REDUCTION TESTS OF SYNTHETIC CALCIUM FERRITES IN TERNARY SYSTEMS OF CaO-FeO-Fe_2O_3

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ABSTRACT

Four calcium ferrites of a CaO-FeO-Fe_2O_3 system were synthesized at 1100°C, while $3CaO \cdot FeO \cdot 7Fe_2O_3$ and $4CaO \cdot FeO \cdot 4Fe_2O_3$ were synthesized in an argon gas and $CaO \cdot FeO \cdot Fe_2O_3$ and $CaO \cdot 3FeO \cdot Fe_2O_3$ were synthesized in a gas mixture of $CO/CO_2 = 30/70$. Synthetic $CaO \cdot 3FeO \cdot Fe_2O_3$ was not distinguished by one phase but rather at least by two phases, i.e. one was of an Asada-Omori type and the other was of a Cirilli-Burdese type. Reduction tests of these four compounds were carried out with various CO-CO_2 gas mixtures by thermogravimetric balance.

Oxygen partial pressure equilibrated with each ternary ferrite at 800°C was roughly determined. Oxygen partial pressure ranges, where $3CaO \cdot FeO \cdot 7Fe_2O_3$ and $4CaO \cdot FeO \cdot 4Fe_2O_3$ were equilibrated, agreed with that of magnetite. $CaO \cdot FeO \cdot Fe_2O_3$ and $CaO \cdot 3FeO \cdot Fe_2O_3$ were stable in the same range of oxygen partial pressure as wüstite. All calcium ferrites were reduced to the assemblage of $2CaO \cdot Fe_2O_3$ + metallic iron at 800°C with a gas mixture of $CO/CO_2 = 80/20$. Reducibility of each ferrite in this condition was nearly equal but $CaO \cdot 3FeO \cdot Fe_2O_3$ of Cirilli-Burdese type had a very low reducibility. However, these ternary calcium ferrites were more reducible than wüstite.

INTRODUCTION

Calcium ferrites exist very commonly in self-fluxing sinters. Especially, the increase of basicity has an affect on larger amounts of calcium ferrite than other iron oxides. The relation between basicity and over-all reducibility of sinters has been reported many researchers[1)~3)] in spite of this the thermochemical properties of each calcium ferrite in the sinter remain unknown.

Phillips and Muan[4)] have presented a basic study on the systems of CaO and Fe_2O_3 and have determined a stable field of binary calcium ferrites in air. However, ternary calcium ferrites of CaO–FeO–Fe_2O_3 appear in reducing gas atmosphere, and it is well known that, at least, four types of ternary calcium ferrites exist in this system, namely $3CaO \cdot FeO \cdot 7Fe_2O_3$ (abbreviated as C_3WF_7), $4CaO \cdot FeO \cdot 4Fe_2O_3$ (C_4WF_4), $CaO \cdot FeO \cdot Fe_2O_3$ (CWF) and $CaO \cdot 3FeO \cdot Fe_2O_3$ (CW_3F) Asada et al synthesized these calcium ferrites at 1000–1200°C from oxide mixtures of CaO, FeO and Fe_2O_3 which were sealed in vacuum silica capsules and obtained detailed X-ray data of these ferrites. They also measured the weight loss of these samples in reduction by hydrogen and discussed the reducibility of these ternary ferrites.

The thermodynamical stabilities of calcium ferrites are determined by oxygen partial pressure. Thus, in weaker reducing gas such as a CO–CO_2 gas mixture as compared against hydrogen, the reducibility of these ferrites should be studied

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in detail. It is expected that an increase of CO/CO_2 ratio may lead to a change from a calcium ferrite to another lower calcium ferrite. In this paoer, the synthesis and reduction of ternary calcium ferrites were carried out in a flowing gas of a given ratio of CO–CO_2 equivalent to low oxygen pressure.

EXPERIMENTAL METHOD

Synthesis of ternary calcium ferrite: CaO was prepared by calcining pure calcium carbonate. For wüstite, reagent grade Fe_2O_3 was reduced at 800°C with a mixture of CO–CO_2 in a ratio which equilibrated with wüstite. Oxides blended in a composition of ternary calcium ferrites were thoroughly mixed in an agate mortar and then compressed with a load pressure of 1 ton/cm^2 to form a cylinder of 10 mm in diameter and about 8 mm in thickness. The apparatus for preparation of a sample is illustrated schematically in Fig. 1. A sample was placed in a platinum crucible and heated at 1100°C in a given atmosphere. Argon gas was allowed to flow through during preheating of a sample. After a test run was completed, synthesized ferrite was quenched in a mercury pot. The condition of preparation of ternary calcium ferrites are summarized in Table 1.

