Experimental Study of Phase Equilibria in the MnO–SiO₂–“TiO₂”–“Ti₂O₃” System

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Phase equilibria and liquidus surface in the system MnO–SiO₂–“TiO₂”–“Ti₂O₃” under controlled atmosphere have been investigated in the temperature range from 1 200 to 1 500°C and in the range of log pO_2 from -7.6 ($pCO/pCO_2=1$) to -16.6 (C–CO equilibration). High-temperature equilibration, quenching and electron probe microanalysis (EPMA) were employed to obtain equilibrium compositions of liquid and several solid solutions. The following primary phases have been observed; molten oxide, manganosite (MnO), rutile (TiO₂), tridymite and cristobalite (SiO₂), tephroite (Mn₂SiO₄), rhodonite (MnSiO₃), spinel (Mn₂TiO₄–MnTi₂O₄), pyrophanite (MnTiO₃–Ti₂O₃) and pseudobrookite (“MnTi₂O₅”–Ti₃O₅) solid solutions. By decreasing oxygen partial pressure, homogeneous liquid oxide area becomes smaller. No ternary compounds or ternary solid solutions were observed.

KEY WORDS: MnO–SiO₂–“TiO₂”–“Ti₂O₃” system; phase equilibria; oxygen partial pressure; spinel; pyrophanite; pseudobrookite; tephroite; rhodonite; oxide metallurgy; inclusion.

1. Introduction

Manganese and titanium are both transition metals and they have several valences in oxides; Mn²⁺, Mn³⁺, Mn⁴⁺, Ti²⁺, Ti³⁺ and Ti⁴⁺ depending on temperature, oxygen partial pressure and phase in which they reside. Although their proportions in oxide systems are still not clear, it is acceptable that Mn²⁺ is predominant under moderate reducing condition among several valences of manganese. On the other hand, Ti⁴⁺ is stable under strongly reducing condition which can be achieved in usual experimental technique.¹⁾

Phase relations in the MnO–SiO₂–“TiO₂”–“Ti₂O₃” quaternary system are still unclear. These systems are main system of non-metallic inclusions in steel product. For example, inclusions in HSLA (High Strength Low Alloyed) steel consist mainly MnO–TiO_x–SiO₂ and these act as nucleation site of intragranular ferrite transformation.^{2,3)}

The purpose of the present study is to experimentally determine phase equilibria and liquidus surfaces of the MnO–SiO₂–“TiO₂”–“Ti₂O₃” quaternary system under various oxygen partial pressures and temperatures. This study is a part of thermodynamic and experimental study on the MnO–SiO₂–“TiO₂”–“Ti₂O₃” system. Experimental study in the MnO–“TiO₂”–“Ti₂O₃” system is presented in previous article by the authors.⁴⁾ Thermodynamic modeling in this system will be followed subsequently.^{5,6)}

2. Previous Works

Previous studies for the MnO–“TiO₂”–“Ti₂O₃” and

MnO–SiO₂ systems are critically reviewed by the present authors,⁴⁾ and Eriksson and Pelton,⁷⁾ Eriksson *et al.*⁸⁾ Several possible phases in the MnO–SiO₂–“TiO₂”–“Ti₂O₃” system is shown in Fig. 1.

Sub-solidus in the MnO–SiO₂–“TiO₂”–“Ti₂O₃” system has not been well known. Smolensky⁹⁾ reported liquidus and solidus in the pseudobinary system MnSiO₃–MnTiO₃ by thermal analysis. He reported that an extensive solid solution was observed from 0 to 61.7 mol% of MnSiO₃ in MnTiO₃ and this solid solution decomposes below 1 050°C in MnSiO₃ and MnTiO₃. Later, however, O'Neill measured phase relations in the Mn–Fe–Ti–Si–O system at 1 100°C by employing chemical equilibration followed by EPMA.¹⁰⁾ He reported that Si did not dissolve in ilmenite (MnTiO₃) structure while small amount of Ti, in terms of $n_{Ti}/(n_{Ti}+n_{Si})=0.06$, was observed in Mn₂SiO₄ with olivine

Fig. 1. Compositional tetrahedron of the MnO–SiO₂–“TiO₂”–“Ti₂O₃” system.

structure at 1 100°C.

Liquidus compositions in the MnO–SiO₂–“TiO₂” system were measured by Amitani *et al.*¹⁾ at 1 500°C under CO/CO₂ atmosphere ($p_{O_2}=2.3\times10^{-6}$ atm). They employed chemical equilibrium with saturating pellets followed by wet chemical analysis of liquid slag. They¹⁾ also measured liquidus in the MnO–SiO₂–“Ti₂O₃” system at 1 300°C and 1 500°C under Ar atmosphere with graphite holder. Ito *et al.*¹¹⁾ reported liquidus in the MnO–SiO₂–“TiO₂” system at 1 400°C under Ar atmosphere using same method of Amitani *et al.* Tabaian *et al.*¹²⁾ measured SiO₂ liquidus compositions in the MnO–SiO₂–TiO_x system in equilibrium with Mn–Si–Ti molten alloy in the silica crucible under Ar atmosphere at 1 300°C and 1 400°C. All these measurements can be categorized as “primary phase saturating method”. Except for the liquidus of MnO–SiO₂–“TiO₂” at 1 500°C by Amitani *et al.*,¹⁾ actual oxygen partial pressures were not exactly known.

