Effects of SiO_2 and Al_2O_3 on the Lattice Parameter and CO Gas Reduction of CaO-containing Dense Wustite

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The effects of SiO_2 and Al_2O_3 on the lattice parameter and the initial reduction rate of CaO-containing wustite were studied at 1273 K. Wustite plates containing 0.5–2 mass% CaO, 0.2–2 mass% SiO_2 and 1 mass% Al_2O_3 were prepared at the mass fractions of $\text{CaO}/\text{SiO}_2=0.5\text{--}5$. The lattice parameter of CaO– SiO_2 -containing wustite decreased with decreasing CaO/ SiO_2 ratio at a constant CaO content. This corresponded to a decrease of the dissolved content of CaO in the wustite due to a formation of CaO–FeO– SiO_2 compounds. Similarly, the dissolved content of CaO decreased in CaO– SiO_2 – Al_2O_3 -containing wustite. The process of CO gas reduction within the wustite phase field was traced with the lattice parameter measurement of the partially reduced samples and was analyzed with a mixed-control model of chemical reaction at the surface and the solid state diffusion in the wustite. The chemical reaction rate constant, k' , decreased with increasing the amount of SiO_2 addition at a constant CaO content. The dependence of k' on SiO_2 (and Al_2O_3) addition was in good accordance with the change in the dissolved content of CaO in the wustite owing to the formation of the compounds containing CaO. The inter-diffusion coefficient, $\tilde{D}$, tended to decrease slightly with increasing the amount of compound.

KEY WORDS: wustite; CO gas reduction; chemical reaction rate constant; inter-diffusion constant; mixed-control model; lattice parameter; iron making.

1. Introduction

As iron ores charged into blast furnace contain many gangue elements, it is practically important to clarify the effects of the elements on the reduction process of iron oxides. In the previous work,¹⁾ it was clarified that the rate of CO reduction within the wustite phase field was remarkably increased by adding CaO and the metallic iron was formed on the surface of wustite plate after the rapid attainment of iron-saturated composition at the surface. In addition, it was shown that the chemical reaction rate constant of 0.5 mass% CaO-containing wustite increased by ten times or more than that of pure wustite. In practical reduction process of iron oxide, this remarkable increase of the reduction rate in CaO-containing wustite may be associated with other coexisting gangue elements. The effects of the coexisting oxides on H_2 reduction of CaO-containing wustite have been reported by Shigematsu and Iwai.^{2,3)} However, little study of these effects on CO reduction has been performed.

In this work, the effect of SiO_2 , known as the most general gangue element in iron ores, on CO reduction of CaO-containing wustite was examined. It has been shown that the composition change of the wustite partially reduced was traced by using the lattice parameter of the wustite.¹⁾ Then, the reduction process within the wustite phase field was evaluated from the concentration profile of the iron ion in the partially reduced wustite estimated by measuring the

lattice parameter of the wustite and analyzed with a mixed-control model of chemical reaction at the surface and mass transport in the solid. In addition, several examinations were performed on CaO– SiO_2 – Al_2O_3 -containing wustite as well.

2. Experimental method

The wustite samples employed in this work were prepared by the same method as that described in the previous paper.¹⁾ Electrolytic iron-, reagent grade hematite-, CaO-, SiO_2 - and Al_2O_3 -powder, whose purities were 99.9 mass% or more, were used as starting materials. Mixed powders of hematite and electrolytic iron added 0.2–2 mass% CaO and 0.5–2 mass% SiO_2 were melted in Ar atmosphere at 1670 K and then cast into the flat-bottomed pure iron mold. The mass ratio of CaO/ SiO_2 in the samples denoted by C/S ranged from 0.5 to 5. The sample of 2mass%CaO–2mass% SiO_2 –1mass% Al_2O_3 -containing wustite was also prepared. The wustite ingot was cut into small plates, $10 \times 10 \times 1.2$ mm, so that the broad-side surface of the plate might become parallel to the bottom surface of the ingot. The wustite plates were equilibrated at 1273 K with CO– CO_2 gas mixture ($P_{\text{CO}_2}/P_{\text{CO}}=50/50$, hereafter Ks) for 90 ks after pre-annealing at 1370 K for 14 ks. The oxygen activity in the wustite is defined as $a_{(\text{O,w})} \equiv P_{\text{CO}_2}/P_{\text{CO}}$ where P_{CO_2} and P_{CO} are the partial pressure of CO_2 and CO in the gas mixture, respectively. The apparent density of the equili-

brated wustite samples was about $5.4 \times 10^3 \text{ kg/m}^3$ and slightly less than that of pure wustite summarized by Onoda and Sasaki.⁴⁾

