Liquidus Surface and Isothermal Section Diagram at 1073 K in SrO-Fe₂O₃-(0 ~ 50 mol%)B₂O₃ Pseudo-Ternary System[†]

Hiroshi Sato

Faculty of Education, Yamanashi University, Kofu 400, Japan

The isothermal section at 1073 K and the liquidus surfaces of the phase diagram of the pseudo-ternary SrO-Fe₂O₃-B₂O₃ system were determined in a composition range of the B₂O₃ content less than 50 mol% by using the thermal analyses and X-ray diffraction. The liquidus surface which is in equilibrium with Fe₃O₄ spreads over a wide composition range and that in equilibrium with SrO·6Fe₂O₃ extends long and narrow to SrO·B₂O₃. The pseudo-ternary SrO-Fe₂O₃-B₂O₃ compound does not exist in the composition range investigated. The ternary eutectic reaction is L→SrO·6Fe₂O₃+SrO·B₂O₃+2SrO·B₂O₃, occurring at 1213 K at the composition 51 mol%SrO-18 mol%Fe₂O₃-31 mol%B₂O₃.

(Received May 20, 1996)

Keywords: phase diagram, strontium ferrite, liquidus surface, SrO-Fe₂O₃-B₂O₃ system, isothermal section

I. Introduction

For the pseudo-ternary SrO-Fe₂O₃-B₂O₃ and BaO-Fe₂O₃-B₂O₃ systems, the amorphous (glass)-crystallization method of the ferrite magnet materials such as SrO·6Fe₂O₃ and BaO·6Fe₂O₃ (M-type ferrite) is very useful to produce ultrafine powders⁽¹⁾⁻⁽¹²⁾. In the previous paper, the relation between the kinds of precipitated crystalline phases and relative quantities of phases, and starting composition and effects of cooling rate on the magnetic properties of the SrO·6Fe₂O₃ particles were investigated for the heat-treated samples⁽¹³⁾. The amorphous state was observed using a transmission electron microscope (TEM) and the relationship between the average particle size and the magnetic properties of SrO·6Fe₂O₃ particles were examined⁽¹⁴⁾⁽¹⁵⁾. However the ranges of composition and temperature at which the individual phases including SrO·6Fe₂O₃ are in stable equilibria have not been clarified yet. Phase diagrams are important to study relationships between properties and microstructures of material, especially in the case of designing SrO·6Fe₂O₃ magnet. Although the pseudo-binary phase diagrams of the SrO-Fe₂O₃ and SrO-B₂O₃ systems are available, however, the pseudo-ternary phase diagram of the SrO-Fe₂O₃-B₂O₃ system has not been reported. In the present study, an isothermal section and the liquidus surfaces of the pseudo-ternary phase diagram of the SrO-Fe₂O₃-B₂O₃ system have been determined in a composition range of the B₂O₃ content less than 50 mol% by thermal analyses and X-ray diffraction.

II. Experimental Procedure

The starting materials used were reagent-grade SrCO₃,

α-Fe₂O₃ and H₃BO₃ powders. These powders were well mixed to obtain the prescribed compositions. A mixed powder was melted in air in a Pt crucible placed in an electric furnace. Specimens were prepared by pouring the molten samples directly on a steel plate after heating for 2.7 ks at 1723 K. Specimens were then heat treated at 1073 K for 3.6 to 108 ks. Figure 1 shows compositions of specimens together with the pseudo-binary phase diagrams of SrO-Fe₂O₃ and SrO-B₂O₃ systems⁽¹⁶⁾⁽¹⁷⁾. Several vertical pseudo-binary section of pseudo-ternary SrO-Fe₂O₃-B₂O₃ phase diagram are defined as follows. The section, through the line connecting the compositions of SrO·Fe₂O₃ and B₂O₃ is named as Section A. Similarly, the section connecting (SrO)_{0.63}·(Fe₂O₃)_{0.37} and B₂O₃ is called Section B, and those of (SrO)_{0.77}·(Fe₂O₃)_{0.23}-B₂O₃, (SrO)_{0.825}·(B₂O₃)_{0.175}-(Fe₂O₃)_{0.825}·(B₂O₃)_{0.175}, (SrO)_{0.75}·(B₂O₃)_{0.25}-(Fe₂O₃)_{0.75}·(B₂O₃)_{0.25}, and (SrO)_{0.68}·(B₂O₃)_{0.32}-(Fe₂O₃)_{0.68}·(B₂O₃)_{0.32}, are named as Section C, D, E and F, respectively.

