Synthesis of Iron-Titanium Oxides under Hydrothermal Conditions

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(Received August 5, 1970)

The solid solutions in the system FeO-Fe_2O_3-TiO_2 were synthesized under hydrothermal conditions up to 700°C and 2.5 kb (P_{H_2O}). The results of X-ray diffraction, chemical and thermomagnetic analyses indicated that the products always consisted of magnetite-ulvöspinel or hematite-ilmenite solid solutions and, in some cases, rutile was also formed. The presence of the solid solutions of magnetite and ulvöspinel indicates a reducing atmosphere during the treatment. When P_{H_2O} increased from 1 kb to 2.5 kb, the FeO contents in the products decreased.

Minerals belonging to the system FeO–Fe_2O_3–TiO_2 are abundant in the earth's crust. Magnetite (Fe_3O_4), a representative mineral, is known to have a spinel structure and to be ferrimagnetic.[1] Ulvöspinel (Fe_2TiO_4) also has a spinel structure but is not ferrimagnetic at room temperature. These two minerals form a continuous solid solution.[2] Hematite (α-Fe_2O_3) has a rhombohedral structure which makes this substance parasitic ferromagnetic.[3] The crystallographic structure of ilmenite ($FeTiO_3$) is analogous to that of hematite, with some differences in magnetic properties.[4] Hematite and ilmenite are the final components of solid solutions, and the relations between chemical composition and cell dimensions have been investigated in detail.[5] Another series of solid solutions is found in the system $FeTi_2O_5$-pseudobrookite (Fe_2TiO_5). These solid solutions have orthorhombic structures and exhibit paramagnetism.[6] Of the three polymorphic forms of TiO_2 (rutile, brookite, and anatase), rutile is the most commonly occurring phase and found to be stable in a wide region of temperature and pressure.[7]

Most investigators have studied the synthesis and stability concerning the FeO–Fe_2O_3–TiO_2 system at atmospheric pressure or below (Ref. 8). In the present investigation, a synthesis of minerals belonging to the above system was attempted in relation to the determination of stable phases under hydrothermal conditions. If this attempt is successful, the results are expected to be useful for explaining the occurrence of these minerals in nature.

Experimental

Starting Materials. A series of solutions containing titanium (IV) chloride and iron (III) chloride in various ratios were mixed with ammonia. The resulting precipitate was washed with ammonia, air-dried, and ground to powder. The powder was confirmed to be amorphous by X-ray diffraction. After ignition, the content of Fe_2O_3 in the powder was determined by the Reinhardt method. The molar ratio of TiO_2 and Fe_2O_3 in the powder was then calculated. The powder was used as the starting material. The chemical compositions of the starting materials are shown in Table 1.

TABLE 1. COMPOSITION (MOL%) OF STARTING MATERIALS

Starting material	TiO_2	Fe_2O_3
A	70.0	30.0
B	59.2	40.9
C	50.9	49.1
D	29.2	70.8
E	15.0	85.0

Apparatus and Procedure of Synthesis. Each starting material was sealed in a gold capsule together with a nearly constant amount of water, and was treated in a test-tube type reactor[9] under various conditions of temperature and pressure from 400° to 700°C and at 1 kb or 2.5 kb (P_{H_2O}). After being kept for 48 to 454 hours, the reactor was quenched to room temperature within three minutes.

Examination of Specimens. *Chemical Analysis*: The FeO content in the quenched specimen was determined by permanganate titration. The molar ratio of TiO_2, Fe_2O_3, and FeO was then calculated.

X-Ray Diffraction: X-Ray powder patterns, obtained with iron-filtered Co-$K\alpha$ radiation, were used for identification of phases and determination of the chemical composition of the solid solutions.

The values of a and c were calculated for the hematite-ilmenite solid solution. The value of c, which is sensitive to variation of the chemical composition, was compared with Lindsley's result[10] to determine the chemical composition. In the case of the magnetite-ulvöspinel solid solution, the chemical composition was also determined by referring to the relation obtained by Lindsley.[10]

Thermomagnetic Analysis: A magnetic balance similar to the apparatus reported by Shimada *et al.*[11] was used for the thermomagnetic analysis at room temperature and above.