The reduction experiments were conducted at 1273 K by using a thermo-balance. CO–CO₂–Ar gas mixtures ($P_{\text{CO}_2}/P_{\text{CO}}=0.04$ and 0.16, hereafter α), flowing at a rate of $2.5 \times 10^{-5} \text{ m}^3/\text{s}$, were used as reducing gas in order to avoid carbon-deposition from the gas mixtures. Under these conditions, the effect of gas-side resistance on the over all rate of reduction is negligibly small as demonstrated previously.¹⁾ X-ray diffraction analysis was performed for the partially reduced sample and the change in lattice parameter in the depth direction of the samples was measured by stepwise polishing of the samples. As the lattice parameter has been reported to be a parameter corresponding to wustite composition,⁵⁾ the concentration profile of iron ion in the samples partially reduced was estimated from the lattice parameter profile measured. Moreover, morphological observation and analysis of elements on the section of samples were carried out with EPMA. Thereafter, prepared wustite samples were distinguished as follows: The SiO₂– and CaO–SiO₂–wustite denoted the wustite containing only SiO₂ and both CaO and SiO₂, respectively.

3. Experimental Results

3.1. Lattice Parameter and Morphology of CaO–SiO₂–Wustite before Reduction

The dependences of lattice parameter on oxide content in

Fig. 1. Relation between lattice parameter a and additive oxide content in the wustite equilibrated with CO–CO₂ gas mixture ($K_s (=P_{\text{CO}_2}/P_{\text{CO}})=50/50$) at 1273 K. (a) CaO–, SiO₂– and Al₂O₃–wustite, (b) CaO–SiO₂– and CaO–SiO₂–Al₂O₃–wustite.

CaO–,⁵⁾ SiO₂–, and Al₂O₃–wustite equilibrated with the CO–CO₂ gas mixture ($K_s=50/50$) at 1273 K are shown in Fig. 1(a). The lattice parameter a increased linearly with an increase of CaO content in CaO–wustite. The solubility limit of CaO was about 6mass% as represented in previous work.⁵⁾ On the other hand, the a of SiO₂– and Al₂O₃–wustite decreased with increases of SiO₂ and Al₂O₃ contents and became constant above 0.3 mass% SiO₂ and 0.6 mass% Al₂O₃, respectively. Therefore, these values correspond to the solubility limit of each oxide on the analogy of CaO–wustite previously reported.⁵⁾ As shown in Fig. 1(b), the a of CaO–SiO₂–wustite decreased drastically with an increase of SiO₂ content. When 2 mass% SiO₂ was added to the 1mass%CaO–wustite ($C/S=0.5$), the a decreased to the value at the solubility limit in SiO₂–wustite. Such dependence of a on SiO₂ content was also found in 2mass%CaO–SiO₂–wustite. In the 2mass%CaO–2mass%SiO₂–wustite ($C/S=1$), the a was slightly larger than that of pure wustite. By the addition of 1 mass% Al₂O₃ to the CaO–SiO₂–wustite, the a decreased to the value at the solubility limit in Al₂O₃–wustite.

The composition images in the vertical section of 2mass%CaO–SiO₂–wustite were observed by EPMA and shown in Fig. 2. In both samples of $C/S=1$ and 2, the stripe- or point-like compounds were observed. The amount of the compound in the sample of $C/S=1$ was more than that in the sample of $C/S=2$. Large stripe-like compounds seemed to be deposited during solidification and exist vertically, that is, along the depth direction of the sample. Wustite phase was a continuous phase without being divided into dispersed phase. The results of quantitative analysis

Fig. 2. Cross section of the wustite samples before reduction; (a) 2mass%CaO–SiO₂–wustite ($C/S=2$) and (b) 2mass%CaO–SiO₂–wustite ($C/S=1$). Gray matrix: wustite, stripe- and point-like black portions: compound.

