

On the Constitution of Copper-Ferrite

By

Isao KUSHIMA and Tsuyoshi AMANUMA

Department of Metallurgy

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1. Introduction

Copper-ferrite is considered as a compound of equimolar of CuO and Fe_2O_3 such as CuOFe_2O_3 or $\text{Cu}(\text{FeO}_2)_2$ and it is well known that the compound is formed when the powdered copper ore are roasted. When it is formed in wet smelting process, a problem arises because of the fact that it is difficult to dissolve in dilute acid. For this reason, the relationship between the roasting temperature and the formation ratio of Cu-ferrite or the leaching ratio of copper in the ore have been studied by many researchers.

It is also well known that this material is ferro-magnetic and Cu-ferrite formed in the roasted ore can be segregated by magnetic separation. On the other hand, since the successful application of Néel's "Ferrimagnetism" theory in 1948 to these compounds, developments of ferrite are quite admirable both practically and theoretically. Recently, Cu-ferrite itself is utilized not only as a ferro-magnetic material or semi-conductor but also as a solid solution of Cu-ferrite with other substance as Zn-ferrite.

The authors have conducted an investigation of the formation temperature of Cu-ferrite on oxide mixture and sulphide mixture and have found that in both cases the formation of ferrite begins at over 700°C . We have also studied the constitution of the compounds between CuO- Fe_2O_3 system by measurement of its magnetic properties, X-ray analyses, chemical analyses and microscopic studies. However, in this paper, we wish to report on the constitution of copper-ferrite. Readers of this report are requested to take notice of the fact that the authors have used the term cuprous-ferrite for $\text{Cu}_2\text{OFe}_2\text{O}_3$, cupric-ferrite for CuOFe_2O_3 , and copper-ferrite or Cu-ferrite for a compound of ferric oxide and copper oxide, not to distinguish cuprous and cupric oxide on purpose.

2. Outline of Previous Studies

As has been mentioned above, the fundamental constitution of Cu-ferrite is the

equimolar compound of CuO and Fe₂O₃, but at high temperature, it is not always so as in the case of Zn-ferrite. For instance, CuO decomposes to Cu₂O at high temperature so that the formation of cuprous-ferrite (Cu₂OFe₂O₃) and of the solid solution of cupric-ferrite (CuOFe₂O₃) and Fe₂O₃ are conceivable and, because of this fact, the magnetic property and microscopic structure of the sample are changed.

Kohlmeyer¹⁾ had already reported in 1910 on the formation of Dicopper-ferrite (CuO)₂Fe₂O₃, but the existence of this compound is doubtful. Recently, N. A. Toropov and A. I. Borisenko¹¹⁾ studied on the system CuO-Fe₂O₃ and explained that the ferrite obtained by 40 hours of heating at 1000°C is stable and does not decomposed even at 1200°C. The quenched CuO+5Fe₂O₃ sample has a single phase, but it possesses two phases when it is annealed, owing to its decomposition into Cu-ferrite and Fe₂O₃. The spinel structure of CuFe₂O₄ is preserved in the components rich in Fe₂O₃ up to and including CuO+5Fe₂O₃. This system forms a series of solid solutions between 66.74 and 83.38% Fe₂O₃.

It is said that the structure of Cu-ferrite belongs to the inversed spinel type which is represented by Fe⁺⁺⁺(Cu⁺⁺, Fe⁺⁺⁺)O₄; but F. Bertaut^{2),3)} reported that the arrangement is not of completely inversed type but it takes a form in which the normal spinel type is admixed to a small degree, i.e. (Fe_{2λ}⁺⁺⁺, Cu_{1-2λ}⁺⁺)(Cu_{2λ}⁺⁺, Fe_{2-2λ}⁺⁺⁺)O₄^{''} where 0.50 > λ > 0.333 (in normal type λ=0 and in inversed type λ=½), in other words, the kind of ion is changed in Néel's sites of A and B.

H. Forestier^{4),5)} conducted crystallographical and electromagnetic research work on Cu-ferrite and others. It was explained in detail by F. S. Wartman⁶⁾ in 1933, F. S. Wartman and A. T. Thompson⁷⁾ in 1934, more recently by L. Weil, F. Bertaut and L. Bochirol⁸⁾, F. Bertaut⁹⁾, and T. Inoue¹⁰⁾, that Cu-ferrite has two crystal types, one is cubic at high temperature and other is tetragonal at low temperature. The axial ratio c/a of tetragonal Cu-ferrite is about 1.06, and N. A. Toropov and A. I. Borisenko¹¹⁾ stated an endothermal effect at 415°C, which is caused by polymorphic transformation is observed. F. S. Wartman reported that the magnetism of cubic Cu-ferrite is stronger than that of magnetite, on the other hand, that of tetragonal Cu-ferrite is much weaker. He said also that cuprous-ferrite is formed by direct union of both oxides at high temperature using excess Cu₂O and quenching; and it is a hexagonal crystal having a density of 5.47, slightly magnetic and black in colour.

L. A. Wels and O. Baudisch¹²⁾ studied the magnetic properties of various ferrites and said that Cu-ferrite has extremely soft magnetic properties since its lattice is strained because of Cu ions being larger than Fe ions, and the ferrite with the most Cu is the softest.

The authors studied systematically on the system of CuO-Fe₂O₃ using Cu-ferrite

formed from oxide mixtures of various molar ratio, and observed that the cupric-ferrite dissolves excess Fe_2O_3 at high temperature, and over 1100°C , it forms cuprous-ferrite in a part of itself and, due to this formation, changes its nature in magnetic properties and the microscopical structure. The results obtained up to the present are as reported below.

3. Experimental Methods

The constitution of Cu-ferrite was studied by X-ray examination, the magnetic and chemical-analyses, and microscopical investigation, etc. Each sintered tablet sample was crushed under 100 mesh and photographed by Debye-Scherrer X-ray. The magnetic properties were measured by the ballistic galvanometer method shown in the previous report¹³⁾ pertaining to the sintered square bar samples. After these experiments, the samples crushed under 100 mesh was chemically analysed.

For it was considered in this case that the decomposition from cupric-ferrite to cuprous-ferrite would occur as from CuO to Cu_2O at high temperature, the CuO sample, heated at various temperature in the air, was examined at first by X-ray and chemical-analyses in order to see the aspect of decomposition of CuO to Cu_2O . As the result of heating CuO, Cu_2O was formed at above 950°C and the formation reached 44% at 1000°C and 89.5% at 1050°C . The analytical procedure of the mixed sample of CuO and Cu_2O was as follows¹⁴⁾. Approximately 500 mg of the sample was dissolved in $\text{Fe}_2(\text{SO}_4)_3$ solution to which was added 10 c.c. of 1:1 H_2SO_4 ; in this solution, Cu_2O reacted upon $\text{Fe}_2(\text{SO}_4)_3$ reduced it to FeSO_4 . Fe^{2+} thus formed was determined by titration with KMnO_4 std. solution and converted into the corresponding volume of Cu'.

In the heated Cu-ferrite sample, Cu_2O and Fe_3O_4 , which are formed by decomposition of CuO and Fe_2O_3 , existed simultaneously, but it was difficult to determine both Cu' and Fe^{2+} at the same time.

Free CuO and Cu_2O in the heated sample were leached in ammoniac ammonium chloride solution by boiling for 2 hours. CuO and Cu_2O individually, and their mixture with Fe_2O_3 were tested by this method previously and it was found that the free Cu oxide in the sample was almost completely leached out after 1 hour.

Cu-ferrites containing Cu oxide in excess of 1:1 ratio melted at comparatively low temperatures and the melting points of these samples were measured by thermal analyses.

4. Preparation of Samples

CuO was obtained from pure CuSO_4 by heating it at $850^\circ\sim 900^\circ\text{C}$ for several hours and decomposing it completely. This CuSO_4 was prepared by dissolving ele-

ctrolytic copper into H_2SO_4 and crystallizing it. In the sample heated under 950°C , the formation of Cu_2O was very little (about 0.5%).

In order to prepare Cu_2O , CuCl_2 was reduced by electrolytic copper sheet in the aqueous solution of HCl , letting white CuCl precipitate in water and then hydrolyzing it by soda acetate in a weak HCl solution. The red cuprous oxide thus obtained was refined by boiling it in acetic acid solution. This Cu_2O sample contained 90.0% Cu (in theoretical Cu content is 88.82%).

Fe_2O_3 was prepared by heating the ferrous oxalate at $700^\circ\sim 750^\circ\text{C}$ for several hours and completely decompsing and oxidizing it. Since in the case of Zn -ferrite, Fe_2O_3 obtained from ferrous oxalate was most reactive with ZnO , the same sample was used in this case also.

