

On the Constitution of Zinc-ferrite

By

Isao KUSHIMA and Tsuyoshi AMANUMA

Department of Metallurgy

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1. Introduction

Zinc-ferrite is known as the compound of the equimolar of ZnO and Fe₂O₃ as ZnO·Fe₂O₃ or ZnFe₂O₄, and distinguished from other various ferrites, such as CuO·Fe₂O₃, NiO·Fe₂O₃, Fe₃O₄, and MgO·Fe₂O₃, as its structure is a normal spinel type as CdO·Fe₂O₃, and is non-magnetic.

For the physical and electrical properties of various ferrites, many important results are obtained, but the chemical constitution of ferrites is not generally known up to the present except in a few instances. In a previous paper¹⁾, the authors reported on formation temperature and the formation ratio of zinc-ferrite. At that time, it seemed that zinc-ferrite (ZnFe₂O₄) was capable of forming a solid solution with Fe₂O₃ or ZnO and forming ferrite of various molar ratio (ZnO:Fe₂O₃) depending upon the condition of formation. Pertaining to this point, the authors have conducted a research on the constitution of the compounds between ZnO-Fe₂O₃ system and also inquired into the formation of magnetite in this system.

2. Preparation of Samples

ZnO was prepared from purified ZnSO₄ and its purity was over 99.0%. Fe₂O₃ was prepared from ferrous oxalate. It is said that ferrous oxalate is decomposed and oxidized between 180°C. to 280°C. in the air²⁾. In our case, ferrous oxalate was heated at 600°-650°C. in the air for more than 5 hours.

Fe₂O₃ and ZnO were mixed so that the molar ratio of ZnO:Fe₂O₃ became exactly 1:4 (Sample No. 2), 1:3 (No. 32), 1:2 (No. 33), 2:3 (No. 3 or 34), 4:5 (No. 35), 1:1 (No. 4 or 36), 5:4 (No. 37), 3:2 (No. 5 or 38), 7:3 (No. 8), 3:1 (No. 10), 4:1 (No. 6), and 9:1 (No. 9). These mixed samples were pressed in the mould into tablets of 15 mm. diameter and about 3 mm. wide or into square bars of 5 mm.²×50 mm. under 50-75 kg./cm.² pressure and they were sintered at 800°, 1000°,

1150°, 1250°, 1350°, and 1440°C. for many hours. Table 1 shows the analyses of these samples.

Table 1. Analyses of the various Samples.

Sample No.	Chemical analysis		Molar ratio of ZnO:Fe ₂ O ₃	Results of X-ray study
	ZnO (Wt. %)	Fe ₂ O ₃ (Wt. %)		
1 or 31	—	100	—	Observed only Fe ₂ O ₃ lattice
2	11.7	88.3	1 : 4	Observed Fe ₂ O ₃ and ZnFe ₂ O ₄
32	13.0	87.0	1 : 3.4	"
33	20.8	79.2	1 : 2	Observed only ZnFe ₂ O ₄
3 or 34	25.2	74.8	2 : 3	"
35	28.8	71.2	4 : 5	"
4 or 36	33.9	66.1	1 : 1	"
37	39.0	61.0	5 : 4	Observed ZnFe ₂ O ₄ and ZnO
5 or 38	43.2	56.8	3 : 2	"
8	55.2	44.8	7 : 3	"
10	59.4	40.6	3 : 1	"
39	64.2	35.8	3.5 : 1	"
6	68.3	31.7	4 : 1	"
9	81.0	19.0	8.5 : 1	"
7	100	—	—	Observed only ZnO

3. Experimental Method

Each sintered tablet sample was crushed under 100 mesh and photographed by the Debye-Scherrer X-ray. The magnetic property was measured with the sintered square bar sample. After these experiments, the sample was chemically analysed and i) free ZnO, ii) constitution of the ferrite (ZnO:Fe₂O₃), iii) and the concentration of magnetite were determined. The free ZnO in the sample was leached in

