Phase Diagram of FeO-TiO₂-SiO₂-5%Al₂O₃ Slag (Phase Diagram of Smelting Slag of Titanium Oxide Bearing Iron Sand)

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To provide a more reliable measures of understanding ancient ironmaking process, an FeO-TiO₂-SiO₂-5%Al₂O₃ phase diagram was determined using microscopic observation, EPMA (Electron Probe Micro Analysis), XRD (X-ray Diffraction), DTA (Differential Temperature Analysis) and stepwise heating observation. Crystal phases were almost the same as predicted by a conventional phase diagram except hercynite which was identified only by XRD for many samples. Compared with the conventional FeO-TiO₂-SiO₂ phase diagram, addition of 5% Al₂O₃ decreased the temperatures of eutectic points remarkably by between 63 and 114°C.

KEY WORDS: FeO-TiO₂-SiO₂; Al₂O₃; phase diagram; DTA; ancient ironmaking; iron sand.

1. Introduction

Ancient iron making in Japan is characterized by the usage of iron sand. A great number of studies have been done based on archeological ironmaking remains. The operation parameters such as smelting temperature have been evaluated on the basis of a ternary phase diagram for the FeO-TiO₂-SiO₂ system.¹⁾ **Figure 1** shows the chemical

compositions of the slag dug from remains on the phase diagram of FeO-TiO₂-SiO₂. The compositions are divided into three regions depending on the TiO₂ content in the iron sand. Melting points of slag in high TiO₂ and low FeO region may easily exceed 1500°C based on this phase diagram. In ancient times such high temperatures could not be attained in smelting process which charcoal was used as

Fig. 1. Chemical composition of actual smelting slag from archeological remains. (Online version in color.)

Table 1. Chemical composition of smelting slag of iron sand.

TiO ₂ in iron sand	remain	T.Fe	FeO	Fe ₂ O ₃	TiO ₂	SiO ₂	Al ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O
25–30%	A	32.6	17.1	27.0	30.1	14.0	3.5	2.2	3.1	0.5	0.3
	B	32.2	32.9	8.9	29.0	16.4	3.5	2.5	3.1	0.6	0.3
	C	28.5	12.3	26.6	32.6	16.8	3.5	1.7	3.9	0.4	0.2
10–16%	D	45.7	27.7	34.2	12.0	15.1	5.4	1.0	2.3	0.5	0.2
	E	34.0	29.3	15.5	21.7	19.0	4.8	1.6	2.5	0.6	0.3
	F	37.3	36.0	12.4	16.7	20.0	5.8	2.4	1.3	1.3	0.3
	L	34.8	43.6	1.2	19.1	17.4	5.3	0.5	0.7		
≤ 6%	K	29.0	23.5	15.4	13.0	29.1	4.7	2.6	1.7	1.3	0.6
	M	41.9	45.7	8.7	10.7	21.0	6.5	2.5	0.7	1.4	0.3
	N	37.4	42.7	6.2	12.8	23.5	5.9	3.2	2.4	1.3	0.4
	O	43.3	49.1	6.4	11.1	19.3	6.4	1.9	1.2	0.3	1.2
	G	38.3	32.3	18.0	5.0	28.2	7.3	2.8	2.5	1.0	0.5
	H	48.4	57.0	5.4	5.3	18.5	5.3	2.7	0.8	0.5	0.6
	I	46.1	51.2	7.9	2.8	22.3	6.2	2.8	2.0	0.5	0.7
	J	45.0	50.5	8.0	4.0	24.6	6.6	1.7	0.7	1.4	0.4
	average						5.38	2.14	1.93	0.82	0.45

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fuel. Microscopic observation showed that these slags were solidified from molten state and the actual melting points must be lower than those estimated from the phase diagram. Examples of chemical compositions of smelting slag from iron sand are shown in **Table 1**. About 5% Al_2O_3 , 2.5% CaO and MgO , and more than 1% of $\text{Na}_2\text{O}+\text{K}_2\text{O}$ are contained and these oxides may decrease the melting point. For more reliable evaluation of the ancient smelting process, the effect of these oxides on the melting point must be considered. In this study, a phase diagram for $\text{FeO}-\text{TiO}_2-\text{SiO}_2-5\%\text{Al}_2\text{O}_3$ was determined by microscopic observation, EPMA, ordinal and high temperature XRD and DTA of slags synthesized under Fe and FeO equilibrium.