CuO and Fe_2O_3 were mixed so that the molar ratio of $\text{CuO}:\text{Fe}_2\text{O}_3$ would become exactly 9:1, 7:1, 4:1, 3:1, 2:1, 1:1, 1:2, 1:3 and 1:9; and Cu_2O and Fe_2O_3 were also mixed so that the ratio $\text{Cu}_2\text{O}:\text{Fe}_2\text{O}_3$ would be 2:1, 1:1 and 1:2. The chemical analyses of some of these samples are shown in Table 1. These mixed samples were

Table 1. Analyses of several samples.

Sign of sample	Mixed ratio	CuO %	Fe_2O_3 %	Molar ratio $\text{CuO}:\text{Fe}_2\text{O}_3$
7-1	7:1	78.0	22.2	7:1
4-1	4:1	66.5	32.4	4.1:1
3-1	3:1	60.9	38.0	3.2:1
2-1	2:1	46.7	51.3	1.8:1
1-1	1:1	31.7	67.0	1:1.05
1-2	1:2	19.6	79.7	1:2.04
1-3	1:3	13.4	86.5	1:3.2

pressed in mold into tablets of 15 mm diameter and about 3 mm wide, or into square bars $5\text{ mm}^2 \times 50\text{ mm}$ under 100 kg/cm^2 pressure, and they were sintered at 900° , 950° , 1000° , 1050° , 1100° , 1150° , 1200° and 1300°C for 3 or more hours. Several of these samples were annealed at 400° or 800°C after the abovementioned heat treatment. The heated samples were then cooled rapidly in the air, quenched in water, or cooled slowly in the furnace according to our experimental purposes.

5. Experimental Results

1) X-ray experiments

The X-ray diffraction patterns of the samples are shown in Photos 1~36. Those in respect to Cu oxide shown in Photos 1~5.

Photo 1 shows the X-ray picture of refined CuO ; Photos 2, 3 and 4 show the X-ray pictures of CuO after heating them at 950° , 1000° and 1050°C respectively for 3 hours, and they clearly indicate various stages of transformation from CuO to Cu_2O .

Photo 5 shows the X-ray picture of refined Cu_2O .

Photos 6~13 show the X-ray pictures of the samples containing excess CuO over 1:1 ratio. Photo 6 shows the X-ray picture of the 9-1 sample heated at 1000°C for 3 hours and the existence of free CuO and a small amount of Cu-ferrite. Photo 7 and 8 show the X-ray pictures of the 7-1 and 4-1 samples respectively heated at 1000°C which indicate that both free CuO and Cu-ferrite are contained. In addition, Photo 8 shows a small content of free Fe_2O_3 . Photos 9 and 10 are the X-ray pictures of the 3-1 sample heated at 1100° and 1150°C respectively for 3 hours and indicate the fact that the samples melt and they contain cupric-ferrite, cuprous-ferrite, and free cuprous oxide. Photos 11~13 show the X-ray pictures of the 2-1 samples heated at 1000° , 1100° and 1150°C respectively for 3 hours, Photo 11 shows the fact that cupric-ferrite and free CuO are contained, but this CuO is considered still changing to Cu_2O and, for this reason, the X-ray picture of CuO in this picture may be blurred. Photos 12 and 13 show the content of Cu_2O in addition to CuOFe_2O_3 and $\text{Cu}_2\text{OFe}_2\text{O}_3$.

Photos 14~17 show all the 1:1 samples heated at 900° , 1000° , 1100° and 1200°C respectively. In the sample heated at 900°C , are shown CuOFe_2O_3 and a small amount of free CuO and Fe_2O_3 ; however, in the sample heated at 1000°C , free CuO and Fe_2O_3 are not recognized, but only CuOFe_2O_3 . The samples heated at 1100° and 1200°C consist of CuOFe_2O_3 and a small quantity of $\text{Cu}_2\text{OFe}_2\text{O}_3$. In the samples of equimolar mixture or those containing excess Fe_2O_3 over 1:1 ratio, the formation of $\text{Cu}_2\text{OFe}_2\text{O}_3$ at above 1100°C is very little; however, in the samples containing CuO over 1:1 ratio, the formation of $\text{Cu}_2\text{OFe}_2\text{O}_3$ is considerable large.

Photos 18~22 show the X-ray pictures of the 1-2 samples; namely, the sample containing Fe_2O_3 over 1:1 ratio. Photo 18 is of the mixed sample, Photos 19 and 20 are of the samples heated at 1000° and 1100°C for 3 hours. In Photo 20, no free Fe_2O_3 is observed whereas it is observed in Photo 19. They consist almost entirely of CuOFe_2O_3 and contain very little $\text{Cu}_2\text{OFe}_2\text{O}_3$ as has been mentioned above. In this case, the excess Fe_2O_3 gradually dissolves in Cu-ferrite and, by heating the sample up to 1100°C , a solid solution, whose ratio of $\text{CuO}:\text{Fe}_2\text{O}_3$ is up to 1:2, is formed. Photos 21 and 22 show the X-ray pictures of the 1-2 sample annealed at 400° and 800°C for 2 hours after heating them at 1200°C for 3 hours. In the sample heated at 1200°C , free Fe_2O_3 is not observed as above mentioned. This dissolved Fe_2O_3 cannot be educed by annealing the sample up to 400°C , as shown in Photo 21, but clearly shown in Photo 22 that this Fe_2O_3 is educed from the solid solution of Cu-ferrite and Fe_2O_3 by annealing the sample at 800°C . The lattice constant "a" of

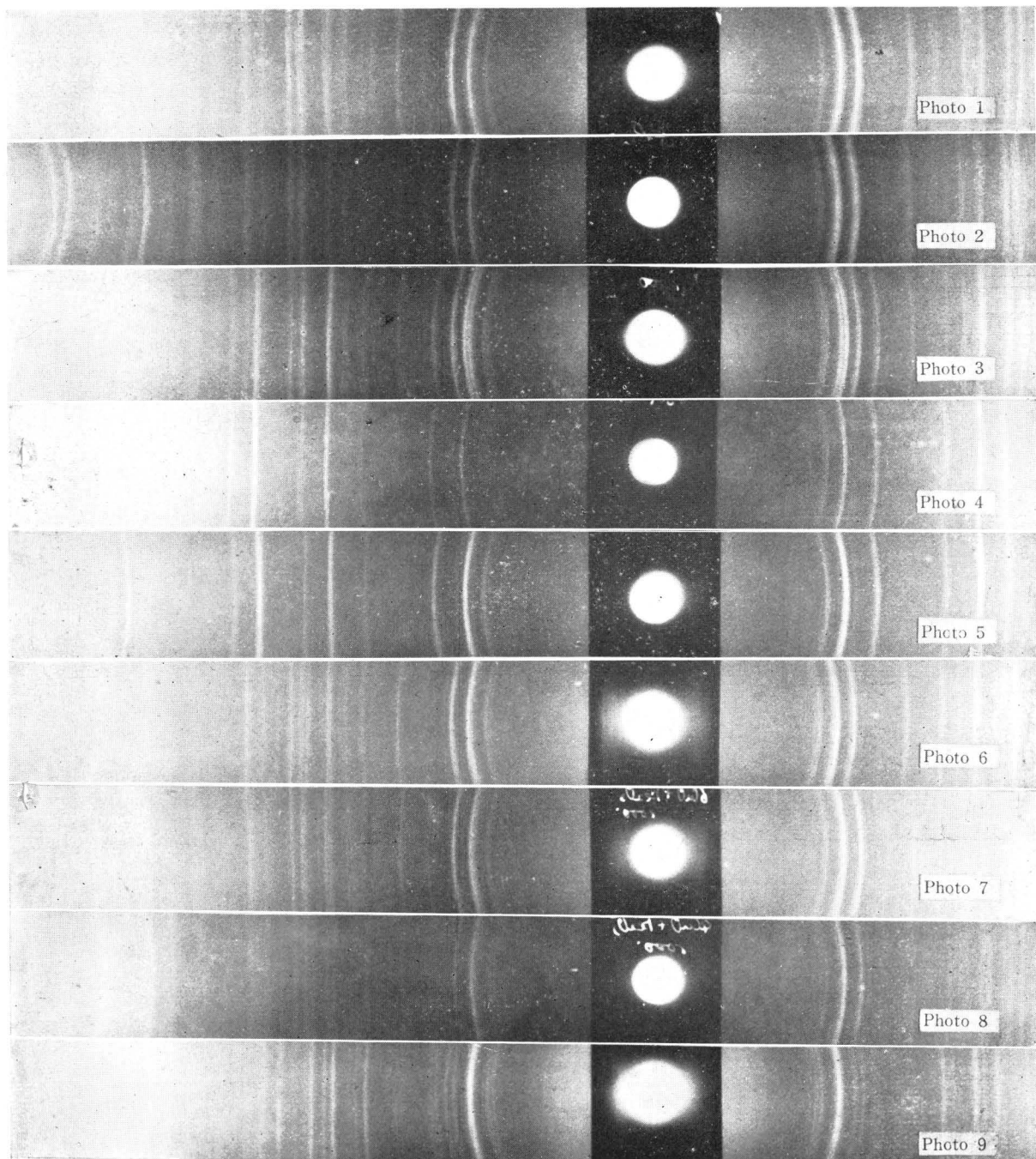


Photo 1. CuO.
 Photo 2. CuO heated at 950°C.
 Photo 3. CuO heated at 1000°C.
 Photo 4. CuO heated at 1050°C.
 Photo 5. Cu₂O.