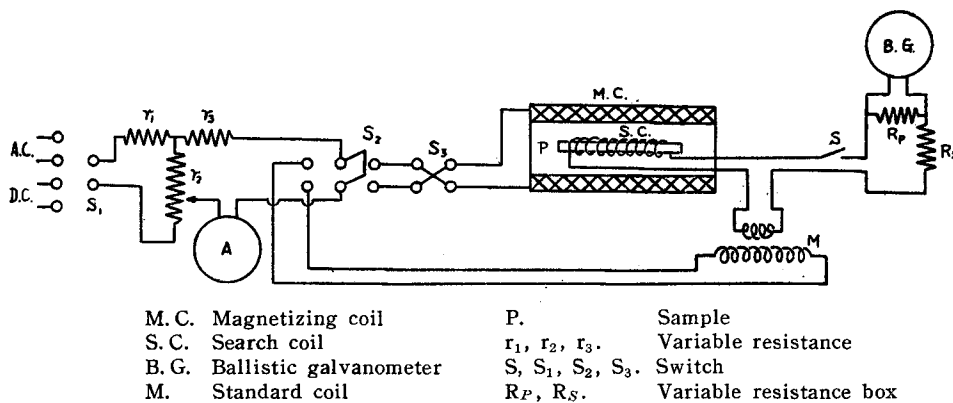


Fig. 1. Measurement apparatus of the magnetic property of samples.

ammoniac ammonium chloride solution. The magnetite concentration was determined from Fe⁺⁺ percent which was decided by dissolving the sample in 1:1 HCl solution under CO₂ atmosphere, and immediately titrated by the 0.1N. KMnO₄ solution.

The intensity of magnetization and H-I curves of samples were both obtained by the ballistic galvanometer method shown in Fig. 1.

4. Experimental Results

A. Electrical resistance

The resistivity of the sample was measured by Wheatstone bridge at room temperature. Plotting the value of $\log \rho$ attained as a function of constitution of zinc-ferrite, Fig. 2 is obtained. Table 2 shows the value of ρ measured. The 1-1 ferrite (No. 4 or No. 36) shows the least resistivity, and when the ferrite forms a solid solution with Fe₂O₃, the value rises slightly. On the contrary, existence of the free ZnO makes the ρ remarkably high.

In Fig. 2, it seems that the samples 1-4, 2-3, and 1-1 (No. 2, 3 and 4) belong to one group, and the samples 3-2, 7-3, 3-1, 9-1 and ZnO (No. 5, 8, 10, 9 and 7) belong to another group.

B. X-ray experiments

The X-ray diffraction patterns of the samples are shown in photo. 1~20 together with the X-ray diffraction picture of magnetite. All of these pictures were taken by the same Debye-Scherrer camera with iron radiation. Since the X-ray diffraction photograph of zinc-ferrite are very much alike that of magnetite and when they exist together, they cannot be distinguished from each other. The chemical constitution of the sample investigated by X-ray is shown in Table 1.

Photo. 1 shown the X-ray diffraction pattern of the mixed sample of ZnO and Fe₂O₃. This photograph contains the patterns of ZnO and Fe₂O₃.

Photo. 2 shows the X-ray figure of pure Fe₂O₃ heated at 1250°C. for 3 hours. Only the pure Fe₂O₃ pattern is seen and the pattern of Fe₃O₄ could not be observed.

Photo. 3 shows the X-ray figure of the 1-3 sample (No. 32) sintered at 1250°C. for 3 hours. Here, the patterns of zinc-ferrite and free Fe₂O₃ both could be seen.

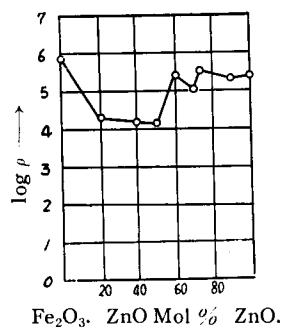


Fig. 2. ρ value of various samples.

Table 2. Value of ρ

Sample No.	Resistivity (Ω cm.)
1	7.15×10^5
2	1.9×10^4
3	1.4×10^4
4	1.3×10^4
5	2.3×10^5
8	9.7×10^4
10	2.9×10^5
9	1.7×10^5
7	1.8×10^5

Photo. 4, 5 and 6 show the X-ray figures of the 1-2, 2-3, and 1-1 samples (No. 33, 3 or 34, and 4 or 36) respectively sintered at 1250°C. for 3 hours. They all show only the complete spinel (zinc-ferrite) pattern and that of free Fe_2O_3 could not be observed even in the ferrite containing initially as high as 81.5 wt. pct. (66.6 mol pct.) Fe_2O_3 , could not be observed.