2. Experiment

2.1. Preparation of Slag

Slag compositions used for this study are shown in **Table 2** and **Fig. 2**. Fine iron powder and Fe_2O_3 powder were blended as to be $\text{Fe}_{0.975}\text{O}$ and mixed well. The mixture was pressed to pellet and packed in an iron crucible of 50 mm in diameter and 65 mm in height. $\text{Fe}_{0.975}\text{O}$ was synthesized by heating at 950°C for 16 hours in $\text{CO}-\text{CO}_2-\text{Ar}$ atmosphere of which the CO/CO_2 ratio was 38/16. The product was pulverized and used for making slag as FeO. It was confirmed that the FeO did not contain other phase by X-ray diffraction analysis. The pulverized FeO, chemical reagent

Table 2. Chemical composition of used slag and results microscopic observation and XRD.

Sample	FeO	TiO ₂	SiO ₂	Al ₂ O ₃	structure observed by microscope *1	identified phase by XRD *2
A1	40.5	45.0	9.5	5.0	needle like IL including Ps	IL●, Ps△, Hc□
A2	37.8	42.0	15.2	5.0	square shaped IL including Ps & rice ear type IL in matrix	IL●, Ps△, Hc□
A3	36.6	40.7	17.8	5.0	Ps surrounded by thin IL & rice ear type IL in matrix	IL●, Ps●, Hc◇
A4	35.1	39.0	20.9	5.0	diamond like IL including Ps and IL in matrix	IL●, Ps◎, Hc◇, Cr◎
A5	33.7	37.5	23.8	5.0	Ps surrounded by thin IL & rice ear type IL in matrix	IL◎, Ps◇, Hc□, Cr●
B1	46.7	38.8	9.5	5.0	IL tangled by UL & obscure Fay in matrix	IL●, UL△, Hc□, Fay□
B2	47.3	32.5	15.2	5.0	dendritic IL & Fay in matrix	IL●, UL◇, Hc□, Fay□
B3	48.6	26.4	20.0	5.0	feather like IL & Fay in matrix	IL●, UL◇, Hc□, Fay◇
B4	49.1	23.0	22.9	5.0	dendritic IL, partly UL & Fay in matrix	IL●, UL◇, Hc□, Fay◇
B5	50.3	18.1	26.6	5.0	skeleton like IL & obscure matix	IL◎, UL△, Hc□, Fay◇
C1	54.9	30.6	9.5	5.0	almost UL & IL in matrix	UL●
C3	47.4	26.4	21.2	5.0	small square shaped IL & fine phase in matrix	IL●, Fay△
C4	45.8	25.5	23.8	5.0	small island IL	IL●, Fay△
C5	43.3	24.1	27.6	5.0	network and rice ear type IL, obscure matrix	IL●, Fay◎, Cr△, Hc□
D1	56.5	15.7	22.8	5.0	skeleton like UI & obscure matix	UL●, Fay◎, Hc□
D2	55.5	12.4	27.1	5.0	skeleton like UI & obscure matix	UL●, Fay△, Hc◇
D3	54.8	9.7	30.5	5.0	skeleton like UI & obscure matix	UL●, Fay△, Hc◇
E1	63.6	21.9	9.5	5.0	square shaped UL & Fay in matrix	UL●, Fay□,
E2	65.7	10.3	19.0	5.0	skeleton type UL in Fay matrix	UL●, Fay●, Hc□
E3	66.7	6.8	21.6	5.0	skeleton type UL in Fay matrix	Fay●, UL●, Hc□
E4	66.7	6.1	22.2	5.0	skeleton type UL in big Fay matrix	Fay●, UL◎, Hc□
E5	67.3	4.0	23.8	5.0	almost very big Fay & obscue UL	Fay●, UL△, Hc□
F1	79.1	6.4	9.5	5.0	egg shaped Wus, star shape UL and Fay matrix	UL●, Fay◎, Wus△
F2	73.0	3.0	19.0	5.0	dendritic Wus in glassy matrix	Fay●, UL◇, Wus◇
F3	71.9	2.4	20.7	5.0	dendritic Wus in glassy matrix	Fay●, UL□, Wus□
F4	70.4	1.5	23.1	5.0	big Fay & obscure UL	Fay●, UL◇, Wus□,
G1	61.2	3.4	30.4	5.0	big Fay & UL between Fay	UI●, Fay●, Hc□
G2	59.0	4.7	31.4	5.0	big Fay & UL between Fay	UI◇, Fay●, Hc□
G3	55.9	6.6	32.5	5.0	stick type and plate like Fay and UL	Cr●, Fay◎, UL△, Hc□
EU1	72.6	3.8	18.6	5.0	dendritic Wus in glassy matrix	Fay●, Wus □, UI□
EU2	57.6	8.8	28.6	5.0	skeleton like UI & obscure matix	UI●, Fay◎, Hc□
EU3	53.8	15.3	25.8	5.0	skeleton like UI & obscure matix	UI●, Fay◇, Hc□
EU4	45.2	30.6	19.2	5.0	only small square shaped IL	IL●, Qu□