Photo 6. 9-1 Sample heated at 1000°C.
 Photo 7. 7-1 Sample heated at 1000°C.
 Photo 8. 4-1 Sample heated at 1000°C.
 Photo 9. 3-1 Sample heated at 1000°C.

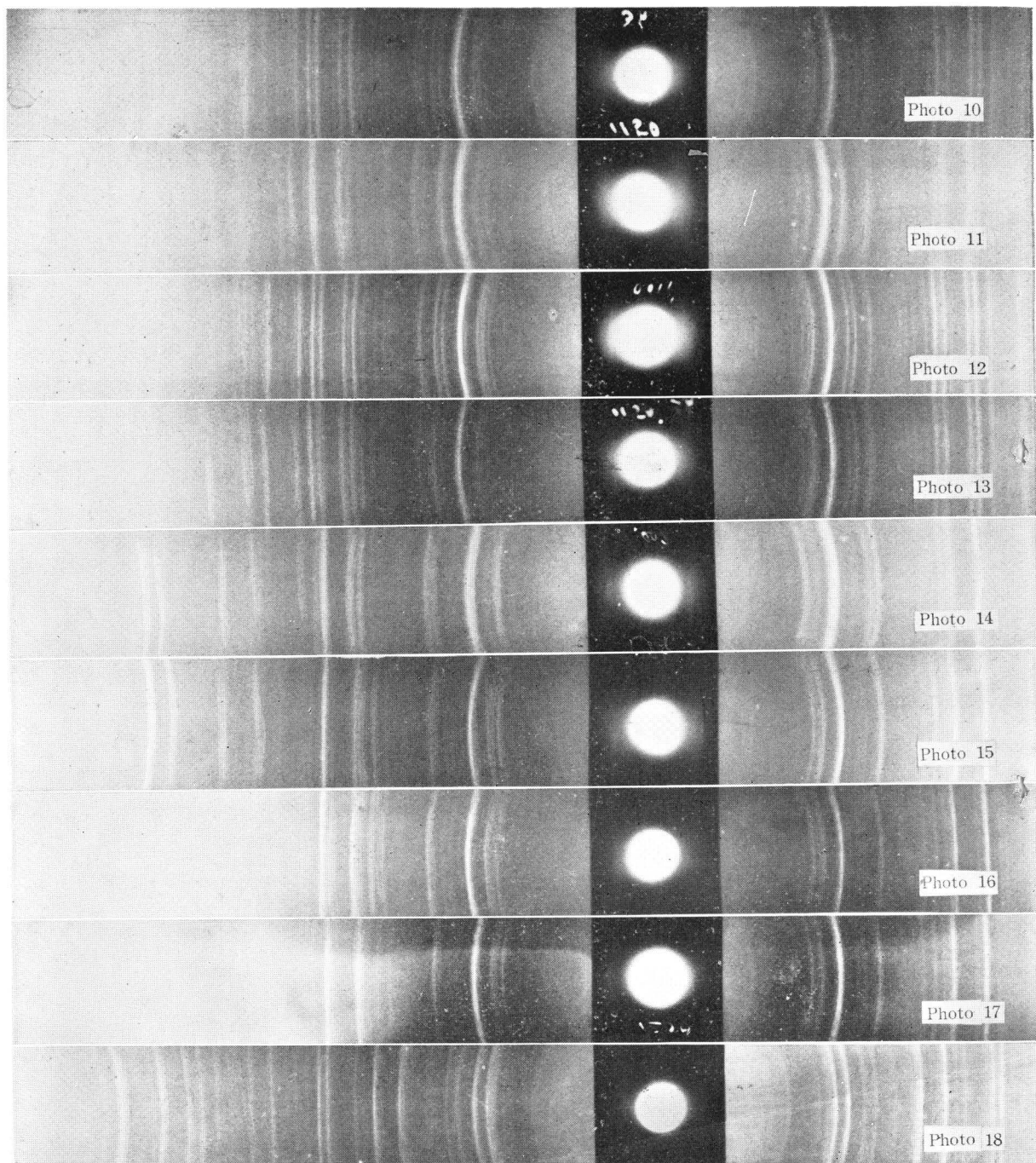


Photo 10

Photo 11

Photo 12

Photo 13

Photo 14

Photo 15

Photo 16

Photo 17

Photo 18

Photo 10. 3-1 Sample heated at 1150°C.
 Photo 11. 2-1 Sample heated at 1000°C for 13 hrs.
 Photo 12. 2-1 Sample heated at 1100°C.
 Photo 13. 2-1 Sample heated at 1150°C.
 Photo 14. 1-1 Sample heated at 900°C.

Photo 15. 1-1 Sample heated at 1000°C.
 Photo 16. 1-1 Sample heated at 1100°C.
 Photo 17. 1-1 Sample heated at 1200°C.
 Photo 18. Mixed sample of 1CuO and 2Fe₂O₃.

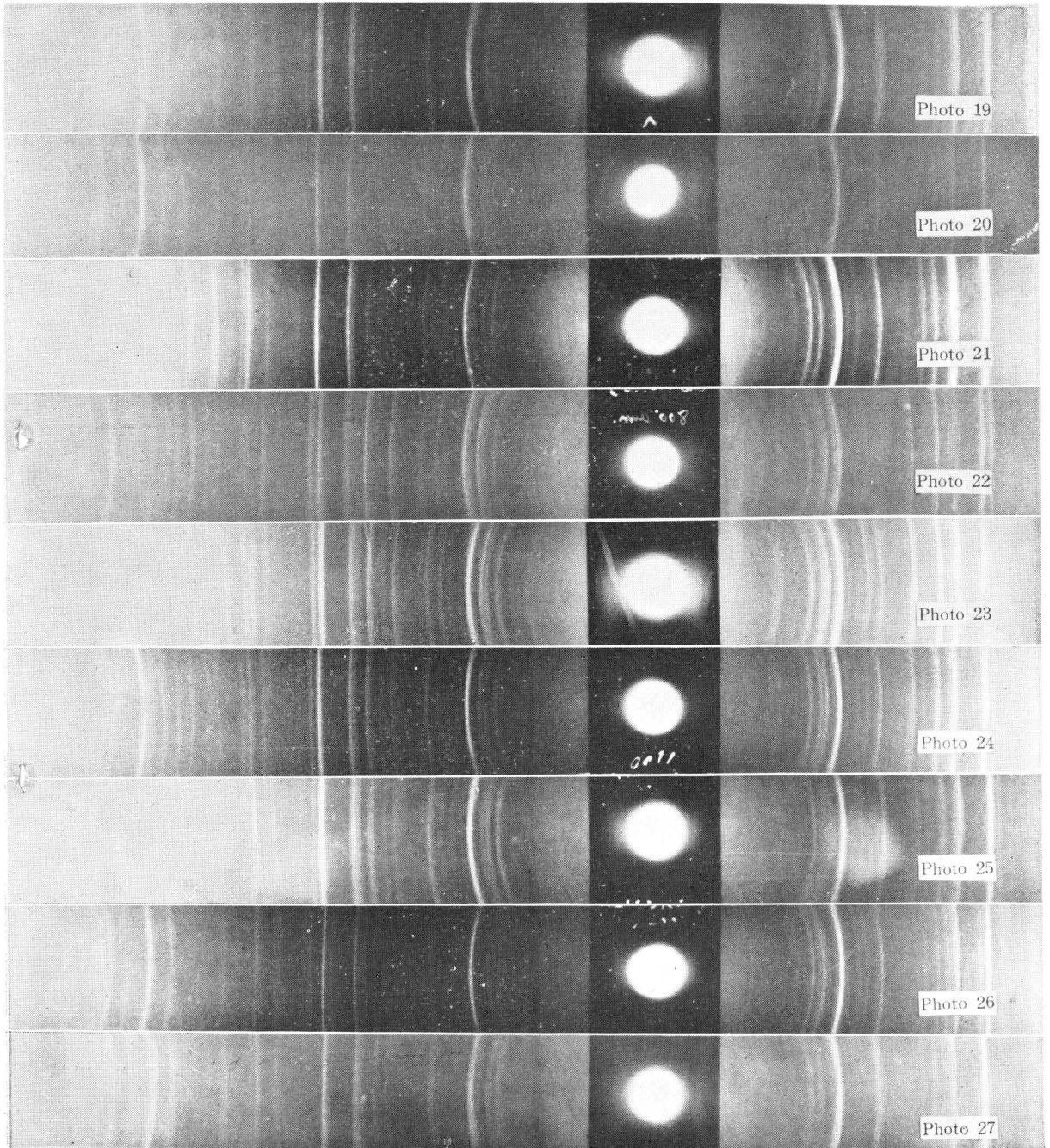


Photo 19. 1-2 Sample heated at 1000°C.

