Effect of Al_2O_3 or MgO on Liquidus Line in the FeO_X Corner of FeO_X-SiO_2-CaO System at 1523 K under Various Oxygen Partial Pressures

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Abstract. The liquidus line in the FeO_X corner of FeO_X-SiO_2-CaO system and the effect by adding Al_2O_3 or MgO to this plain system on the liquidus line were experimentally investigated at 1523 K in a wide range of oxygen partial pressure between about 10^{-12} and about 10^{-4} atm and for given (mass% CaO/mass% SiO_2) ratios in the system between 0 and about 1. It was found for the plain system that the liquidus line remarkably shifted toward the low FeO_X-content region when the partial pressure of oxygen was increased from 10^{-10} to 10^{-8} atm. It was clarified that the addition of Al_2O_3 made the homogeneous region wide only in a strongly reducing atmosphere while the addition of MgO made the homogeneous liquid region remarkably narrow at all the oxygen partial pressures and all the (mass% CaO/mass% SiO_2) ratios investigated in the study.

Keywords. Liquidus line, FeOx-SiO_2-CaO-Al_2O_3 system, FeOx-SiO_2-CaO- MgO system, oxygen partial pressure.

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1 Introduction

The FeO_X-SiO_2-CaO base slag is common in the matte smelting and the slag cleaning of copper at about 1550 K and oxygen partial pressures in a range between 10^{-9} and 10^{-7} (the partial pressure expressed as dimensionless one, defined by $p_{O_2} = P_{O_2}$ Pa/101 325 Pa). The phase diagram

data of this system in these conditions are of practical importance, specially, those on the liquidus line in the FeO_X corner of the system to avoid the formation of solid magnetite (Fe_3O_4) which causes some serious troubles in the operations. However, only a little is known about the phase diagram [1–3].

The plain slag in the matte smelting commonly contains a few mass% Al_2O_3 and MgO as the minor components, which are considered to give serious effects to the homogeneous liquid region around the FeO_X corner in the FeO_X-SiO_2-CaO base slag, but the experimental data on the phase relations in the slag with Al_2O_3 or MgO in the condition of copper smelting or slag cleaning are very few [4].

In the present study, followed by the investigations on the plain FeO_X-SiO_2-CaO ternary system at 1573 K [5, 6], the liquidus lines were experimentally determined for the system containing given amounts of Al_2O_3 or MgO at 1523 K under a very wide range of oxygen partial pressure between about 10^{-12} corresponding to the iron saturation and about 10^{-4} corresponding to the CO_2 atmosphere, and for the (mass% CaO/mass% SiO_2) ratio of the system between 0 and about 1.

2 Experimental Procedure

Details of the experimental method and procedure were reported in the previous papers [5, 6]. Firstly, the liquidus lines were determined for the plain slag without Al_2O_3 and MgO; (1) the Fe_3O_4 (spinel)-SiO_2-CaO system at p_{O_2} of 10^{-8}, 10^{-6} and 2.27×10^{-4} (CO_2 atmoshere) (2) the FeO-SiO_2-CaO system at p_{O_2} of 4.21×10^{-12} (iron saturation) and 10^{-10}. The ratios of mass% CaO to mass% SiO_2 in the slag were fixed at given values between 0 and about 1. In the second experiments, the effect of Al_2O_3 or MgO on the liquidus line was investigated by adding Al_2O_3 or MgO to the plain FeO_X-SiO_2-CaO system in the same conditions as those in the first experiments.

A premelted FeO-Fe_2O_3-SiO_2-CaO mother slag was mixed with Fe_2O_3, SiO_2 and CaO (and Al_2O_3 or MgO in the second experiments) to obtain the required initial composition and was held in a platinum foil crucible with 20-mm height, 6-mm diameter and 0.03-mm thickness. An iron crucible with the same size was used for the experiments at p_{O_2} of 4.21×10^{-12}. The sample was heated at

the desired temperature and oxygen pressure. The temperature was controlled within 2 K by a SCR controller with a Pt-Pt · Rh thermocouple. CO-CO$_2$ gas mixtures were used to control the partial pressures of oxygen at 10^{-6}, 10^{-8} and 10^{-10} according to Eq. (1) [7].

$$CO(g) + 1/2O_2 = CO_2(g), \qquad (1)$$

$$\Delta G°/J = -279\,710 + 84.08 \text{ T.}$$
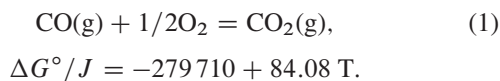
The gas mixture, which was regulated using a capillary flow meter, was introduced into a reaction chamber through an alumina tube with a flow rate of 1.7×10^{-6} m^3/s. For the experiments at p_{O_2} of 2.27×10^{-4} and the iron saturation, pure CO$_2$ gas and argon gas were respectively introduced in the reaction chamber. It was indicated in the preliminary experiments that the equilibrium with the platinum or iron crucible could be obtained in 86.4 ks. Thus, after the holding time of 86.4 ks, the sample was taken from the upper side of the furnace and quenched in a jet stream of argon.