Photo. 7, 8, 9, 10 and 11 respectively show the X-ray figures of the 3-2, 7-3, 3-1, 4-1, and 9-1 samples (No. 5 or 38, 8, 10 or 39, 6, and 9) heated at 1250°C. for 3 hours. They all show the patterns of zinc-ferrite and free ZnO. The more the quantity of ZnO, the more distinct the pattern of ZnO.

Photo. 12 shows the X-ray figure of the pure ZnO.

Photo. 13 shows the X-ray figure of 2-3 sample (No. 34) heated at 1150°C. for 3 hours, and it contains the patterns of both zinc-ferrite and free Fe_2O_3 . But the pattern of free Fe_2O_3 in photo. 13 is weaker compared with that in photo. 14, which shows the X-ray figure of the 2-3 sample (No. 34) heated at 1000°C for 3 hours.

Photo. 15 shows the X-ray figure of 2-3 sample (No. 34) annealed at 800°C. for 2 hours after being heated at 1250°C. for 3 hours. This picture is very much similar to photo. 14, and it is obvious that the Fe_2O_3 is educed from the solid solution of zinc-ferrite and Fe_2O_3 by annealing.

Photo. 16, 17, 18, and 19 show the X-ray figures of 3-2 sample (No. 5 or 38) heated for 3 hours at 800°, 1000°, 1200°, and 1250°C. respectively, and the decreasing strength of the pattern of free ZnO with the increase of the heating temperature can be seen.

Photo. 20 shows the X-ray figure of natural magnetite, which is very much alike that of zinc-ferrite (Photo. 6).

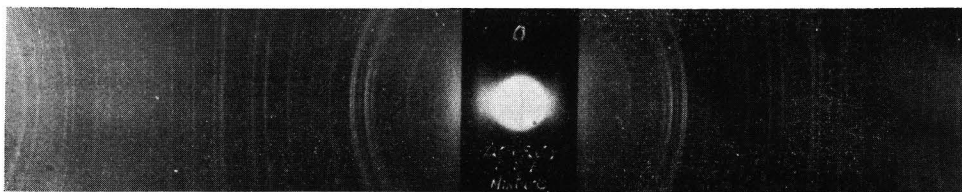


Photo. 1. Mixed Sample of ZnO and Fe_2O_3 .

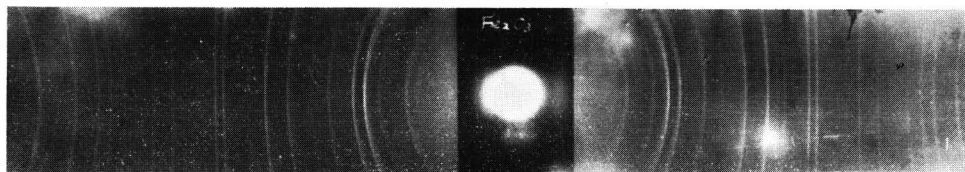


Photo. 2. Fe_2O_3 (No. 1) heated at 1250°C.

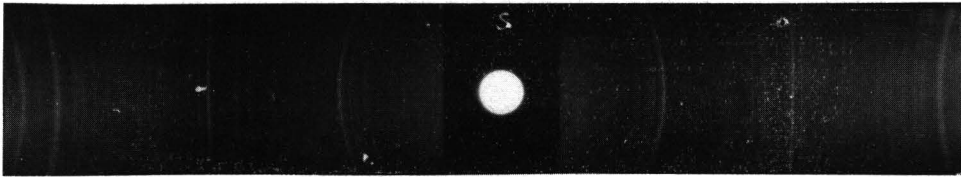


Photo. 3. 1-3 Sample (No. 32) heated at 1250°C.

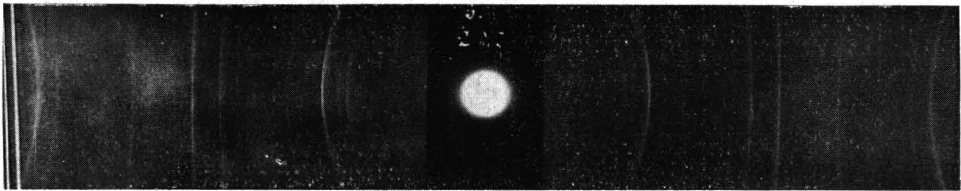


Photo. 4. 1-2 Sample (No. 33) heated at 1250°C.