*1 Ps: pseudobrookite, IL: ilmenite, UL:ulvospinel, Fay: Fayalite, Wus: wustite, Cr: cristobalite, Hc: hercynite

*2 Intensity of Xray diffraction: ●very strong, ◎strong, △medium, ◇weak, □slight

Fig. 2. Chemical composition of sample slags. (Online version in color.)

Fig. 3. Iron crucible and the sealing method. (Online version in color.)

grade TiO_2 and SiO_2 were weighed accurately to meet the composition of Table 2. Al_2O_3 was added to be 5% and mixed thoroughly. As the molten slag wets extraordinarily well to iron and might creep out from the crucible, the mixture was sealed in a crucible of 9 mm ID and 25 mm height by two pure and thin iron sheets as shown in Fig. 3. The mixture was melted at 1350°C in an Ar gas flow, and the upper part of the crucible was filled with iron powder as to protect the mixture against contact with oxygen in Ar atmosphere and to keep the equilibrium between Fe and FeO.

The synthesized slag was roughly crushed. Lumpy parts were supplied to microscopic observation and EPMA measurement and remainder was finely pulverized to use for XRD, DTA and stepwise heating observation.

2.2. Microscopic Observations, EPMA, XRD

Primarily solidified phase, eutectically solidified phases and others were identified by microscopic observation, and the change in morphology with change in composition was studied. Further, microscopic observation and chemical analysis of the phases were carried out by EPMA. The XRD used was a parallel beam system as to compensate the location shift of the sample by temperature change in the high temperature measurement. In this system a platinum heater is used, and X-ray diffraction analysis can be possible up to 1500°C with the condition of air and inert gas atmosphere. High temperature measurement was conducted up to 1200°C in this research. Further, phase transformations were determined by XRD analysis of slags quenched from around the assumed transformation temperatures. In this case, the slag melted in a sealed crucible and cooled to the upper and lower temperature of assumed transformation was quenched in water after keeping at each temperature to stabilize the crystal phase.

Fig. 4. EPMA mapping of sample A1 (40.5%FeO-45.0%TiO₂-9.5%SiO₂-5.0%Al₂O₃). (Online version in color.)

