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. Fig. 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

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

| TiO₂ in iron sand remain T.Fe FeO Fe₂O₃ TiO₂ SiO₂ Al₂O₃ CaO MgO K₂O Na₂O |
|-----------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 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       |
| 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       |
| G               | 34.8      | 43.6      | 12.9      | 19.1      | 17.4      | 5.3        | 0.5        | 0.7        |           |           |
| H               | 29.0      | 23.5      | 15.4      | 13.0      | 29.1      | 4.7        | 2.6        | 1.7        | 1.3       | 0.6       |
| I               | 41.9      | 45.7      | 8.7       | 10.7      | 21.0      | 6.5        | 2.5        | 0.7        | 1.4       | 0.3       |
| J               | 37.4      | 42.7      | 6.2       | 12.8      | 23.5      | 5.9        | 3.2        | 2.4        | 1.3       | 0.4       |
| K               | 43.3      | 49.1      | 6.4       | 11.1      | 19.3      | 6.4        | 1.9        | 1.2        | 0.3       | 1.2       |
| L               | 38.3      | 32.3      | 18.0      | 5.0       | 28.2      | 7.3        | 2.8        | 2.5        | 1.0       | 0.5       |
| M               | 48.4      | 57.0      | 5.4       | 5.3       | 18.5      | 5.3        | 2.7        | 0.8        | 0.5       | 0.6       |
| N               | 46.1      | 51.2      | 7.9       | 2.8       | 22.3      | 6.2        | 2.8        | 2.0        | 0.5       | 0.7       |
| O               | 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% Al₂O₃, 2.5% CaO and MgO, and more than 1% of Na₂O+K₂O 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 FeO-TiO₂-SiO₂-5%Al₂O₃ 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 Fe₂O₃ powder were blended as to be Fe₀.₉₇₅O 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. Fe₀.₉₇₅O was synthesized by heating at 950°C for 16 hours in CO–CO₂–Ar atmosphere of which the CO/CO₂ 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>
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<tr>
<th>Sample</th>
<th>FeO</th>
<th>TiO₂</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>structure observed by microscope *1</th>
<th>identified phase by XRD *2</th>
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<td>40.7</td>
<td>17.8</td>
<td>5.0</td>
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<td>3.4</td>
<td>30.4</td>
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<td>19.2</td>
<td>5.0</td>
<td>only small square shaped IL</td>
<td>IL, Qu</td>
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</tbody>
</table>

*2 Intensity of Xray diffraction: ◇very strong, ◌strong, ◌medium, ◄weak, ◆slight

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grade TiO₂ and SiO₂ were weighed accurately to meet the composition of Table 2. Al₂O₃ 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.
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 1 030°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.

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<th>Run No</th>
<th>cristobalite °C</th>
<th>EU1* °C</th>
<th>EU2* °C</th>
<th>EU3* °C</th>
<th>EU4* °C</th>
<th>MP °C</th>
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<td>1285</td>
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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

Table 3. Results of DTA measurement.

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SiO$_2$ slag, high TiO$_2$ and high SiO$_2$ slag and low TiO$_2$ and low SiO$_2$ slag, respectively. The melting points of these slags must be lower than 1 350°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 TiO$_2$ exists only as pseudobrookite and ilmenite and is not distributed to the final melt. SiO$_2$ dissolves slightly in pseudobrookite and not in ilmenite and is concentrated in the boundary between both phases. The main part of SiO$_2$ is contained in the final melt and solidified as glass. Al$_2$O$_3$ dissolves slightly in pseudobrookite, non-dissolved Al$_2$O$_3$ 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. SiO$_2$ 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 predicted from the conventional phase diagram. Al$_2$O$_3$ 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 Al$_2$O$_3$ in the final liquid phase. Sasabe et al.\textsuperscript{2) showed in a study of Fe$_2$SiO$_4$–TiO$_2$ phase diagram that cristobalite appeared in the range which TiO$_2$ content exceeded 12%. In this investigation cristobalite is detected only in the region where the SiO$_2$ 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 SiO$_2$ region by an addition of Al$_2$O$_3$. Figure 8 shows the diffraction patterns of sample G1 quenched from 1 030°C and 980°C. Strong diffractions of fayalite and ulvospinel are observed at 1 030°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, Al$_2$O$_3$ 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 heated up to 1 327°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 1 000°C was observed. This transformation is thought to represent the appearance of quartz explained in section 3.2. Heat absorption between 1 025 and 1 050°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 1 130°C and 1 141°C and melting occurs at about 1 150°C. Figure 12 shows the stepwise heating observation of G3. The sample is in a powder state at 1 047°C. Liquid phase appears at 1 086°C but is not melted completely. It is melted completely and crept out from iron boat at 1 135°C. This observation showed that the DTA change at lower temperature of 1 047°C is caused by solid state transformation and that the change between 1 047°C and 1 086°C is due to eutectic transformation. The temperature of the wustite-ulvospinel-fayalite eutectic point is estimated to about 1 050°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% Al$_2$O$_3$ decreased the eutectic point of EU1 (wustite-ulvospinel-fayalite), EU2 (ulvospinel-fayalite-cristobalite), EU3 (ulvospinel-ilmenite-cristobalite), and EU4 (pseudobrookite-
The measurements suggest that 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


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.)

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