The isothermal section at 1073 K and the liquidus surfaces of the phase diagram of the pseudo-ternary SrO-Fe₂O₃-B₂O₃ system were determined by thermal analysis, differential thermal analysis (DTA) and X-ray diffraction. In DTA, specimens of about 10 × 10⁻³ kg were heated in air to specified temperatures at fixed heating rates between 0.08 and 0.25 K/s. Al₂O₃ was employed as a standard sample for DTA. The temperatures detected by the DTA were compared with the known melting points of standard substances, and the difference were within 10 K in both heating and cooling operations.

In order to identify existing phases in the specimens, X-ray diffraction analysis was conducted for specimens prepared under various conditions, i.e. quenched for various annealing temperatures. When primary phase was hardly identified in the composition range of the high SrO or Fe₂O₃ content, a rapid quenching method was conducted by pouring the molten sample on a rotating twin rollers, and the primary phases were conformed.

[†] This paper was originally published in Japanese in J. Japan Inst. Metals, 59 (1995), 593.

The primary phases of $3\text{SrO} \cdot \text{Fe}_2\text{O}_3$, $3\text{SrO} \cdot 2\text{Fe}_2\text{O}_3$, $\text{SrO} \cdot 6\text{Fe}_2\text{O}_3$, $3\text{SrO} \cdot \text{B}_2\text{O}_3$, $2\text{SrO} \cdot \text{B}_2\text{O}_3$, $\text{SrO} \cdot \text{B}_2\text{O}_3$, $\text{SrO} \cdot 2\text{B}_2\text{O}_3$, SrFeO_{3-x} , Fe_2O_3 and Fe_3O_4 were identified from the results of X-ray diffraction analysis using the powder diffraction file by JCPDS. For X-ray diffraction, the samples were pulverized to about $50\text{ }\mu\text{m}$ in diameter, and the X-ray of $\text{CuK}\alpha$ was used at a voltage of 40 kV and at an electric current of 30 mA.

III. Experimental Results and Discussion

Liquidus temperatures of specimens of the respective

In Fig. 2, the cooling and heating curves obtained by the DTA are shown for a specimen of 47.5 mol%SrO-47.5 mol%Fe₂O₃-5.0 mol%B₂O₃. For this specimen, reproducible two peaks were observed. The peak at the

Fig. 2 Typical curves obtained by differential thermal analysis.

Fig. 3 Change of X-ray diffraction patterns of samples after the heat treatment of various annealing time at 30.5 mol% SrO-52.0 mol% Fe₂O₃-17.5 mol% B₂O₃.

higher temperature corresponds to the liquidus temperature and the one at the lower temperature denotes a reaction for the formation of a secondary phase. The temperatures of 1419 and 1346 K obtained in heating were adopted as the temperatures at which the thermal reactions occurred because the supercooling was observed on cooling. In order to clarify these reactions, the samples on cooling were quenched from 1373 or 1253 K during the analysis and the existing phases were identified by X-ray diffraction analysis; SrFeO_{3-x} when quenched from

Fig. 4 Heating time dependence on relative intensity of X-ray diffraction of sample containing 30.5 mol% SrO-52.0 mol% Fe₂O₃-17.5 mol% B₂O₃ heat-treated at 1073 K.

1373 K, and SrFeO_{3-x} and SrO·6Fe₂O₃ when quenched from 1253 K. It was concluded from these results that SrFeO_{3-x} precipitated as the primary phase at 1419 K and SrO·6Fe₂O₃ precipitated as the secondary phase at 1346 K.