Fig. 5. EPMA mapping of sample A5 (33.7%FeO-37.5%TiO₂-23.8%SiO₂-5.0%Al₂O₃). (Online version in color.)

2.3. DTA Measurement and Stepwise Heating Observation

DTA equipment with an infrared ray radiation heating system was used for phase transformation analysis in which heating and cooling at constant rate were possible. In this system a platinum plated alumina shell was used to enlarge the homogeneous temperature region and played the role of indirect heater. Ordinarily alumina or platinum cells are

used in this system. A steel cell made of ultra-low carbon thin sheets was used in this study, since the high FeO content slag reacts with the ordinary cells. A powder sample was sealed in the cell and DTA measurement was carried out in Ar gas atmosphere. A heating rate of 5°C/min and cooling rate of 10°C/min was adopted on the basis of prior experiments. The measured temperature was calibrated using NaF melting point and MgF₂ melting point as refer-

Fig. 6. EPMA mapping of sample F1 (79.1%FeO-6.4%TiO₂-9.5%SiO₂-5.0%Al₂O₃). (Online version in color.)

Fig. 7. X-ray diffraction patterns of sample A1.

Fig. 8. X-ray diffraction patterns of G1 quenched from 980 and 1030°C.

ences. Heating and cooling patterns were as follows; heated up to 900°C at the rate of 30°C/min, kept for 15 minutes, heated up to the given temperature at 5°C/min, kept for 10 minutes and cooled to 900°C at 10°C/min. The maximum temperature was varied between 1 275°C and 1 457°C. Further, appearance of melt and fusion were observed during stepwise heating. Pulverized slag put in a pure iron boat was set up in a transparent silica tube and heated in Ar gas atmosphere. At each heating step the silica tube was drawn out and the change in the feature of slag in hot and cold state was observed.

3. Results and Discussion

3.1. Microstructure and Crystal Phase

Results of microscopic observation are shown in Table 2. Pseudobrookite and ilmenite are the main crystal phases in high TiO₂ slag and the phases change to ulvospinel and fayalite in the middle TiO₂ slag. Wustite and fayalite become the main phases in the low TiO₂ slag. These are not so different from those predicted from the conventional phase diagram. Hercynite was not found by the optical microscopic observation in spite of the identification by XRD. EPMA mappings of slag A1, A5 and F1 are shown in **Figs. 4 to 6**. These are the representative examples of high TiO₂ and low

Table 3. Results of DTA measurement.

Run No	cristobalite °C	EU1* °C	EU2* °C	EU3* °C	EU4* °C	MP °C	Run No	cristobalite °C	EU1* °C	EU2* °C	EU3* °C	EU4* °C	MP °C
A1-1					1 141	1 285	D1-1	1 008		1 052			1 171
A1-2					1 138	1 277	D1-2			1 056			
A2-5	1 004				1 142	1 215	D1-3	1 010		1 054			1 183
A2-6	1 006				1 141	1 217	D2-2	1 018		1 057			1 145
A2-7	1 014				1 145	1 216	D2-3	1 016		1 048			1 136
A3-1					1 141	1 217	D3-2	1 014		1 056			1 106
A3-2	1 002				1 144	1 214	D3-3	1 012		1 056			1 109
A3-3	1 010				1 137	1 215	EU3-1	1 016		1 057			
A3-4	998				1 143	1 218	EU3-2	1 022		1 052			
A4-2					1 143	1 219	EU3-3	1 017		1 056			1 164
A4-3					1 135	1 210	EU3-3	1 011		1 046			1 167
A5-1					1 141	1 214	E1-1	1 015		1 056			1 347
A5-2					1 142	1 217	E2-2	1 008		1 051			1 153
EU4-1			1 052	1 113			E3-1	1 009		1 042			
EU4-2			1 053	1 115		1 265	E3-2	1 001		1 048			1 152
EU4-3	1 015		1 055	1 117		1 275	E4-2	1 009		1 043			1 150
B1-1			1 050	1 111		1 311	E5-2	1 008		1 047			1 150
B1-2	1 013		1 049	1 105		1 307	G1-2	1 016		1 052			1 126
B2-3	1 015		1 054	1 119			G2-1	1 015		1 053			1 105
B2-4	1 009		1 049	1 113			G3-1	1 014		1 054			1 132
B2-5	1 007		1 048	1 112		1 295	G3-3	1 016		1 058			
B3-2	1 013		1 051	1 128		1 250	G3-4	1 013		1 056			1 124
B4-2			1 055	1 143		1 223	EU2-1	1 014		1 053			1 102
B4-3	1 012		1 041	1 137		1 234	EU2-2	1 009		1 053			1 122
B5-2			1 051	1 151			EU2-2	1 006		1 047			1 122
B5-3	1 012		1 048	1 148		1 197	F1-2		1 135				
C1-1	1 016		1 055	1 110		1 289	F1-2		1 134				1 263
C3-2	1 013		1 055	1 128		1 256	F2-3		1 138				1 144
C4-2	1 014		1 053	1 125		1 242	F3-2		1 138				1 144
C5-1	1 000		1 055	1 128		1 239	F4-2		1 137				1 145
							F4-3		1 134				1 141
							EU1-1		1 137				1 160