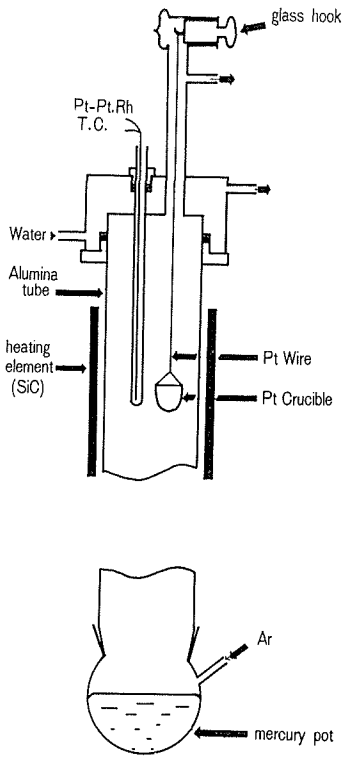

Fig. 1 Schematic illustration of the apparatus for preparation of samples.

Table 1 Relations between synthetic ferrites and the condition of synthesis

Ratio of oxide mixtures	Atmosphere (300 cc/min.)	Temperature (°C) and time (hours)	Product
$3CaO \cdot FeO \cdot 7Fe_2O_3$	argon	1100, 3	C_3WF_7
$4CaO \cdot FeO \cdot 4Fe_2O_3$	argon	1100, 3	C_4WF_4
$CaO \cdot FeO \cdot Fe_2O_3$	$CO/CO_2=30/70$	1100, 1	CWF
$CaO \cdot 3FeO \cdot Fe_2O_3$	$CO/CO_2=30/70$	1100, 1	CW_3F

Reduction test: 200 mg of powdered ferrite sample was placed in a platinum crucible in thermogravimetric balance and heated to 800°C in argon gas which was removed oxygen through magnesium chips at 350°C, and then reduced with a gas mixture of CO–CO_2 at the rate of 300 cc/min. The weight loss of a sample was measured continuously by thermogravimetric balance with an accuracy of ± 0.5 mg until the reaction was accomplished. After reduction, the product was examined by X-ray powder diffraction analysis.

RESULTS AND DISCUSSION

Identification of ternary calcium ferrite: X-ray diffraction patterns of calcium ferrites agreed with that reported by Asada et al[5] except for CW_3F. X-ray diffraction data of CW_3F were reported by Asada-Omori and Cirilli-Burdese.[6] In the present study, it was recognized that the diffraction pattern of CW_3F changed slowly with the reaction time from an Asada-like type to a Cirilli-like type as shown in Fig. 2. A sample of CW_3F in the present study appeared to be of an Asada-like type at the first stage of preparation which changed to a Cirilli-like type at the final stage. However, when they were reduced by thermogravimetric

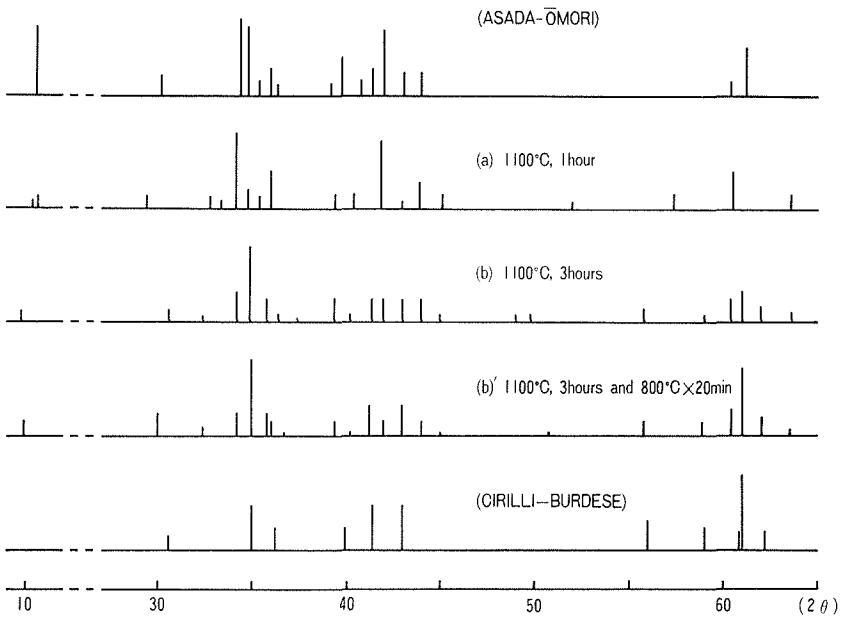

Fig. 2 Variation *X*-ray diffraction patterns of CW_3F

Table 2 Phase assemblages after reduction of ferrites at 800°C with various CO/CO_2 ratios