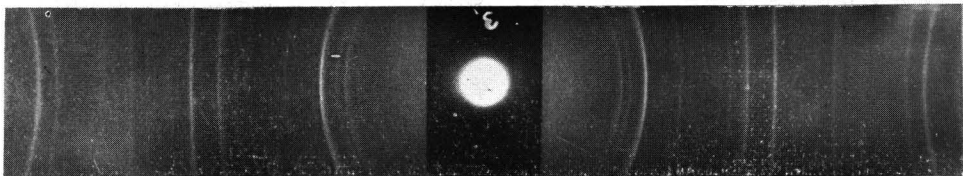


Photo. 5. 2-3 Sample (No. 3 or 34) heated at 1250°C.

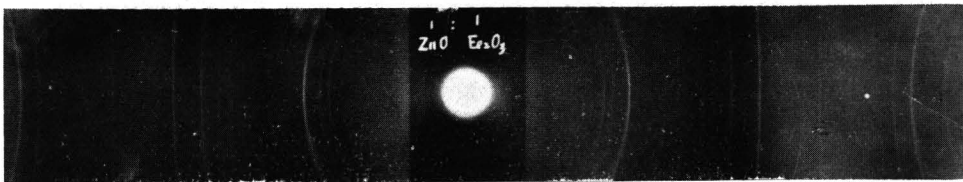


Photo. 6. 1-1 Sample (No. 4 or 36) heated at 1250°C.

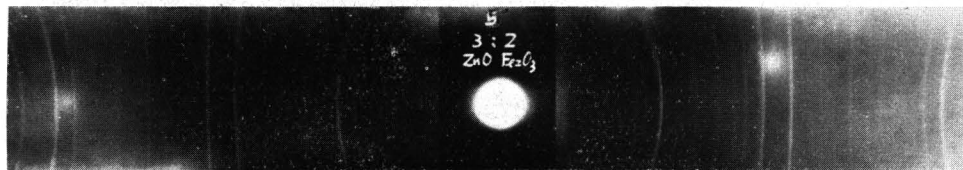


Photo. 7. 3-2 Sample (No. 5 or 38) heated at 1250°C.

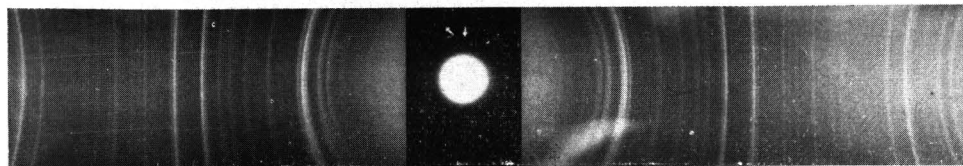


Photo. 8. 7-3 Sample (No. 8) heated at 1250°C.

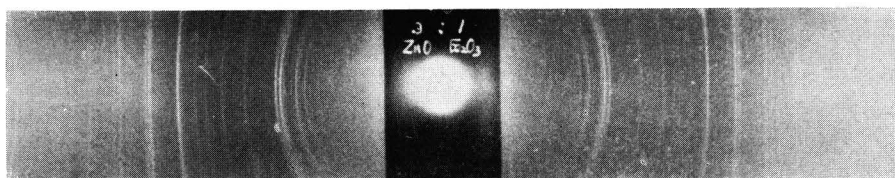


Photo. 9. 3-1 Sample (No. 10 or 39) heated at 1250°C.

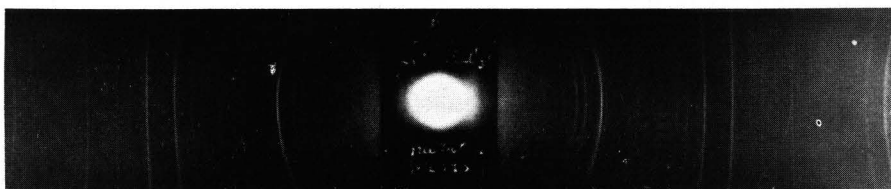


Photo. 10. 4-1 Sample (No. 6) heated at 1250°C.

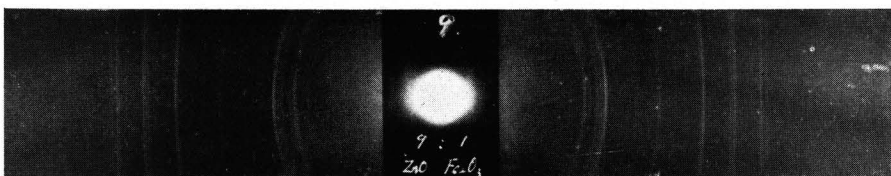


Photo. 11. 9-1 Sample (No. 9) heated at 1250°C.