A vertical section of the quenched sample composing of a glassy part, which was formed during quenching the liquid slag with the liquidus composition, and a crystalline part corresponding to the solid solution of Fe$_3$O$_4$ or FeO, which was in equilibrium with the liquid slag at 1523 K, was analyzed by the EPMA technique using a JEOL*8200L with wavelength dispersive detectors (*Japan Elecron Optics Ltd., Tokyo, Japan). The analysis of the glassy slag by EPMA was carried out with the method of scanner area analysis at more than 8 different places on each sample, each covering an area of 100 μm × 100 μm, while the conventional point analysis was carried out for the crystalline solid solution.

3   Results and Discussion

3.1   FeO$_X$-SiO$_2$-CaO System

The liquidus lines in the FeO$_X$ corner of the plain FeO$_X$-SiO$_2$-CaO system with the (mass% CaO/(mass% SiO$_2$ + mass% CaO)) ratios of less than 0.5 at 1523 K are shown in Figure 1. It is found that the solid iron oxide coexisting with the liquid slag was solid Fe$_3$O$_4$ containing few SiO$_2$ or CaO of less than 0.5 mass% at p_{O_2} of 10^{-8}, 10^{-6} and 2.27×10^{-4} , while solid FeO also with very few SiO$_2$ and CaO contents at p_{O_2} of 4.21×10^{-12} and 10^{-10}. It is also found in Figure 1 that the liquidus line at p_{O_2} of 2.27×10^{-4} protrudes toward the SiO$_2$ corner and solid SiO$_2$ coexists along with solid Fe$_3$O$_4$ at the terminal point of the liquidus line. On the other hand, the liquidus line at p_{O_2} of 10^{-6} is almost parallel to the FeO$_X$-CaO axis of the ternary diagram and joins together the triple point of the liquid, solid Fe$_3$O$_4$ and solid SiO$_2$ phases and another triple point of the liquid, solid Fe$_3$O$_4$ and solid CaO · SiO$_2$ phases. The liquidus line at p_{O_2} of 10^{-8} is also closely parallel to the
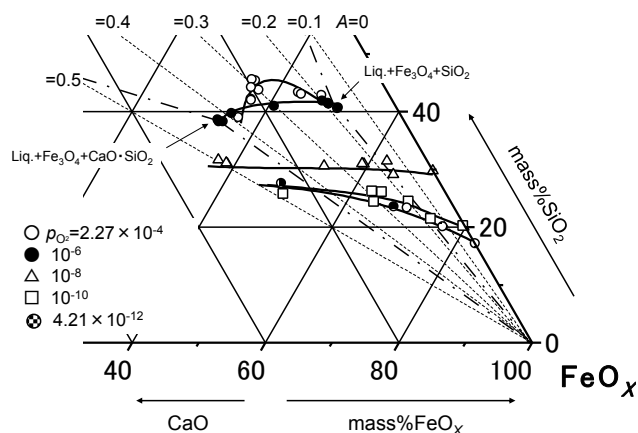

Figure 1. Liquidus line in the FeO$_X$ corner of FeO$_X$-SiO$_2$-CaO system at 1523 K and at different partial pressures of oxygen (dotted lines: iso-A given by mass% CaO/(mass% SiO$_2$ + mass% CaO)).

FeO$_X$-CaO axis but it simply terminates at the FeO$_X$-SiO$_2$ axis with no triple point being formed. The liquidus lines at p_{O_2} of 10^{-10} and 4.21×10^{-12} are very similar to each other and both represent slightly convex curvatures against the FeO$_X$-CaO axis.

