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On the Formation and Constitution of Calcium-Ferrite

By

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Abstract

We studied the formation, constitution, melting point, and micro-structures of Ca-ferrite prepared from the mixtures of CaO and Fe_2O_3 by chemical- and X-ray analyses. Main results obtained are as follows. 1) Ca-ferrite has two kinds of compound which are represented by CaOFe_2O_3 (monocalcium-ferrite) and $2\text{CaOFe}_2\text{O}_3$ (dicalcium-ferrite). 2) CaOFe_2O_3 is formed over 700° and the formation is completed at about 1000°C . 3) When the sample contains excess CaO, $2\text{CaOFe}_2\text{O}_3$ is formed over 1000°C by the reaction of CaOFe_2O_3 and excess CaO and this reaction is completed at about 1200°C . 4) CaOFe_2O_3 dissolves Fe_2O_3 at high temperature and the sample containing 60 mol% of Fe_2O_3 shows single phase at 1200°C . 5) The compound represented by $3\text{CaOFe}_2\text{O}_3$ or $\text{CaO}2\text{Fe}_2\text{O}_3$ cannot be observed by X-ray examination; the former is nothing but a mixture of CaO and $2\text{CaOFe}_2\text{O}_3$, and the latter, simply a mixture of solid solution of CaOFe_2O_3 and Fe_2O_3 and free Fe_2O_3 . 6) CaOFe_2O_3 melts at 1220° and is dissolved in hot 1:1 HCl by heating while $2\text{CaOFe}_2\text{O}_3$ melts at 1280°C and is dissolved immediately in cold dil HCl, and they both have paramagnetic property. 7) CaOFe_2O_3 forms fine hexagonal crystals near its melting point and shows growth steps, but $2\text{CaOFe}_2\text{O}_3$ is apt to become glassy and its definite crystal forms are difficult to recognize under microscope.

1. Introduction

Ca-ferrite is known as one of compositions in slags and also as a constitution in ceramic or refractory materials. As Tafel¹⁾ said, zinc-ferrite or copper-ferrite can be decomposed and formation of zinc-ferrite and copper-ferrite can be prevented by heating with CaO as follows: $\text{ZnOFe}_2\text{O}_3 + \text{CaO} \rightarrow \text{CaOFe}_2\text{O}_3 + \text{ZnO}$.

Prior to the studies on the decomposition of Cu- or Zn-ferrite by CaO, the authors have investigated on the formation temperature, constitution, microscopic structures, and melting point of Ca-ferrite. The results obtained differ somewhat from previous works.

2. Experimental Methods

The formation temperature and constitution of Ca-ferrite was studied by the chemical analyses and X-ray examinations. Different from other ferrites, Ca-ferrite is a paramagnetic material, therefore, the magnetic analysis could not be adopted in this investigation.

a) Chemical analyses.

The formation ratio of Ca-ferrite at various temperatures was studied by chemical analyses by the samples which were heated at $700^{\circ}\sim 1200^{\circ}\text{C}$ for 2 or 3 hours. 0.3 g each of the heated sample was leached in 2% formic acid solution for 1 hour at room temperature (about 15°C), the sample was agitated every 15 minutes by hand.²⁾ By this treatment, free CaO, which is not reacted with Fe_2O_3 , are leached out almost completely and, at the same time, Ca-ferrite (CaOFe_2O_3) is slightly dissolved in formic acid solutions while free Fe_2O_3 does not dissolve in formic acid solution at all. The formation ratio was calculated from percentages of CaO in leaching solution and CaO and Fe_2O_3 in the residue.

As will be mentioned afterwards Ca-ferrite has two kinds of composition represented by the formula CaOFe_2O_3 and $2\text{CaOFe}_2\text{O}_3$ respectively. These two can be distinguished from their mixture by the following analytical treatment. First, a small amount of free CaO contained in the sample is leached out by 2% formic acid solution for 10 minutes, the residue is treated with cold 1:1 HCl for 1 minute to dissolve dicalcium-ferrite ($2\text{CaOFe}_2\text{O}_3$) only and let monocalcium-ferrite (CaOFe_2O_3) remain. Filtrate and residue are analysed for CaO and Fe_2O_3 . The filtrate representing CaO: Fe_2O_3 is about 2:1 and the residue is about 1:1.

b) X-ray analyses.

Each sintered tablet sample was crushed and photographed by Debye-Scherrer X-ray.

3. Preparation of Samples

CaO: CaO was obtained from Merk's CaCO_3 by heating it at 1000°C for several hours and decomposing it completely. However, since CaO thus obtained was very active and changed readily into carbonate, the mixed sample of CaCO_3 and Fe_2O_3 was used to prepare Ca-ferrite.

Fe_2O_3 : As in the cases of the other ferrites,³⁾ Fe_2O_3 was prepared by heating ferrous oxalate at $600\sim 700^{\circ}\text{C}$ for several hours and completely decomposing and oxidizing it.

Mixed sample: CaCO_3 and Fe_2O_3 were mixed so that the molar ratio of CaO and Fe_2O_3 would become 3:1, 2:1, 1.7:1, 1.4:1, 1:1, 4:5, 2:3, 1:2 and 1:4. These samples are represented respectively as 3-1, 2-1 ... and so on. The chemical analyses

of these samples are shown in Table 4. These mixed samples were pressed in mold into tablets of 15 mm diameter and about 3 mm wide under 100 Kg/cm² pressure, and they were heated at 700°~1200°C for 2 or 3 hours for every 100°C interval. The heated samples were then cooled rapidly in the air, and after they were crushed, chemical and X-ray analyses were performed.

