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Experimental Study on the X-Ray Powder Diffraction Pattern of Fayalite

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Abstract

X-ray powder diffraction was carried out for fayalite, Fe_2SiO_4, artificially prepared from the mixture of ferrous oxide and silica gel, and fairly complete data for fayalite was obtained. The effect of ferrous oxide on the transformation of silica gel into cristobalite and quartz, and the formation of solid solution of fayalite with the excess ferrous oxide are described and discussed.

Introduction

The system of ferrous oxide and silica is commonly encountered in the study of pyro-metallurgical slags. This system had been throughly investigated by Bowen and Schairer[1] and they obtained a phase diagram of this system. The diagram indicates that there is only one complex compound Fe_2SiO_4 between ferrous oxide and silica, and the compound is called as fayalite.

Actually, fayalite is known as a major component in copper smelting slags[2]. In ferrous metallurgy there are also many cases in which fayalite is concerned. Fayalite is often a chief constituent of commercial iron ore sinter, causing an increase in strength of the material at the expense of its low reducibility[3]. According to Evans and Sloman[4] fayalite was found even in deoxidation products of steel which had been deoxidized with silicon metal. Lismer and Pickering[5] also reported that fayalite was observed among siliceous inclusions in steel ingots. Shioya[6] described that sand marks in steel ingots consisted mainly of iron-manganese silicate. Endo[7] obtained a single crystal of fayalite in slags of an ingot heating furnace and examined its crystal characters by using the technique developed by Laue.

As fayalite usually exists in a state of association with some other phases, identification of the mineral is troublesome. X-ray diffraction analysis seems to be one of the most useful method in the identification of this compound, since this method is quick and brief in both qualitative and quantitative determination.

Up to date, four patterns of fayalite of X-ray powder diffraction have been reported. As shown in Table 1, there are poor coincidence of the values of I, d, and hkl among those data. Data obtained by Chatteree and Sidu[8] can not be compared with others because the detail of their conditions, especially the
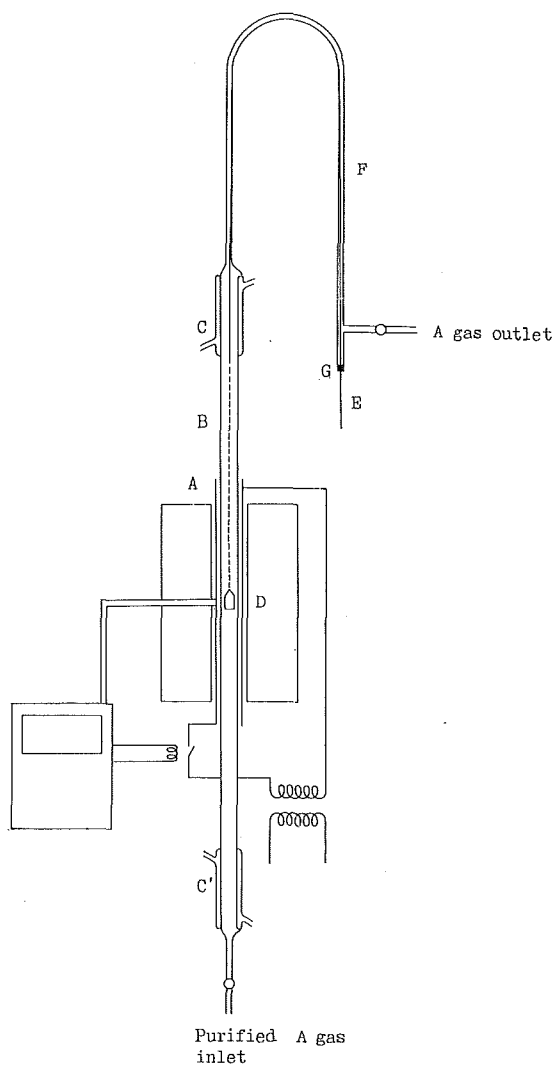
F