EU1*: eutectic point of ulvospinel-wustite-fayalite

EU2*: eutectic point of ulvospinel-fayalite-cristobalite

EU3*: eutectic point of ilmenite-ulvospinel-cristobalite

EU4*: eutectic point of pseudobrookite-ilmenite-cristobalite

SiO₂ slag, high TiO₂ and high SiO₂ slag and low TiO₂ and low SiO₂ slag, respectively. The melting points of these slags must be lower than 1350°C as these phases are solidified evidently from molten state. In the case of A1 dark grayish pseudobrookite is seen as a primary solidified phase and gray ilmenite is so seen to surround it as a secondary solidified phase. Ilmenite appears also in a skeleton-like shape in matrix phase. Cristobalite is not found though it seems to appear from the conventional phase diagram. These results show that TiO₂ exists only as pseudobrookite and ilmenite and is not distributed to the final melt. SiO₂ dissolves slightly in pseudobrookite and not in ilmenite and is concentrated in the boundary between both phases. The main part of SiO₂ is contained in the final melt and solidified as glass. Al₂O₃ dissolves slightly in pseudobrookite, non-dissolved Al₂O₃ remains in the final melt. In the case of A5, rectangle-shaped dark gray pseudobrookite and its surrounding ilmenite are observed. Ilmenite is also found in the matrix. Black cristobalite is found around ilmenite. SiO₂ seems to be super saturated in melt due to the low solubility in ilmenite and solidifies around the secondary ilmenite. Relative position of this cristobalite solidification to other phases suggests that the cristobalite is not a primarily solidified phase. Another phase is found sparsely in the matrix. Its composition was near to that of fayalite but was not identified by XRD. In the case of F1, grayish ulvospinel, slightly white and oval wustite, and obscure fayalite in a matrix are found. These phases are those predicted from the conventional phase diagram. Al₂O₃ is relatively well soluble in ulvospinel.

3.2. X-ray Diffraction Analysis

Figure 7 shows the X-ray diffraction patterns of sample A1. Pseudobrookite, ilmenite and hercynite were identified. Scarcely, hercynite is detected in actual smelting slags from remains; this suggests that CaO and alkaline oxide may increase the solubility of Al₂O₃ in the final liquid phase. Sasabe *et al.*²⁾ showed in a study of Fe₂SiO₄-TiO₂ phase diagram that cristobalite appeared in the range which TiO₂ content exceeded 12%. In this investigation cristobalite is detected only in the region where the SiO₂ content is higher than the eutectic line of pseudobrookite and cristobalite of the conventional phase diagram. This suggests that the eutectic line is shifted to higher SiO₂ region by an addition of Al₂O₃. **Figure 8** shows the diffraction patterns of sample G1 quenched from 1030°C and 980°C. Strong diffractions of fayalite and ulvospinel are observed at 1030°C and quartz is appeared at 980°C. This means the formation of quartz occurs between these temperatures. Results of XRD are summarized in Table 2. Though hercynite is not found by microscopic observation, it is identified for many slags. As is mentioned above, Al₂O₃ concentrates to final liquid and seems to solidify at low temperature to form fine crystal and may be difficult to observe.