Since stability of titanium containing oxide could be affected by oxygen partial pressure, its careful control during experiment is very important to understand phase equilibria of the system. Most experimental reports above mentioned did not specify the actual oxygen partial pressure. Information on solid solutions in MnO–SiO₂–“TiO₂”–“Ti₂O₃” system is rare and most investigators did not consider possible solid solutions during their measurement of liquidus in the system. Further careful experimental studies are, therefore, required to provide accurate phase diagram and develop thermodynamic database. The aim of the present study is to provide new experimental data on the phase equilibria in the MnO–SiO₂–“TiO₂”–“Ti₂O₃” system including liquidus and sub-solidus phase relations. This newly provided experimental data will be used by the present authors for thermodynamic optimization to develop a consistent thermodynamic data set.^{5,6)}

3. Experimental

The general experimental procedures used in the present study are high temperature equilibration, quenching and followed by electron probe X-ray microanalysis (EPMA). The present investigation was carried out in a controlled atmosphere using CO/CO₂ gas mixture or C/CO equilibration. Initial oxide mixtures were prepared from reagent grade oxides powders. The MnO (99.9 mass%, Kosundo), SiO₂ (99.9 mass%, Kosundo) and TiO₂ (99.9 mass%, Kosundo) were dried at 110°C, and weighed in the desired proportions. Those powders were then mixed by ball-milling under ethyl alcohol for 12 h and dried at 200°C in air.

Each sample was weighed from 0.5 to 1.0 g, pelletized and placed in a boat made from thin molybdenum foil (0.07–0.1 mm thick) or a platinum crucible (diameter 10 mm×height 10 mm×thickness 0.1 mm) depending on temperature and oxygen partial pressure during experiment. The samples were then placed in the hot zone of a recrystallized alumina tube equipped for gas-mixing, which is tightly sealed by water-cooled brass end cap. A vertical MoSi₂ resistance furnace was used for heating samples. Temperatures were controlled to $\pm 2^\circ\text{C}$ using a B type Pt/Rh thermocouple placed externally to the alumina tube,

and were continuously monitored throughout the runs using another B type thermocouple placed immediately above the sample.

Oxygen partial pressure was controlled using a flowing CO/CO₂ gas mixture or CO with graphite holder. Moistures in CO, CO₂ gases were removed by passing over CaSO₄ and CO₂ impurities in CO gas was purified by passing sodium hydroxide. In former case ($p_{CO}/p_{CO_2}=1$) in the temperature range between 1 200 to 1 500°C, the stable form of Ti oxide is rutile (TiO_{2- δ}). On the other hand, under the condition of C/CO equilibration, rutile reduces to Ti₃O₅ (below 1 457°C) and to Ti₂O₃ (above 1 457°C).⁷⁾ Experiments in the present study were conducted at those two different gas conditions ($p_{CO}/p_{CO_2}=1$ and C/CO equilibration) to reveal effect of oxygen partial pressure on the phase equilibria in the MnO–SiO₂–“TiO₂”–“Ti₂O₃” system.

Total flow rate was 400 ml/min and the volume ratio of each gas was controlled. Mass flow controllers for CO and CO₂ gas were preliminarily calibrated using soap-bubble-column-technique. Oxygen partial pressures were monitored in some runs using an yttria-stabilized zirconia sensor with air as the reference.

After equilibration, runs were terminated by rapid quenching the sample into ice water. Whole part of each sample was then mounted in epoxy resin, and polished for examination by optical microscopy and electron microprobe analysis.

The electron microprobe analysis was carried out on a JEOL 8100-JXA in the WDS mode. Operating conditions were 15 kV accelerating voltage, 20 nA probe current. Data were reduced using ZAF correction routine. For standards, pure MnO, SiO₂ (quartz) and TiO₂ (rutile) crystals supplied from JEOL Ltd. were used for manganese, silicon and titanium concentrations. Additionally, the calibration was also checked using some larger crystals of MnTiO₃. The MnTiO₃ sample was prepared from commercially available MnTiO₃ powder (99.9 mass%, Kosundo). The powders were made into pellet under a pressure of 200 MPa. The prepared pellet was sintered at 1 400°C under $p_{CO}/p_{CO_2}=9$ for 3 d. The compositions of samples were measured by EPMA as described above (using MnO and TiO₂ as standard crystals). Measured cationic ratio ($n_{Ti}/(n_{Mn}+n_{Ti})$) was 0.501 ± 0.002 so that pure MnO and pure TiO₂ seem suitable as standards in the present study.

At least five analyses were made of each phase in a sample and averaged. The STD of the measurement was within 1 mass% in most cases. Because the liquid phase in the MnO–SiO₂–TiO_x with low silica content was very fluid and hence gave rise to the formation of large numbers of precipitates, even during rapid quenching, EPMA analysis were carried out more than ten analyses with a broad probe size ($\sim 30\ \mu\text{m}$), as done by Roberts and Muan in the similar systems NiO–SiO₂–TiO₂.¹³⁾ When Mo was used for sample holder, Mo dissolution into the oxide was checked during EPMA measurement. At high temperature with high oxygen partial pressure, noticeable amount of Mo dissolution into molten oxide was observed. In that case, the sample was rejected for further analysis and platinum crucible was used as container.