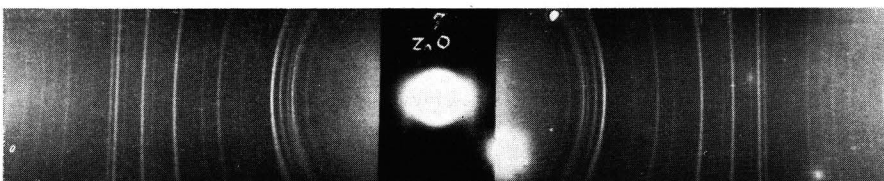


Photo. 12. ZnO (No. 7) heated at 1250°C.

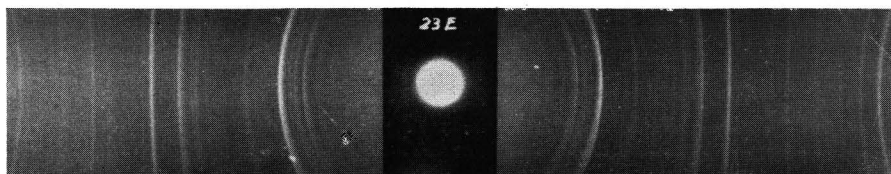


Photo. 13. 2-3 Sample (No. 3 or 34) heated at 1150°C.

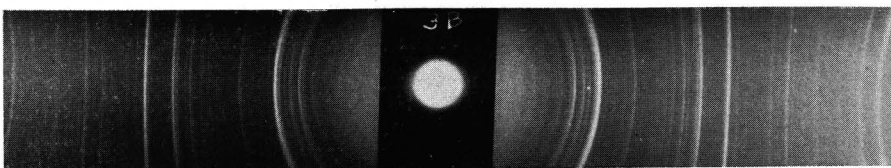


Photo. 14. 2-3 Sample (No. 3 or 34) heated at 1000°C.

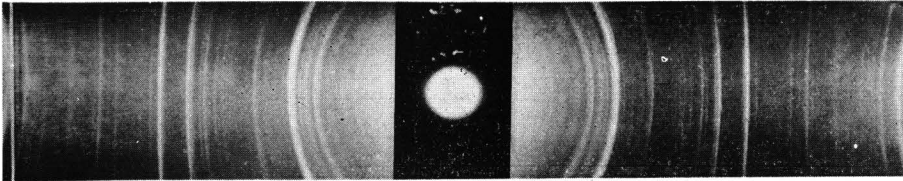


Photo. 15. 2-3 Sample (No. 3 or 34) annealed at 800°C.

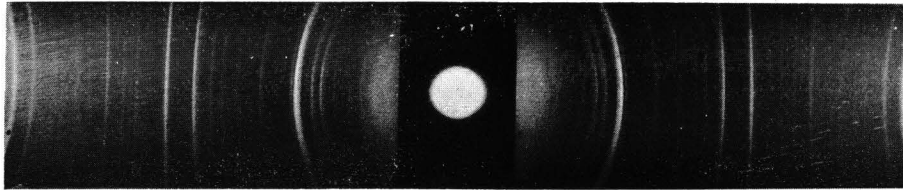


Photo. 16. 3-2 Sample (No. 5 or 38) heated at 800°C.

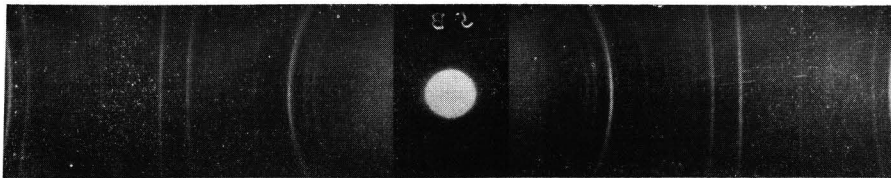


Photo. 17. 3-2 Sample (No. 5 or 38) heated at 1000°C.

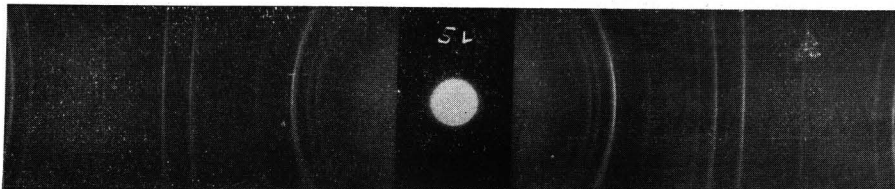


Photo. 18. 3-2 Sample (No. 5 or 38) heated at 1200°C.

