Lattice Parameter and Redox Equilibria in CaO-containing Wustite

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Equilibrium relation among oxygen potential in atmosphere, composition and lattice parameter in CaO-containing wustite have been studied at 1273 K. Wustite plates with the molar cation fraction $M_{\text{Ca}}/(M_{\text{Fe}} + M_{\text{Ca}})$ ($=M_{\text{Ca-Fe}}$) ranging from 0.0058 to 0.079 were equilibrated with CO–CO₂ gas mixtures. Composition of the wustite specimens was determined by chemical analysis and thermo-gravimetric method. Lattice parameter of the CaO-containing wustite was measured by X-ray diffraction method. The relation between the lattice parameter a and the gas ratio K_s ($=P_{\text{CO}_2}/P_{\text{CO}}$) in the gas mixture was expressed by

$$a = (4.2975 + 0.560 \cdot M_{\text{Ca-Fe}}) - 1.470 \times 10^{-2} \cdot \ln(K_s) \quad (\text{\AA})$$

The variation of a with $M_{\text{Ca-Fe}}$ and molar ratio $M_{\text{Fe}}/M_{\text{O}}$ in the CaO-containing wustite was given by

$$a = 1.916 + 0.565 \cdot (M_{\text{Ca-Fe}}) + 4.719 \cdot (M_{\text{Fe}}/M_{\text{O}}) - 2.316 \cdot (M_{\text{Fe}}/M_{\text{O}})^2 \quad (\text{\AA})$$

Then the lattice parameter may be used as the index of the composition in CaO-containing wustite. The 'iso-lattice-parameter' line was drawn within the wustite field in the isothermal section of the system FeO–Fe₂O₃–CaO. The molar ratio $M_{\text{Fe}_2\text{O}_3}/M_{\text{FeO}}$ of the CaO-containing wustite on the Fe₂O₃-rich side slightly increases with an increase in CaO content but the ratio on the FeO-rich side does not change. The solubility of CaO in the wustite equilibrated with both metallic iron and 2CaO·Fe₂O₃ was estimated to be ~9 mol% CaO.

KEY WORDS: ironmaking; phase diagram; CaO-containing wustite; lattice parameter; solubility of CaO; molar ratio of Fe₂O₃ to FeO; gas composition.

1. Introduction

The redox equilibria between oxygen potential and the composition of wustite are the most important relation to understand the high temperature performance of iron or wustite. Therefore, many works have been done by using various methods.^{1,2)} On the other hand, it was reported that the lattice parameter of pure wustite measured at room temperature changed almost linearly with oxygen content in wustite.^{3,4)} Moreover, it was found that the lattice parameter of CaO-containing wustite increased with an increase in CaO content of the wustite at constant oxygen potential.^{1,5)} Therefore, the lattice parameter would be considered as a useful parameter which relates to the composition of wustite.

We have been examined the initial reduction stage of pure and CaO-containing wustite with CO–CO₂ gas mixtures.^{6–8)} In these works, mass changes of the reduced wustite were estimated by measuring the changes in the lattice parameter of wustite. The estimated mass changes were in good agreement with the measured ones by an usual thermo-balance and the reduction process was analyzed quantitatively.

In the present paper, the lattice parameter of CaO-con-

taining wustite was measured over the wide range of the composition by X-ray diffraction method, and the change in the lattice parameter with the wustite composition and the oxygen potential in the atmosphere was revealed. In addition, the phase boundaries between the wustite and the co-existing phases in the system FeO–Fe₂O₃–CaO were examined.

2. Experimental

2.1. Preparation of Specimen

Wustite containing CaO was prepared by the same procedure as the previous work.⁸⁾ The powder mixture of reagent grade CaO (more than 99.9 mass%), Fe₂O₃ and electrolytic iron (99.9 mass% both) well mixed in a mortar, was charged into an iron crucible and melted with high frequency induction furnace under an Ar atmosphere. The cation molar fraction $M_{\text{Ca}}/(M_{\text{Fe}} + M_{\text{Ca}})$ (hereinafter $M_{\text{Ca-Fe}}$) in the mixture was ranging from 0.0058 to 0.079. The temperature was held at 1673 K for 1.8 ks and then the melt was cast into the shallow flat-bottomed pure iron mold preheated at ~1170 K. The obtained wustite ingot was cut into small plates with 10×10×1.2 mm so that the broad-side surface of the plate might become parallel to the bottom surface of