Table 1. Results of EPMA analysis of the compounds existed in 2mass%CaO–SiO₂–wustite before reduction

Mass ratio CaO/SiO ₂	Concentration (at%)			
	Fe	Ca	Si	O
1	15.8	14.5	14.4	55.3
2	10.2	19.5	14.4	55.9

Fig. 3. Reduction curves of 1mass%CaO–SiO₂–, 1mass%CaO– and pure-wustite. The samples were reduced with CO–CO₂–Ar gas mixtures having the following P_{CO} and α at 1273 K. Pure wustite: P_{CO} =0.075 MPa and α =0.04, SiO₂ free: P_{CO} =0.046 MPa and α =0.16, C/S=1 and 2: P_{CO} =0.055 MPa and α =0.04.

of the compounds by EPMA are shown in **Table 1**. The mean concentration of each element was obtained from ten times measurements. The compound in the sample of C/S=1 appears to be CaO·FeO·SiO₂ from a result of the atomic ratio being nearly Fe:Ca:Si=1:1:1. In the sample of C/S=2, 2CaO·SiO₂ is most likely deposited besides CaO·FeO·SiO₂ from a result of the ratio being Fe:Ca:Si 2:4:3. These results were almost in accordance with those predicted from FeO–CaO–SiO₂ phase diagram.⁶⁾ Considering the change in a with SiO₂ content in CaO–SiO₂–wustite, one predicts that the amount of dissolved CaO in the wustite decreased with the decrease of C/S due to the deposition of CaO–FeO–SiO₂ compounds. As shown in Fig. 1(b), the a of 1mass%CaO–2mass%SiO₂–wustite (C/S=0.5) decreased to the value at the solubility limit in SiO₂–wustite. It is thought that the amount of dissolved CaO is virtually 0 and only SiO₂ is dissolved in the wustite. Similarly, only Al₂O₃ is dissolved in 2mass%CaO–2mass%SiO₂–1mass%Al₂O₃–wustite because of the deposition of the dissolved CaO as compounds due to Al₂O₃ addition.

3.2. Reduction Curve

Mass changes in the initial reduction stage of 1mass%CaO–SiO₂–wustite are shown in **Fig. 3** together with those of CaO–¹⁾ and pure wustite.⁷⁾ A remarkable mass change took place in CaO–wustite at the initial stage of reduction. In contrast, the initial mass change in CaO–SiO₂–wustite of C/S=2 was smaller than that of CaO–wustite in despite of higher reduction potential in the gas mixture employed. The mass change in the sample of C/S=1 became small and was substantially similar to that in pure wustite. The same dependence of reduction curve on SiO₂ content was observed in 2mass%CaO–SiO₂–wustite.

Fig. 4. Depth profiles of a in 1mass%CaO–SiO₂–wustite plates reduced at 1273 K. The samples were reduced with CO–CO₂–Ar gas mixtures having the following P_{CO} and α . The solid lines denote profiles estimated by using a mixed-control model. SiO₂ free: P_{CO} =0.017 MPa and α =0.16, C/S=5: P_{CO} =0.029 MPa and α =0.04, C/S=1 and 2: P_{CO} =0.055 MPa and α =0.04, C/S=0.5 and 0.5mass%SiO₂ (CaO free): P_{CO} =0.096 MPa and α =0.04.