4. Experimental results and Considerations

a) On the Formation of Ca-ferrite

The formation ratio of Ca-ferrite at 700~1200°C measured by chemical analyses is shown in Fig. 1. At 700°C, the formation ratio becomes over 10% and it increases linearly as the temperature rises. This solid reacton is completed at about 1000°C. Differences in the reaction rate between the cases of two- and three-hour heating is only a few percent, and it has been shown that most of the reaction takes place in a comparatively short time as in the case of other ferrites.³⁾ The colour of the sample changes from reddish brown to dark violet by heating, at 1200°C the colour turns black and its surface crystallizes and shines slightly.

By Huttig, et al.⁴⁾ it is said that the formation of Ca-ferrite can be recognized from its increment of magnetic intensity. Cirilli and Brisi^{5,6)} said that rhombic CaOFe₂O₃ is normally paramagnetic and it shows unstable ferromagnetic property when its crystal form is tetragonal. In the authors' experiment, the little pieces of the crushed sample heated

over 1000°C was attracted by magnet when it was brought near, but their magnetic intensity was so weak that it could not be measured by ballistic galvanometer method under about 1000 Oersted magnetic field. From these facts, we consider our samples paramagnetic. Further, Brisi⁶⁾ said that 2CaOFe₂O₃ is purely ferromagnetic with a Curie point of about 400°C, but our dicalcium-ferrite did not show ferromagnetism. Photo 1 shows the B-H curve of our CaOFe₂O₃ sample.

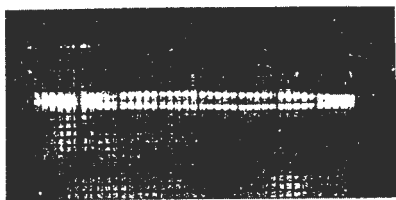


Photo. 1 B-H Curve of 1 1 Ca ferrite.

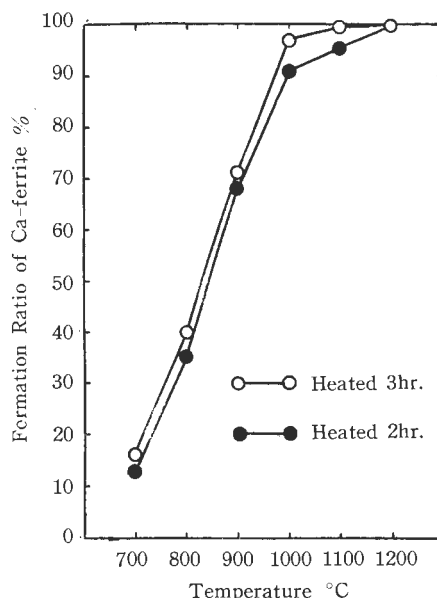


Fig. 1 The formation ratio of Ca-ferrite at various temperature.