Photo 20. 1-2 Sample heated at 1100°C.

Photo 21. 1-2 Sample annealed at 400°C after being heated at 1200°C.

Photo 22. 1-2 Sample annealed at 800°C after being heated at 1200°C.

Photo 23. 1-3 Sample heated at 1000°C.

Photo 24. 1-3 Sample heated at 1100°C.

Photo 25. 1-3 Sample heated at 1150°C for 15 hrs.

Photo 26. 1-3 Sample heated at 1200°C.

Photo 27. 1-3 Sample heated at 1300°C.

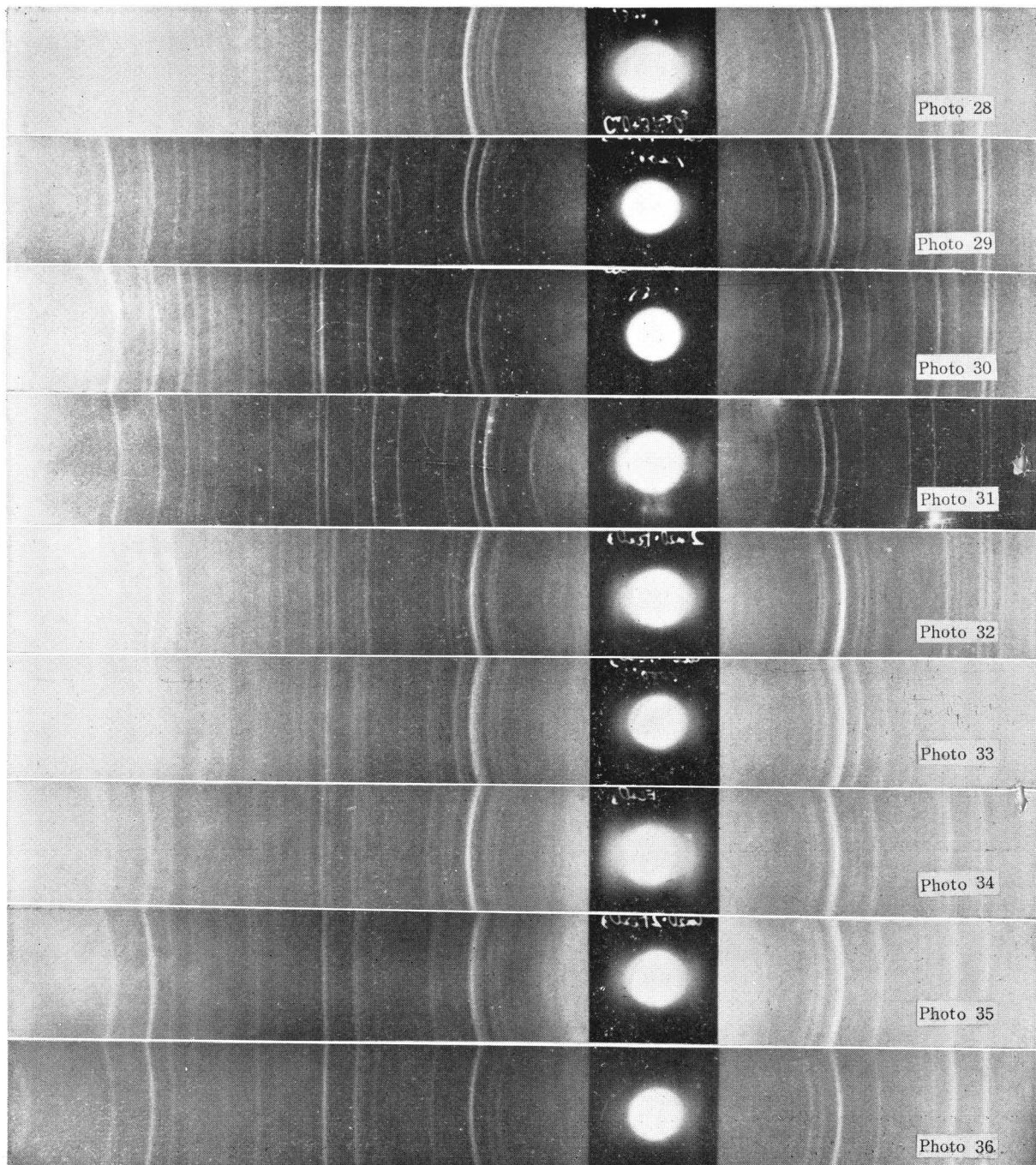


Photo 28. 1-3 Sample annealed at 800°C after being heated at 1300°C.

Photo 29. 1-9 Sample heated at 1200°C.

Photo 30. 1-9 Sample heated at 1300°C.

Photo 31. Fe_2O_3 .

Photo 32. $2\text{Cu}_2\text{O} + \text{Fe}_2\text{O}_3$ Sample heated at 1100°C and quenched.

Photo 33. $\text{Cu}_2\text{O} + \text{Fe}_2\text{O}_3$ Sample heated at 1000°C and quenched.

Photo 34. $\text{Cu}_2\text{O} + \text{Fe}_2\text{O}_3$ Sample heated at 1100°C and quenched.

Photo 35. $\text{Cu}_2\text{O} + 2\text{Fe}_2\text{O}_3$ Sample heated at 1100°C and quenched.

Photo 36. Fe_3O_4 .

the 1-2 sample annealed at 400°C becomes more or less smaller in comparison with the samples sintered at 1200°C and is about 8.34 Å.

Photos 23~28 show the X-ray pictures of the 1-3 samples. Photos 23, 24, 26, and 27 are the X-ray pictures of the samples heated at 1000°, 1100°, 1200° and 1300°C for 3 hours, and Photo 25 shows that of the 1-3 sample heated at 1150°C for 15 hours. As in Photos 22~26, namely in the sample heated under 1200°C, the lines of CuOFe_2O_3 and of free Fe_2O_3 , which become weaker with the increase of temperature, can be observed. In Photo 27, as in Photo 20, the free Fe_2O_3 is not observed; in other words, by heating the sample up to 1300°C, a solid solution having the $\text{CuO}:\text{Fe}_2\text{O}_3$ ratio of 1:3 is formed. Unlike the case shown by Photo 20, however, in this case a part of free Fe_2O_3 is dissociated to Fe_3O_4 and the solid solution is considered to consist of CuOFe_2O_3 , Fe_2O_3 and some Fe_3O_4 . Photo 28 shows the X-ray picture of the 1-3 sample annealed at 800°C after being heated at 1300°C and shows the existence of CuOFe_2O_3 and free Fe_2O_3 deduced from solid solution as in the case shown by Photo 22.

Photos 29 and 30 show X-ray pictures of the 1-9 samples heated at 1200°C and 1300°C for 3 hours. Both Fe_2O_3 and a small amount of CuOFe_2O_3 are observed, but the dissolution of Cu-ferrite into solid Fe_2O_3 cannot be seen up to 1300°C.

Photo 31 shows the X-ray picture of pure Fe_2O_3 .

Photos. 32~35 show the X-ray picture of the mixed sample of Cu_2O and Fe_2O_3 . Photo 32 is of the mixed sample of $2\text{Cu}_2\text{O}+1\text{Fe}_2\text{O}_3$ heated at 1100°C for 3 hours and quenched in water. Photo 33 is of the mixed sample of $1\text{Cu}_2\text{O}+1\text{Fe}_2\text{O}_3$ heated at 1000°C, and Photo 34 is the same specimen heated at 1100°C, both quenched in water. Photo 35 is the X-ray picture of the mixed sample of $1\text{Cu}_2\text{O}+2\text{Fe}_2\text{O}_3$ heated at 1100°C for 3 hours and quenched in water. From these photographs, it can be explained that, in spite of the use of Cu_2O as a mixing material and heated over the melting point of Cu_2O and then quenched, the samples contain both CuOFe_2O_3 and $\text{Cu}_2\text{OFe}_2\text{O}_3$ and fail to form pure $\text{Cu}_2\text{OFe}_2\text{O}_3$ alone. In $2\text{Cu}_2\text{O}+1\text{Fe}_2\text{O}_3$ and $1\text{Cu}_2\text{O}+1\text{Fe}_2\text{O}_3$ specimens, both CuOFe_2O_3 and $\text{Cu}_2\text{OFe}_2\text{O}_3$ are plainly shown, but, in the $1\text{Cu}_2\text{O}+2\text{Fe}_2\text{O}_3$ specimen, CuOFe_2O_3 is formed for the most part, and $\text{Cu}_2\text{OFe}_2\text{O}_3$ is very scanty and free Fe_2O_3 is not observed. Photo 36 shows the X-ray picture of the synthetic Magnetite.