3.3. Depth Profile of Lattice Parameter in Partially Reduced Wustite

In progress of the reduction within the wustite phase field, oxygen is removed from the sample and the iron ion concentration at the sample surface increases. Then the diffusion of the iron ion into the sample takes place and results in its concentration profile. In the previous work,¹⁾ the reaction rate constant in the reduction of CaO–wustite was estimated from the iron ion concentration profiles with a mixed-control model of the surface reaction and the solid state diffusion in the wustite. In this work, the a of CaO–SiO₂–wustite before and after partial reduction in the depth direction was measured to determine the iron ion concentration profile. The lattice parameter profiles in the depth direction of 1mass%CaO–SiO₂–wustite reduced for 100 and 200 s are shown in **Fig. 4** together with the results of CaO–¹⁾ and SiO₂–wustite. In this figure, the mean value and the error of five measurements of a before and after reduction were shown as a function of the distance, x , from sample surface. Taking account of different reduction potentials in the reducing gases used, we noticed that the lattice parameter change in 1mass%CaO–SiO₂–wustite (C/S=1, 2, and 5) was considerably smaller than that in 1mass%CaO–wustite as shown in Fig. 4(a). Moreover, the increase of the a at the surface became small with the decrease of C/S. In 1mass%CaO–SiO₂–wustite of C/S=0.5, the lattice parameter profile was almost similar to that in 0.5mass%SiO₂–wustite reduced under the same condition as shown in Figs. 4(b) and 4(c). The changes in the a of 2mass%CaO–SiO₂–

Fig. 5. Depth profiles of a in 2mass%CaO-SiO₂-wustite plates reduced at 1273K. The samples were reduced with CO-CO₂-Ar gas mixtures. The solid lines denote profiles estimated by using a mixed-control model. C/S=4: P_{CO} =0.029 MPa and α =0.04, C/S=1 and 2: P_{CO} =0.055 MPa and α =0.04.

wustite reduced for 100 s are shown in Fig. 5. Comparing Fig. 5 with Fig. 4(a), one notices the larger lattice parameter change in the sample with 2mass%CaO content under the same C/S. Nevertheless the decreasing tendency of a with the decrease of C/S was similar in both cases. The solid lines shown in Figs. 4 and 5 are described later.

4. Discussion

4.1. Analysis with Mixed-control Model

The mixed-control model previously reported¹⁾ was used for the kinetic analysis. The amount of the compounds shown in Fig. 2 was too small to detect in a usual X-ray diffraction measurement. These compounds did not form a so-called cell structure and the wustite phase existed as a continuous phase in the depth direction from the sample surface. Therefore, the effects of the compounds on the surface reaction and the solid state diffusion seem to be insignificant. In the reduction reaction (1) within the wustite phase field for such CaO-SiO₂-wustite, the rate-determining step may be the elementary reaction (2)⁸⁾ and the removal rate of oxygen from the surface is given by Eq. (3).^{9,10)}

$$dW_O/dt = k' \cdot (1 - \alpha/K_s) \cdot P_{CO} (\text{kg-oxygen/m}^2 \cdot \text{s}) \dots\dots\dots (3)$$

- $|\text{Fe}^{2+}|''$: vacant site of Fe^{2+}
 $|\text{e}\cdot|$: positive hole
 $|\text{Fe}^{2+}| \text{Fe}^{2+}$: Fe^{2+} in lattice site of Fe^{2+}
 $\text{O}(\text{ads})$: oxygen atom adsorbed on wustite surface
 W_O : removed amount of oxygen (kg-oxygen/m²)
 t : reduction time (s)
 k' : apparent chemical reaction rate constant (kg-oxygen/m²·s·Pa)
 α : partial pressure ratio of reducing gas ($=P_{CO_2}/P_{CO}$)
 K_s : partial pressure ratio of gas mixture in equilibrium with the surface wustite ($=P_{CO_2}/P_{CO}$)
 P_{CO} : partial pressure of CO in reducing gas mixture (Pa).

In Eq. (3), k' and K_s seem to depend on the composition of the surface wustite.

The oxygen removal from the wustite surface results in an excess of iron ion. The iron ion diffuses into the wustite and forms a concentration profile in the depth direction. This concentration profile can be obtained by solving the diffusion Eq. (4) under the initial and the boundary conditions (Eq. (5)).

$$\partial C/\partial t = \tilde{D} \cdot \partial^2 C/\partial x^2 \dots\dots\dots (4)$$

$$t=0, 0 \leq x \leq 2L: C = C_0 \dots\dots\dots (5)$$

$$t>0, x=0, x=2L: -\tilde{D} \cdot (\partial C/\partial x) = (M_{Fe}/M_O) \cdot (dW_O/dt) \dots\dots\dots (5)$$