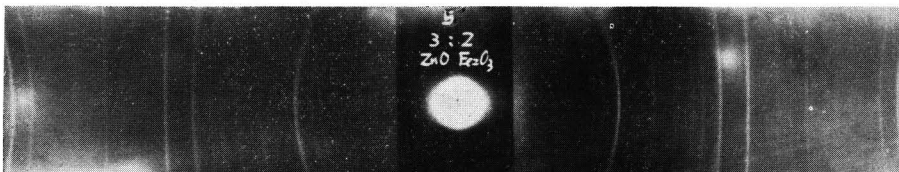


Photo. 19. 3-2 Sample (No. or 38) heated at 1250°C.

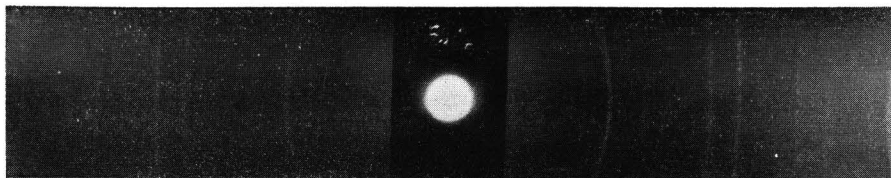


Photo. 20. Natural Magnetite.

The calculated values of d of Fe_2O_3 , zinc-ferrite and ZnO are shown in Table 3.

Table 3. d Values of Samples

No.	No. 1 Fe_2O_3		Fe_2O_3		No. 4 ZnFe_2O_4		ZnFe_2O_4		No. 7 ZnO		ZnO	
	d .	I.	d .	I.	d .	I.	d .	I.	d .	I.	d .	I.
1	4.075	v.w.			3.23	v.w.			3.06	w.		
2	3.611	w.	3.68		2.933	s.	2.97	s.	2.808	w.		
3	3.05	s.			2.77	w.			2.771	s.	2.81	s.
4	2.687	v.s.	2.69	v.s.	2.51	v.s.	2.53	v.s.	2.705	w.		
5	2.435	v.s.			2.075	v.w.			2.568	s.		
6	2.187	s.			1.744	v.w.			2.44	v.s.	2.46	v.s.
7	1.915	v.w.			1.70	v.w.	1.71		2.07	v.w.		
8	1.827	s.	1.84	s.	1.612	v.w.			1.89	s.	1.91	
9	1.688	v.s.	1.69		1.60	s.	1.61		1.774	w.		
10	1.627	v.w.			1.474	s.	1.484	s.	1.612	v.s.	1.61	s.
11	1.59	w.	1.60		1.30	v.w.			1.536	v.w.		
12	1.48	v.s.	1.485	s.	1.24	v.w.	1.24		1.480	v.w.		
13	1.446	v.s.	1.452	s.	1.121	w.	1.122		1.464	v.s.	1.474	s.
14	1.307	s.	1.308		1.096	s.	1.093		1.396	v.w.		
15	1.252	w.	1.259		1.048	w.	1.049		1.371	v.s.	1.378	s.
16	1.185	w.			0.991	v.w.			1.35	s.	1.355	
17	1.165	w.	1.163						1.29	v.w.	1.302	
18	1.137	w.							1.229	w.	1.236	
19	1.109	s.	1.104						1.197	v.w.		
20	1.053	v.s.	1.056						1.173	v.w.	1.179	
21	1.035	v.w.							1.143	v.w.		
22	0.986	w.							1.088	v.s.		
23									1.072	v.w.		
24									1.058	w.	1.063	
25									1.039	v.s.	1.042	
26									1.011	v.s.	1.016	

v.s. very strong s. strong w. weak v.w. very weak

Of special interest to note from the results of these X-ray experiments, are the followings. i), The 1-1 sample (No. 4 or 36) furnishes the complete spinel structure by heating at 800°C for 3 hours. ii), When the sample contain excess Fe_2O_3 over 1:1 ratio, the excess Fe_2O_3 gradually dissolves in the zinc-ferrite (ZnFe_2O_4) and by the heat of up to 1250°C . a solid solution whose ratio of $\text{ZnO}:\text{Fe}_2\text{O}_3$ is up to 1:2 is formed. In other words, the solubility limit of Fe_2O_3 in the solid zinc-ferrite (ZnFe_2O_4) is about 33 mol. pct. Fe_2O_3 at 1250°C . iii), The solid solution of zinc-ferrite (ZnFe_2O_4) and Fe_2O_3 thus obtained, educe the excess Fe_2O_3 again when it is annealed at low temperature (800°C .). iv), From these results, we obtained the

equilibrium diagram for the system ZnO-Fe₂O₃ as shown in Fig. 3.