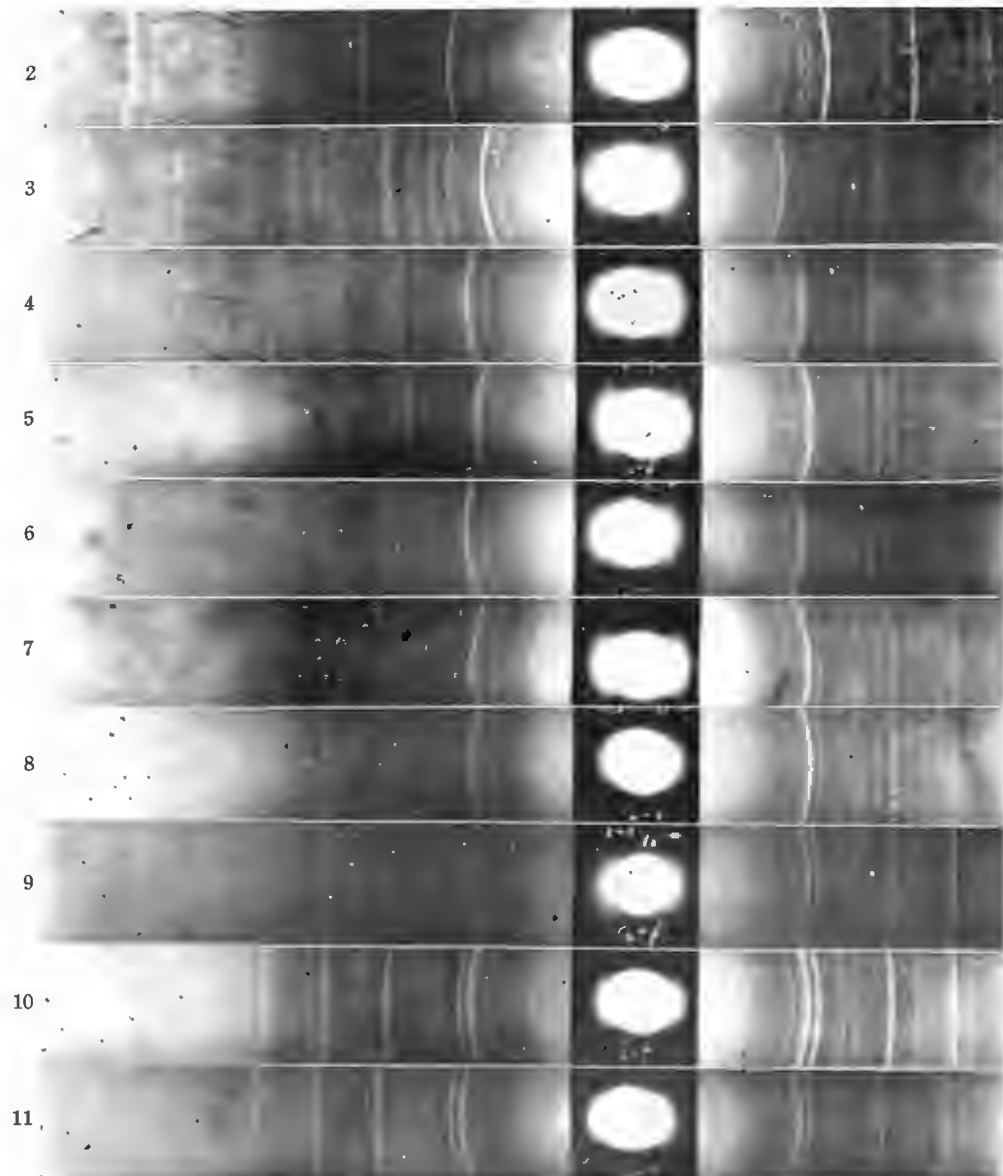


Photo. 2. CaO.
Photo. 3. CaCO₃.
Photo. 4. 3-1 Sample heated at 1100°C.
Photo. 5. 2-1 Sample heated at 1200°C.
Photo. 6. 1.7-1 Sample heated at 1100°C.
Photo. 7. 1.7-1 Sample heated at 1000°C.
Photo. 8. 1.4-1 Sample heated at 1100°C.
Photo. 9. 1-1 Sample heated at 1100°C.
Photo. 10. 1-1.3 Sample heated at 1000°C.
Photo. 11. 2-3 Sample heated at 1100°C.

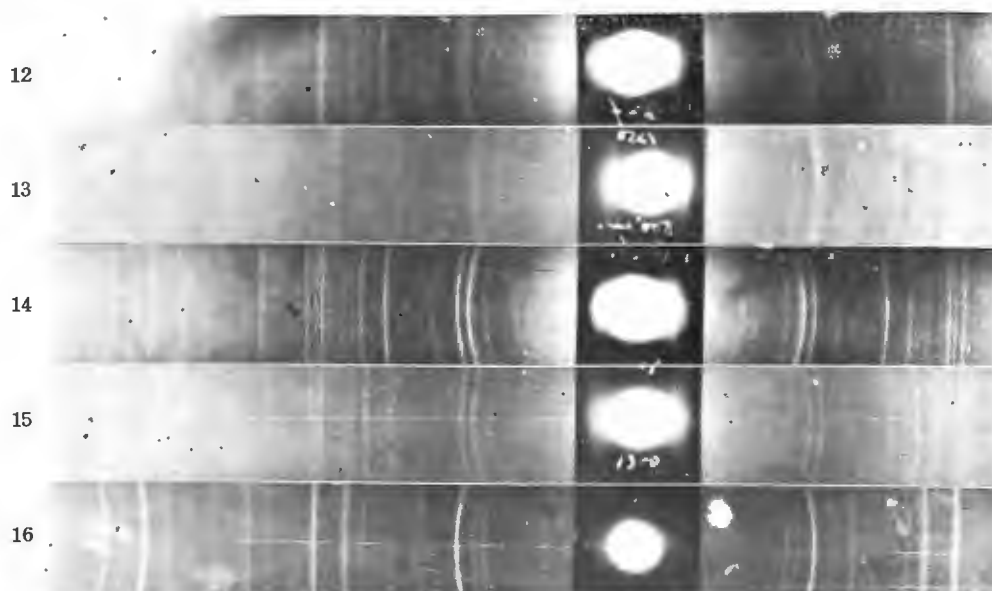


Photo. 12. 2-3 Sample heated at 1200°C.
 Photo. 13. 2-3 Sample heated at 1250°C and annealed at 800°C for 6 hrs.
 Photo. 14. 1-2 Sample heated at 1100°C.
 Photo. 15. 1-4 Sample heated at 1375°C.
 Photo. 16. Fe₃O₄.

Table 1 "d" Values of several Samples.