- C : iron ion concentration in wustite (kg/m³)
 C_0 : initial concentration of iron ion in wustite (kg/m³)
 x : distance from sample surface (m)
 $2L$: thickness of sample (m)
 $\tilde{D}$: inter-diffusion coefficient in wustite (m²/s)
 M_{Fe} : molar mass of iron (kg/mol)
 M_O : molar mass of oxygen (kg/mol)

Comparing the obtained concentration profile with that estimated from the lattice parameter measurement, we can determine k' and inter-diffusion coefficient, D . The boundary condition expressed by Eq. (5) shows the material balance between the oxygen ion removed from the surface and the iron ion diffusing into the wustite. The Crank-Nicolson method¹¹⁾ was used for solving the diffusion equation.

The relation among the composition, a and $a_{(O,w)}$ was examined on CaO-SiO₂-wustite. Figure 6 shows the relation between a and $a_{(O,w)}$. The relations in pure- and CaO-wustite, expressed by using Eq. (6) in the previous work,⁵⁾ were shown by the solid line and the dashed line, respectively.

$$a = (4.2975 + 0.560 \cdot M_{Ca-Fe}) - 1.470 \times 10^{-2} \cdot \ln(a_{(O,w)}) (\text{\AA}) \dots\dots\dots (6)$$

Here, M_{Ca-Fe} is a molar fraction of Ca ion to (Ca+Fe) ions. As shown with marks in the figure, the dependence of a on $a_{(O,w)}$ in CaO-SiO₂-wustite is almost the same as that in pure- and CaO-wustite. The relative difference of a in CaO-SiO₂-wustite is thought to correspond to the difference of M_{Ca-Fe} in the wustite. Substituting a of CaO-SiO₂-wustite at $a_{(O,w)}=1$ in Eq. (6) gives the apparent value of M_{Ca-Fe} in each sample. Then, the relations between a and $a_{(O,w)}$ in each sample were estimated by using Eq. (6) and the apparent value of M_{Ca-Fe} and these results were shown as the single dotted and dashed line in Fig. 6. As the calculated a of each sample at $a_{(O,w)}=0.67$ was in good accordance with the measured one, it is clear that the relation between a and $a_{(O,w)}$ in CaO-SiO₂-wustite is also represented by Eq. (6). In Fig. 6, a of 1mass%CaO-2mass%SiO₂-wustite (C/S=0.5) is smaller than that of pure wustite. Therefore, an apparent negative value of M_{Ca-Fe} was used in the application of Eq. (6).

The relation between the composition and a of CaO-SiO₂-wustite was examined. In the present analysis, it is required to know not the wustite composition itself but a relative change in the iron ion concentration due to the oxygen removal. Hence, the relation between the change in the iron

Fig. 6. Relation between a and oxygen activity $a_{(O,w)}$ in CaO-SiO₂-wustite.

Fig. 7. Relation between $\Delta C/C_0$ and a in CaO-SiO₂-wustite of various $a_{(O,w)}$.

ion concentration and a of CaO-SiO₂-wustite was clarified. Here, it is assumed that the evaporation of each element from the wustite sample during equilibration in various CO-CO₂ gas mixtures is negligibly small and the mass change in the sample corresponds to the change in the oxygen content of the wustite. **Figure 7** shows the relation between $\Delta C/C_0$ and a of the wustite, where C_0 is the iron ion concentration at $a_{(O,w)}=1$ and ΔC is the iron ion concentration difference between $a_{(O,w)}=1$ and other activities. The relations between $\Delta C/C_0$ and a in the pure- and 1mass%CaO-wustite are also shown in the figure. The iron ion concentrations of pure- and 1mass%CaO-wustite at each $a_{(O,w)}$ were estimated from the chemical analysis and by using Eq. (7) in consideration of the lattice parameter, respectively. This equation was derived experimentally in previous work.⁵⁾

$$a = 1.916 + 0.565 \cdot (M_{Ca-Fe}) + 4.719 \cdot (M_{Fe}/M_O) - 2.316 \cdot (M_{Fe}/M_O)^2 \quad (\text{\AA}) \quad (7)$$

Here, M_{Fe}/M_O represents the molar ratio of iron to oxygen ion. It can be seen from Fig. 7 that the dependences of $\Delta C/C_0$ on a in pure-, 1mass%CaO- and CaO-SiO₂-wustite