It is notable that the content of FeO$_X$ on the liquidus line in the FeO$_X$ corner of FeO$_X$-SiO$_2$-CaO system at 1523 K is drastically decreased with increasing partial pressure of oxygen when the pressure is over 10^{-10}. The similar dependency on the partial pressure of oxygen was observed in the phase diagram at 1573 K [5]. This dependency has a very important implication in copper smelting to avoid the formation of solid Fe$_3$O$_4$ in the liquid slag phase because it causes the bottom-up of smelting furnace and also increases the viscosity of the slag, that may enhance the loss of copper in the slag due to the suspension of copper matte droplets. The matte smelting is practically operated at the oxygen partial pressure of about 10^{-8} and about 1523 K. The content of FeO$_X$ in the slag is usually controlled at about 35 mass%. This selection for the FeO$_X$ content is reasonable because the slag is homogeneously liquid with no solid Fe$_3$O$_4$ being formed. It should be noted that even the slight increase in the oxygen partial pressure above 10^{-8} may drastically decrease the FeO$_X$ content on the liquidus line and a careful control of the oxygen partial pressure will be required to avoid the formation of solid Fe$_3$O$_4$.

3.2   FeO$_X$-SiO$_2$-CaO-Al$_2$O$_3$ System

The effect of Al$_2$O$_3$ on the liquidus line in the FeO$_X$ corner of FeO$_X$-SiO$_2$-CaO system, which is illustrated in Figure 1, was investigated at 1523 K. Some amounts of Al$_2$O$_3$ were added to the fixed points on the liquidus line in the FeO$_X$ corner, which have given values of A in a range between 0 and about 0.5, as defined by $A =$ mass% CaO/(mass%

(a) p_{O_2}=4.21 × 10^{-12}

○A=0, △0.19, □0.51
●, ▲, ■Liq.+FeO+FeO·Al$_2$O$_3$

(b) p_{O_2} =10^{-10}
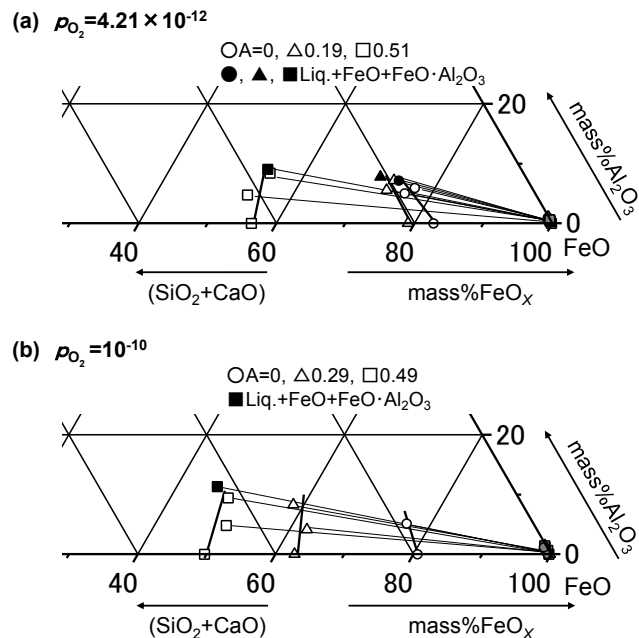
○A=0, △0.29, □0.49
■Liq.+FeO+FeO·Al$_2$O$_3$

Figure 2. Effect of Al$_2$O$_3$ on the liquidus line in the FeO$_X$ corner of FeO$_X$-SiO$_2$-CaO system (1523 K) with given A (A = mass% CaO/(mass% SiO$_2$ + mass% CaO)) at p_{O_2} = 4.21 × 10^{-12} (a) and p_{O_2} = 10^{-10} (b).

(a) p_{O_2} =10^{-8} ○A=0, △0.24, □0.49

(b) p_{O_2} =10^{-6} ○A=0.18, △0.30, □0.48

(c) p_{O_2} =2.27 × 10^{-4} ○A=0.25, △0.33, □0.48

Figure 3. Effect of Al$_2$O$_3$ on the liquidus line in the FeO$_X$ corner of FeO$_X$-SiO$_2$-CaO system (1523 K) at p_{O_2} = 10^{-8} (a), p_{O_2} = 10^{-6} (b) and p_{O_2} = 2.27 × 10^{-4}.