Achievement of equilibrium has been confirmed by same final phases and compositions with different starting com-

Fig. 2. Representation of experimental data of the MnO-SiO₂-“TiO₂”-“Ti₂O₃” system onto MnO-SiO₂-“TiO₂” plane.

position, well grown facets of crystals. At least one common final equilibrium assemblages starting from different initial compositions in each run were confirmed.

The EPMA provides information only on the metal cation content present in a phase and does not distinguish the proportion of the cations of the same element with different valences. In the investigated oxides, titanium is present as Ti⁴⁺ and Ti³⁺ (while all manganese could be assumed in divalent state). In the present study, for construction of the phase diagram in the quaternary for MnO-SiO₂-“TiO₂”-“Ti₂O₃”, all the titanium was recalculated to the Ti⁴⁺ oxidation state. This is equivalent to projecting the phase composition from the oxygen corner of the MnO-SiO₂-“TiO₂”-“Ti₂O₃” quaternary onto the MnO-SiO₂-“TiO₂” surface. This projection is shown by an arrow in Fig. 2, where the compositions of the real oxide are schematically illustrated with a dark surface.

4. Results

Details of the compositions of the liquid and the solid phases determined in the present studies for the MnO-SiO₂-“TiO₂”-“Ti₂O₃” system are given in Table 1.

Under the conditions investigated in the present study, the following phases have been observed: molten oxide, manganosite (MnO rich s.s.), rutile (TiO₂ rich s.s.), spinel (Mn₂TiO₄-MnTi₂O₄), pyrophanite (MnTiO₃-Ti₂O₃), pseudobrookite (“MnTi₂O₅”-Ti₃O₅) solid solutions, tridymite and cristobalite (SiO₂), tephroite (Mn₂SiO₄) and rhodonite (MnSiO₃).

The backscattered electron images of typical microstructures in the system MnO-SiO₂-“TiO₂”-“Ti₂O₃” are shown in Figs. 3 through 8. Figure 3 illustrates the microstructures of the SiO₂ and rutile (TiO₂) crystalline phases in equilibration with liquid oxide under controlled CO/CO₂ gas mixture. In Fig. 4, globular manganosite (MnO) and irregular shape of spinel (Mn₂TiO₄) with molten oxide are shown. Pyrophanite was observed as platelike-form or blocky-form, as shown in Fig. 5. Equilibrium morphologies of rhodonite in equilibrium with SiO₂ and molten oxide are seen in Fig. 6. Sub-solidus phase equilibria among rutile, SiO₂ and pyrophanite are presented in Fig. 7. Figure 8 shows equilibrium morphology of pseudobrookite in equilibrium with molten oxide. Each solid phase was identified on the basis of the atomic compositions obtained from EPMA.

Table 1. Results of experiments on the system MnO-SiO₂-“TiO₂”-“Ti₂O₃” in equilibrium with various gas conditions.