the ingot. After pre-annealing at 1420 K for 14 ks, the wustite specimens were equilibrated at 1273 K with CO–CO₂ gas mixtures having gas ratio of $P_{\text{CO}_2}/P_{\text{CO}}=40/60$ (hereinafter K_s) for several hours and then cooled quickly to room temperature. The lattice parameter of wustite in the specimens was measured by X-ray diffraction method. Then the specimens were re-equilibrated under the same condition. These processes were repeated up to 90 ks. The equilibration was confirmed to be attained at 50 ks by ensuring no change in the lattice parameter of wustite. Composition of the wustite specimens equilibrated with the gas mixture was determined by chemical analysis for total iron, FeO and CaO. These specimens were designated as the ‘standard specimen’. The equilibration with other gas mixture was conducted for the gas mixtures with K_s ranging from 70/30 to 32/68. The composition of these specimens was determined from the mass change of the specimen during equilibration. In the experimental run, evaporation of CaO and iron oxides from the specimen was assumed to be negligibly small.

2.2. Determination of Lattice Parameter

The wustite specimens used in this work were consisted of many columnar crystal grains directed almost perpendicularly to the specimen surface. The longitudinal direction of the grains was almost coincided with $\langle 100 \rangle$. X-ray diffractometry of the specimen surface indicated strong 400 reflection ($K_{\alpha 1}$ and $K_{\alpha 2}$ peaks were separated clearly) at the relatively high diffraction angle, and the lattice parameter was calculated from these peaks. The lattice parameter at the polished surface of the specimen is the same as that of the surface within experimental error. In addition, it was confirmed that this result was in agreement with that from 420 reflection obtained on the cutting surface which was inclined at $\sim 25^\circ$ to the broad-side surface of the specimen.

3. Results and Discussion

3.1. Lattice Parameter of Pure Wustite

Figure 1 shows the relation between lattice parameter a of the pure wustite and K_s of the gas mixtures. The figure also presents the calculated values by the present authors from the composition dependence of lattice parameter³⁾ and the relation between composition and the gas ratio in the gas mixtures equilibrated⁹⁾ and the observed values by Bredesen and Kofstad.⁴⁾ The present results are in good agreement with the others except for the calculated value at $K_s > 2.0$. From these results, the dependence of a on K_s is expressed by Eq. (1).

$$a = 4.2975 - 1.470 \times 10^{-2} \cdot \ln(K_s) \quad (\text{\AA}) \quad \dots\dots\dots (1)$$

The lattice parameter of iron-saturated wustite (a^*) was reported to be 4.311(Å) by Levin and Wagner.³⁾ Extrapolating Eq. (1) to $a = a^*$, one has the gas ratio in equilibrium with iron-saturated wustite (K_s^*) as 0.40. This value agrees well with the value 0.396 by Darken and Gurry.¹⁰⁾

The relation between a and molar ratio of Fe and O ion (hereinafter $M_{\text{Fe}}/M_{\text{O}}$) on the pure wustite is shown in Fig. 2. The boundaries of the wustite field reported by Darken and Gurry¹⁰⁾ were also shown in this figure. Levin and Wagner³⁾ and Bredesen and Kofstad⁴⁾ reported a linear relation be-

Fig. 1. Relation between lattice parameter and $K_s (=P_{\text{CO}_2}/P_{\text{CO}})$ in the pure wustite equilibrated with CO–CO₂ gas mixtures. The solid line represents the result calculated from Eq. (1).

Fig. 2. Relation between lattice parameter and molar ratio $M_{\text{Fe}}/M_{\text{O}}$ in pure wustite.

tween a and the composition over a wide range of the homogeneous wustite field. The present results seem to be in accordance with those results. The change in a , however, tends to become small as $M_{\text{Fe}}/M_{\text{O}}$ approaches the composition of both phase boundaries, indicating that the linear relation mentioned above can not be applicable consistently over the entire range of the wustite composition. This point will be discussed in the next section including the results of CaO-containing wustite.