SiO$_2$ + mass% CaO), which corresponds to the basicity of slag. The results are shown in Figures 2 and 3 in the FeO$_X$-(SiO$_2$ + CaO)-Al$_2$O$_3$ quasi-ternary composition diagrams. The tie lines connecting between the solid FeO and the liquidus point at p_{O_2} of 4.21 × 10^{-12} and 10^{-10} are shown in Figure 2(a) and (b), respectively. It is noted that the solubility of Al$_2$O$_3$ in the solid FeO is small at less than 1.5 mass% and that the second solid phase of FeO · Al$_2$O$_3$ (hercynite) is formed when the content of Al$_2$O$_3$ in the liquid phase is increased up to about 10 mass%. At p_{O_2} of 10^{-8}, 10^{-6} and 2.27 × 10^{-4}, as shown in Figure 3(a), (b) and (c), respectively, solid Fe$_3$O$_4$ is in equilibrium with the liquid phase in the FeO$_X$ corner. It is notable that the solubility of Al$_2$O$_3$ in the solid Fe$_3$O$_4$ is considerably large and that the tie line connecting between the solid and liquid phases is almost parallel to the bottom (SiO$_2$ + CaO)-FeO$_X$ axis in the quasi-ternary diagram, indicating that the solubility of Al$_2$O$_3$ in the coexisting liquid and solid phases is very similar in the magnitude to each other.

The effect by adding Al$_2$O$_3$ on the liquidus line can be made clear when the mass% FeO$_X$ on the liquidus point is shown against the mass% Al$_2$O$_3$ on the same point for the given A and the slope is compared with that given by
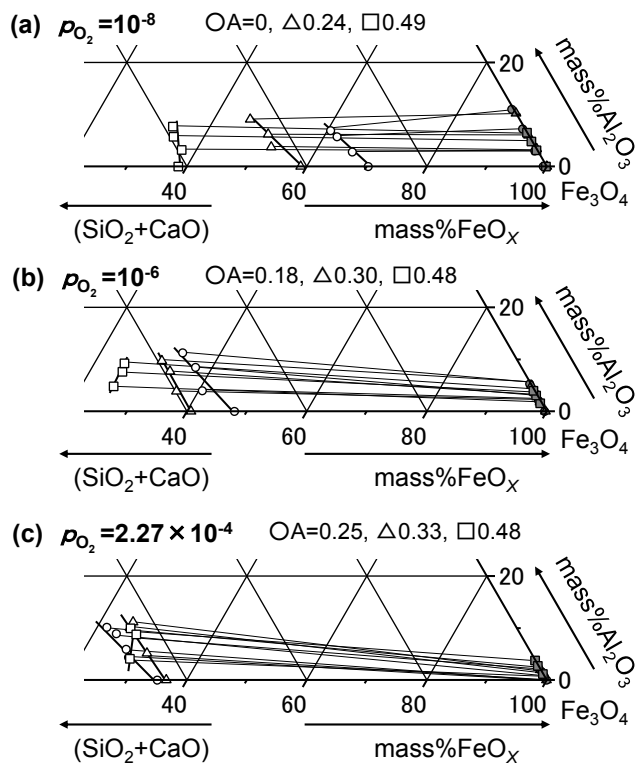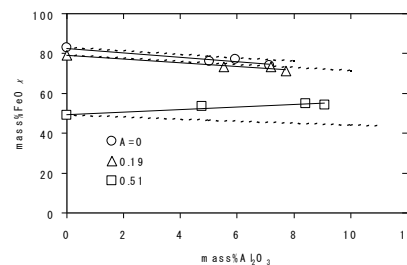

(a) p_{O_2}=4.21 × 10^{-12}

(b) p_{O_2}=10^{-10}

Figure 4. Relationships between the FeO$_X$ and Al$_2$O$_3$ contents on the liquidus line in the FeO$_X$ corner of FeO$_X$-SiO$_2$-CaO system (1523 K) with given A at p_{O_2} = 4.21 × 10^{-12} (a) and p_{O_2} = 10^{-10} (b) (broken lines: from Eq. (2)).

Eq. (2).

$$\text{mass\% FeO}_X(\text{simple}) = \text{mass\% FeO}_X(\text{without Al}_2O_3)$$
$$\times \{1 - (\text{mass\% Al}_2O_3)/100\}. \quad (2)$$

In this equation, mass% FeO_X(without Al_2O_3) is the content of FeO_X in the liquid phase of plain FeO_X-SiO_2-CaO system and mass% Al_2O_3 is that of Al_2O_3 in the liquid phase of FeO_X-SiO_2-CaO-Al_2O_3 system. It is indicated by mass% FeO_X(simple) in Eq. (2) that the plain ternary system is simply diluted by the addition of Al_2O_3 with no chemical and physical effects being given to the liquidus point.