1-1 (1100)		2-1 (1200)		1.4-1 (1100)		2-3 (1100)		2-3 (1200)		1-2 (1100)	
d	I	d	I	d	I	d	I	d	I	d	I
2.638	vs	3.00	vw	2.99	vw	2.72	vw	2.62	w	2.625	w
		2.89	vw	2.86	w						
		2.744	w	2.75	w						
2.49	s	2.64	vs	2.63	vs	2.48	s	2.478	w	2.55	s
				2.21	w						
2.08	w	2.122	vw	2.48	m	2.078	w	2.10	vw	1.805	vs
		2.07	w	2.19	vw						
1.817	s	1.922	s	2.04	vw	2.078	w	2.10	vw	1.805	vs
		1.725	vw	1.915	s	1.915	vw	1.808	vs	1.805	vs
1.654	w	1.578	w	1.81	s	1.803	vs	1.808	vs	1.67	s
		1.528	w	1.57	vw	1.718	vw	1.65	vw	1.69	w
1.501	vs	1.33	m	1.64	vw	1.64	vw	1.516	w	1.517	vw
				1.521	vw	1.57	vw	1.495	s	1.49	s
1.44	vw	1.17	m	1.49	m	1.468	vw	1.436	s	1.467	m
				1.441	m	1.441	m	1.436	s	1.436	s
1.303	m	1.33	m	1.33	vw	1.303	w	1.178	vw	1.178	vw
		1.17	m	1.301	w	1.154	vw	1.154	vw		
1.075	m	1.075	m	1.075	m	1.075	m	1.075	m	1.134	m
		1.018	m	1.075	m	1.075	m	1.075	m	1.072	m
0.998	s	0.998	s	0.998	s	0.998	s	0.998	s	0.998	s

() shows heating Temperature of Samples
 vs: very strong, s: strong, m: medium, w: weak, vw: very weak.

From the facts that in the case of the 2-3 sample which was heated at 1200°C, the patterns of Fe_2O_3 , which is obviously recognized in the sample heated at 1100°C, were vanished and Fe_3O_4 , which was formed by decomposition of Fe_2O_3 , was neither observed, it is considered that Fe_2O_3 dissolves in CaOFe_2O_3 to some extent at high temperature. Free Fe_2O_3 existed in both of the 1-2 samples heated at 1100°C and 1200°C. In general, Fe_2O_3 dissolved in ferrite is easily precipitated by annealing at 800°~900°C, but in the case of Ca-ferrite, as can be determined by comparing the Photo 12 with 13, the precipitation of Fe_2O_3 from solid solution could not be recognized even though the sample was annealed at 800°~920°C for a long time (6~8 hours). Cirilli and Brisi said that the position of the eutectic between Fe_2O_3 and CaOFe_2O_3 is at about 60 mol% of Fe_2O_3 and when this composition is cooled, the solid formed appears to be monophasic under optical inspection but it shows eutectic structure after a long heat treatment. 60 mol% of Fe_2O_3 corresponds to $\text{CaO}:\text{Fe}_2\text{O}_3$ when their ratio is 2:3, so that the eutectic structure recognized by Cirilli et al. can be considered as a mixture of CaOFe_2O_3 and Fe_2O_3 precipitated by prolonged heat treatment. Authors feel inclined to consider that Fe_2O_3 dissolves into Ca-ferrite to some extent.

b) On the Constitution of Ca-ferrite

There are several previous works on this system.^{7,8,9,10)} Sosman and Merwin⁸⁾ showed two compounds, CaOFe_2O_3 (monocalcium-ferrite) and $2\text{CaOFe}_2\text{O}_3$ (dicalcium-ferrite) in this system. Ferguson⁹⁾ in addition showed $3\text{CaOFe}_2\text{O}_3$ (tricalcium-ferrite). In 1935, White, Graham and Hay⁸⁾ obtained the equilibrium diagram of this system and showed two compounds of mono- and di-calcium-ferrite. Nagai and Asaoka¹⁰⁾ obtained the same results. Recently, the existence of $\text{CaO}2\text{Fe}_2\text{O}_3$ has become a question.^{11,12)}

Authors have recognized only two compounds, CaOFe_2O_3 and $2\text{CaOFe}_2\text{O}_3$, in this system by X-ray and chemical analyses. In the case of the samples have a greater molar ratio of $\text{CaO}:\text{Fe}_2\text{O}_3$ than 1:1 and smaller than 2:1, these two kinds of ferrites are formed in a constant proportion.

i) X-ray analyses: Table 1 shows the "d" values of some of the specimens. This table or Photos 4~15 show that the compounds which exist in CaOFe_2O_3 system are only $2\text{CaOFe}_2\text{O}_3$ and CaOFe_2O_3 , and there is no evidence of existence of $3\text{CaOFe}_2\text{O}_3$ or $\text{CaO}\cdot2\text{Fe}_2\text{O}_3$, the former is nothing but the mixture of CaO and $2\text{CaO}-\text{Fe}_2\text{O}_3$ and latter, of solid solution of Ca-ferrite and Fe_2O_3 and free Fe_2O_3 . This result coincides with that of Malquori and Cirilli.¹²⁾

ii) Chemical Analyses.

Based on the fact that $2\text{CaOFe}_2\text{O}_3$ dissolves easily in cold dil HCl and CaOFe_2O_3 , in heated 1:1 HCl, we performed the separation and quantitative analyses following the above-mentioned method.

The leaching residues by 2% formic acid of the 3-1, 2-1, 3-2, 1-1 and 4-5 samples were analysed, and the molar ratios of CaO : Fe₂O₃ of the residue are shown in Table 2.

Table 2 CaO/Fe₂O₃ of leaching Residues by Formic Acid.