3.2. Lattice Parameter of CaO-containing Wustite

3.2.1. Relation between Lattice Parameter and CaO Content in Wustite

Figure 3 represents the relation between a and $M_{\text{Ca-Fe}}$ in CaO-containing wustite. From this figure, it is clear that a increases linearly with an increase in $M_{\text{Ca-Fe}}$ and its slope is almost constant independent of K_s . The similar dependence of a on CaO content was also reported by Iguchi *et al.*¹⁾ and Takami and Yoshii.⁵⁾ At $K_s=50/50$, 60/40 and 70/30, however, the a becomes nearly constant as $M_{\text{Ca-Fe}}$ exceeds a certain value. This suggests that the composition of wustite in these specimens exceeds the homogeneous phase field and the certain value corresponds to the solubility limit of CaO. The values of a at the solubility limit (a_c), K_s , coexisting phases identified by X-ray diffraction and solubility limit

Fig. 3. Lattice parameter as a function of molar cation fraction in the CaO-containing wustite equilibrated with various CO-CO₂ gas mixtures. The a_c^* denotes the lattice parameter of the wustite in equilibrium with both metallic iron and C₂F.

Table 1. Results of equilibration and X-ray diffraction experiments on the CaO-containing wustite with various molar cation fractions.

No.	M_{Ca-Fe}	K_s (=Pco ₂ /Pco)	coexisting phases	a_c (Å)	solubility limit (M_{Ca-Fe})
1	0.032	70/30	W + CWF	4.299	0.025
2	0.059	60/40	W + CWF	4.319	0.05
3	0.079	50/50	W + CW ₃ F	~4.338	0.07
4	0.079	14/86	W + C ₂ F + M · Fe	~4.357	-

The lattice parameter of sample (No.4) corresponds to a_c^* . That sample was reduced with CO-CO₂-Ar gas mixture ($K_s=14/86$) for 600s.

$M_{Ca-Fe} = M_{Ca}/(M_{Fe} + M_{Ca})$, W : wustite, CWF : CaO · FeO · Fe₂O₃,
CW₃F : CaO · 3FeO · Fe₂O₃, C₂F : 2CaO · FeO, M · Fe : metallic iron

are summarized for the specimens with several M_{Ca-Fe} in Table 1. It is confirmed that the solubility limit of CaO increases and the coexisting another phase changes from CaO · FeO · Fe₂O₃ (CWF) to CaO · 3FeO · Fe₂O₃ (CW₃F) with a decrease in K_s , that is, the decrease in the oxygen content of the wustite. These results are almost similar to those in the phase diagram given by Schürman and Wurm.¹¹⁾ The 'standard specimens' were reduced by CO-CO₂ gas mixture ($K_s=14/86$) until metallic iron was slightly formed, and cooled rapidly. Then, the lattice parameter of the surface wustite in contact with the metallic iron was measured. The obtained a was shown in Fig. 3 with the closed circle as the lattice parameter of iron-saturated wustite (a^*). The dependence of a^* on M_{Ca-Fe} is the same as that of a on M_{Ca-Fe} . In the specimen (4) in Table 1, X-ray diffraction analysis was performed on the vicinity of the interface between reduced iron layer and unreduced wustite after reducing for relatively long time (600 s). The formation of 2CaO · Fe₂O₃ (C₂F) besides metallic iron was observed from the diffraction pattern. The a (=4.357 Å) obtained corresponds to the lattice parameter of the wustite in equilibrium with metallic iron and C₂F (a_c^*). The solubility limit of CaO in iron-saturated wustite was estimated to be $M_{Ca-Fe}=0.081$

Fig. 4. Relation between lattice parameter and K_s at various molar cation fractions. The solid lines represent the results calculated from Eq. (2). The a_c^* denotes the lattice parameter of the wustite in equilibrium with both metallic iron and C₂F.

by extrapolation of a^* to a_c^* in the relation between a^* and M_{Ca-Fe} shown in Fig. 3. The double dotted and dashed line in the figure represents the solubility limit of CaO in the wustite at various K_s .