The relationships between the contents of FeO_X and Al_2O_3 on the liquidus point at given A and p_{O_2} of 4.21×10^{-12} and 10^{-10} are shown in Figure 4(a) and (b), respectively, along with the relationships for the simple dilution given by the dotted straight lines. It is noted that the content of FeO_X is obviously larger than that for the simple dilution at A of about 0.5 and at these oxygen partial pressures. This means that the addition of Al_2O_3 shifts the liq-

(a) p_{O_2} =10^{-8}

(b) p_{O_2} =10^{-6}

(c) p_{O_2} =2.27 × 10^{-4}

Figure 5. Relationships between the FeO_X and Al_2O_3 contents on the liquidus line in the FeO_X corner of FeO_X-SiO_2-CaO system (1523 K) at $p_{O_2} = 10^{-8}$ (a), $p_{O_2} = 10^{-6}$ (b) and $p_{O_2} = 2.27 \times 10^{-4}$ (c) (broken lines: from Eq. (2)).

uidus line towards the FeO corner. On the other hand, the content of FeO_X at smaller A is decreased with increasing content of Al_2O_3 and the relationship is very close to that for the simple dilution. It is of technological importance that the addition of Al_2O_3 to the FeO_X-SiO_2-CaO slag will enhance the solubility of FeO_X in the liquid slag with a high (CaO/SiO_2) ratio in a strongly reducing atmosphere.

On the other hand, as for the relationships at p_{O_2} of 10^{-8}, 10^{-6} and 2.27×10^{-4} as shown in Figure 5(a), (b) and (c), respectively, it is noted that the content of FeO_X is proportionally decreased with increasing content of Al_2O_3 in the liquid and the slope for smaller values of A is considerably steeper than that for the simple dilution. This indicates that the addition of Al_2O_3 to the plain FeO_X-SiO_2-CaO system with a low (CaO/SiO_2) ratio will clearly decrease the solubility of FeO_X in the liquid, shifting the liquidus line toward the low FeO_X-content region, in other word, making the homogeneous liquid region in the FeO_X corner narrow. On the other hand, the relationship at a high value of A with about 0.5 closely resembles that for the simple dilution.

3.3 FeO_X-SiO_2-CaO-MgO System

The effect of MgO on the liquidus line, which is illustrated in Figure 1, was investigated at 1523 K. Some amounts of MgO were added to the fixed points on the liquidus line in the FeO_X corner, which have given values of A in a range between 0 and about 0.5. The results are shown in Figure 6 and Figure 7 on the FeO_X-(SiO_2 + CaO)-MgO quasi-ternary composition diagrams. As for the tie lines connecting between the solid FeO and the liquidus point at p_{O_2} of 4.21×10^{-12} and 10^{-10} as shown in Figure 6(a) and (b), respectively, it is noted that the solubility of MgO in the solid FeO phase is considerably large and the tie lines are almost parallel to the bottom FeO_X-(SiO_2 + CaO) axis in the diagram. It is found that the second solid phase of magnesiowustite ((Mg, Fe)O) is formed at $A = 0$ when the content of MgO is increased. At A of about 0.5, a solid compound of 2CaO·MgO·SiO_2 is also formed as the second solid phase when the content of MgO in the liquid phase is increased up to about 4 mass%. As for the tie lines connecting between the solid Fe_3O_4 and the liquidus point at p_{O_2} of 10^{-8}, 10^{-6} and 2.27×10^{-4} as shown in Figure 7(a), (b) and (c), respectively, it is noted that the content of MgO in the solid Fe_3O_4 is also considerably large as compared with that on the liquidus point.

The mass% FeO_X on the liquidus point is shown against the mass% MgO on the same point for the given A and the slope is compared with that given by Eq. (3).

$$\text{mass\% FeO}_X(\text{simple}) = \text{mass\% FeO}_X(\text{without MgO})$$
$$\times \{1 - (\text{mass\% MgO})/100\}. \quad (3)$$

In this equation, mass% FeO_X(without MgO) is the content of FeO_X on the liquidus point of plain FeO_X-SiO_2-CaO