Table 2 shows the summarized results obtained from the above X-ray investigations.

The calculated "d" values and the comparison of these values between some specimens are shown in Table 3. The average lattice constant "a" of CuOFe_2O_3 con-

Table 2. Results of the X-ray Analyses.

No. of photo	Mixed ratio CuO : Fe ₂ O ₃	Heating Temperature	Heating hours	Observed substances
6	9 : 1	1000°	3	CuO and CuOFe ₂ O ₃
7	7 : 1	1000°	3	CuO and CuOFe ₂ O ₃
8	4 : 1	1000°	3	CuO, CuOFe ₂ O ₃ and Fe ₂ O ₃
9	3 : 1	1000°	3	CuO and CuOFe ₂ O ₃
10	"	1150°	3	CuOFe ₂ O ₃ , Cu ₂ OFe ₂ O ₃ , CuO and Cu ₂ O
11	2 : 1	1000°	13	CuOFe ₂ O ₃ and CuO
12	"	1100°	3	CuOFe ₂ O ₃ , Cu ₂ OFe ₂ O ₃ and CuO
13	"	1150°	3	CuOFe ₂ O ₃ , Cu ₂ OFe ₂ O ₃ and Cu ₂ O
—	1 : 1	950°	3	CuOFe ₂ O ₃ and Fe ₂ O ₃
15	"	1000°	3	CuOFe ₂ O ₃
16	"	1100°	3	"
19	1 : 2	1000°	3	CuOFe ₂ O ₃ and Fe ₂ O ₃
20	"	1100°	3	CuOFe ₂ O ₃
21	"	1200° and annealed at 400°		"
22	"	1200° and annealed at 800°		CuOFe ₂ O ₃ and Fe ₂ O ₃
25	1 : 3	1150°	15	CuOFe ₂ O ₃ and Fe ₂ O ₃
26	"	1200°	3	"
27	"	1300°	3	CuOFe ₂ O ₃
28	"	1300° and annealed at 800°		CuOFe ₂ O ₃ and Fe ₂ O ₃
	1 : 9	1300°	3	Fe ₂ O ₃ and CuOFe ₂ O ₃
	Cu ₂ O : Fe ₂ O ₃			
32	2 : 1	1100°	3	CuOFe ₂ O ₃ , Cu ₂ OFe ₂ O ₃ and Cu ₂ O
33	1 : 1	1000°	3	CuOFe ₂ O ₃ and CuO
34	1 : 1	1100°	3	CuOFe ₂ O ₃ and Cu ₂ OFe ₂ O ₃
35	1 : 2	1100°	3	CuOFe ₂ O ₃

ducted from these "d" values is about 8.37Å, and the change of it owing to the dissolution of Fe₂O₃ is not so remarkable.

2) Magnetic Experiments.

Cu-ferrite is known as a ferro-magnetic material belonging to the mixed type of normal- and inversed-spinels and its magnetic properties are varied by heat treatment.

In our experiments, the samples, which were all air-cooled after heating at a constant temperature were used for magnetic analyses. Since the samples containing excess CuO over 1:1 ratio melt when they are heated over 1100° and 1150°C for a long time, the magnetic properties were measured only on the samples which were heated at 1000°C: and since the samples containing excess Fe₂O₃ over 1:1 ratio shrink

Table 3. "d" values of several samples, Fe₂O₃, CuO, Cu₂O, and CuOFe₂O₃, and Cu₂OFe₂O₃.

Photo No. Sample Line No.	11		16		19		20		21		27		28		34		35		31		1		5		16		32, 34					
	2-1:1100		1-1:1100		1-2:1000		1-2:1100		1-2:400*		1-3:1300		1-3:800*		Cu ₂ O+Fe ₂ O ₃		Cu ₂ O+2Fe ₂ O ₃		Fe ₂ O ₃		CuO		Cu ₂ O		CuOFe ₂ O ₃		Cu ₂ OFe ₂ O ₃					
	d.	I.	d.	I.	d.	I.	d.	I.	d.	I.	d.	I.	d.	I.	d.	I.	d.	I.	d.	I.	d.	I.	d.	I.	d.	I.	d.	I.				
1																																
2	2.96	vw	2.96	w	2.96	vw	2.96	w	2.94	m	2.96	m	2.96	m	2.97	w	2.96	w	2.99							(2.97)						
3	2.86	w												2.86	w											2.96	w					
4																																
5	2.78	w	2.79	w	2.79	vw	2.79	w	2.77	vw	2.80	m	2.80	m	2.80	vw	2.80	w	2.80	vw	2.80	vw										
6					2.698	vw			2.676	m			2.698	m					2.71	vs												
7	2.62	w							2.60	w			2.597	vw	2.625	w										(2.53)			2.625	w		
8	2.53	vs	2.54	vs	2.53	vs	2.54	vs	2.52	vs	2.54	vs	2.54	vs	2.54	vs	2.54	vs								2.53	vs		(2.50)			
9																																
10																																
11			2.41	vw					2.41	vw	2.42	vw	2.42	vs																		
12	2.32	vw	2.31	vw			2.32	vw	2.30	vw	2.32	vw	2.31	vw	2.33	vw																
13	2.23	m	2.23	vw			2.24	vw							2.25	vw																
14													2.216	w																		
15																			2.216	m												
16	2.093	w	2.094	m	2.10	w	2.101	w	2.086	s	2.101	m	2.104	m	2.10	vw																
17													1.86	m																		
18	1.77	vw	1.77	vw			1.78	vw	1.76	w	1.78	w	1.77	w	1.77	vw	1.77	vw	1.85	s	1.86	w										
19									1.70	m			1.69	m					1.69	s												
20	1.65	s	1.66	w			1.66	w					1.65	vw	1.663	m																
21			1.63	w					1.62	w			1.63	w					1.628													
22	1.60	s	1.60	s	1.60	w	1.60	m	1.588	vs	1.60	m	1.60	m	1.60	m	1.60	s	1.60	w												
23	1.58	vw											1.58	m							1.58	vw										
24	1.51	m											1.51	vw	1.518						1.50	m										
25																																
26	1.485	s	1.48	s	1.486	vs	1.486	vs	1.478	vs	1.491	vs	1.487	s	1.48	s	1.483	vs	1.49	s												
27													1.45	m																		
28	1.43	w	1.43	vw			1.43	vw							1.43	w																
29	1.41	vw	1.41	vw			1.41	vw	1.41	vw	1.41	vw																				
30	1.37	m																														
31	1.34	vw	1.34	vw			1.34	vw							1.341	vw																
32			1.32	vw							1.32	vw	1.306	vw																		
33	1.282	vw	1.28	m	1.28	w	1.28	m	1.275	m	1.284	m	1.284	w																		
34									1.26	w			1.25	vw																		
35	1.22	vw	1.21	vw	1.21	vw	1.21	vw	1.20	w	1.21	w	1.21	w	1.22	w																
36													1.18	w																		
37					1.16	vw			1.155	vw			1.16	w					1.188	w												
38					1.139	vw							1.139	w					1.162	w												
39	1.125	m	1.125	m	1.125	vw	1.123	m	1.120	m	1.127	m	1.121	w	1.121	w	1.121	w	1.138	m												
40													1.103	vw																		
41	1.097	s	1.097	vs	1.097	vs	1.097	vs	1.091	vs	1.099	vs	1.097	vs	1.097	s	1.09	vs														
42									1.06	vw																						
43	1.049	vw	1.049	m	1.049	vw	1.049	vw	1.047	s	1.050	s	1.049	vw	1.049	w	1.049	s														
44	1.038	s													1.038	w																

Notes: 1) vs: very strong, s: strong, m: medium, w: weak, vw: very weak
 2) * annealing temperature

3) "d" values in () is cited from A.I.M.E. vol. 182, 163 (1949)¹⁷⁾
 4) Mixed samples of Cu₂O and Fe₂O₃ (Photo 34 and 35) are heated at 1100°C.

remarkably when they are heated over 1300°C, the magnetic properties were measured on the samples which were heated up to 1200°C. The results obtained are shown in Fig. 1 and 2. Fig. 1 shows the intensity of magnetization of various Cu-ferrites heated at the same temperature, and Fig. 2 shows the effect of the heating temperature on the intensity of magnetization for the 1-1, 1-2 and 1-3 samples.