3.2.2. Relation between Lattice Parameter and K_s

Figure 4 shows the relation between a and K_s on the CaO-containing wustite. The dependence of a on K_s seems to be almost similar to that in the pure wustite. This relation is expressed by Eq. (2).

$$a = (4.2975 + 0.560 \cdot M_{Ca-Fe}) - 1.470 \times 10^{-2} \cdot \ln(K_s) \quad (\text{Å}) \quad (2)$$

The solid lines in the figure represent the results calculated from Eq. (2) and are in good accordance with the measurements. Equation (2) can also express the dependence of a on M_{Ca-Fe} given in Fig. 3. Here, the gas ratio in equilibrium with iron-saturated wustite (K_s^*) are obtained by extrapolating Eq. (2) to $a=a^*$. The closed symbols in Fig. 4 show the calculated K_s^* . Extrapolating the relation between a^* and K_s^* to $a^*=a_c^*$, one has the gas ratio in equilibrium with the wustite saturated with both metallic iron and C₂F ($(K_s)_c^*$) as 0.392. Thus the K_s^* in high M_{Ca-Fe} is considered to become slightly smaller than that on pure wustite. This tendency accords with the result reported by Schurman and Janhsen.²⁾ The double dotted and dashed line shows the a_c at various M_{Ca-Fe} .

3.2.3. Composition Dependence of Lattice Parameter

Figure 5 demonstrates the relation between a and the composition M_{Fe}/M_O in CaO-containing wustite. At constant M_{Ca-Fe} , the a seems to increase almost linearly with an increase in M_{Fe}/M_O . However, the value of a deviates from linear relation as M_{Fe}/M_O approaches both phase boundary compositions. Then, the relation between a and M_{Fe}/M_O is expressed by Eq. (3).

$$a = 1.916 + 0.565 \cdot (M_{Ca-Fe}) + 4.719 \cdot (M_{Fe}/M_O) - 2.316 \cdot (M_{Fe}/M_O)^2 \quad (\text{Å}) \quad (3)$$

Fig. 5. Relation between lattice parameter and $M_{\text{Fe}}/M_{\text{O}}$ at various molar cation fractions. The solid lines represent the results calculated from Eq. (3) and the dotted line represents the results for pure wustite. The a_c^* denotes the lattice parameter of the wustite in equilibrium with both metallic iron and C_2F .

The results calculated from Eq. (3) are in accord with the measurements as shown in the figure. Extrapolating Eq. (3) to $a=a^*$, the molar ratios of iron-saturated wustite ($(M_{\text{Fe}}/M_{\text{O}})^*$) are obtained and shown with the closed symbols in Fig. 5. Though the observed values of $(M_{\text{Fe}}/M_{\text{O}})^*$ are somewhat scattered, they tend to become smaller slightly with an increase in $M_{\text{Ca-Fe}}$. The dotted and dashed line shows the boundary of wustite and (wustite+metallic iron) fields. On the other hand, the double dotted and dashed line shows the boundary of wustite and (wustite+coexisting phase) fields estimated from the solubility limits of CaO at various K_s . The intersection of these two lines shows a_c^* and $(M_{\text{Fe}}/M_{\text{O}})_c^*$ in the wustite equilibrated with metallic iron and C_2F . The value of $(M_{\text{Fe}}/M_{\text{O}})_c^*$ is estimated to be 0.954.

It may be considered that Eq. (3) is possible to represent the dependence of a on $M_{\text{Fe}}/M_{\text{O}}$ in pure wustite. Then, the values of a calculated at $M_{\text{Ca-Fe}}=0$ are shown with the dotted line in Fig. 5. The results obtained are consistent with the values measured at high $M_{\text{Fe}}/M_{\text{O}}$ but inconsistent with those at low $M_{\text{Fe}}/M_{\text{O}}$. This suggests that the dependence of a on $M_{\text{Fe}}/M_{\text{O}}$ in the CaO-containing wustite may be not extrapolated linearly to that in pure wustite. The $M_{\text{Fe}}/M_{\text{O}}$ is considered to be related immediately to the defect structure of wustite. Therefore, it is thought that an atomistic examination on the defect structure *etc.* is necessary to describe the dependence of a on $M_{\text{Fe}}/M_{\text{O}}$ more strictly.