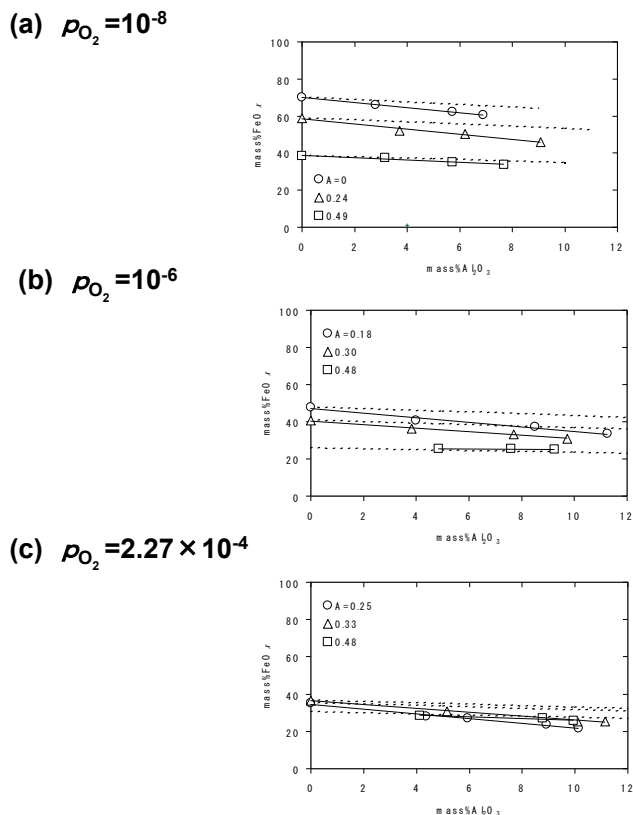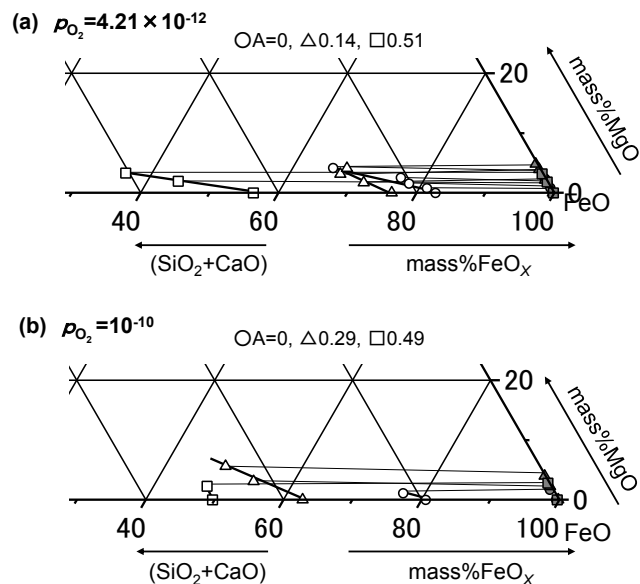(a) $p_{O_2} = 4.21 \times 10^{-12}$

$\bigcirc A = 0$, $\triangle 0.14$, $\square 0.51$

(b) $p_{O_2} = 10^{-10}$

$\bigcirc A = 0$, $\triangle 0.29$, $\square 0.49$

Figure 6. Effect of MgO on the liquidus line in the FeO$_X$ corner of FeO$_X$-SiO_2-CaO system (1523 K) with given A (A = mass% CaO/(mass% SiO_2 + mass% CaO)) at $p_{O2} = 4.21 \times 10^{-12}$ (a) and $p_{O_2} = 10^{-10}$ (b).

(a) $p_{O_2} = 10^{-8}$

$\bigcirc A = 0$, $\triangle 0.24$, $\square 0.49$

(b) $p_{O_2} = 10^{-6}$

$\bigcirc A = 0.18$, $\triangle 0.30$, $\square 0.52$

(c) $p_{O_2} = 2.27 \times 10^{-4}$
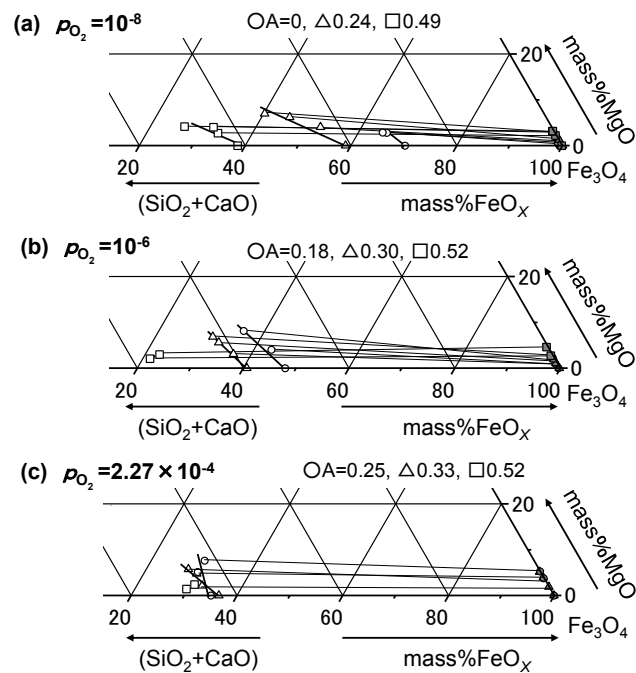
$\bigcirc A = 0.25$, $\triangle 0.33$, $\square 0.52$