C

A gas outlet

G

E

B

A

D

C′

Purified A gas
inlet

Fig. 1.

properties of the sample used, were not explained. It is also shown in Table
1 that the intensity (I) of ASTM (6–0455)[9] appears to be stronger than either
that of ASTM (7–164)[10] or Yoder and Sahama's[11], and the indexes (hkl) of the
first (6–0455) are different from the latter two. The latter two data are closely
related to each other. However, the material corresponding to the (7–164) data
contained a small amount of magnesium silicate as impurity, and the data of
Yoder and Sahama was not filled at high Bragg angle region. The purpose

TABLE 1.

Chatteree and Sidu		ASTM 6–0455			ASTM 7–164			Yoder and Sahama			Authers		
I	d	I	d	hkl	I	d	hkl	I	d	hkl	I	d	hkl
		70	5.2	0̄20	20	5.25	020	16	5.240	020	30	5.241	020
		10	4.37	110				8	4.386	110			
		70	3.96	101				14	3.995	021	32	3.972	021
S	3.71	30	3.78	111	10	3.784	101	7	3.783	101	12	3.780	101
M	3.53	90	3.54	120	30	3.558	111	7.5	3.555	111	60	3.553	111
			3.04	022	10	3.047	002	11	3.052	002	18	3.054	002
		40	2.886	102									
S	2.85	100	2.822	130	100	2.831	130	100	2.829	130	100	2.828	130
					20	2.634	022				25	2.632	022
		80	2.626	040	20	2.621	042	22	2.620	040	20	2.618	040
M	2.55	90	2.562	122	50	2.556	131	60	2.565	131	85	2.563	131
		100	2.495	041	70	2.501	112	80	2.500	112	100	2.499	112
		60	2.461	003									
					5	2.416	200						
		60	2.403	200	20	2.408	041	35	2.408	041	24	2.408	041
		40	2.350	210	5	2.350	210	18	2.350	210			
					20	2.313	122						
M	2.21	80	2.302	140	30	2.303	140	35	2.306	140	28	2.305	140
		70	2.190		10	2.144	211	12	2.191	211	16	2.192	211
W	2.06	60	2.071		5	2.071	132	6	2.074	132			
		60	2.042										
		40	1.984										
		40	1.938										
V.W	1.91				5	1.842	113						
		90	1.837		10	1.834	151						
S	1.76	100	1.778		30	1.778	222				80	1.777	222
					10	1.770	240				28	1.771	240
		60	1.703		10	1.703	241				14	1.703	241
		70	1.677		10	1.679	061				30	1.679	061
		70	1.648		10	1.650	133						
M	1.61	70	1.625		10	1.626	152				11	1.625	152
		70	1.605		10	1.606	043						
		30	1.589										
		70	1.574										
		50	1.537		5	1.539	213						
					5	1.533	242						
		80	1.523		20	1.523	004				27	1.522	004
M	1.51	80	1.514		20	1.516	062				26	1.515	062

of this investigation was to ascertain the discrepancy among those data described above, and to present the complete pattern of fayalite.

a) Experimental Apparatus

The apparatus used was shown schematically in Fig. 1. It was consisted of a silicon carbide spiral heating element (A), which contained a high purity alumina tube (B) having 3 cm inside diameter and being 100 cm long. Ground glass double walled caps (C and C′), through which cooling water can be flowen, were attached to the upper and lower ends of the alumina tube. The sample was held in an iron crucible (D) of 2 cm inside diameter and 3 cm long; it was made of vacuum-melted electrolytic iron. The crucible was suspended in the middle part of alumina tube with a nichrom chain connected with platinum wire (E) which came out of the system through the guide glass tube (F) and rubber stopper (G). In order to heat and cool the sample rapidly, the location of the crucible inside the tube was changed by pulling or pushing the platinum wire. A purified argon was flown through the apparatus to maintain the atmosphere inert. A Pt-Pt 13% Rh thermocouple was fixed at the outside of the middle part of alumina tube and the temperature was automatically controlled and recorded by means of an electronic temperature regulator with an accuracy of $\pm 3°C$. Measured temperatures were checked with melting points of pure copper, silver, aluminum and zinc metals.