Sample	CO/CO_2	Result
CF	30/70	$CWF+C_2F$
C_4WF_4	0/100	C_4WF_4
	30/70	$CWF+C_2F$
	50/50	$CWF+C_2F$
	80/20	C_2F+Fe
C_3WF_7	0/100	$CWF+WF$
	30/70	$CWF+W$
	50/50	$CWF+W$
CWF	50/50	CWF
	65/35	CWF
	70/30	C_2F+W
	80/20	C_2F+Fe
CW_3F	30/70	CW_3F
	50/50	CW_3F
	65/35	CW_3F
	70/30	CW_3F
	80/20	C_2F+Fe

balance, no difference of weight loss was found between the samples of the two types, but the Asada-like type was more reducible than the Cirilli-like type. Samples of the Asada-like type and the Cirilli-like type were respectively designated as type-A and type-B for the reduction test.

Phase assemblages after reduction: The results were summarized in Table 2. The ratio of $CO/CO_2=30/70$, 50/50 and 80/20 correspond to an oxygen pressure of about 10^{-18}, 10^{-19} and 10^{-20} atm. respectively. CWF and CW_3F were not reduced at 800°C in a flow of $CO/CO_2=50/50$, because these ferrites were synthesized in $CO/CO_2=30/70$ at 1100°C. It may be seen that oxygen partial pressure equilibrated with C_3WF_7 and C_4WF_4 agreed with magnetite and oxygen partial pressure equilibrated with CWF and CW_3F were almost the same as in wüstite. Binary calcium ferrites of CaO–Fe_2O_3 are stable in an oxygen pressure range of hematite except for C_2F. C_2F is stable in oxygen pressure in which metallic iron exists.

The system of CaO–FeO–Fe_2O_3 is not a true ternary in this experiment but is a partial system of the CaO–Fe–O ternary. According to the phase rule, two solid phases are allowed to coexist in CaO–Fe–O ternary under equilibrium conditions with a given oxygen partial pressure and temperatute. Phase assemblages in the system are determined by a given oxygen partial pressure and chemical composition, namely the ratio of CaO/Fe. A schematic diagram of the relation between the phase assemblages and oxygen partial pressure are shown in Fig. 3 on the

basis of the result of this experiment.

It was very difficult to decrease the oxygen pressure in argon gas that some calcium ferrites were equilibrated. CWF and CW_3F were not synthesized in argon gas but were synthesized in a mixture of CO–CO_2. The oxygen content of wüstite in ternary calcium ferrites should be different according to their composition.

Reducibility of ferrites: The relation of reduction degree with reaction time in a few types of CO–CO_2 gas atmosphere are shown Fig. 4 and 5. The reduction degree in Fig. 4 and 5 are calculated as 100% when the ferrites are reduced to the state of CaO and metallic iron.

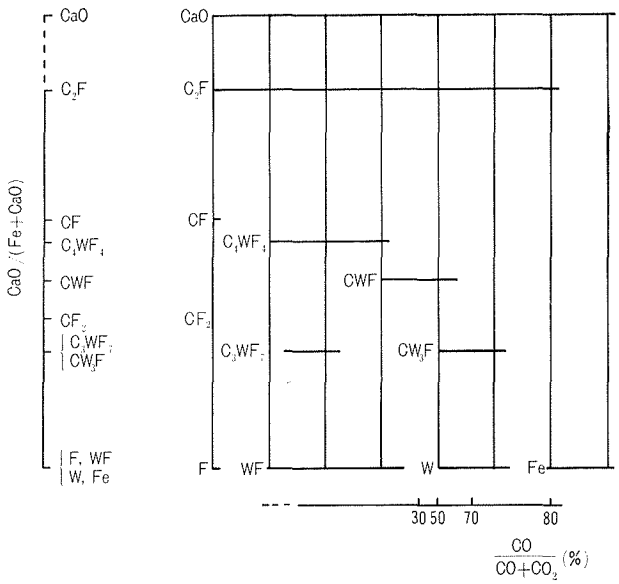

Fig. 3 Schematic diagram of the relation between the phase assemblages and oxygen partial pressure.

Fig. 4 showed that phase transformations from C_3WF_7 to $3 \cdot CWF + 6 \cdot W$ and from $4 \cdot C_4WF_4$ to $10 \cdot CWF + 3 \cdot C_2F$ are accomplished, because the reduction degrees of both calcium ferrites became constant and the values of final weight loss of samples agreed with the values calculated from the above reactions. The fact that the reaction $CWF + 2W = CW_3F$ did not occur at 800°C was not clear. A considerable amount of CaO might be dissolved in a solid solution in wüstite produced in reduction, in as much as the peaks of X-ray diffraction of wüstite in the reduced ferrite were shifted to a lower angle from the peaks of pure wüstite.