Results and Discussion

Synthetic Conditions and Composition of Products. The synthetic conditions and the chemical composition of

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TABLE 2. SYNTHETIC CONDITIONS AND COMPOSITION OF PRODUCTS

Starting material		No.	Product composition (mol%) TiO$_2$	Fe$_2$O$_3$	FeO	R*
(a) 1 kb (P_{H_2O})						
700°C 70hr	A	1	55.6	3.5	40.7	0.85
	B	2	44.1	5.0	50.9	0.84
	C	3	39.1	14.6	46.3	0.61
	D	4	21.7	26.6	51.7	0.49
	E	5	11.0	35.2	53.8	0.43
600°C 114hr	A	6	58.5	8.8	32.6	0.65
	B	7	45.7	8.9	45.5	0.72
	C	8	39.9	17.0	43.2	0.56
	D	9	22.3	30.2	47.5	0.44
	E	10	11.4	40.6	48.0	0.37
500°C 168hr	A	11	69.5	29.1	1.4	0.02
	B	12	56.5	34.6	8.9	0.11
	C	13	49.1	44.0	6.9	0.07
	D	14	28.1	64.0	7.9	0.06
	E	15	14.2	73.7	12.2	0.08
400°C 454hr	A	16	69.6	29.3	1.1	0.02
	B	17	58.3	38.8	2.9	0.04
	C	18	49.2	44.2	6.6	0.07
	D	19	28.5	66.5	5.0	0.04
	E	20	14.6	79.3	6.2	0.04
(b) 2.5 kb (P_{H_2O})						
700°C 48hr	A	21	67.2	24.6	8.2	0.14
	B	22	54.1	28.9	17.0	0.23
	C	23	45.0	31.8	23.3	0.27
	D	24	25.2	47.1	27.7	0.23
	E	25	13.5	66.0	20.5	0.13
600°C 212hr	A	26	68.4	27.0	4.5	0.08
	B	27	56.4	34.2	9.4	0.12
	C	28	44.0	29.0	27.0	0.32
	D	29	24.5	43.0	32.5	0.27
	E	30	13.7	68.9	17.4	0.11
500°C 422hr	A	31	68.9	27.9	3.2	0.05
	B	32	56.2	33.8	10.0	0.13
	C	33	47.5	39.2	13.3	0.15
	D	34	27.6	61.3	11.1	0.08
	E	35	14.0	72.4	13.6	0.09

R*: FeO/(2Fe$_2$O$_3$+FeO) calculated from composition.

the products are summarized in Table 2. Since no Fe (II) ion was contained in any of the starting materials, the ratio FeO/(2Fe$_2$O$_3$+FeO) shows the extent of reduction which occurred during the treatment. Figs. 1 (a) and (b) give ternary diagrams in which the composition of the starting materials and the products are plotted. A comparison of these results with those in Table 2 reveals the following. (1) The extent of reduction increases under conditions of temperature and pressure above 600°C and 1 kb. (2) The extent decreases at 600°C, when P_{H_2O} increases from 1 kb to 2.5 kb.

In the range from 400 to 500°C, hematite-like and rutile-like crystals are formed regardless of the starting materials. When temperature increases, the composition of the hematite-like crystals approaches that of ilmenite.

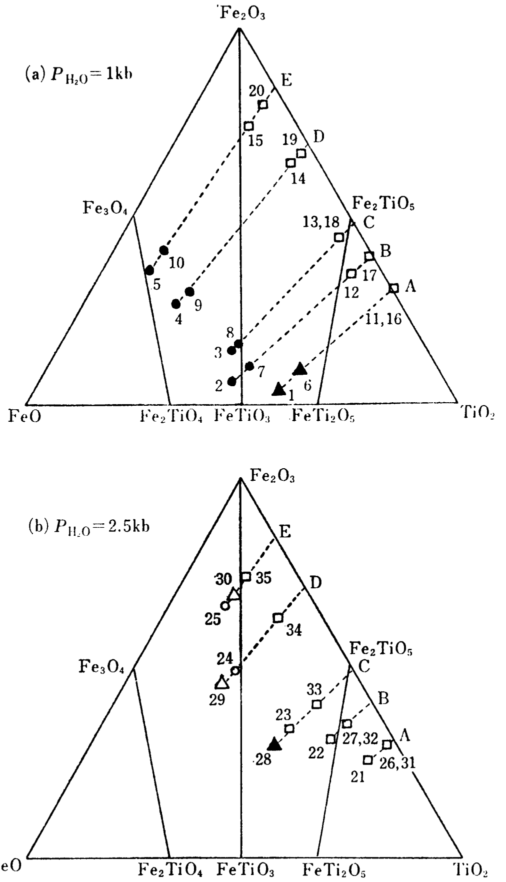

Fig. 1. Ternary diagrams in the system FeO-Fe$_2$O$_3$-TiO$_2$ on which the chemical composition of the starting materials and those of the hydrothermal products are plotted. The letters A, B, *etc.* in the diagrams correspond to those in Table 1. The numbers also correspond to those in Table 2.
●: coexistence of ilmenite-like crystal with magnetite.
○: hematite-like crystal.
□: coexistence of hematite-like crystal with rutile.
△: coexistence of hematite-like crystal with magnetite.
▲: coexistence of ilmenite-like crystal with rutile.