b) Experimental Technique

The lower glass cap (C′) was removed and the suspension line was lowered (by pushing the platinum wire through the rubber stopper) in order that the nichrhom chain with a hook came out of the lower end of alumina tube. An iron crucible, containing the sample to be heated, was suspended from the hook and the glass cap was then replaced. Prior to the run, argon was passed through the tube at a flow rate of 21 cc/min for at least six hours. Results of preliminary experiment showed that the air in the system was completely replaced by argon by this procedure. When the temperature of the furnace was reached to 1000°C the crucible with the specimen was quickly raised to the center of the furnce and heated for ten hours at that temperature. On completion of this heat treatment, the crucible was lowered to the cooling chamber (C′) as quickly as possible, and within two minutes the crucible was cooled lower than about 600°C in the flow of argon. The product was removed from the crucible without any difficulty. After crushing and grinding the product to pass through a 150 mesh sieve, it was analyzed by using Norelco Geigercounter Diffractometer with a Co target.

C) Preparation of Materials

Ferrous oxide was made from ferric oxide and iron powder. Ferric oxide of GR grade contained Fe_2O_3 more than 99.21 per cent. It was carefully ground in an agate mortar and screened with a 200 mesh sieve. The iron powder used had more than 99.87 per cent iron and the perticle size was small enough to pass through 100 mesh sieve. The powder was treated by hydrogen to remove surface oxides. These two materials were mixed to obtain ferrous oxide, and the mixture was pelletized by the procedure described below. The pellet was heated for ten hours at 1000°C and followed by rapid cooling in an argon stream[12]. The apparatus used for the preparation of ferrous oxide was the same as described above. In order to examine the degree of synthesis, the product was analyzed by means of both x-ray diffraction and microscope. The quantitative determination of metallic iron and ferric iron unreacted and ferrous iron produced were carried out by chemical analysis. After completing the reaction, the ferrous oxide pellets were ground in an agate mortar, screened with a 200 mesh sieve and stored in a desiccator.

As a source of silica, guaranteed commercial silica gel having a purity of more than 99.1 per cent was used after drying at 700°C.

These reserved materials of ferrous oxide powder and silica gel were mixed intimately in various proportions as shown in Table 2, and were pressed in an iron mould under a pressure of $700 \, kg/cm^2$ to produce small columnar pellets which were 7.18 mm in diameter and being about 10 mm long. A pellet of the specimen was placed in an iron crucible and heated in the apparatus.

TABLE 2.

No. of sample	Composition in wt. %		Phases found in Fig. 2
	SiO$_2$	FeO	
1	100	0	Crisobalite modification
2	100	0	More ordered cristobalite modification than No. 1
3	97.1	2.9	Cristobalite, quartz, and cristobalite modification
4	94.4	5.6	Nearly the same as No. 3
5	89.3	10.7	Cristobalite, quartz, and a small amount of fayalite
6	80.7	19.3	Quartz, cristobalite, and fayalite
7	62.6	37.4	Nearly the same as No. 6
8	29.5	70.5	Fayalite
9	21.8	78.2	Fayalite
10	17.3	82.7	Fayalite and wustite