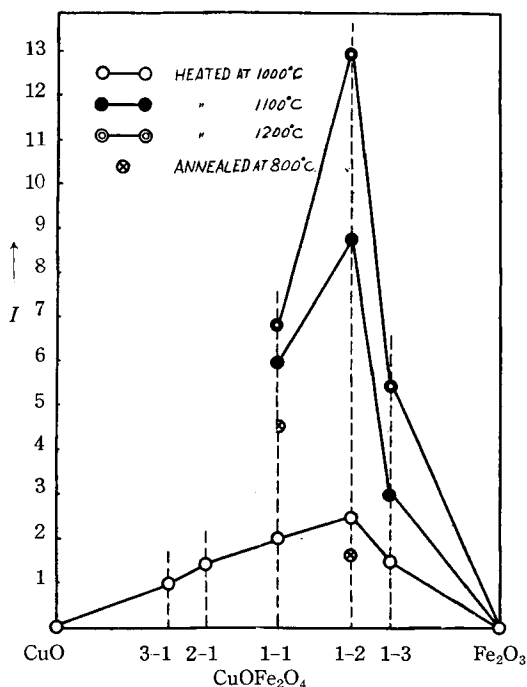


Fig. 1. Intensity of Magnetization of various Cu-ferrite.

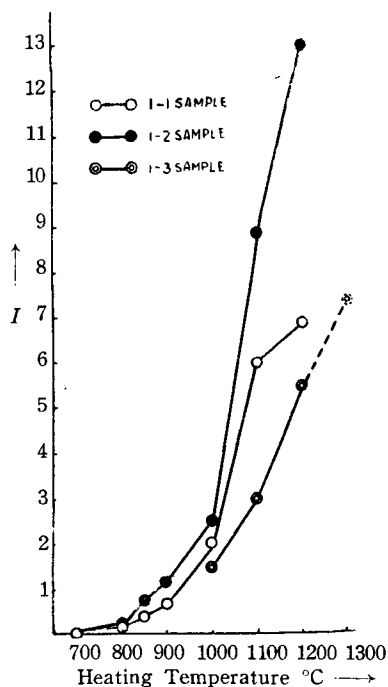


Fig. 2. Effect of the heating temperature on the intensity of magnetization of Cu-ferrite.

It is obvious from Fig. 1 that CuO and Fe_2O_3 are themselves non-magnetic substances, but, when they react upon each other and form a ferrite, the latter becomes a ferromagnetic substance, and the intensity of magnetization is strongest at the constitution of $\text{CuO}_2\text{Fe}_2\text{O}_3$ for each temperature up to 1200°C.

It is considered that the lesser intensity of magnetization of the samples containing excess CuO is due to the existence of $\text{Cu}_2\text{OFe}_2\text{O}_3$ or free CuO, which tends to weaken the magnetic properties.

The H-I curves of various ferrites are shown in Fig. 3. The intensity of magnetization of the 1-2 sample is stronger than that of magnetite,

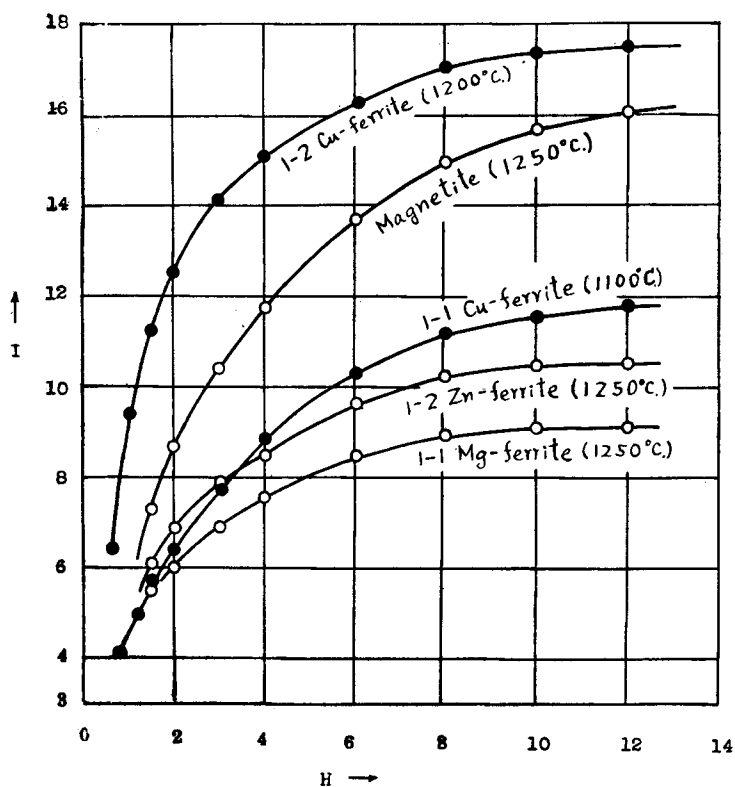


Fig. 3. H-I curves for various ferrite.

Table 4. Results of the chemical analyses.

Sample No.	Sign of sample	Heating temp.	Heating hours	Free CuO %	Residue		Mol. ratio CuO : Fe ₂ O ₃ of residue	Formation ratio of Cu-ferrite (%)
					CuO %	Fe ₂ O ₃ %		
1	3-1	1000	3	32.2	25.6	38.5	1 : 0.75	100
2	"	1100	"	29.8	25.5	38.7	"	"
3	2-1	1000	3	19.4	26.5	49.7	1 : 1	"
4	"	1150	"	18.9	26.5	53.5	"	"
5	"	"	10	18.9	26.3	53.4	"	"
6	1-1	950	3	8.5	22.0	65.7	1 : 1.5	76
7	"	1000	"	2.1	29.3	66.3	1 : 1	95~100
8	"	1050	"	2.0	28.5	65.7	1 : 1.1	"
9	1-2	900	3	3.6	16.3	79.0	1 : 2.4	81
10	"	1000	"	0.5	19.2	79.5	1 : 2	100
11	"	1100	"	0.2	19.4	80.7	1 : 2	"
12	1-3	1100	3	0.6	13.2	86.7	1 : 3.2	"

3) Chemical Analyses.

Results are summarised in Table 4. In this table, free CuO (in some cases a part of them changes to Cu_2O) and the molar ratio of $\text{CuO}:\text{Fe}_2\text{O}_3$ of the residues are shown. The residual Fe_2O_3 contain free Fe_2O_3 . It is difficult to determine this free Fe_2O_3 by direct chemical analyses. In the 3-1 samples, as in sample No. 1 and 2 in this Table, the constitution of leaching residue is 1CuO and $0.75\text{Fe}_2\text{O}_3$ (namely $\text{CuO}:\text{Fe}_2\text{O}_3$ is 4:3) and it appears that the ferrite dissolves excess CuO, but since the ferrite in this case consists of both cupric- and cuprous-ferrites, the value obtained by calculation on the base of CuO alone is considered too excessive.

4) Thermal Analyses.

As has been already mentioned, the samples containing excess CuO melt over 1100°C . It is considered that the ceramic material like ferrite does not have a constant melting point and gradually softens and at last melts. The melting point of Cu-ferrite containing excess CuO could not be determined by the thermal analyses but we could determine the range of temperature in which the samples softened. The results are shown in Table 5. The samples containing excess Fe_2O_3 melt over

Table 5. Results of the thermal analyses.

Sample	$\text{CuO}(\text{CuO} + \text{Cu}_2\text{O})$	$3\text{CuO} + \text{Fe}_2\text{O}_3$	$2\text{CuO} + \text{Fe}_2\text{O}_3$	$\text{CuO} + \text{Fe}_2\text{O}_3$
Temperature range of softening	(M.p.) 1083°C .	$1120^\circ \pm 20^\circ\text{C}$.	$1160^\circ \pm 20^\circ\text{C}$.	$1280^\circ \pm 30^\circ\text{C}$.

1300°C and the thermal analyses of these samples are very difficult.

5) Microscopic Structures.

Photos 37 and 38 show the microscopic structures of the polished surface of CuO after the thermal analyses. This sample is assumed to be an eutectic consisting 30% of CuO and 70% of Cu_2O and having a melting point of about 1075°C ¹⁵⁾. In Photos 37 and 38, the crystals, thin and grayish, are considered to be CuO and others, to be Cu_2O (CuO belongs to triclinic system and Cu_2O , to cubic system).