3.3. Phase Equilibria in the System $\text{FeO-Fe}_2\text{O}_3\text{-CaO}$

The results obtained in this work are shown as an oxygen potential line in the isothermal section of the system $\text{FeO-Fe}_2\text{O}_3\text{-CaO}$ (Fig. 6(a)). The oxygen potential lines in $K_s=35/65\text{-}50/50$ are almost shown by the straight line and the extension of these lines converges to CaO vertex. Therefore, it is thought that the molar ratio ($M_{\text{Fe}_2\text{O}_3}/M_{\text{FeO}}$) of wustite does not change with the solution of CaO into

Fig. 6. Diagrams illustrating (a) phase equilibria and (b) 'iso-lattice-parameter' line in the wustite field of the system $\text{FeO-Fe}_2\text{O}_3\text{-CaO}$ at 1273 K. The closed symbols at $K_s=50/50, 60/40$ and $70/30$ represent the boundary compositions of wustite.

wustite in the composition range of low Fe_2O_3 . On the other hand, a little increase of $M_{\text{Fe}_2\text{O}_3}/M_{\text{FeO}}$ is observed in $K_s=60/40$ and $70/30$. In the figure, the results in $K_s=50/50$ and $60/40$ given by Iguchi *et al.*¹⁾ are also shown. Their results agree with the present work except for the pure wustite.

The phase boundaries in the isothermal section at 1273 K are also discussed. At $K_s=50/50, 60/40$ and $70/30$, the boundary compositions of wustite were estimated from a_c by using Eqs. (2) and (3) and were shown with the closed symbols in Fig. 6(a). The compositions of wustite specimens within the two-phase field lie close to the tie-line connecting those boundary compositions and CWF or CW_3F at the same K_s . The area enclosed by the phase boundary thus obtained and the iron-saturated compositions in the wustite equilibrated with C_2F and in the pure wustite is thought to be the single phase field of the CaO-containing wustite. This field shown in Fig. 6(a) broadens to high CaO concentration as compared with that by Schürman and Wurm.¹¹⁾ In addition, the iron-saturated composition obtained in the present work slightly swerves to the low Fe_2O_3 side with an increase in CaO content. The solubility limit of CaO in iron-saturated wustite is estimated to be $\sim 9\text{ mol}\%$. Takahashi *et al.*¹²⁾ has reported that the solubility limit at $K_s=40/60$ was 5–7 mass% CaO. Their result is in good accordance with the present work.

The 'iso-lattice-parameter' line of CaO-containing wustite was shown in Fig. 6(b). Only the measured compositions of

the wustite with a ranging from 4.290 to 4.350 (Å) are shown with the symbols in the figure. The results calculated by using Eqs. (2) and (3) are shown with the solid line and in good agreement with the measurements. In addition, the extrapolation of 'iso-lattice-parameter' line at $a=4.310$ (Å) to pure wustite converges to the result by Levin and Wagner³⁾ shown with double circle. From these results, it is confirmed that the relation between the lattice parameter and the composition of the CaO-containing wustite equilibrated with CO–CO₂ gas mixture is expressed by Eqs. (2) and (3). Therefore, the composition of wustite is estimated from only the lattice parameter when the wustite is equilibrated with the prescribed CO–CO₂ gas mixture.

4. Conclusions

The redox equilibria and lattice parameter in CaO-containing wustite were measured and the relation between the lattice parameter and composition was studied at 1273 K. The phase equilibria in the system FeO–Fe₂O₃–CaO were also examined. The results obtained are summarized as follows:

(1) The relation between the lattice parameter of the CaO-containing wustite and the gas ratio $K_s (=P_{\text{CO}_2}/P_{\text{CO}})$ in CO–CO₂ gas mixture are expressed by Eq. (2). The lattice parameter increases with an increase in molar ratio $M_{\text{Fe}}/M_{\text{O}}$ and molar fraction $M_{\text{Ca-Fe}}$, and the relation among them is shown by Eq. (3).

(2) The oxygen potential lines measured and 'iso-lat-

tice-parameter' lines calculated by using Eqs. (2) and (3) were drawn on the isothermal section of the system FeO–Fe₂O₃–CaO. At constant K_s , the molar ratio $M_{\text{Fe}_2\text{O}_3}/M_{\text{FeO}}$ of wustite does not change with the solution of CaO in the low Fe₂O₃ composition, but slightly increases in the high Fe₂O₃. The solubility of CaO was estimated to be ~9 mol% in the wustite equilibrated with both metallic iron and C₂F.

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