Experimental Results

Fig. 2 showed the X-ray powder diffraction patterns of the silica gel used and the specimens prepared by the heat treatment of mixtures of silica gel and ferrous oxide. The phases of the minerals which were most likely to be identified from these patterns were summarized in Table 2. The pattern of the specimen No. 1 shows that the silica gel had a structure of modified cristobalite. As can be seen from the pattern of No. 2 specimen, if this material was heated at 1000°C for ten hours in an argon atmosphere, the structure tended to change toward a more orderd one. When the heat treatment was continued for an additional fourteen hours, the characteristic reflection lines of cristobalite began to develop. From the pattern of No. 3 specimen which contained 3 per cent of ferrous oxide, it is seen that the modified cristobalite was partly changed into cristobalite and quartz during the heat treatment. The more the ferrous oxide addition, the stronger the characteristic lines of respective silica minerals is observed, as is clearly shown in the patterns of No. 4 and No. 5. It is interesting to note here that in the patterns of No. 3, 4 and 5 no line of ferrous oxide does appear owing probably to the fact that the oxide was dissolved into or reacted with silica. In the pattern of No. 5 very weak reflection lines of fayalite was observed. This means that the reaction between ferrous oxide and silica commenced to occur. The patterns from No. 6 to 8 showed that, with a further increase in ferrous oxide addition, the intensity of the characteristic lines of fayalite were increased. The characteristic lines of No. 8 should be attributable to fayalite, since the mixing ratio of ferrous oxide and silica was fixed to that of fayalite (Fe_2SiO_4), and the indexes of the pattern obtained agreed with those expected for the orthorhombic system. The values of I, d and hkl for fayalite were determined precisely with No. 8 specimen using silicon metal powder as a standard, and the result was shown in Table 1.

The specimens of No. 9 and No. 10 were prepared to have the mole ratios of 1/3 and 1/4 respectively in silica to ferrous oxide, as shown in Table 3. The patterns of these specimens were shown in Fig. 2. It was oberved from the patterns that the characteristic lines of fayalite tend to shift to the dirction of lower region of Bragg angle. This tendency was not observed for the specimens of No. 5, 6, 7 and 8. In the pattern of No. 10 specimen, unreacted ferrous oxide was clearly shown to exist, while it was not detected for the other specimens.

It should be pointed out here that the characteristic lines corresponding to grünerite ($FeSiO_3$) could not be observed in the present experiment.
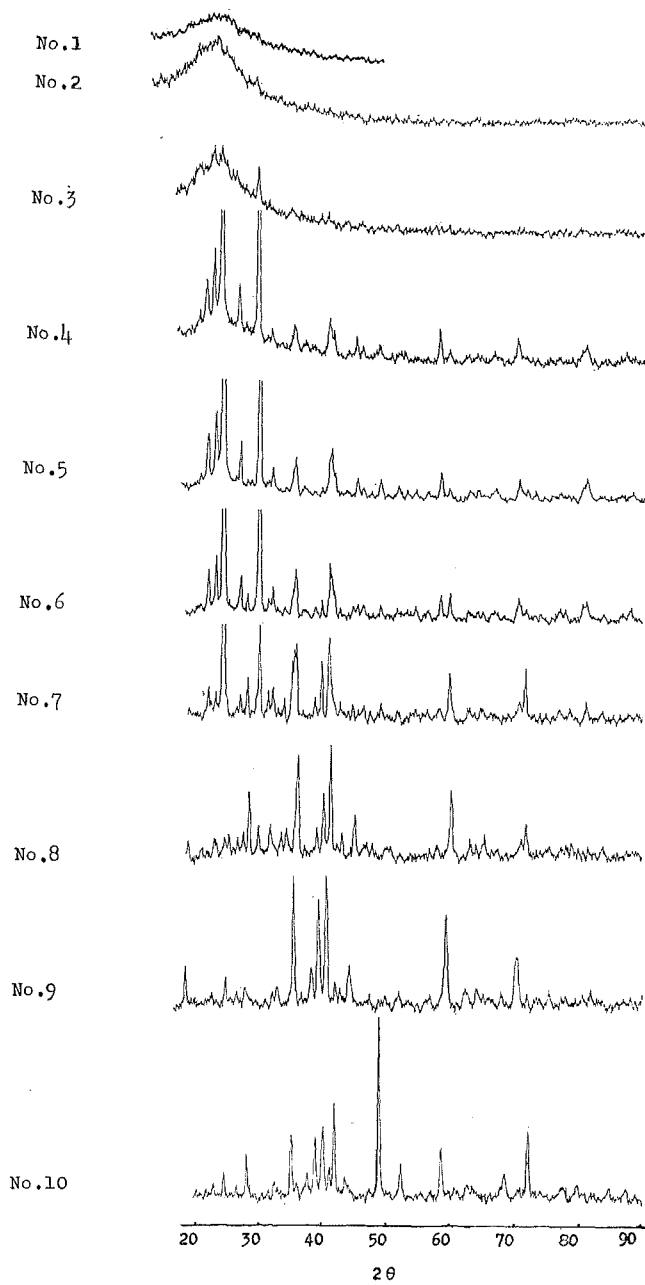
No.1
No.2
No.3
No.4
No.5
No.6
No.7
No.8
No.9
No.10