Fig. 8. Relation between apparent chemical reaction rate constant k' and SiO₂ content in CaO-SiO₂-wustite at 1273 K.

coincide with one another. Then, the dependences of $\Delta C/C_0$ on a in the three systems may be expressed by a simple equation. Using the least squares method, we obtained Eq. (8).

$$\Delta C/C_0 = 1.149418 \times 10^2 + 5.39665 \times 10^1 \cdot a + 6.3338 \cdot a^2 \quad (8)$$

The calculated results by using Eq. (8) were in good accordance with those measured as shown by the lines in Fig. 7. The change in the iron ion concentration was estimated from a by using this equation. However, the applicability of Eq. (8) may be restricted within the range of $a_{(O,w)}$ shown in Fig. 7.

4.2. Evaluation of k' and $\tilde{D}$

As seen from Figs. 4 and 5, the changes in wustite composition were so small that the kinetic analysis was performed by assuming k' and $\tilde{D}$ to be constant in CaO-SiO₂-wustite reduced for 100 and 200 s. The k' and $\tilde{D}$ were estimated as a mean value between the compositions of surface wustite before and after reduction.

The concentration profiles obtained from a mixed-control model are converted to the lattice parameter profiles and shown by the solid lines in Figs. 4 and 5. The observed and calculated results are in good agreement with each other. The relation between k' thus obtained and the amount of SiO₂ addition is shown in **Fig. 8(a)** together with k' in pure-⁷⁾ and CaO-wustite.¹⁾ The k' in SiO₂-wustite was almost the same as that in pure wustite up to 1 mass% SiO₂. In 1mass%CaO-SiO₂-wustite, k' decreased markedly with increasing the amount of SiO₂ addition and became almost the same value as pure wustite at 2 mass% SiO₂ addition.

Fig. 9. Relation between k' and a in CaO-SiO₂-(Al₂O₃)-wustite at 1273 K.

Although k' in 2mass%CaO-SiO₂-wustite decreased with increasing the amount of the SiO₂ addition similarly, the extent of the decrease at the same amount of SiO₂ addition was smaller than that in 1mass%CaO-SiO₂-wustite. The logarithm of k' decreases linearly with SiO₂ addition at a constant CaO content as shown in Fig. 8(b). From this figure, the SiO₂ content at which the k' of 1mass%CaO-SiO₂-wustite decreases to the value of pure wustite is estimated to be 1.1 mass% SiO₂, which corresponds to C/S=0.9. Conversion of the mass ratio C/S=0.9 into the molar ratio gives unity. This molar ratio was in good agreement with that in the mainly deposited compound CaO·FeO·SiO₂ revealed from the elemental analysis by EPMA. Therefore, dissolved CaO in wustite are consumed completely as a result of the compound formation at C/S=0.9 and the k' decreases to the value of pure wustite. This situation is in good agreement with the change in the a according to SiO₂ addition shown in Fig. 1(b). Since the dissolved amount of CaO in wustite corresponds directly to its a as shown in Fig. 1(a), estimated k' are shown as a function of a in Fig. 9. The results in 0.5, 1, and 2mass%CaO-wustite¹⁾ were also shown in the figure. It is clear that k' increases with the increase of the a , that is, the increase of dissolved CaO content in both CaO- and CaO-SiO₂-wustite. Thus, it can be concluded that k' increases with the increase of the dissolved CaO content, not of the added content in the wustite.

The relation between estimated inter-diffusion coefficient $\tilde{D}$ and the amount of SiO₂ addition is shown in Fig. 10 together with $\tilde{D}$ in pure wustite.⁷⁾ Though there was no obvious difference of $\tilde{D}$ among these samples, the $\tilde{D}$ tended to decrease slightly with increasing the amount of CaO and SiO₂ addition which implies the amount of deposited compounds.