2. Isothermal section at 1073 K

The variation of the X-ray diffraction patterns of samples containing 30.5 mol% SrO-52.0 mol% Fe₂O₃-17.5 mol% B₂O₃ is shown in Fig. 3. The relationship between the heating time and the relative quantities of existing phases is shown in Fig. 4 where the relative intensities of the X-ray diffraction peaks for the individual phases are evaluated as the relative quantities present. It is shown that the quantity of Fe₃O₄ decreased with heating time and became 0% after 36 ks. On the other hand, the quantity of SrO·6Fe₂O₃ increased with heating time and became almost constant after 36 ks. The isothermal section at 1073 K was determined in a composition range of less than 50 mol% B₂O₃ as shown in Fig. 5. In the region enclosed by the lines connecting the compositions of Fe₂O₃, SrO·B₂O₃, 3SrO·B₂O₃, SrFeO_{3-x}, and Fe₂O₃, the following five regions of three phases equilibria are present:

3. Section of phase diagram

The vertical pseudo-binary sections were determined by thermal analyses and X-ray diffraction measurements.

Figure 6 shows the SrO·Fe₂O₃-B₂O₃ section (Section A), where two-phase regions of Fe₃O₄+L, SrO·6Fe₂O₃+L, SrFeO_{3-x}+L and 3SrO·2Fe₂O₃+L (L denotes the liquid phase). A eutectic reaction occur be-

 Fig. 5 Isothermal section of the phase diagram of the pseudo-ternary $\text{SrO}-\text{Fe}_2\text{O}_3-\text{B}_2\text{O}_3$ system at 1073 K.

 Fig. 6 $\text{SrO}\cdot\text{Fe}_2\text{O}_3-\text{B}_2\text{O}_3$ section of phase diagram. (Section A)

 Fig. 8 $(\text{SrO})_{0.77}\cdot(\text{Fe}_2\text{O}_3)_{0.23}-\text{B}_2\text{O}_3$ section of the phase diagram. (Section C)

 Fig. 7 $(\text{SrO})_{0.64}\cdot(\text{Fe}_2\text{O}_3)_{0.37}-\text{B}_2\text{O}_3$ section of the phase diagram. (Section B)

tween SrFeO_{3-x} and $\text{SrO}\cdot 6\text{Fe}_2\text{O}_3$ at the composition of 91 mol% $\text{SrO}\cdot\text{Fe}_2\text{O}_3$ -9 mol% B_2O_3 at 1348 K.

Figure 7 shows the $(\text{SrO})_{0.63}\cdot(\text{Fe}_2\text{O}_3)_{0.37}-\text{B}_2\text{O}_3$ section (Section B), where two-phase regions of $\text{SrO}\cdot 6\text{Fe}_2\text{O}_3 + \text{L}$, $3\text{SrO}\cdot \text{B}_2\text{O}_3 + \text{L}$ and $\text{SrFeO}_{3-x} + \text{L}$. Two eutectic reactions are observed between $3\text{SrO}\cdot \text{B}_2\text{O}_3$ and $\text{SrO}\cdot 6\text{Fe}_2\text{O}_3$ with the composition of 79 mol% $(\text{SrO})_{0.63}\cdot(\text{Fe}_2\text{O}_3)_{0.37}$ -29 mol% B_2O_3 at 1283 K and between SrFeO_{3-x} and $3\text{SrO}\cdot \text{B}_2\text{O}_3$ with the composition of 86 mol% $(\text{SrO})_{0.63}\cdot(\text{Fe}_2\text{O}_3)_{0.37}$ -14 mol% B_2O_3 at 1353 K.

The result of Section C is shown in Fig. 8, in which two-phase regions of $\text{SrO}\cdot \text{B}_2\text{O}_3 + \text{L}$, $2\text{SrO}\cdot \text{B}_2\text{O}_3 + \text{L}$ and $3\text{SrO}\cdot \text{B}_2\text{O}_3 + \text{L}$ exist. Two eutectic reactions are found between $2\text{SrO}\cdot \text{B}_2\text{O}_3$ and $\text{SrO}\cdot \text{B}_2\text{O}_3$ with the composition of 20 mol% $(\text{SrO})_{0.77}\cdot(\text{Fe}_2\text{O}_3)_{0.23}$ -30 mol% B_2O_3 at 1280 K and between $3\text{SrO}\cdot \text{B}_2\text{O}_3$ and $2\text{SrO}\cdot \text{B}_2\text{O}_3$ with the composition of 75 mol% $(\text{SrO})_{0.77}\cdot(\text{Fe}_2\text{O}_3)_{0.23}$ -25 mol% B_2O_3 at 1220 K.