X-Ray Diffraction and Composition of Products. The results of X-ray powder diffraction and the composition determined from the cell dimensions are summarized in Table 3. The products consist of one or two phases and each phase corresponds to rutile, hematite, ilmenite or magnetite, although the d-spacings of each phase differ from ideal values. The differences are caused by the fact that these phases are not the final components of solid solution series in the FeO–Fe$_2$O$_3$–TiO$_2$ system but those of an intermediate composition.

Figures 2 (a) and (b) show the variation of d_{104} of the hematite-ilmenite solid solutions with the change in reaction conditions. The values of d_{104} of the hematite-ilmenite solid solutions are plotted against the chemical composition in Fig. 3.

Thermomagnetic Analysis. The results of thermomagnetic analysis indicate that the products have the

TABLE 3. X-RAY EXAMINATION OF PRODUCTS

Product	Ilmenite-Hematite					Rutile		Magnetite-Ulvöspinel			
No.	d_{104}(Å)	I	a (Å)	c (Å)	R_1[a)]	d_{110}(Å)	I	d_{220}(Å)	I	a (Å)	R_2[b)]
(a) 1 kb (P_{H_2O})											
1	2.750	vs	5.090	14.076	100	3.253	m				
2	2.746	m	5.084	14.051	96			2.984	s	8.441	35
3	2.749	m			98			2.979	vs	8.427	27
4	2.746	m	5.084	14.051	96			2.979	s	8.427	27
5	2.746	s			96			2.991	s	8.460	46
6	2.742	s	5.082	14.019	89	3.249	s				
7	2.740	s			87			2.984	s	8.441	35
8	2.740	s			87			2.971	m	8.404	10
9	2.740	s			87			2.979	s	8.425	26
10	2.740	m			87			2.971	s	8.404	10
11	2.700	m			0	3.251	s				
12	2.702	vs	5.038	13.767	8	3.251	m				
13	2.700	vs	5.034	13.752	0	3.251	m				
14	2.700	vs	5.037	13.747	0	3.249	s				
15	2.704	s	5.039	13.776	10	3.251	s				
16	2.700	m			0	3.251	s				
17	2.700	s			0	?	w				
18	2.704	s			10	3.253	m				
19	2.700	vs	5.034	13.752	0	3.253	m				
20	2.700	vs	5.034	13.752	0	?	w				
(b) 2.5 kb (P_{H_2O})											
21	2.704	m			10	3.251	s				
22	2.712	vs	5.050	13.824	30	3.253	m				
23	2.717	s			47	3.255	s				
24	2.714	vs	5.054	13.840	40						
25	2.706	vs	5.041	13.795	20						
26	2.705	m	5.040	13.786	15	3.251	s				
27	2.709	m	5.042	13.815	26	3.253	s				
28	2.720	m	5.057	13.880	53	3.251	m				
29	2.717	vs	5.056	13.860	47			?	vw		
30	2.709	vs	5.042	13.815	26			?	vw		
31	2.701	m	5.035	13.761	5	3.249	m				
32	2.704	s	5.039	13.776	10	3.253	m				
33	2.704	s			10	3.251	m				
34	2.704	vs	5.039	13.776	10	3.251	m				
35	2.702	vs	5.033	13.767	8	3.253	s				

a) Mole percentage of ilmenite in ilmenite-hematite solid solution.

b) Mole percentage of magnetite in magnetite-ulvöspinel solid solution.

R_1 and R_2 were determined using the cell dimensions and Lindsley's results. When diffraction was weak and the calculation of the cell dimensions was difficult, the composition was estimated by the value of d_{104} with reference to Fig. 3.