Sample	3-1		2-1		3-2			1-1	4-5
	1100	1200	1100	1200	1000	1100	1200	1100	1000
CaO/Fe ₂ O ₃ of leaching Residue	2.0/1	2.08/1	1.93/1	1.97/1	1.17/1	1.37/1	1.4/1	1/1	1/1.33

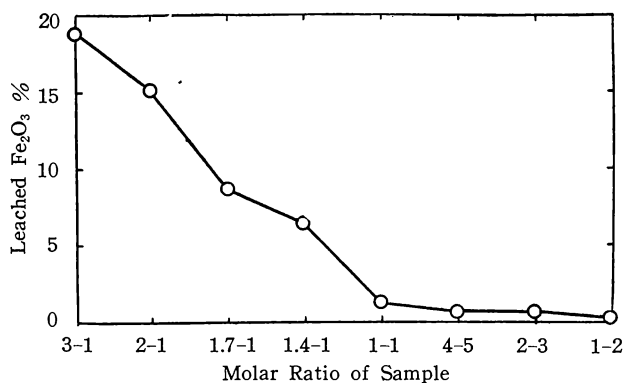
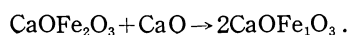
In the cases of the 3-1 and 2-1 sample, both of the residues showed the molar ratio of 2:1 (namely, the residues having the composition of 2CaOFe₂O₃), but the residue of the 3-2 sample varied to some extent its molar ratio of CaO : Fe₂O₃ depending upon the heating temperature. Hence, we prepared the mixed samples of the 1.7-1 and 1.4-1 and analysed the samples, which were heated at 1000° and 1100°C respectively, by the above-mentioned method. The analyses of the leached solution which had been treated by cold dil HCl for 1 minute showed the molar ratio of CaO : Fe₂O₃ to be

Table 3 Component Analyses of 1.7-1 and 1.4-1 Sample.

Sample	Heating Temp °C	CaO/Fe ₂ O ₃		2CaOFe ₂ O ₃ %	CaOFe ₂ O ₃ %
		Leaching Sol. by cold dil. HCl	Residues		
1.7-1	1000	1.9/1	1.02/1	52.5	47.5
	1100	2.02/1	1.18/1	69.5	30.5
1.4-1	1100	2.06/1	1.08/1	44.0	56.0

about 2:1, and that of the residue to be about 1:1; and the quantities of 2CaOFe₂O₃ and CaOFe₂O₃ were calculated by their analytical values and are shown in the right column in Table 3. For example, when heated at 1100°C, the sample 1.7-1 comes to consist of 70% of 2CaOFe₂O₃ and 30% of CaOFe₂O₃. This fact is also considered from leached amount of Fe₂O₃ of various samples (See Fig. 2). The

formation of 2CaOFe₂O₃ takes place in the following manner over 1000°C which is considered to complete at 1200°C.

Fig. 2 Amount of leached Fe₂O₃ by formic acid on various samples.