Figure 7. Effect of MgO on the liquidus line in the FeO$_X$ corner of FeO$_X$-SiO_2-CaO system (1523 K) at $p_{O_2} = 10^{-8}$ (a), $p_{O_2} = 10^{-6}$ (b) and $p_{O_2} = 2.27 \times 10^{-4}$ (c).

system and mass% MgO is that of MgO on the liquidus point of FeO$_X$-SiO_2-CaO-MgO system. The relationships between the contents of FeO$_X$ and MgO on the liquidus at given A at p_{O_2} of 4.21×10^{-12} and 10^{-10} are shown in Figure 8(a) and (b), respectively, together with mass%
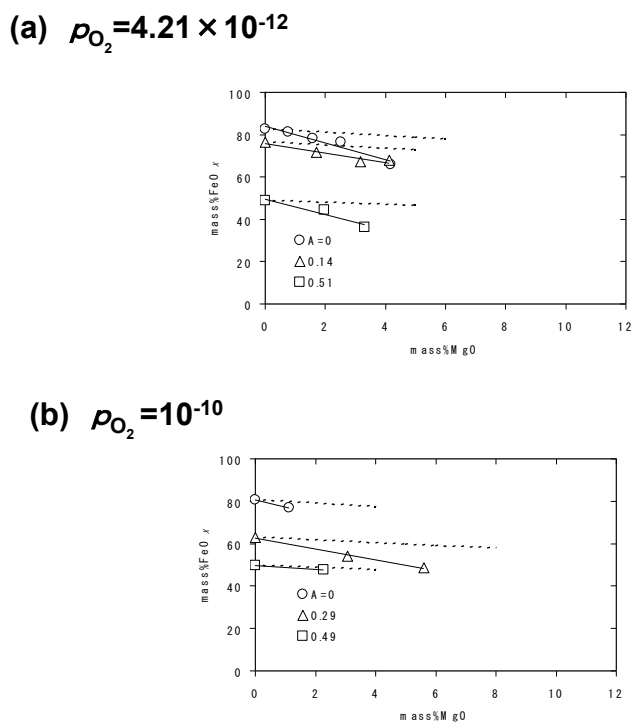
(a) $p_{O_2} = 4.21 \times 10^{-12}$

(b) $p_{O_2} = 10^{-10}$

Figure 8. Relationships between the FeO$_X$ and MgO contents on the liquidus line in the FeO$_X$ corner of FeO$_X$-SiO_2-CaO system (1523 K) with given A at $p_{O_2} = 4.21 \times 10^{-12}$ (a) and $p_{O_2} = 10^{-10}$ (b) (broken lines: from Eq. (3)).

FeO$_X$(simple) given by the dotted lines. It is noted that the content of FeO$_X$ is almost proportionally decreased with increasing content of MgO in the liq1uid and that the slope is considerably steeper than that for the simple dilution. As shown in Figure 9(a), (b) and (c) for p_{O_2} of 10^{-8}, 10^{-6} and 2.27×10^{-4}, respectively, the content of FeO$_X$ is almost proportionally decreased with increasing content of MgO in the liquid and the slope is also considerably steeper than that for the simple dilution. The deviation from the simple dilution by the addition of MgO is much larger than that by the addition of Al_2O_3.