T (°C)	CO/CO ₂ (cm ³ /min)	log <i>p</i> O ₂ (Pa) [†]	Phases in Equilibrium	Phase Name	Equilibrium Composition (mass percent)		
					MnO	"TiO ₂ "	SiO ₂
Equilibria in equilibrium with gas mixture of <i>p</i> CO/ <i>p</i> CO ₂ = 1							
1500	200/200	-2.63	L + M	L	71.7	9.8	18.6
				M	99.5	0.5	0.0
1500	200/200	-2.63	L + M	L	68.6	23.6	7.8
				M	98.2	1.8	0.0
1500	200/200	-2.63	L + M	L	74.6	2.7	22.8
				M	99.8	0.2	0.0
1500	200/200	-2.63	L + M	L	66.1	31.7	2.2
				M	97.5	2.4	0.0
1500	200/200	-2.63	L + S	L	45.8	11.6	42.6
				S	0.7	0.8	98.5
1500	200/200	-2.63	L + S	L	48.0	5.4	46.5
				S	0.7	0.4	98.9
1500	200/200	-2.63	L + S	L	43.1	19.9	37.0
				S	0.5	1.2	98.2
1500	200/200	-2.63	L + S	L	29.4	53.2	17.4
				S	0.2	3.1	96.7
1500	200/200	-2.63	L + S	L	34.8	42.8	22.4
				S	0.3	2.4	97.3
1500	200/200	-2.63	L + S + R	L	28.2	54.1	17.7
				S	0.2	3.2	96.6
				R	0.5	99.1	0.3
1500	200/200	-2.63	L + S + R	L	28.5	53.6	17.9
				S	0.2	3.5	96.4
				R	0.1	99.6	0.3
1500	200/200	-2.63	L + R	L	28.8	57.5	13.6
				R	0.0	99.8	0.2
1500	200/200	-2.63	L + R	L	29.4	66.0	4.6
				R	0.1	99.9	0.1
1400	200/200	-3.61	L + M	L	70.4	11.6	18.0
				M	99.5	0.5	0.0
1400	200/200	-3.61	L + M	L	66.8	24.7	8.4
				M	98.1	1.9	0.0
1400	200/200	-3.61	L + M	L	72.6	2.7	24.7
				M	99.8	0.2	0.0
1400	200/200	-3.61	L + M + SP	L	66.4	25.7	7.9
				M	98.2	1.8	0.0
				SP	63.8	36.2	0.0
1400	200/200	-3.61	L + S	L	50.9	6.1	43.1
				S	0.8	0.4	98.8
1400	200/200	-3.61	L + S	L	44.2	20.2	35.6
				S	0.4	1.2	98.4
1400	200/200	-3.61	L + S	S	37.8	38.7	23.5
				T	0.4	2.1	97.5
1400	200/200	-3.61	L + R + S	L	34.1	46.7	19.1
				S	0.3	2.5	97.2
				R	0.1	99.7	0.2
1400	200/200	-3.61	L + R + S	L	34.1	46.7	19.2
				R	0.1	99.7	0.2
				S	0.2	2.5	97.3
1400	200/200	-3.61	L + R	L	33.4	49.3	17.3
				R	0.1	99.7	0.2
1400	200/200	-3.61	L + R	L	33.9	55.9	10.2
				R	0.1	99.7	0.2
1400	200/200	-3.61	L + IL + R	L	33.0	65.4	1.6
				IL	44.6	55.4	0.0
				R	0.0	99.9	0.0
1400	200/200	-3.61	L + IL	L	38.4	54.9	6.7
				IL	45.7	54.3	0.0
1400	200/200	-3.61	L + IL	L	45.6	46.0	8.3
				IL	45.7	54.3	0.0
1400	200/200	-3.61	L + SP + IL	L	57.9	37.4	4.7
				SP	62.4	37.6	0.0
				IL	46.4	53.5	0.1
1400	200/200	-3.61	L + SP + IL	L	58.6	36.4	5.0
				SP	62.6	37.2	0.2
				IL	46.8	53.1	0.1
1400	200/200	-3.61	L + SP	L	60.1	33.6	6.3
				SP	63.2	36.8	0.0

Table 1. (Continued)