20 30 40 50 60 70 80 90

2θ

Fig. 2.

Discussion of the Results

As described in the proceeding section, non of ferrous oxide and ferrous oxide-silica compound could be detected in the sintered products of No. 3 and 4 samples in spite of the addition of a small amount of ferrous oxide before the reaction. The disappearence of ferrous oxide is considered to be the result of dissolution into silica during the heat treatment. It is well known that any type of silica crystal is composed of a net-work of terahedral crystal unit of silica. Non-crystalline silica gel had a structure of modified cristobalite which is considered to be a structure with disordered net-work of tetrahedral arrangement of silica. The structure can be transformed into the state of ordered net-work (crystalline state) if proper experimental condition is chosen. The transformation is accelerated at high temperature or by the addition of some mineralizers. However, in general the crytallization is quite sluggish because of the strong bonding between the tetrahedral units. When a small amount of ferrous oxide dissolves into the silica gel, it will firstly break the bonding between tetrahedral unit structures at highly disordered positions where the lattice energy is high. Then the each tetrahedron becomes movable and is rearranged to form an ordered structure, ie. cristobalite or quartz. As the amount of ferrous oxide addition is increased, the destruction of the bond advances to a greater extent and finally the orthorhombic composition (fayalite) is reached[2].

The lattice constants of fayalite were calculated for the samples of No. 7, 8, 9 and 10 under the assumption of an orthorhombic system. The results were shown in Table 3. In this table it is clear that the lattice constants of No. 7 (SiO_2/FeO $= 2/1$) and No. 8 are almost identical. This fact shows that the excess amount of silica does not affect the structure of fayalite during the sintering process. On the other hand, the excess amount of ferrous oxide has a remarkable effect on the lattice constants of fayalite. The latter enlarged with the increased amount of the former as shown in Table 3. From the fact it is concluded that the excess silica does not react with fayalite while the excess

TABLE 3.

No. of sample	Composition in mole ratio			Lattice Constant (Orthorhombic) (Å)		
	SiO_2	:	FeO	a	b	c
7	2	:	1	4.81	10.52	6.11
8	1	:	2	4.813	10.518	6.108
9	1	:	3	4.84	10.66	6.16
10	1	:	4	5.07	10.70	6.39

ferrous oxide reacts to form a solid solution with fayalite.

Summary

The mixtures of ferrous oxide and silica gel were heated at 1000°C in an argon atmosphere in order to produce fayalite, the products were analyzed by X-ray diffraction method.

Conclusions are as follows :

(1) powder X-ray diffraction data of fayalite was obtained which is considered to be more accurate and complete compared to that hitherto reported,

(2) the excess ferrous oxide forms a solid solution with fayalite but the excess silica has no influence,

(3) grünerite was not recognized as the sintered product for all mixing ratios of silica and ferrous oxide, and

(4) the mechanism of transformation of silica gel into cristobalite · or quartz was explained by the mineralizing action of ferrous oxide dissolved in silica.

Acknowledgement

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