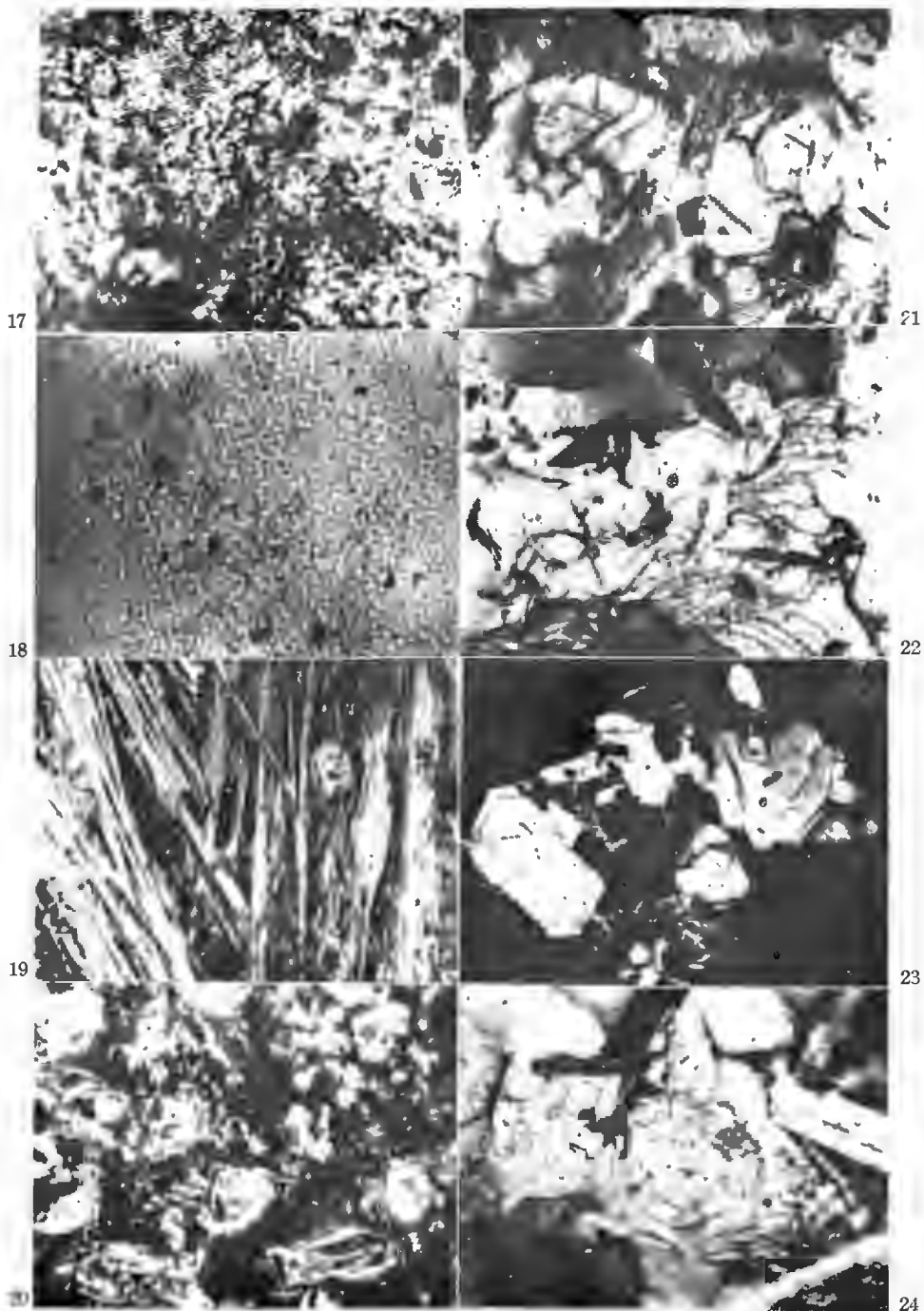


Photo. 17. 2-1 Sample heated at 1280°C. ×400
 Photo. 18. 2-1 Sample after melt ×400
 Photo. 19. 1.7-1 Sample heated at 1250°C. ×400
 Photo. 20. 1.7-1 Sample heated at 1250°C. ×400
 Photo. 21. 1.4-1 Sample heated at 1250°C. ×400
 Photo. 22. 1.4-1 Sample heated at 1250°C. ×400
 Photo. 23. 1.4-1 Sample heated at 1250°C. ×400
 Photo. 24. 1-1 Sample heated at 1220°C. ×400