4.3. Effect of Al₂O₃ in CaO-SiO₂-Wustite on k'

In general, calcium ferrites are the main mineral constituent in self-fluxing sinters, main charge for blast furnace.¹²⁾ Many works have been done on the reduction and the expansion during reduction of these calcium ferrites. It has been reported that quaternary and part of ternary calcium ferrite decomposed into the wustite, which contains CaO, SiO₂ and Al₂O₃, and that they were reduced to metal-

Fig. 10. Relation between inter-diffusion coefficient $\tilde{D}$ and SiO₂ content in CaO-SiO₂-(Al₂O₃)-wustite at 1273 K.

Fig. 11. Comparison of the observed lattice parameter profiles in CaO-SiO₂-Al₂O₃-wustite plates with those estimated by using a mixed-control model. The sample was reduced with CO-CO₂-Ar gas mixtures ($P_{\text{CO}}=0.096 \text{ MPa}$, $\alpha=0.04$) for 300 s.

lic iron at the final reduction stage.^{13,14)} In this study, the relation between the reduction rate and the dissolved content of CaO in CaO-SiO₂-Al₂O₃-wustite was examined. The 2mass%CaO-2mass%SiO₂-1mass%Al₂O₃-wustite sample was prepared and the a of the sample was measured. As the obtained a was almost the same as that at solubility limit of Al₂O₃-wustite as shown with a double rhombic mark in Fig. 1(b), the dissolved content of CaO was virtually 0 and only Al₂O₃ seemed to be dissolved in the wustite. The depth profile of the a in 2mass%CaO-2mass%SiO₂-1mass%Al₂O₃-wustite reduced for 300 s is represented in Fig. 11. The change in a was extremely small even at the surface. From the analysis of this profile with the mixed-control model mentioned above, the k' and the $\tilde{D}$ were estimated to be $6 \times 10^{-11} \text{ kg-oxygen/m}^2 \cdot \text{s} \cdot \text{Pa}$ and $5.8 \times 10^{-10} \text{ m}^2/\text{s}$, respectively. The obtained k' is smaller than that of the pure wustite as shown in Fig. 9. The decreasing tendency of k' in Al₂O₃-containing wustite was in accordance with the result by Piepenbrock *et al.*¹⁵⁾ Therefore, coexisting Al₂O₃ in CaO-SiO₂-wustite leads to a decrease in the dissolved content of CaO and in the reduction rate. The obtained $\tilde{D}$ is almost the same as that of CaO-SiO₂-wustite as shown in Fig. 10. To maintain the enhanced reduction rate of CaO-containing wustite, it may be necessary to decrease the amount of coexisting oxides such as SiO₂ and Al₂O₃ to secure the dissolved content of CaO in the wustite.

5. Conclusions

The CaO–SiO₂–wustite was reduced with CO–CO₂–Ar gas mixtures at 1273 K. In the reduction within the wustite phase field, the concentration profile of iron ion was formed in the wustite. These profiles were estimated from the lattice parameter measurements. The reduction process was examined by using a mixed-control model of chemical reaction at the wustite surface and solid state diffusion in the wustite. Some examinations were also performed on CaO–SiO₂–Al₂O₃–wustite. The results obtained are summarized as follows.

(1) The lattice parameter of CaO–SiO₂–wustite decreases with the decrease of mass ratio CaO/SiO₂. The amount of dissolved CaO content seems to decrease due to the compound formations such as CaO·FeO·SiO₂ and 2CaO·SiO₂. This amount decreases further with coexisting Al₂O₃. In 1mass%CaO–2mass%SiO₂– and 2mass% CaO–2mass%SiO₂–1mass%Al₂O₃–wustite, dissolved CaO content is virtually 0 and only SiO₂ and Al₂O₃ are dissolved in the wustite, respectively.

(2) The apparent chemical reaction rate constant in the reduction of CaO–SiO₂–wustite decreases with decreasing the amount of dissolved CaO. The rate constant which increases remarkably in 1mass%CaO–wustite decreases to almost the same value as pure wustite in 1mass%CaO–SiO₂–wustite with CaO/SiO₂ ≤ 0.9. The rate constant of 2mass%CaO–2mass%SiO₂–wustite with coexisting 1mass%Al₂O₃ becomes smaller than that of pure wustite.

(3) The inter-diffusion coefficients in CaO–SiO₂–wustites tend to decrease slightly with increasing the

amount of deposited compounds.

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