Fig. 9 $(\text{SrO})_{0.825} \cdot (\text{B}_2\text{O}_3)_{0.175} - (\text{Fe}_2\text{O}_3)_{0.825} \cdot (\text{B}_2\text{O}_3)_{0.175}$ section of the phase diagram. (Section D)

Fig. 10 $(\text{SrO})_{0.76} \cdot (\text{B}_2\text{O}_3)_{0.24} - (\text{Fe}_2\text{O}_3)_{0.76} \cdot (\text{B}_2\text{O}_3)_{0.24}$ section of phase diagram. (Section E)

Fig. 11 $(\text{SrO})_{0.68} \cdot (\text{B}_2\text{O}_3)_{0.32} - (\text{Fe}_2\text{O}_3)_{0.68} \cdot (\text{B}_2\text{O}_3)_{0.32}$ section of phase diagram. (Section F)

The result of Section D is shown in Fig. 9, in which two-phase regions of $\text{Fe}_3\text{O}_4 + \text{L}$, $\text{SrO} \cdot 6\text{Fe}_2\text{O}_3 + \text{L}$ and $3\text{SrO} \cdot \text{B}_2\text{O}_3 + \text{L}$ exist. A eutectic reaction occurs between $3\text{SrO} \cdot \text{B}_2\text{O}_3$ and $\text{SrO} \cdot 6\text{Fe}_2\text{O}_3$ with the composition of 47.5 mol% SrO–35.0 mol% Fe_2O_3 –17.5 mol% B_2O_3 at 1335 K.

The result of Section E is shown in Fig. 10, in which two-phase regions of $\text{Fe}_3\text{O}_4 + \text{L}$, $\text{SrO} \cdot 6\text{Fe}_2\text{O}_3 + \text{L}$ and $3\text{SrO} \cdot \text{B}_2\text{O}_3 + \text{L}$ exist. A eutectic reaction is observed between $3\text{SrO} \cdot \text{B}_2\text{O}_3$ and $\text{SrO} \cdot 6\text{Fe}_2\text{O}_3$ with the composition of 53 mol% SrO–24 mol% Fe_2O_3 –23 mol% B_2O_3 at 1263 K.

The result of Section F is shown in Fig. 11. Two-phase regions of $\text{Fe}_3\text{O}_4 + \text{L}$, $\text{SrO} \cdot 6\text{Fe}_2\text{O}_3 + \text{L}$, $\text{SrO} \cdot \text{B}_2\text{O}_3 + \text{L}$ and $2\text{SrO} \cdot \text{B}_2\text{O}_3 + \text{L}$ exist. Two eutectic reactions are found between $\text{SrO} \cdot \text{B}_2\text{O}_3$ and $\text{SrO} \cdot 6\text{Fe}_2\text{O}_3$ with the composition of 48 mol% SrO–20 mol% Fe_2O_3 –32 mol% B_2O_3 at 1215 K and between $2\text{SrO} \cdot \text{B}_2\text{O}_3$ and $\text{SrO} \cdot \text{B}_2\text{O}_3$ with the composition of 56 mol% SrO–12 mol% Fe_2O_3 –32 mol% B_2O_3 at 1225 K.

4. The liquidus surfaces of the pseudo-ternary phase diagram

The liquidus surfaces of the pseudo-ternary phase diagram of the $\text{SrO}-\text{Fe}_2\text{O}_3-\text{B}_2\text{O}_3$ system were determined according to the results shown in Figs. 3 to 11. The resultant liquidus surfaces of the pseudo-ternary phase diagram are shown in Fig. 12 in the composition range of the B_2O_3 content less than 50 mol%. The ternary $\text{SrO}-\text{Fe}_2\text{O}_3-\text{B}_2\text{O}_3$ compound does not exist in this region. The following phase transformations occur in cooling on the lines of L_1 to L_{10} shown in Fig. 12;