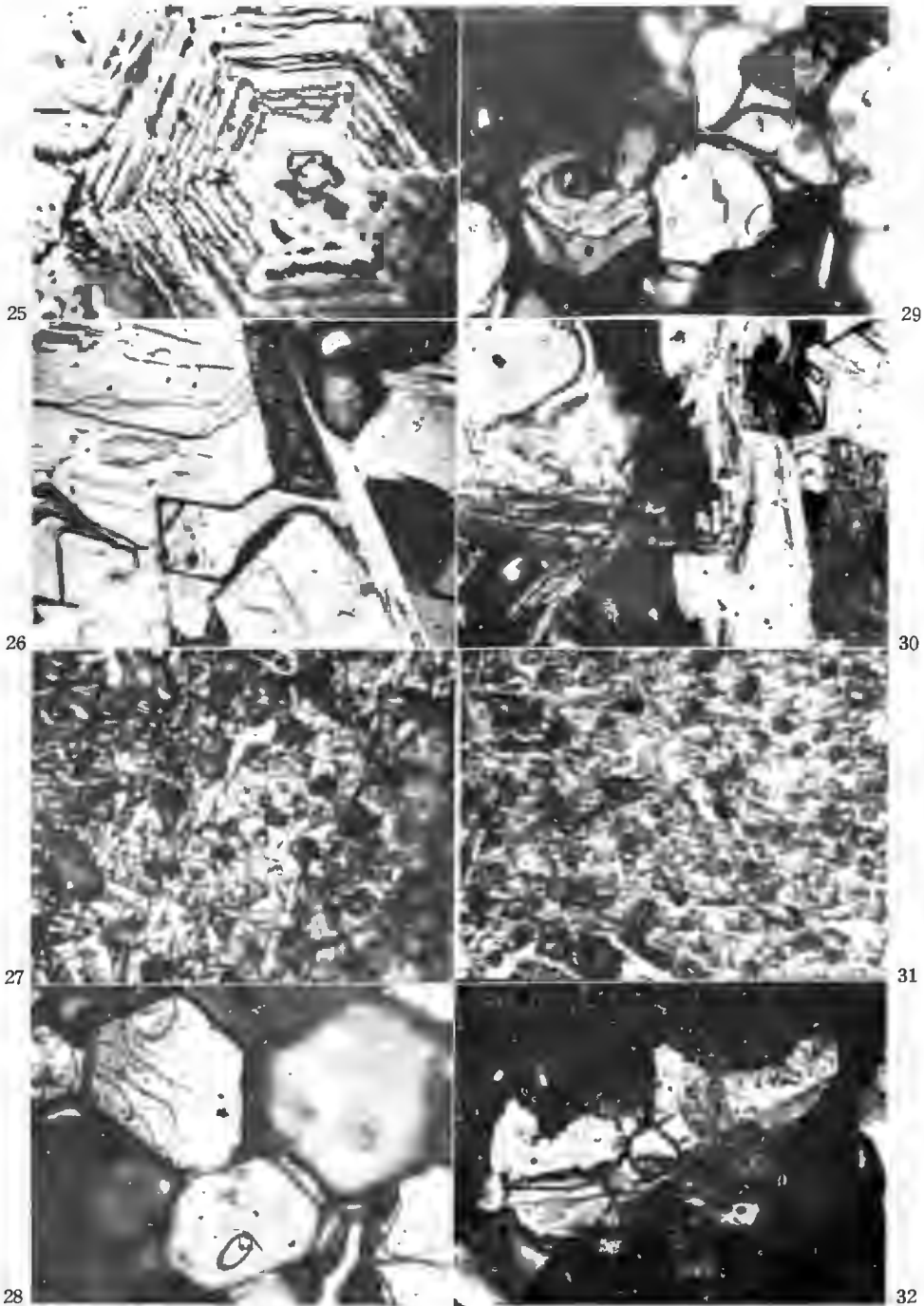


Photo. 25. 1-1 Sample heated at 1220°C. $\times 400$ Enlarged.
 Photo. 26. 1-1 Sample heated at 1220°C. $\times 400$ Enlarged.
 Photo. 27. 2-3 Sample heated at 1200°C. $\times 400$
 Photo. 28. 2-3 Sample heated at 1250°C. $\times 400$
 Photo. 29. 1-2 Sample heated at 1250°C. $\times 400$
 Photo. 30. 1-2 Sample heated at 1300°C. $\times 400$
 Photo. 31. 1-4 Sample heated at 1220°C. $\times 400$
 Photo. 32. 1-4 Sample heated at 1375°C. $\times 400$

c) Microscopic Structure of Ca-ferrite

Photo 17~32 show the micro-structures of the unpolished surfaces of the CaOFe_2O_3 system. Since the samples containing more than twofold of CaO contained in Fe_2O_3 become glassy near their melting point, their micro-structures are difficult to find, but in the case of other samples, the fine crystal structures are observed near their melting point. In the 1.7-1 and 1.4-1 samples both thin crystals and polygonal crystals are found, especially in the 1.4-1 sample, hexagonal board like crystals, hexagonal eddy crystals or parallelogramic crystals are shown. In the 1-1 samples as shown in Photo 25, regular hexagonal crystals are formed and they develop step by step showing the so-called growth steps and, further, some of them appear to grow vortically (Photo 24). In the samples containing excess Fe_2O_3 , the crystals develop well and as Fe_2O_3 increases, the crystals become circular as shown in Photo 28 and 29. The growth steps are also recognized in these samples, but the number of the steps become less. In the 1-2 sample, crystals change into square timber.

From these observations, it is considered that CaOFe_2O_3 crystallizes into hexagonal board, and the growth steps develop on its surfaces, but $2\text{CaOFe}_2\text{O}_3$ sample is apt to become glassy and its crystal is hard to grow.

d) Melting Point of Ca-ferrite

The melting point of $\text{CaO-Fe}_2\text{O}_3$ system are shown in equilibrium diagram by White, Graham and Hay⁹⁾ and the melting points of CaOFe_2O_3 and $2\text{CaOFe}_2\text{O}_3$ are 1216° and 1438°C respectively. By Cirilli and Brisi⁵, they are 1245° and 1435°C respectively. Besides, it is well known that, in the side which is richer in Fe_2O_3 , Fe_2O_3 is apt to decompose into Fe_3O_4 .

In the authors' experiments, as shown in Fig. 3, CaOFe_2O_3 has the lowest melting point and it melts at about 1220°C which agrees with the previous results reported in literatures. However, $2\text{CaOFe}_2\text{O}_3$ melts at about 1280°C which is very much lower than the temperature reported in literatures. In both sides, in which CaO or Fe_2O_3 is richer than CaOFe_2O_3 , the melting point of the samples is higher than that of CaOFe_2O_3 . In literatures, the eutectic point of this system shown at the site of Fe_2O_3 is 60 or 80 mol% and they melt at 1203° or 1216°C respectively, but from our results, could not be made clear.

Table 4 shows our results.

e) On $\text{CaO-Fe}_2\text{O}_3$ System

Summarising the results mentioned, above, we obtain Fig. 4, which shows the existing form of $\text{CaO-Fe}_2\text{O}_3$ system at high temperatures. The main differences from the results of White et al. are as follows. i) Fe_2O_3 dissolves gradually in CaOFe_2O_3 over 1000°C , and shows at 1200°C single phase in the range of Fe_2O_3 containing up

Table 4 Analyses of Samples and Sammarizing of Results.

No. of Sample	1	2	3	4	5	6	7	8	9
	Component	CaO (%) 52.0	43.3	38.0	32.8	26.1	21.6	20.0	14.8
	Fe ₂ O ₃ (%) 48.0	56.7	62.0	67.0	74.0	78.5	80.1	85.2	92.0
Molar Ratio CaO/Fe ₂ O ₃	3.1/1	2.17/1	1.74/1	1.4/1	1.02/1	1/1.28	1/1.48	1/2.05	1/4.02
Symbol of Sample	3-1	2-1	1.7-1	1.4-1	1-1	4-5	2-3	1-2	1-4
Melting point °C	1310	1280	1250	1250	1220	1220	1200~1250	1250	1375
CaO/Fe ₂ O ₃ of leaching Residue by Formic Acid	$\frac{2.1 \sim 2}{1}$	$\frac{1.97 \sim 1.93}{1}$	1.69/1	$\frac{1.42 \sim 1.37}{1}$	1/1	1/1.33	—	1/2.15	—
State of Crystal under Microscope	indistinct	indistinct	needle like, board like	hexagonal board like	hexagonal board like, distinct growth steps	roundish tiny hexagonal board like, distinct growth steps	roundish tiny hexagonal board like, distinct growth steps	roundish tiny crystals and hexagonal board like crystals	ceramic fracture like crystals
Existing Substance recognized by X-ray	2CaO·Fe ₂ O ₃ and CaO	2CaO·Fe ₂ O ₃	2CaO·Fe ₂ O ₃ and CaO·Fe ₂ O ₃	CaO·Fe ₂ O ₃ and 2CaO·Fe ₂ O ₃	CaO·Fe ₂ O ₃	Solid Solution of CaO·Fe ₂ O ₃ and Fe ₂ O ₃	Solid Solution of CaO·Fe ₂ O ₃ and Fe ₂ O ₃	CaO·Fe ₂ O ₃ and Fe ₂ O ₃ or Fe ₃ O ₄	CaO·Fe ₂ O ₃ , Fe ₂ O ₃ and Fe ₃ O ₄
No. of Photographs	4	5, 17, 18	6, 7, 19, 20	8, 21, 22, 23	9, 10, 24, 25, 26		11, 12, 13, 27, 28, 29.	14, 30.	15, 31, 32.