1400	200/200	-3.61	L + SP	L	65.3	27.4	7.3	1500	C/CO	-10.71	L + S + IL	S	0.2	0.9	98.8
				SP	63.6	36.3	0.0					IL	35.4	33.1	31.6
1300	200/200	-4.72	L + M	L	68.8	11.6	19.6					S	7.5	92.5	0.0
				M	99.5	0.5	0.0	1500	C/CO	-10.71	L + M	L	0.1	1.0	98.9
1300	200/200	-4.72	L + M + OL	L	70.0	7.9	22.1					L	67.8	18.0	14.1
				M	99.6	0.4	0.0	1500	C/CO	-10.71	L + IL	M	97.5	2.5	0.0
				OL	70.1	0.3	29.6					L	47.8	33.8	18.4
1300	200/200	-4.72	L + S	L	52.1	6.0	42.0	1500	C/CO	-10.71	L + IL	IL	18.6	81.4	0.0
				S	0.8	0.4	98.8					L	39.8	36.2	23.9
1300	200/200	-4.72	L + S	L	47.0	20.5	32.5	1400	C/CO	-11.12	L + S	IL	12.5	87.5	0.0
				S	0.4	1.0	98.5					L	48.1	11.5	40.4
1300	200/200	-4.72	L + S + R	L	42.0	34.5	23.6	1400	C/CO	-11.12	L + S	S	0.6	0.4	99.0
				S	0.5	2.1	97.4					L	50.3	5.6	44.1
				R	0.1	99.8	0.1	1400	C/CO	-11.12	L + S + IL	S	0.7	0.2	98.9
1300	200/200	-4.72	L + S + R	L	41.5	35.2	23.3					L	40.4	26.0	33.6
				S	0.3	1.9	97.9	1400	C/CO	-11.12	L + S + IL	S	0.2	1.0	98.8
				R	0.1	99.8	0.1					IL	9.6	90.3	0.1
1300	200/200	-4.72	L + IL + R	L	39.6	42.9	17.5	1400	C/CO	-11.12	L + S + IL	L	41.5	25.0	33.5
				IL	45.1	54.8	0.0					S	0.3	0.9	98.8
				R	0.0	99.8	0.1	1400	C/CO	-11.12	L + SP	IL	10.9	89.1	0.0
1300	200/200	-4.72	L + IL	L	50.4	27.8	21.8					L	53.2	26.3	20.5
				IL	46.7	53.2	0.1	1400	C/CO	-11.12	L + M	SP	45.4	54.6	0.1
1300	200/200	-4.72	L + SP	L	63.5	20.2	16.3					L	69.5	10.6	19.9
				SP	63.5	36.5	0.0	1400	C/CO	-11.12	L + SP	M	98.1	1.8	0.0
1300	200/200	-4.72	L + M + OL	L	70.5	8.5	21.0					L	55.3	22.8	21.9
				M	99.6	0.3	0.1	1400	C/CO	-11.12	L + M + SP	SP	46.3	53.7	0.0
				OL	70.2	0.7	29.2					L	61.8	21.1	17.1
1300	200/200	-4.72	L + OL	L	62.5	3.3	34.2					M	98.0	2.0	0.1
				OL	70.0	0.1	29.9	1400	C/CO	-11.12	L + SP	SP	53.1	46.9	0.0
1300	200/200	-4.72	L + OL	L	63.5	8.6	27.9					L	57.5	20.8	21.7
				OL	70.5	0.4	29.1	1400	C/CO	-11.12	L + SP + IL	SP	47.4	52.5	0.0
1300	200/200	-4.72	L + IL	L	42.2	38.6	19.2					L	49.0	29.3	21.7
				IL	46.0	54.0	0.0					SP	41.9	58.1	0.0
1300	200/200	-4.72	L + IL	L	52.4	24.8	22.8	1400	C/CO	-11.12	L + IL	IL	20.3	79.7	0.0
				IL	46.5	53.5	0.0					L	50.3	25.3	24.4
1300	200/200	-4.72	L + M + SP	L	68.6	13.0	18.4	1300	C/CO	-11.59	L + S	IL	16.1	83.9	0.0
				M	98.7	1.3	0.0					L	47.7	12.4	40.0
				SP	63.8	36.1	0.1	1300	C/CO	-11.59	L + S	S	0.6	0.5	98.9
1300	200/200	-4.72	L + M + SP	L	67.6	15.9	16.5					L	52.7	6.0	41.2
				M	99.2	0.8	0.0	1300	C/CO	-11.59	L + PB + S	S	0.9	0.3	98.9
				SP	64.3	35.6	0.1					L	46.7	18.6	34.7
1200	200/200	-5.99	L + RH + S	L	49.6	16.7	33.7					PB	6.6	93.6	0.1
				RH	53.8	1.0	45.2	1300	C/CO	-11.59	L + PB + S	S	0.4	1.1	98.5
				S	0.8	0.6	98.6					L	45.3	19.4	35.3
1200	200/200	-5.99	L + RH + S	L	49.7	17.1	33.2					PB	6.2	93.7	0.1
				RH	54.4	1.0	44.5	1300	C/CO	-11.59	L + M + SP	S	0.3	1.1	98.5
				S	0.9	0.8	98.3					L	68.9	9.7	21.4
1200	200/200	-5.99	L + S + IL	L	49.8	16.4	33.8					M	97.3	2.6	0.1
				S	0.5	0.8	98.6	1300	C/CO	-11.59	L + M + OL	SP	58.1	41.4	0.5
				IL	46.6	53.3	0.1					L	70.7	7.6	21.7
1200	200/200	-5.99	IL + R + S	IL	45.9	53.7	0.6					M	98.6	1.4	0.0
				R	0.4	99.4	0.2	1300	C/CO	-11.59	L + OL	OL	71.1	0.7	28.3
				S	0.6	2.2	97.2					L	64.3	3.4	32.3
1200	200/200	-5.99	IL + R + S	IL	46.3	53.7	0.0	1300	C/CO	-11.59	L + SP	OL	70.7	0.2	29.1
				R	0.4	99.5	0.1					L	66.3	10.8	22.9
				S	0.6	2.2	97.2	1300	C/CO	-11.59	L + SP	SP	56.2	43.8	0.0
1200	200/200	-5.99	L + IL	L	50.4	16.3	33.3					L	62.4	12.3	25.3
				IL	46.7	53.3	0.0	1300	C/CO	-11.59	L + SP	SP	52.2	47.8	0.0
1200	200/200	-5.99	L + IL + OL	L	56.4	12.1	31.5					L	57.1	14.6	28.3
				IL	47.1	52.9	0.0	1300	C/CO	-11.59	L + IL	SP	47.3	52.7	0.0
				OL	70.4	0.7	28.9					L	49.0	24.8	26.2
1200	200/200	-5.99	L + IL + OL	L	56.6	12.6	30.8	1300	C/CO	-11.59	L + IL	IL	27.5	72.5	0.0
				IL	47.2	52.8	0.0					L	50.3	24.8	25.0
				OL	70.3	0.7	29.0	1300	C/CO	-11.59	L + IL + PB	IL	27.1	72.9	0.0
1200	200/200	-5.99	L + RH	L	49.6	16.8	33.6					L	49.3	24.0	26.7
				RH	54.6	0.9	44.4	1300	C/CO	-11.59	L + PB	IL	18.9	81.0	0.1
												PB	10.4	89.6	0.0
								1300	C/CO	-11.59	L + PB	L	48.7	21.7	29.7
												PB	9.2	90.6	0.1
1500	C/CO	-10.71	L + S	L	43.8	12.7	43.4	1300	C/CO	-11.59	L + OL	L	63.8	5.2	31.0
				S	0.4	0.4	99.2					OL	70.3	0.3	29.4
1500	C/CO	-10.71	L + S	L	41.2	20.1	38.7								
				S	0.5	0.6	98.9								
1500	C/CO	-10.71	L + S + IL	L	33.7	32.4	33.9								
				IL	7.4	92.6	0.0								

Equilibria in equilibrium with C(s)/CO(g)

 M: Manganosite, SP: Spinel, IL: Pyrophanite, PB: Pseudobrookite, R: Rutile, L: Liquid oxide, S: SiO₂ (cristobalite and tridymite), OL: Mn₂SiO₄, RH: MnSiO₃
 †1 Pa = 1/101325 atm

Fig. 3. Microstructure of SiO_2 and rutile in equilibrium with molten oxide. Legend: L=molten oxide, S= SiO_2 , R=rutile s.s. The specimen was held at 1300°C under $0.5\text{CO}-0.5\text{CO}_2$ atmosphere with initial composition of 20mass%MnO+50mass% TiO_2 +30mass% SiO_2 .