Photos 39, 40, 41 and 42 show all the 3-1 samples. Photos 39, 40 and 41 show the different parts of the same sample. The black portions in these photographs in reality are reddish violet and black and a part of them indicates the melting. These portions are considered to be caused by excess free CuO or Cu_2O . The white crystals that had occurred look like boards are presumably CuOFe_2O_3 , and the thin white crystals that look like the ears of rice may be $\text{Cu}_2\text{OFe}_2\text{O}_3$.

Photo 43 shows the structure of the 2-1 sample, in which the white crystals, looking like the boards of CuOFe_2O_3 , the thin white crystals of $\text{Cu}_2\text{OFe}_2\text{O}_3$ and reddish violet portions of the eutectic of CuO and Cu_2O are discernible.

Photo 44 shows the structure of the 1-1 sample, which consists mainly of the white crystals, that look like boards, of CuOFe_2O_3 . Between these crystals, some of

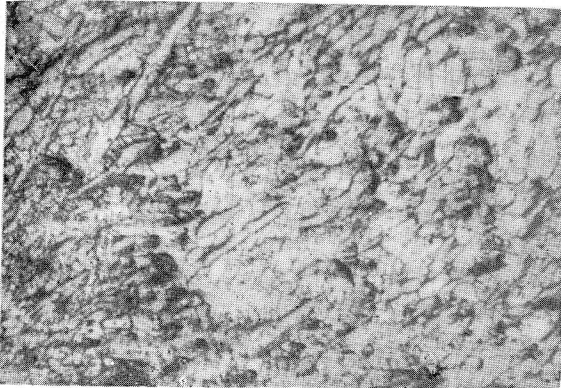


Photo 37. CuO after melted. $\times 180$
(polished surface)

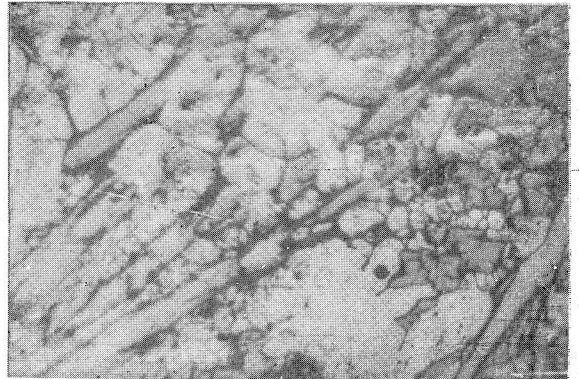


Photo 38. CuO after melted. $\times 400$
(polished surface)



Photo 39. 3-1 Sample after melted. $\times 400$
(polished surface)



Photo 40. 3-1 Sample after melted. $\times 400$
(polished surface)

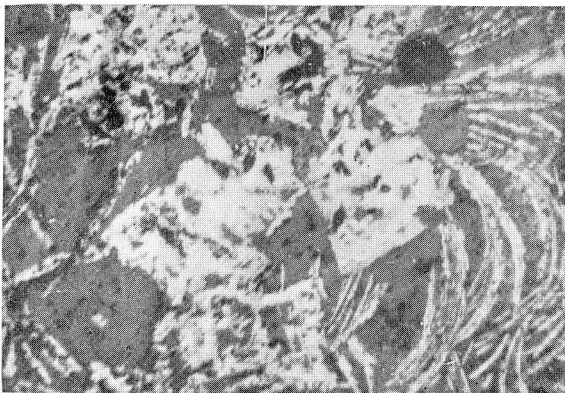


Photo 41. 3-1 Sample after melted. $\times 180$
(polished surface)



Photo 42. 3-1 Sample after melted. $\times 180$
(polished surface)



Photo 43. 2-1 Sample after melted. $\times 180$
(polished surface)

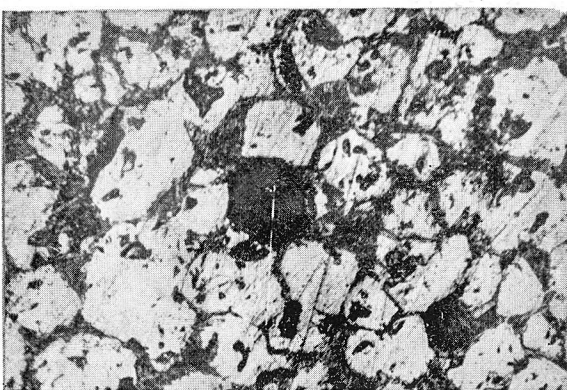


Photo 44. 1-1 Sample after melted. $\times 100$
(polished surface)

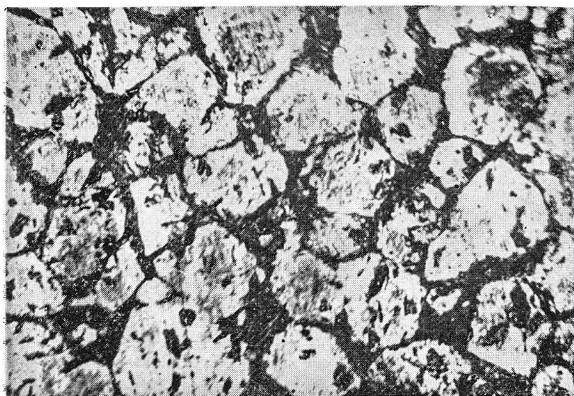


Photo 45. 1-1 Sample after annealed at 400°C. $\times 100$
(polished surface)



Photo 46. 1-1 Sample. $\times 400$
(unpolished surface as sintered)



Photo 47. 1-3 Sample. $\times 700$
(unpolished surface as sintered)

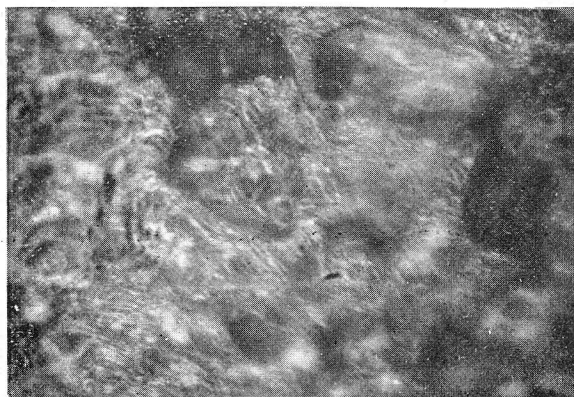


Photo 48. 1-3 Sample. $\times 400$
(unpolished surface as sintered)

the crystals, small and thin, of $\text{Cu}_2\text{OFe}_2\text{O}_3$ can be seen. Photo 45 shows the structure of above-mentioned sample annealed at $350^\circ\sim 400^\circ\text{C}$ for 2 hours and cooled in the furnace. This sample is not transformed from cubic to tetragonal by this heat treatment. But its lattice constant "a" becomes rather smaller. The differences between Photo 44 and 45 are not remarkable, but in the latter CuOFe_2O_3 crystals are more or less angular and the grain boundary is distinct, and the crystals which appear to be $\text{Cu}_2\text{OFe}_2\text{O}_3$ are considerably decreased. The size of CuOFe_2O_3 crystals in these photographs is about $50\sim 200\mu$ dia. The structure of the sample annealed at 800°C has not been changed in spite of its crystal transformation.

Photo 46 shows the unpolished surface of the 1-1 sample as they are sintered at 1200°C , and Photo 47 and 48 show the same kind of surface of the 1-2 and 1-3 sample. On account of the high melting point of these specimens having excess Fe_2O_3 , no crystal is observed on the polished surface of sintered samples. On the contrary, small squar, pentagonal or hexagonal skeletal figures are distinctly shown on its unpolished surface as sintered. These growth steps on the sintered surfaces recognized on the specimens of equimolar mixture or of containing excess Fe_2O_3 . The sketches of these skeleton

crystals are shown in Fig. 4 and 5. As is shown in these sketches, it is clear that the symmetrical crystals gradually grow following each step of development. The size of these crystals is as follows: the diameter of the upper surface is $3.5\sim 15\mu$, the diameter of the base is about $20\sim 30\mu$, and the height of crystal is about 10μ . In Fig. 6, we have shown a assumed model of this

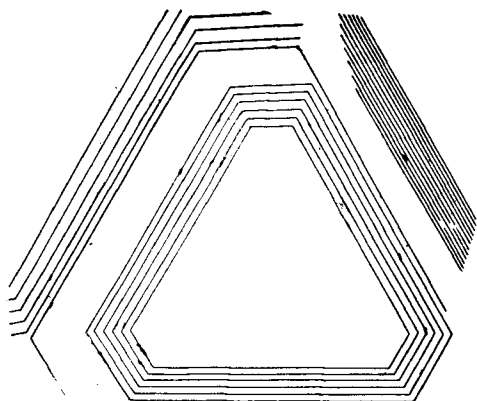


Fig. 4. Sketch of the growth steps on the sintered 1-3 sample.