It is found in the present study that the addition of MgO to the plain FeO$_X$-SiO_2-CaO slag definitely shifts the liquidus line around the FeO$_X$ corner toward the low FeO$_X$-content region and makes the homogeneous liquid region narrow at A between 0 and 0.5 and at the oxygen partial pressures between the extremely reducing(iron saturation) and oxidizing (CO$_2$) atmospheres. This result suggests for practical operations of the matte smelting and the slag cleaning of copper that MgO is a refractory component which makes the slag less fusible and its involvement in the slag system causes some serious problems in the operations due to the formation of the solid oxides in the liquid slag phase.
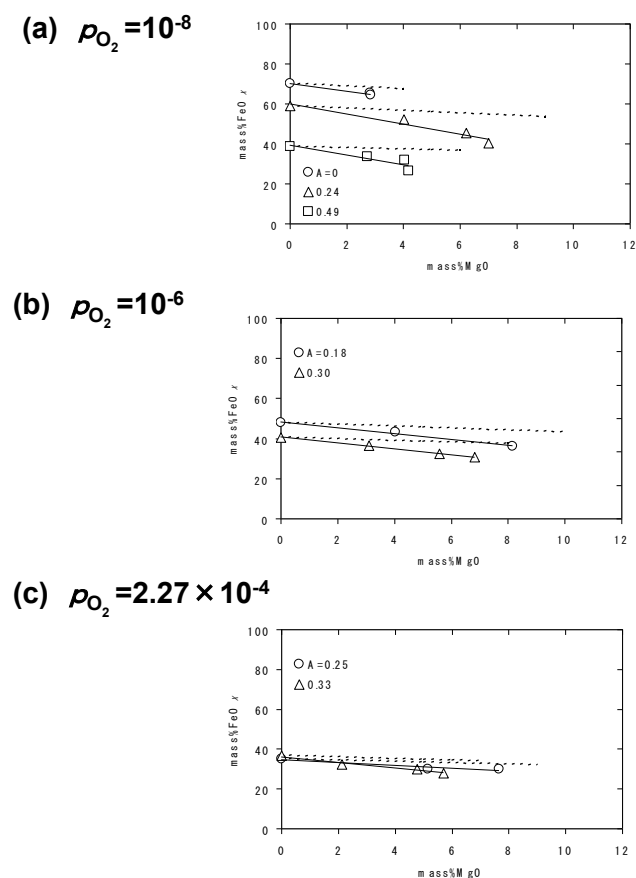
(a) $p_{O_2} = 10^{-8}$

(b) $p_{O_2} = 10^{-6}$

(c) $p_{O_2} = 2.27 \times 10^{-4}$

Figure 9. Relationships between the FeO_X and MgO contents on the liquidus line in the FeO_X corner of FeO_X-SiO_2-CaO system (1523 K) at $p_{O_2} = 10^{-8}$ (a), $p_{O_2} = 10^{-6}$ (b) and $p_{O_2} = 2.27 \times 10^{-4}$ (c) (broken lines: from Eq. (3)).

It is considered thermodynamically that MgO makes the activity coefficient of FeO_X in the slag system positively large at the conditions in the present study even though Al_2O_3 makes the activity coefficient of FeO_X small only in the extremely reducing atmosphere.

4   Conclusion

Despite of the importance in the matte smelting and the slag cleaning of copper, the effects of oxygen partial pressure and minor components of Al_2O_3 and MgO on the range of homogeneous liquid region in the FeO_X corner of FeO_X-SiO_2-CaO base system are not well known quantitatively. In the present study, the liquidus line in the FeO_X corner of FeO_X-SiO_2-CaO system and the effect by adding Al_2O_3 or MgO to this plain system on the liquidus line

were experimentally investigated at 1523 K and at various ratios of A defined by (mass% CaO/(mass% SiO_2 + mass% MgO)) under various partial pressures of oxygen between 4.21×10^{-12} (iron saturation) and 2.27×10^{-4} (atmosphere of CO_2). The results are summarized as follows:

(1) In the plain FeO_X-SiO_2-CaO system, the liquidus line in the corner of FeO_X shifts remarkably toward the low FeO_X-content region, making the homogeneous liquid region narrow when the partial pressure of oxygen is increased from 10^{-10} to 10^{-8}. The change of solid FeO_X phase in the corner from FeO (wustite) to Fe_3O_4 (magnetite) is considered to be responsible for this remarkable shift.

(2) The addition of Al_2O_3 to the plain FeO_X-SiO_2-CaO system at p_{O_2} of 4.21×10^{-12} and 10^{-10} and at a high A of about 0.5 shifts the liquidus line in the FeO_X corner toward the FeO_X-rich region, making the homogeneous liquid region wide but, at the higher partial pressures, makes the homogeneous liquid region considerably narrow. It must be noted that the effect of Al_2O_3 on the liquidus line is considerably different by the oxygen partial pressure and by A.

(3) The addition of MgO to the plain FeO_X-SiO_2-CaO system remarkably shifts the liquidus line toward the low FeO_X-content region, making the homogeneous liquid region considerably narrow, at any oxygen partial pressure and at any A.

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