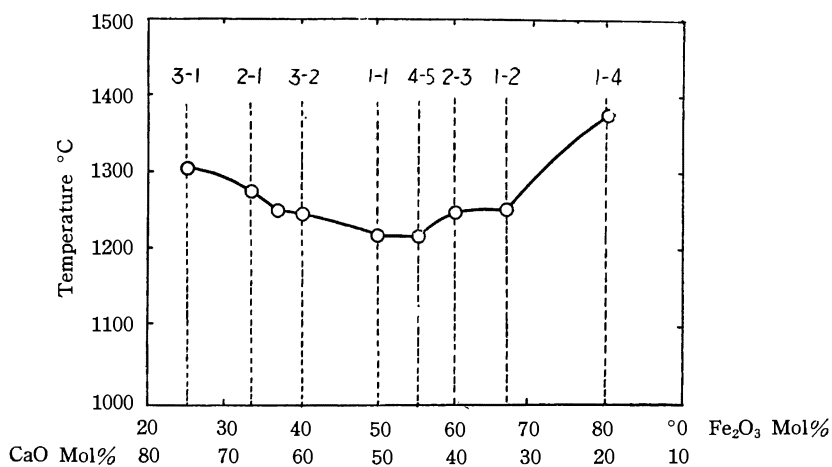


Fig. 3 The melting point of CaO-Fe₂O₃ system.

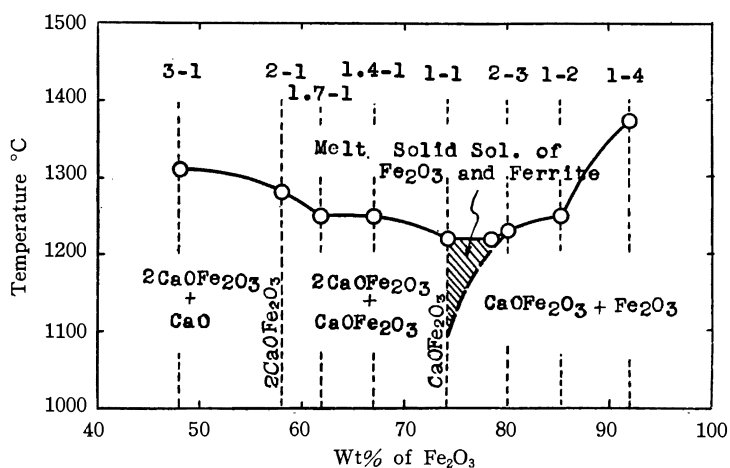


Fig. 4 The existing form of CaO-Fe₂O₃ at high temperature.

to 60 mol% and, for that reason, eutectic between CaOFe₂O₃ and Fe₂O₃ cannot be observed. ii) The melting point of 2CaOFe₂O₃ is considerably lower than that shown in the previous works.

5. Conclusions

A large number of mixtures of various molar ratio of CaO : Fe₂O₃ were prepared and investigated for formation temperature, constitution and compounds of Ca-ferrite, and the following results were obtained :

- 1) Ca-ferrite has two kinds of compound represented by the formula CaOFe₂O₃ (monocalcium-ferrite) and 2CaOFe₂O₃ (dicalcium-ferrite).
- 2) CaOFe₂O₃ is formed over 700°C and this reaction is completed at about 1000°C.

- 3) In the case the samples contain excess CaO, dicalcium-ferrite is formed over 1000°C by the reaction between CaOFe_2O_3 and CaO.
- 4) Both of these two kinds of Ca-ferrite have no ferromagnetism.
- 5) $2\text{CaOFe}_2\text{O}_3$ dissolves easily in cold dil HCl and CaOFe_2O_3 , in 1:1 hot HCl.
- 6) CaOFe_2O_3 dissolves Fe_2O_3 at high temperature to some extent, and the sample containing 60 mol% of Fe_2O_3 shows single phase at 1200°C.
- 7) The melting points of CaOFe_2O_3 and $2\text{CaOFe}_2\text{O}_3$ are 1200° and 1280°C respectively.
- 8) CaOFe_2O_3 forms hexagonal crystals near its melting point and shows growth steps, but in $2\text{CaOFe}_2\text{O}_3$, it is difficult to recognize under microscope a definite crystal formation.

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