3.3. DTA Measurement

DTA results are summarized in Table 3. **Figure 9** shows the DTA curves of F series samples. Endothermic peaks in the heating stage and super cooled exothermic peaks in the cooling stage are observed clearly, though some noises appear when the temperature control is changed. F1 was

Fig. 9. DT curves of F series samples (different heat pattern for F1-2). (Online version in color.)

Fig. 10. DT curves of samples around the eutectic point of ulvospinel-fayalite- cristobalite. (Online version in color.)

heated up to 1327°C and the appearance of exothermic peak is delayed. **Figure 10** shows the DTA curves of samples around the ulvospinel-fayalite-cristobalite eutectic point. An endothermic transformation around 1000°C was observed. This transformation is thought to represent the appearance of quartz explained in section 3.2. Heat absorption between 1025 and 1050°C accompanied with eutectic reaction are seen. Heat absorptions related to melting are observed at higher temperatures. In this figure, to make the difference between samples clear, the baselines of the DTA curves are shifted. **Figure 11** shows the DTA curves for samples around the eutectic point of wustite-ulvospinel-fayalite. Heat absorption by eutectic phase transformation appears between 1130°C and 1141°C and melting occurs at about 1150°C. **Figure 12** shows the stepwise heating observation of G3. The sample is in a powder state at 1047°C. Liquid phase appears at 1086°C but is not melted completely. It is melted completely and crept out from iron boat at 1135°C. This observation showed that the DT change at lower temperature of 1047°C is caused by solid state transformation and that the change between 1047°C and 1086°C is due to eutectic transformation. The temperature of the wustite-ulvospinel-fayalite eutectic point is estimated to about 1050°C, which is lowered by 93°C than that presumed from the conventional phase diagram. **Figure 13** is the phase diagram determined by this study. Addition of 5% Al₂O₃ decreased the eutectic point of EU1 (wustite-ulvospinel-fayalite), EU2 (ulvospinel-fayalite-cristobalite), EU3 (ulvospinel-ilmenite-cristobalite), and EU4 (pseudobrookite-

Fig. 11. DT curves of samples around the eutectic point of ulvospinel-wustite-fayalite. (Online version in color.)

Fig. 12. Change in features of powder sample G3 by stepwise heating. (Online version in color.)

ilmenite-cristobalite) from 1169°C to 1136°C, from 1145°C to 1052°C, from 1180°C to 1115°C and 1254°C to 1140°C, respectively. These measurements suggest that

Fig. 13. FeO-TiO₂-SiO₂-5%Al₂O₃ phase diagram. (Online version in color.)

the ancient iron making was operated at lower temperatures than those estimated from the conventional FeO-TiO₂-SiO₂ phase diagram.

4. Conclusion

A phase diagram of FeO-TiO₂-SiO₂-5%Al₂O₃ system and the crystal phases were successfully determined by microscopic observation, EPMA, XRD, DTA and stepwise heating to enable a more reliable evaluation of ancient iron making process. Compared with the conventional phase diagram the temperatures of eutectic points are decreased remarkably by addition of 5% Al₂O₃.

REFERENCES

- 1) Slag Atlas, 2nd ed., VdEh, Verlag Sthleisen, (1995), 146.
- 2) M. Sasabe, S. Yamashita, S. Uno and M. Tate: *Tetsu-to-Hagané*, **91** (2005), 33.