Fig. 6. Microstructure of SiO_2 and rhodonite in equilibrium with molten oxide. Legend: L=molten oxide, S= SiO_2 , RH=rhodonite. The specimen was held at 1300°C under $0.5\text{CO}-0.5\text{CO}_2$ atmosphere with initial composition of 40mass%MnO+10mass% TiO_2 +50mass% SiO_2 .

Fig. 4. Microstructure of manganosite and spinel in equilibrium with molten oxide. Legend: L=molten oxide, SP=spinel s.s., M=manganosite s.s. The specimen was held at 1300°C under $0.5\text{CO}-0.5\text{CO}_2$ atmosphere with initial composition of 73mass%MnO+22mass% TiO_2 +5mass% SiO_2 .

Fig. 7. Microstructure of SiO_2 , pyrophanite and rutile. Legend: S= SiO_2 , IL=pyrophanite s.s., R=rutile s.s. The specimen was held at 1200°C under $0.5\text{CO}-0.5\text{CO}_2$ atmosphere with initial composition of 20mass%MnO+40mass% TiO_2 +40mass% SiO_2 .

Fig. 5. Microstructure of pyrophanite in equilibrium with molten oxide. Legend: L=molten oxide, IL=pyrophanite s.s. The specimen was held at 1200°C under $0.5\text{CO}-0.5\text{CO}_2$ atmosphere with initial composition of 50mass%MnO+30mass% TiO_2 +20mass% SiO_2 .

Fig. 8. Microstructure of pseudobrookite in equilibrium with molten oxide. Legend: L=molten oxide, PB=pseudobrookite s.s. The specimen was held at 1300°C under C/CO atmosphere with initial composition of 26.5 mass% MnO+60 mass% TiO_2 +13.5 mass% SiO_2 .

5. Discussion

Previous studies of phase diagram measurement^{1,11,12)} have been carried out by “primary phase saturating method” as mentioned. In this method, equilibrium compositions of molten oxide phase were determined by wet chemical analysis after separating quenched molten oxide from the saturating pellet. Equilibrium solid phase was assumed to be a same phase with oxide pellet which was initially put in crucible. This assumption would not be right, in some cases, when the solid phase forms extensive solid solution and the MnO–SiO₂–“TiO₂”–“Ti₂O₃” system corresponds to the case. For example, Ti₂O₃ absorbs a considerable amount of Mn and forms pyrophanite solid solution.⁴⁾ Even pure Ti₂O₃ pellet was allowed to equilibrate with molten oxide which contain MnO, the final equilibrium solid phase is not pure Ti₂O₃ but (Ti,Mn)₂O₃ pyrophanite s.s. Thus, simultaneous analyses for all equilibrium phases in a sample are required to characterize phase equilibria.

On the other hand, the experimental techniques used in the present study differ from those used by previous investigators. The compositions of liquid and solid phases formed

have been directly measured after equilibration. The use of EPMA provides the equilibrium compositions of co-existing phases, either liquid or solid, simultaneously so that it is possible to measure solid solubility as well as liquid composition. This is more important in studying sub-solidus phase equilibria. Also phase identification during analysis is possible by electron microscope in back scattered electron mode. The oxygen partial pressure in equilibrium can be known by the equilibration of CO/CO₂ gas mixture or C/CO equilibration. This makes phase equilibria in the system be characterized accurately while using Ar gas does not provide the exact oxygen partial pressures. Homogeneity of particular phase can be confirmed by analyzing several positions or line analysis on the sample by using EPMA. General advantages of using EPMA in phase diagram measurement are discussed more detail by Jak *et al.*¹⁴⁾ and Jak and Hayes.¹⁵⁾

5.1. Phase Diagram of the MnO–SiO₂–“TiO₂”–“Ti₂O₃” System under $p_{\text{CO}}/p_{\text{CO}_2}=1$

Figures 9(a)–(d) show the experimentally determined liquidus compositions in the present study from 1 200 to

Fig. 9. Phase equilibrium data in the MnO–SiO₂–“TiO₂”–“Ti₂O₃” system under $p_{\text{CO}}/p_{\text{CO}_2}=1$, listed in Table 1. Legend: L=molten oxide, M=manganosite s.s., S=SiO₂, R=rutile s.s., SP=spinel s.s., IL=pyrophanite s.s., OL=tephroite (Mn₂SiO₄), RH=rhodonite (MnSiO₃).