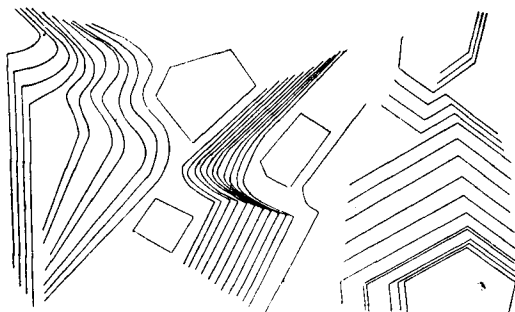


Fig. 5. Sketch of the growth steps on the sintered 1-2 sample.

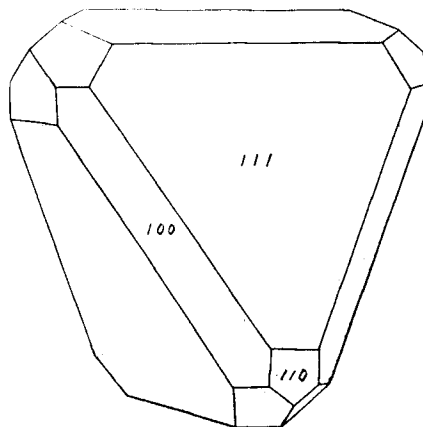


Fig. 6. Rhombic dodecahedron.

crystal, an imaginary drawing based upon the above description.

- 6) On the phase diagram of CuO-Fe₂O₃ system.

By summarizing the above results, the phase diagram of CuO-Fe₂O₃ system is obtained as shown in Fig. 7. In this figure, the dissociation of CuO into Cu₂O over 950°C, and of Fe₂O₃ into Fe₃O₄ over 1100°C, the formation of eutectic of CuO and Cu₂O, and the formation of Cu₂OFe₂O₃, etc. are not explained at the same time.

6. Considerations

From the results of the X-ray analyses, it is explained

that the samples containing excess CuO over 1:1 ratio is apt to form Cu₂OFe₂O₃ in addition to CuOFe₂O₃ by heating them over 1100°C. Even when the mixture of Cu₂O and Fe₂O₃ are used from the beginning, both ferrites are also formed. On the contrary, the samples containing excess Fe₂O₃ are apt to form mainly CuOFe₂O₃ and the formation of Cu₂OFe₂O₃ is little.

It is considered that CuOFe₂O₃ and Cu₂OFe₂O₃ do not make solid solution because the former belongs to the cubic crystal system at high temperature, but latter belongs to the hexagonal system. The structural difference between CuOFe₂O₃ and Cu₂OFe₂O₃ be seen in Photos 34 and 35.

In copper- or magnesium-ferrite, the arrangements of ions are mixed type of normal- and inverted- type as previous mentioned, and it is said that these arrangements are affected by heat treatment. In our case, the intensity of magnetization was strongest at the constitution of 1-2 ferrite for each temperature under 1200°C. In the 1-2 sample, the excess Fe₂O₃ dissolves into ferrite at 1100°C but not at 1000°C, and the formation of magnetite at 1100°C is almost nil. From these points, we considered that the remarkable increase of magnetism of the 1-2 sample at 1100°C may

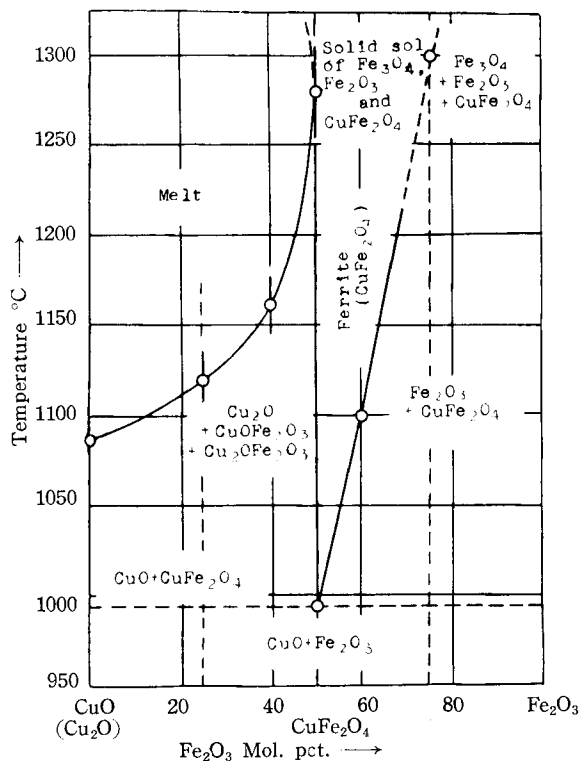


Fig. 7. Phase diagram for the system CuO-Fe₂O₃. (in mol. pct.)

be related to the formation of the solid solution of copper-ferrite and Fe_2O_3 . It is true that the change of magnetism of ferrite is affected by the arrangements of Cu^{2+} and Fe^{3+} in the 8-f and 16-c positions caused by the heat treatment; however, in our case, this arrangements have presumably been affected both by the heat treatment and the existence of dissolved excess Fe^{3+} . In other words, the existence of dissolved excess Fe^{3+} may affect on the arrangements of Cu^{2+} and Fe^{3+} in their normal positions.

In the case of the 1-3 sample, excess Fe_2O_3 dissolves in ferrite over 1300°C , but a part of Fe_2O_3 converts into Fe_3O_4 by its dissociation. On the other hand, the excess CuO or Cu_2O hardly dissolves in ferrite by heating them at 1150°C which is over the melting point of the sample, but in higher temperatures, it may dissolve to a small extent as in the case of zinc ferrite¹³⁾. Since the ion radius of Cu^{2+} is bigger than that of Zn^{2+} , it is considered that the solubility of CuO in Cu-ferrite may be smaller than that of ZnO in Zn-ferrite.

The growth steps on the sintered surfaces could not be observed on the samples containing excess CuO . Since these loop steps develop at a considerably high temperature, the samples containing excess CuO may melt under that temperature or else the growth steps under their melting point may be so small that we are unable to recognize them under the optical microscope of less than one thousand magnification.

These steps grown on the sintered surface are known also in the cases of other oxides such as BaTiO_3 or TiO_2 ¹⁶⁾ and many explanations are given on them. We consider that these loop steps are the expression of the skeleton crystal of Cu-ferrite belongs to cubic system at high temperature. We may consider, for instance, (111), (110), or (100) faces on the "Rhombic dodecahedron" (Fig. 6) belonging to cubic system, develop step by step, and the skelton crystal having the square, pentagonal, or hexagonal upper faces also grow. However, there is no proof that Cu-ferrite has the crystal form of rhombic dodecahedron. But it is known that Franklinite [$(\text{Zn}, \text{Fe})\text{O}\cdot\text{Fe}_2\text{O}_3$] has some times the crystal from of rhombic dodecahedron¹⁸⁾.

7. Conclusion

The constitution of Cu-ferrite and its nature which is affected by its constitution were studied and the following results were obtained.

1) Cupric-ferrite dissolves excess Fe_2O_3 over 1:1 ratio at above 1100°C . At 1100°C , the single phase spinel is obtained up to 1:2 ratio and up to 1:3 ratio at 1300°C . Namely, this system forms a solid solution in the range of the content of Fe_2O_3 is from 66.74% to 85.75% in weight at 1300°C .

2) Cupric-ferrite dissolving excess Fe_2O_3 becomes to possess two phases by annealing at 800°C owing to its decomposition into CuOFe_2O_3 and Fe_2O_3 .

- 3) Copper-ferrite does not dissolve excess CuO or Cu₂O under 1150°C.
- 4) Cuprous-ferrite, Cu₂OFe₂O₃, is apt to form in the sample contain excess CuO over 1100°C; but the formation of pure Cu₂OFe₂O₃ is very difficult.
- 5) Cupric-ferrite (CuOFe₂O₃) and cuprous-ferrite (Cu₂OFe₂O₃) do not form solid solution because of the differences in shape and size of the crystals.
- 6) Copper-ferrite is a ferro-magnetic compound and the intensity of magnetization is strongest on the 1-2 sample. After being annealed at 800°C, the magnetic property weakens approximately to the original 15%. These facts may be attributable to dissolved excess Fe₂O₃ and also the transformation of the crystal form.
- 7) Copper-ferrite has not constant melting point but it gradually softens with the increase of temperature.
- 8) By summarizing the above results, we obtained the phase diagram for CuO and Fe₂O₃ systems.
- 9) The growth steps are recognized on the sintered surfaces of copper-ferrite of equimolar or of containing excess Fe₂O₃ heated at above 1200°C.

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