2-x}$ + α-MnS are in equilibrium was estimated using the results of a study parallel to that reported here for the five-component system $Fe_{0.394-x}$–Mn_x–$Ti_{0.606}$–O–S (to be published). The intersection of this proposed boundary with that experimentally determined defines the maximum oxygen fugacity for stability of the M_3O_5 phase at 1380°K to be $10^{-15.8}$ atm.

The results of equilibration and quench experiments in the $Mn_{0.394}$–$Ti_{0.606}$–O system at 1380°K, given in Table III, show that the three oxides M_2O_3, M_3O_5, and MO_{2-x} are in equilibrium at $f_{O_2} = 10^{-15.75}$ atm. This result is consistent with the proposed set of boundaries and suggests that the boundary where the three oxide phases are in equilibrium is independent of sulfur fugacity as is drawn in Fig. 3.

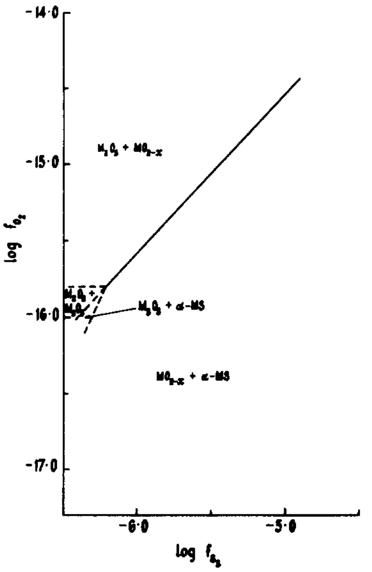

FIG. 3. The equilibrium phase assemblages and phase boundaries for the system $Mn_{0.394}$–$Ti_{0.606}$–O–S at 1380°K on a plot of $\log f_{S_2}$ vs $\log f_{O_2}$.

TABLE III

PHASES FOUND IN SAMPLES FROM THE $Mn_{0.394}$–$Ti_{0.606}$–O SYSTEM AT 1380°K

$\log f_{O_2}$	M_2O_3	M_3O_5	MO_{2-x}
−15.708[a]	P		P
−15.708[b]	P	?	P
−15.805[c]	P	P	T
−15.805[b]	P	P	?
−15.891[b]	P	P	?

[a] Starting material contained a mixture of M_2O_3 and M_3O_5 formed by twice heating a mixture of Mn_2O_3 and TiO_2 at $\log f_{O_2} = -15.805$.

[b] Starting material contained a mixture of Mn_2O_3 and TiO_2.

[c] Starting material contained a mixture of M_2O_3, M_3O_5, and MO_{2-x} formed by twice heating a mixture of Mn_2O_3 and TiO_2 at $\log f_{O_2} = -15.966$.

4.3. Comparison of the Results at 1485 and 1380°K

The results at the two temperatures give rise to consistent phase diagrams. The effect of lowering the temperature is to shift phase boundaries to higher values of both the gas ratios H_2/H_2S and H_2/CO_2. This is shown in Fig. 4 where the phase diagrams are presented together on a plot of log H_2/H_2S vs log H_2/CO_2. The shift to higher gas ratios is the reason why it was not possible to observe experimentally the M_3O_5 as an equilibrium phase at 1380°K.

The experimental results of this work may be compared with previously published data at intermediate temperatures by using linear plots of the logarithms of the equilibrium constant against reciprocal temperature. For the boundaries where $M_2O_3+M_3O_5+MO_{2-x}$ are in equilibrium the plot of log f_{O_2} vs $1/T$ was used to estimate a figure of log $f_{O_2}=-13.88$ for the boundary at 1473°K. Within the combined experimental uncertainties this value agrees with that of log $f_{O_2}=-13.95$ given by Grey *et al.* (*2*).

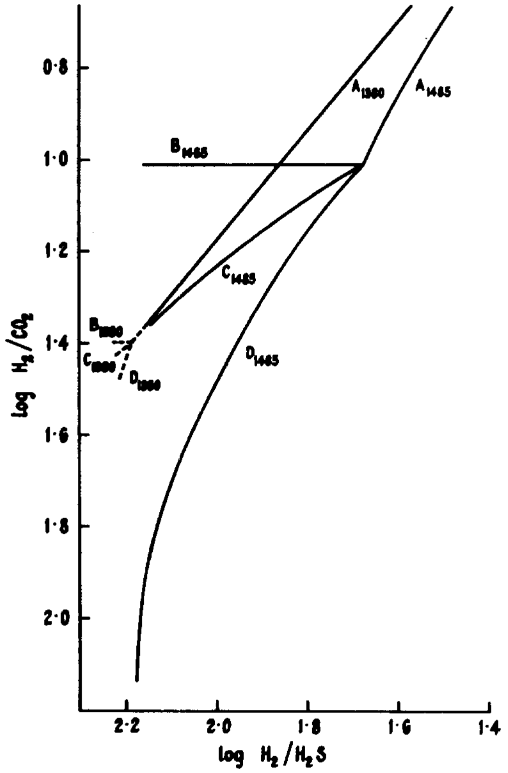

FIG. 4. The equilibrium phase boundaries for the $Mn_{0.394}$–$Ti_{0.606}$–O–S system at 1380 and 1485°K shown together on a plot of log H_2/H_2S vs log H_2/CO_2. The boundaries are lettered with the temperature (in °K) shown as a subscript. A shows the three-phase equilibrium $M_2O_3+MO_{2-x}+\alpha$-MnS. B shows the three-phase equilibrium $M_2O_3+M_3O_5+MO_{2-x}$. C shows the three-phase equilibrium $M_2O_3+M_3O_5+\alpha$-MnS. D shows the three-phase equilibrium $M_3O_5+MO_{2-x}+\alpha$-MnS.

5. Summary

Equilibrium phase data are presented for the system $Mn_{0.394}$–$Ti_{0.606}$–O–S at 1485 and 1380°K. These data are presented on two self-consistent log f_{S_2} vs log f_{O_2} isothermal phase diagrams which are in agreement with previously published data for the subsystems Mn–Ti–O, Mn–O–S, Mn–S, and Ti–O–S. The oxygen fugacity predicted by the data for the three-phase equilibrium $M_2O_3+M_3O_5+MO_{2-x}$ at 1473°K agrees with the published value for the same boundary in the Mn–Ti–O subsystem.

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