1500°C with the previously reported data by Amitani *et al.*¹⁾ at 1300 and 1500°C, Ito *et al.*¹¹⁾ at 1400°C. Measured tie-lines by EPMA are shown as dotted lines. Liquidus lines are estimated from the experimental data. MnO–SiO₂ system contains two intermediate compounds, tephroite (Mn₂SiO₄) and rhodonite (MnSiO₃) and MnO–“TiO₂” system has spinel (Mn₂TiO₄) and pyrophanite (MnTiO₃). No intermediate compound has been reported in the SiO₂–“TiO₂” system.¹⁶⁾ Wide immiscibility was reported in SiO₂–“TiO₂” system by DeVries *et al.*¹⁶⁾ and in MnO–SiO₂ system by Glasser.¹⁷⁾ Below 1500°C, miscibility gap has not been observed in the MnO–SiO₂–“TiO₂”–“Ti₂O₃” system under $p\text{CO}/p\text{CO}_2=1$ during the present study.

No ternary compounds or ternary solid solutions were found under the conditions in the present study. SiO₂ absorbs Ti up to ~3.5 mass% at 1500°C. The solubility was found to be decreased by decreasing temperature. No Ti solubility¹⁸⁾ or extensive solid solubility^{19,20)} had been reported. However, the result of the present study is in good agreement with DeVries *et al.*¹⁶⁾ (less than 5 mass%) and recent work by Kaneko *et al.*²¹⁾ (~4.7 mass% TiO₂ at 1450°C). Si solubility in rutile and manganosite are negligible. It was also found that Si concentration in pyrophanite and spinel measured in the present study was less than STD (>~0.1 mass%). Ti dissolution into tephroite and rhodonite were also negligible (>~1.0 mass%). Wide solid solution between MnSiO₃ and MnTiO₃ reported by Smolensky⁹⁾ were never observed. Solubility of Ti in Mn₂SiO₄ observed in the present study at 1200°C was 0.68 ± 0.04 while those in the earlier study by O'Neill¹⁰⁾ was 1.5 ± 0.5 at 1100°C, in terms of mass percent of “TiO₂” in olivine. However, at the present stage, it is questionable whether Mn₂SiO₄ with olivine structure and Mn₂TiO₄ with spinel structure form extensive solid solution at lower temperature.

Phase equilibria at 1200°C were difficult to characterize because liquidus compositions in equilibrium with rhodonite+SiO₂, pyrophanite+SiO₂, pyrophanite, rhodonite were very close each other. It seems that an eutectic reaction ($L \rightarrow \text{rhodonite} + \text{pyrophanite} + \text{SiO}_2$) occurs near this composition and near 1200°C.

5.2. Phase Diagram of the MnO–SiO₂–“TiO₂”–“Ti₂O₃” System under C/CO Equilibrium

Figures 10(a)~(c) show the experimentally determined liquidus composition in the present study from 1300 to 1500°C with the previously reported data by Amitani *et al.*¹⁾ Measured tie-lines by EPMA are shown as dotted lines. Liquidus lines are estimated from the experimental data. MnO–“TiO₂”–“Ti₂O₃” system at C/CO equilibrium gas condition has spinel as intermediate solid solution while pyrophanite (extending from Ti₂O₃) and pseudobrookite (extending from Ti₃O₅) solid solutions locate in TiOx corner.⁴⁾ No intermediate compound, which is composed of SiO₂–“TiO₂”–“Ti₂O₃”, has been found in the system at this gas condition. This is in good agreement with the result of Muan who investigated SiO₂–“TiO₂”–“Ti₂O₃” systems.²²⁾ Similarly discussed in previous section, below 1500°C, no miscibility gap has been observed in the MnO–SiO₂–“TiO₂”–“Ti₂O₃” system under C/CO equilibrium gas condition during the present study.

At this gas condition, it was found that there was no no-

ticeable solubility of the third component in any solid phases. That is, Si solubility in MnO–“TiO₂”–“Ti₂O₃” solid system is negligible, *etc.*

Fig. 10. Phase equilibrium data in the MnO–SiO₂–“TiO₂”–“Ti₂O₃” system under C/CO equilibrium, listed in Table 1. Legend: L=molten oxide, M=manganosite s.s., S=SiO₂, SP=spinel s.s., IL=pyrophanite s.s., OL=tephroite (Mn₂SiO₄), PB=pseudobrookite s.s.

Distinctive change of phase equilibria in this reducing condition is shrinkage of homogeneous liquid area as seen in Fig. 11. Liquidus of manganosite and SiO_2 at low Ti oxide content are close to those at $p\text{CO}/p\text{CO}_2=1$. However, solid phases in MnO –“ TiO_2 ”–“ Ti_2O_3 ” system become more stable at this reducing condition so that liquidus boundary of spinel, pyrophanite move toward MnO – SiO_2 . Also, as observed in phase relations in the MnO –“ TiO_2 ”–“ Ti_2O_3 ” system at C/CO equilibrium gas condition,⁴⁾ pseudobrookite appears below 1400°C and form small primary phase field. This results in change of three phase equilibria from SiO_2 +molten oxide+pyrophanite (1400°C and 1500°C) to SiO_2 +molten oxide+pseudobrookite (1300°C). It should be noted that three phase equilibria, molten oxide+ SiO_2 + Ti_2O_3 as reported by Amitani *et al.*, is not exact because TiO_x (either Ti_2O_3 as pyrophanite or Ti_3O_5 as pseudobrookite) absorbs certain amount of Mn at reducing condition. Thus, exact phase relation for the three phase equilibria is molten oxide+ SiO_2 +pyrophanite s.s. (or pseudobrookite s.s.).

