Effects of Potassium Chloride on the Reduction of Iron Oxides*

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I. Introduction

Alkaline metal compounds enter a blast furnace accompanying the burden gangue and coke ash. Although their input is usually very low, they are circulated and consequently accumulated over a period of time in the blast furnace. The alkali compounds circulating in the blast furnace create serious problems to the smooth functioning of the furnace by causing the disintegration of ore and coke, the formation of scaffolds on the furnace wall, *etc.*^{1,2)} A study of their effects on various blast furnace reactions is therefore very important.

One of the effects of alkali compounds is the acceleration of the reduction of iron oxides. Khala-falla and Weston, Jr.³⁾ found that alkaline and alkaline-earth metal oxides increased the reduction rate of wustite pellets by carbon monoxide. Itaya *et al.*⁴⁾ found in the stepwise reduction of hematite pellets by carbon monoxide that sodium chloride increased the rate of reduction step of $\text{FeO} \rightarrow \text{Fe}$ but it had no effect on the reduction steps of $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ and $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$.

In this paper, effects of potassium chloride on the rate of reduction of dense hematite, magnetite and wustite plates by carbon monoxide have been investigated in order to find a reduction step or steps on which the alkali compound has effects.

II. Experimental Method

Hematite, magnetite and wustite samples were prepared by oxidizing electrolytic iron plates ($25 \times 15 \times 0.1$ mm) according to the method shown in Table 1. The samples thus obtained were dense oxide plates, which were more suitable than porous pellets for examining the effects of KCl on the change of microstructure of the oxides during reduction.

Potassium chloride was added to an oxide sample by dipping the sample in a KCl-saturated aqueous solution and then drying it at 120°C . The potassium chloride adsorbed on the oxide surface was gradually evaporated while the sample was heated to a reduction temperature in a nitrogen atmosphere. The KCl content at the start of reduction was less than 100 ppm.

Reduction experiments were carried out in a thermobalance under a flow of 2 NL/min of a $\text{CO}-\text{CO}_2$ gas mixture at 900°C . The gas composition was 10% $\text{CO}-90\% \text{CO}_2$ for the reduction step of

$\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$, 50% $\text{CO}-50\% \text{CO}_2$ for $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$, and 90% $\text{CO}-10\% \text{CO}_2$ for $\text{FeO} \rightarrow \text{Fe}$ and $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}$.

The surface and cross section of samples were examined with a SEM before and after reduction.

III. Results and Discussion

1. Reduction of Hematite Plates

Figure 1 shows the reduction curves for the reduction of hematite plates with and without KCl addition by 90% $\text{CO}-10\% \text{CO}_2$ at 900°C . From this figure, the accelerating effect of potassium chloride on the continual reduction of hematite to iron is evident.

Figures 2 to 4 show the results of stepwise reduction of hematite plates with and without the addition of KCl. As it is apparent from these figures, potassium chloride accelerates the reduction rate of all the reduction steps: $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$, $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$, and $\text{FeO} \rightarrow \text{Fe}$.

Photograph 1 shows SEM micrographs of lightly polished cross section of magnetite, wustite, and iron produced by stepwise reduction of hematite plates.

Table 1. Preparation of oxide samples.

Sample	Material	Oxidizing condition		
		Temper- ature ($^\circ\text{C}$)	Time (hr)	Atmosphere
FeO	Fe plate	1 250	8	$\text{CO}-\text{CO}_2$ (1 : 1)
Fe_3O_4	Fe plate	1 000	5	$\text{CO}-\text{CO}_2$ (1 : 9)
Fe_2O_3	FeO plate	850	24	air

Fig. 1. Effect of KCl addition on the continual reduction of dense Fe_2O_3 plate to Fe by 90% $\text{CO}-10\% \text{CO}_2$ at 900°C .

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Fig. 2. Effect of KCl addition on the reduction step from Fe_2O_3 to Fe_3O_4 in the stepwise reduction of dense Fe_2O_3 plate.

Fig. 3. Effect of KCl addition on the reduction step from Fe_3O_4 to FeO in the stepwise reduction of dense Fe_2O_3 plate.

Fig. 4. Effect of KCl addition on the reduction step from FeO to Fe in the stepwise reduction of dense Fe_2O_3 plate.