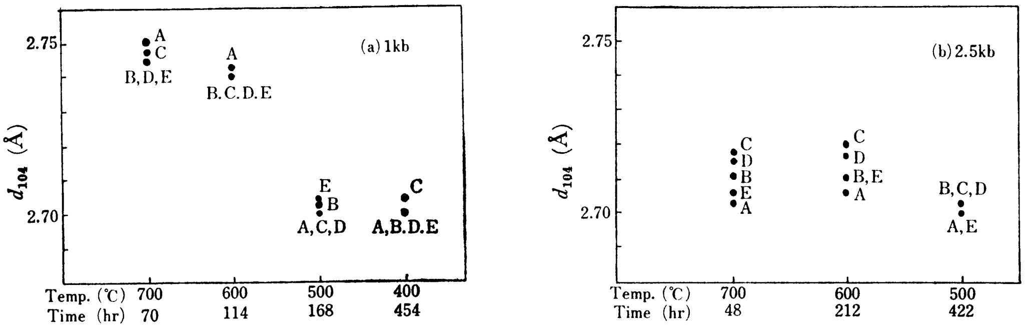

Fig. 2. Variation of d_{104} of hematite-ilmenite solid solutions with change in the reaction conditions. The letters A, B, *etc.* correspond to those in Fig. 1.

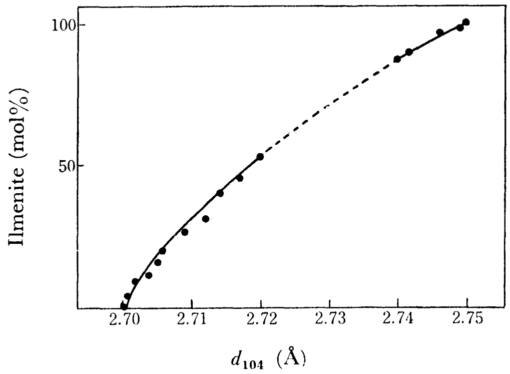

Fig. 3. Relation between the chemical composition and d_{104} in hematite-ilmenite solid solutions.

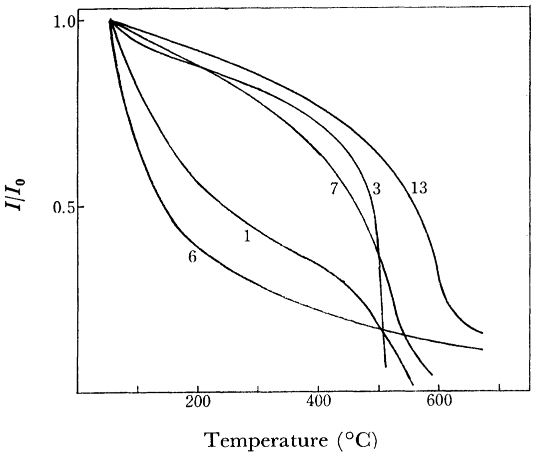

Fig. 4. Magnetization of the products as a function of temperature. The numbers on each curve correspond to those in Table 2. I_0 : Magnetic moment at 50°C.

intermediate composition of solid solution series in the $FeO–Fe_2O_3–TiO_2$ system. This is in line with the results obtained by X-ray diffraction. In Fig. 4 the curves (3) and (7) show a similar temperature dependency to magnetite. In these cases, the magnetite-ulvöspinel solid solutions are found by X-ray diffraction. From the curve (13), the presence of a hematite-like crystal is expected which agrees with the result of X-ray diffraction.

It is thought that the decreasing P_{O_2} at elevated temperatures is established either by the dissociation of water or by the reaction of water and the metal wall of the reactor.[12] This has not been clarified in the present experiments.

From the results, the following conclusions are obtained.

(i) All the crystals that belong to the system $FeO–Fe_2O_3–TiO_2$ and remain stable under hydrothermal conditions up to 700°C and 2.5 kb are classified into rutile, magnetite-ulvöspinel solid solutions and hematite-ilmenite solid solutions.

(ii) Synthesis of a new mineral is unsuccessful under the conditions of the present investigation, when the starting materials belonging to the system $Fe_2O_3–TiO_2$ are used.

(iii) Atmosphere surrounding the samples under the hydrothermal conditions was reducing to a certain extent. The cause of this reduction is not clearly shown at this stage of investigation, but P_{O_2} acting on the samples at 700°C and 1 kb corresponds to the value of the order of 10^{-8} atm at 1300°C proposed by Taylor.[13]

(iv) The common occurrence of magnetite-ulvöspinel or hematite-ilmenite solid solutions in nature is explained if these minerals remain stable even under hydrothermal conditions as was proved by the present experiments.

The author wishes to thank Professor Mitsue Koizumi and Professor Shoichi Kume of Osaka University for their kind guidance and help. Thanks are also due to Professor Jumei Yamasaki of Kôchi University for his encouragement throughout this work.

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