As discussed in the previous article for the MnO –“ TiO_2 ”–“ Ti_2O_3 ” system,⁴⁾ C/CO equilibrium gas condition is so low enough to reduce oxide to metallic form. In the previous study by the present authors, manganosite s.s was not stable at 1500°C under C/CO equilibrium condition. Thus, in Fig. 10(a), equilibrium between manganosite and molten oxide seems metastable against metallic liquid. It seems that silica in molten oxide retards reduction from oxide to metallic phase.

5.3. Comparison with Earlier Studies

It was difficult to compare phase equilibrium data in the present study directly with those in previous study¹⁾ due to different gas condition (oxygen partial pressure) employed in the studies. Liquidus compositions of SiO_2 (cristobalite and tridymite), rutile, $\text{SiO}_2/\text{TiO}_x$ (rutile, pyrophanite and pseudobrookite) co-saturation are in good agreement with the previous study¹⁾ although they did not distinguish Ti_2O_3 (pyrophanite) and Ti_3O_5 (pseudobrookite). However, liquidus compositions of manganosite at low silica region, spinel and pyrophanite show discrepancies between the present study and previous studies. This results from discrepancies in MnO –“ TiO_2 ”–“ Ti_2O_3 ” system. That is, liquidus compositions of spinel and pyrophanite in the previous studies locate in two phase regions (liquid+solid) in the view of present study. Probably, in the previous studies, prepared solid oxide pellet might break into small particles and it resulted in overestimation of molten oxide composition during chemical analysis. Appearance of pseudobrookite phase at low oxygen partial pressure was also not noticed by the earlier researchers.¹⁾ This is because exact phase equilibrium relations in the MnO –“ TiO_2 ”–“ Ti_2O_3 ” system was not reported to the researchers at that time. In the present study, phase equilibrium data in MnO – TiO_x side coincide with the result of the MnO –“ TiO_2 ”–“ Ti_2O_3 ” system by the present authors.⁴⁾

5.4. Effect of Oxygen Partial Pressure on the Phase Equilibria in the MnO – SiO_2 –“ TiO_2 ”–“ Ti_2O_3 ” System

Given that Mn^{3+} does not appear in the oxygen partial

Fig. 11. Effect of oxygen partial pressure on the 1400°C isotherm in the MnO – SiO_2 – TiO_x system. Experimental data are listed in Table 1.

pressure range employed in the present study ($\log p\text{O}_2 < -7.6$), phase equilibria in binary MnO – SiO_2 system do not change by oxygen partial pressure. Change of phase equilibria in this system by oxygen partial pressure seems strongly related with the change of phase equilibria by oxygen partial pressure in the MnO –“ TiO_2 ”–“ Ti_2O_3 ” system. Since reducing oxygen partial pressure results in increasing stability of solid phases against liquid oxide in the MnO –“ TiO_2 ”–“ Ti_2O_3 ” system, liquidus temperatures in spinel, pyrophanite primary phase field in MnO – SiO_2 –“ TiO_2 ”–“ Ti_2O_3 ” system increase. This means that homogeneous liquid area becomes smaller at reducing condition as well as primary phase fields of tephroite and rhodonite. Moreover, stoichiometry of solid phases in the MnO –“ TiO_2 ”–“ Ti_2O_3 ” system changes considerably by reducing oxygen partial pressure so that primary phase regions in MnO – SiO_2 –“ TiO_2 ”–“ Ti_2O_3 ” system also moves to TiO_x corner.

6. Conclusions

The phase relations, liquidus as well as solid solubility in several solid solutions in the MnO – SiO_2 –“ TiO_2 ”–“ Ti_2O_3 ” system have been determined experimentally under controlled atmosphere in the temperature range from 1200 to 1500°C . High-temperature equilibration under controlled atmosphere followed by EPMA was employed to measure equilibrium compositions in equilibrium phases. The following primary phases have been observed; molten oxide, manganosite (MnO), rutile ($\text{TiO}_{2-\delta}$), tridymite and cristobalite (SiO_2), tephroite (Mn_2SiO_4), rhodonite (MnSiO_3), spinel (Mn_2TiO_4 – MnTi_2O_4), pyrophanite (MnTiO_3 – Ti_2O_3) and pseudobrookite (“ MnTi_2O_5 ”– Ti_3O_5) solid solutions.

The phase equilibrium data in the present study was consistent with the phase diagram reported by the present authors in the MnO –“ TiO_2 ”–“ Ti_2O_3 ” system.⁴⁾ It was found that there was no noticeable solubility of the third component in any solid phases. That is, Si solubility in MnO –“ TiO_2 ”–“ Ti_2O_3 ” solid system is negligible, *etc.*

Decreasing oxygen partial pressure resulted in decreasing homogeneous area of molten oxide at a given temperature.

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