Reduction proceeded from the right on the photographs to the left. Although hematite samples were dense, pores were formed during their reduction. In the magnetite reduced from the hematite sample without KCl addition, the pores were regularly extended from the surface of the sample inward. On the other hand, in the magnetite reduced from KCl-added hematite, the pores were randomly distributed and had much larger contact area with reducing gas. Further reduction of magnetite to wustite and to iron increased the pore volume but did not change the pore morphology. The increase in the contact area with reducing gas by the addition of KCl seems to be responsible for the acceleration of reduction.

A, B, C: without KCl addition
a, b, c: with KCl addition

Photo. 1. SEM micrographs of cross sections of Fe_3O_4 (A, a), FeO (B, b), and Fe (C, c) produced by stepwise reduction of dense Fe_2O_3 plates.

2. Reduction of Magnetite and Wustite Plates

Reduction experiments were carried out by using dense magnetite and wustite plates, in order to investigate whether potassium chloride influenced *directly* the reduction of magnetite and wustite or *indirectly* through the difference in the pore structure of magnetite made during the reduction of hematite to magnetite.

Figure 5 shows the reduction curves for the reduction of dense magnetite plates to wustite. As is seen from this figure, potassium chloride added to the surface of magnetite also accelerates the reduction rate of magnetite.

Photograph 2 shows SEM micrographs of the surfaces of magnetite before reduction. As shown in Photo. 2(B), the grain boundary of magnetite was strongly eroded by KCl, while the sample was heated to 900 $^{\circ}\text{C}$ in a nitrogen atmosphere.

Photograph 3 shows SEM micrographs of the surfaces of wustite produced by reduction of dense magnetite plates. Cubic crystals of wustite grew regularly on the surface of a magnetite sample without KCl addition, whereas the growth of wustite crystals was irregular on the surface of a magnetite sample with KCl addition. The potassium chloride adsorbed

Fig. 5. Effect of KCl addition on the reduction of dense Fe_3O_4 plate to FeO by 50% CO -50% CO_2 at 900 °C. (The broken line refers to the reduction step from Fe_3O_4 to FeO in the stepwise reduction of KCl-added dense Fe_2O_3 plate shown in Fig. 3.)

Fig. 6. Effect of KCl addition on the reduction of dense FeO plate to Fe by 90% CO -10% CO_2 at 900 °C. (The broken line refers to the reduction step from FeO to Fe in the stepwise reduction of KCl-added dense Fe_2O_3 plate shown in Fig. 4.)

A: without KCl addition
B: with KCl addition

Photo. 2. SEM micrographs of surfaces of dense Fe_3O_4 plates before reduction.

A: without KCl addition
B: with KCl addition

Photo. 3. SEM micrographs of FeO surfaces produced by reduction of dense Fe_3O_4 plates.

on the surface of magnetite probably affected the nucleation and growth of wustite phase and caused the irregular and distorted crystals to grow. The

diffusion of Fe^{2+} ions and vacancies can be greatly facilitated in the distorted lattice, which may be responsible for the accelerating effect of KCl on magnetite reduction.

In Fig. 5, the reduction curve of porous magnetite reduced from dense hematite with KCl addition was also shown in a broken line. The difference in the reduction rate between dense hematite and dense magnetite samples for the same reduction step of $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$ is due to the difference in the porosity of magnetite at the start of reduction.

Figure 6 shows the reduction curves for the reduction of dense wustite plates. Potassium chloride had also an accelerating effect on the reduction of wustite but the effect was smaller, especially at the beginning of reduction, than that on the reduction of porous wustite reduced from dense hematite sample, the reduction curve of the latter being shown in a broken line in Fig. 6. No significant difference in the microstructure of wustite samples before and after reduction with and without the addition of KCl was found and the effect of KCl could not be clarified in terms of morphology.

IV. Summary

Effects of potassium chloride on the reduction of iron oxides were investigated by using dense hematite, magnetite, and wustite samples prepared by the oxidation of electrolytic iron plates.

The addition of small amount of KCl to the surfaces of oxide samples was found to greatly increase the reduction rate of all the reduction steps: $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$, $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$, and $\text{FeO} \rightarrow \text{Fe}$.

Reduction of hematite with KCl addition produced very porous magnetite having larger contact area with reducing gas. In the reduction of magnetite with KCl addition, the grain boundary on the surface was strongly eroded and distorted wustite crystals were formed on the magnetite surface. These phenomena were considered to be responsible for the accelerating effects of KCl on the reduction of hematite and magnetite. However, the accelerating effect of KCl on wustite reduction could not be clarified in terms

of morphology.

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