- $\text{L}_1: \text{L} \rightarrow 2\text{SrO} \cdot \text{B}_2\text{O}_3 + 3\text{SrO} \cdot 2\text{Fe}_2\text{O}_3$
- $\text{L}_2: \text{L} \rightarrow 3\text{SrO} \cdot \text{B}_2\text{O}_3 + 2\text{SrO} \cdot \text{B}_2\text{O}_3$
- $\text{L}_3: \text{L} \rightarrow \text{SrO} \cdot 6\text{Fe}_2\text{O}_3 + \text{SrFeO}_{3-x}$
- $\text{L}_4: \text{L} \rightarrow 2\text{SrO} \cdot \text{B}_2\text{O}_3 + \text{SrO} \cdot \text{B}_2\text{O}_3$
- $\text{L}_5: \text{L} \rightarrow \text{SrO} \cdot 6\text{Fe}_2\text{O}_3 + \text{SrO} \cdot \text{B}_2\text{O}_3$
- $\text{L}_6: \text{L} \rightarrow \text{SrO} \cdot 6\text{Fe}_2\text{O}_3 + 3\text{SrO} \cdot \text{B}_2\text{O}_3$
- $\text{L}_7: \text{L} \rightarrow \text{SrO} \cdot 6\text{Fe}_2\text{O}_3 + 2\text{SrO} \cdot \text{B}_2\text{O}_3$
- $\text{L}_8: \text{Fe}_3\text{O}_4 + \text{L} \rightarrow \text{SrO} \cdot 6\text{Fe}_2\text{O}_3$
- $\text{L}_9: \text{SrFeO}_{3-x} + \text{L} \rightarrow 3\text{SrO} \cdot 2\text{Fe}_2\text{O}_3$
- $\text{L}_{10}: \text{L} \rightarrow \text{SrO} \cdot 6\text{Fe}_2\text{O}_3 + 3\text{SrO} \cdot 2\text{Fe}_2\text{O}_3$

For the pseudo-binary $\text{SrO}-\text{Fe}_2\text{O}_3$ or $\text{SrO}-\text{B}_2\text{O}_3$ system, phase transformations occur at the points of e_1 , e_2 , p_1 , p_2 and p_3 in Fig. 12 which are expressed as follows;

- $e_1: \text{L} \rightarrow \text{SrO} \cdot 6\text{Fe}_2\text{O}_3 + 3\text{SrO} \cdot 2\text{Fe}_2\text{O}_3 \quad (1468 \text{ K})$
- $e_2: \text{L} \rightarrow 2\text{SrO} \cdot \text{B}_2\text{O}_3 + \text{SrO} \cdot \text{B}_2\text{O}_3 \quad (1335 \text{ K})$
- $p_1: \text{Fe}_3\text{O}_4 + \text{L} \rightarrow \text{SrO} \cdot 2\text{FeO} \cdot 8\text{Fe}_2\text{O}_3 \quad (1693 \text{ K})$
- $p_2: \text{SrFeO}_{3-x} + \text{L} \rightarrow 3\text{SrO} \cdot 2\text{Fe}_2\text{O}_3 \quad (1498 \text{ K})$
- $p_3: \text{SrO} \cdot 2\text{FeO} \cdot 8\text{Fe}_2\text{O}_3 + \text{L} \rightarrow \text{SrO} \cdot 6\text{Fe}_2\text{O}_3 \quad (1663 \text{ K})$

The transformation points of e_1 , e_2 , p_1 , p_2 and p_3 were reported by Kojima *et al.*⁽¹⁶⁾ and that of e_2 was report-

Fig. 12 Phase diagram of the pseudo-ternary SrO-Fe₂O₃-B₂O₃ system, showing liquidus surface. Fig. 13 Phase diagram of the pseudo-ternary SrO-Fe₂O₃-B₂O₃ system, showing isotherm lines of the liquidus surface.

ed by Witzmann and Beulich⁽¹⁷⁾. The point of e_3 is also a eutectic point and is already shown in the pseudo-binary phase diagram of the SrO-B₂O₃ system in Fig. 1. In the region examined in the present study, a ternary eutectic reaction (E_1) is $L \rightarrow \text{SrO} \cdot 6\text{Fe}_2\text{O}_3 + \text{SrO} \cdot \text{B}_2\text{O}_3 + 2\text{SrO} \cdot \text{B}_2\text{O}_3$, occurring at 1213 K with the composition of 51 mol% SrO-18 mol% Fe₂O₃-31 mol% B₂O₃. The points of R_1 , R_2 , R_3 and R_4 are those of phase transformation obtained from the results of this study.