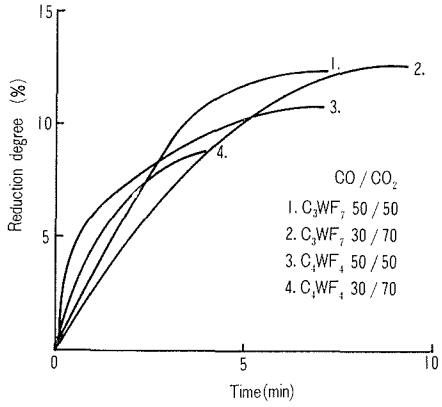

Fig. 4 Reduction degree of C_3WF_7 and C_4WF_4 vs. reduction time at 800°C in some CO/CO_2 gas mixtures.

In a gas mixture of $CO/CO_2 = 80/20$, all ternary calcium ferrites were reduced to form metallic iron and C_2F. The reduction degree was calculated under the assumption that total oxygen was removed except for the oxygen combined with calcium. The relation between the reduction degree and reaction time was shown in Fig. 5. The reducibility of CW_3F (A) and CW_3F (B) was quite different. CW_3F (A) was reduced more rapidly than CW_3F (B). In fact, CW_3F (B) showed the lowest reducibility in ternary calcium ferrites.

The degree of reduction shown in Fig. 5 could not clearly be classified in accordance with the reducibility of various ferrites. And it was recalculated to form metallic iron and C_2F as the final product. The results were shown in Fig. 6 in $CO/CO_2 = 80/20$. C_2F could not be reduced to metallic iron and CaO. CWF, C_3WF_7 and C_4WF_4 showed the same rate of reduction at the first stage.

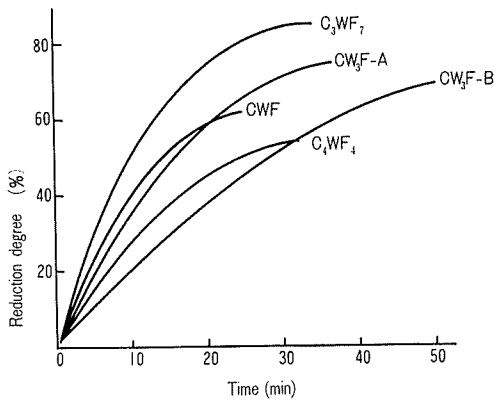

Fig. 5 Reduction degree of calcium ferrites vs. reduction time at 800°C in gas mixture of CO/CO_2 = 80/20.

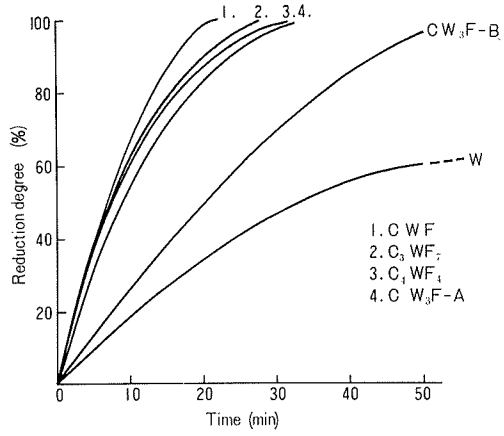

Fig. 6 Recalculated reduction degree vs. reduction time at the same condition as Fig. 5.

At the final stage, CWF was the most reducible and C_4W_4F had the lowest reducibility in these calcium ferrites. All ternary calcium ferrites in so far as examined showed a higher reducibility than pure wüstite.

SUMMARY

1) Four ternary calcium ferrites in the CaO–FeO–Fe_2O_3 system were synthesized at 1100°C, while C_3WF_7 and C_4WF_4 were synthesized in argon gas and CWF and CW_3F were synthesized in a gas mixture of CO/CO_2 = 30/70.

2) CW_3F existed as a phase of Asada-Omori type at the first stage and was transformed to a phase of Cirilli-Burdese type after long time reaction.

3) Oxygen partial pressure equilibrated with each ternary calcium ferrite was roughly determined at 800°C. It seemed that stable ranges of C_3WF_7 and C_4WF_4 agreed with that of magnetite and CWF and CW_3F were almost the same as wüstite. Oxygen partial pressure of CW_3F, CWF, C_3WF_7 and C_4WF_4 was larger in the above indicated order.

4) All calcium ferrites were changed to the assemblage of metallic iron and C_2F after reduction at 800°C with a gas mixture of CO/CO_2=80/20. Reducibility of each ferrite in this atmosphere was almost equal but CW_3F (especially Cirilli-Burdese type) showed a very low reducibility.

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