$$R_1: 1440 \pm 10 \text{ K}$$

$$R_2: 1293 \pm 10 \text{ K}$$

$$R_3: 1228 \pm 10 \text{ K}$$

$$R_4: 1253 \pm 10 \text{ K}$$

The region where the liquidus surface is in equilibrium with Fe₃O₄ widely spreads toward SrO·B₂O₃. The liquidus surface equilibrated with SrO·6Fe₂O₃ also extends long and narrow in the same direction.

Figure 13 shows the isothermal lines on the liquidus surface of the pseudo-ternary phase diagram of the SrO-Fe₂O₃-B₂O₃ system. The temperature at which liquidus phase and the Fe₃O₄ primary phase are in equilibrium is relatively high in region of the B₂O₃ content higher than 20 mol% and abruptly decreases when the B₂O₃ content exceeds 40 mol%. The liquidus surface in equilibrium with SrO·6Fe₂O₃ forms a steep slope, while the slopes of the liquidus surface equilibrated with SrO·B₂O₃ or 2SrO·B₂O₃ are more gentle than those in equilibrium with Fe₃O₄ and SrO·6Fe₂O₃.

IV. Conclusions

The isothermal section at 1073 K and the liquidus surface of the pseudo-ternary phase diagram of the $\text{SrO}-\text{Fe}_2\text{O}_3-\text{B}_2\text{O}_3$ system have been determined in a composition range of the B_2O_3 content less than 50 mol%. The pseudo-ternary compound does not exist in this range. The ternary eutectic reaction is $\text{L} \rightarrow \text{SrO} \cdot 6\text{Fe}_2\text{O}_3 + \text{SrO} \cdot \text{B}_2\text{O}_3 + 2\text{SrO} \cdot \text{B}_2\text{O}_3$, occurring at 1213 K at the composition 51 mol% SrO –18 mol% Fe_2O_3 –31 mol% B_2O_3 .

REFERENCES

- (1) M. Tanigawa and M. Tanaka: Osaka Kogyo Gijutsu Shikenjyo Kiyo, **15** (1964), 285.
- (2) B. T. Shirk and W. R. Buessem: J. Amer. Ceram. Soc., **53** (1970), 192.
- (3) D. V. Ratnam and W. R. Buessem: IEEE Trans. Magn., **MAG-6** (1970), 610.
- (4) D. V. Ratnam and W. R. Buessem: J. Appl. Phys., **43** (1972), 1291.
- (5) B. T. Shirk and W. R. Buessem: IEEE Trans. Magn., **MAG-7** (1971), 659.
- (6) O. Kubo, T. Ido and H. Yokoyama: IEEE Trans. Magn., **MAG-18** (1982), 1122.
- (7) T. Ido: Electronic Ceramics, **15** (1985), 49.
- (8) O. Kubo, T. Doi, H. Yokoyama and Y. Koike: J. Appl. Phys., **57** (1985), 4280.
- (9) T. Fujigawa: IEEE Trans. Magn., **MAG-21** (1985), 1480.
- (10) T. Ido, O. Kubo and H. Yokoyama: IEEE Trans. Magn., **MAG-21** (1985), 704.
- (11) K. Oda T. Yoshio and K. O-oka: J. Materials Science Letters, **3** (1984), 1007.
- (12) T. Ido, T. and K. O-oka: J. Materials Science Letters, **4** (1985), 876.
- (13) H. Sato, T. Umeda and Y. Kimura: J. Japan Inst. Metals, **54** (1990), 101.
- (14) H. Sato and T. Umeda: J. Japan Inst. Metals, **55** (1991), 92.
- (15) H. Sato and T. Umeda: Mater. Trans., JIM, **34** (1993), 76.
- (16) Y. Kojima, M. Higashimoto and K. Takahashi: Powder and Powder Metallurgy, **21** (1974), 21.
- (17) H. Witzmann and W. Beulich: Z. Physic. Chem., **225** (1964), 336.