C. Magnetic experiments.

Zinc-ferrite is known as a non-magnetic material belonging to the normal spinel type. But it has been explained by Kato and Takei⁴⁾ that when zinc-ferrite makes a solid solution with magnetite or ferro-magnetic Fe₂O₃ at high temperature, it assumes ferro-magnetism.

We also conducted our study on magnetic properties of our various zinc-ferrite. In Fig. 4 the H-I curves of magnetite and various kinds of zinc-ferrites are shown. From Fig. 4, it is made clear that the magnetic intensity increased in order of the sample 1-3

(No. 32), 4-5 (No. 35), 2-3 (No. 34) and 1-2 (No. 33). The 1-2 sample (No. 33) has the strongest intensity of magnetization; however, pure Fe₂O₃ (No. 1) and 1-1 ferrite (No. 4 and 36) do not assume ferro-magnetism even if they are heated at 1250°C. for 3 hours. Since the dissociation of Fe₂O₃ to Fe₃O₄ originates vigorously when the sample is heated in vacuum, the sample forms a solid solution with magnetite and it shows a stronger intensity of magnetization compared with the

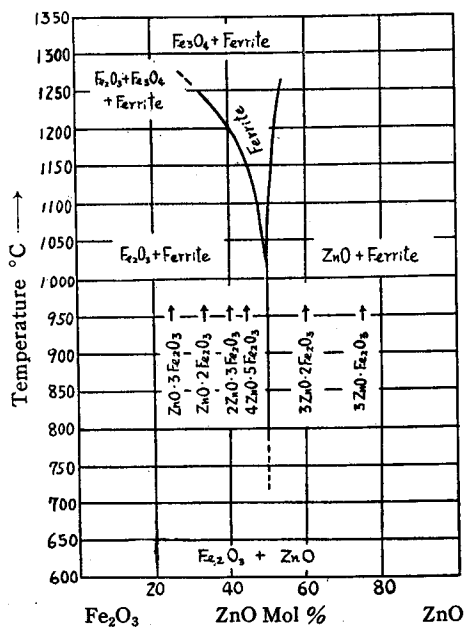


Fig. 3. Phase diagram for the system ZnO-Fe₂O₃ (in mol. pct.)

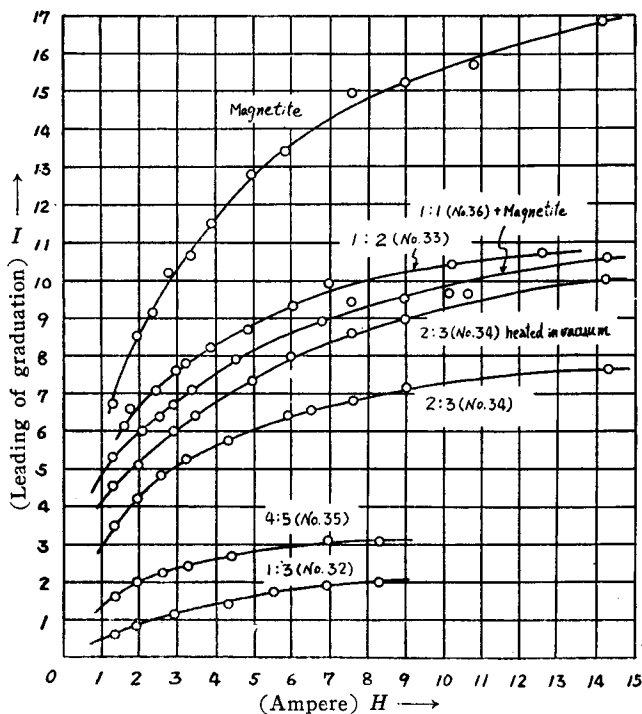


Fig. 4. H-I Curves for various samples.

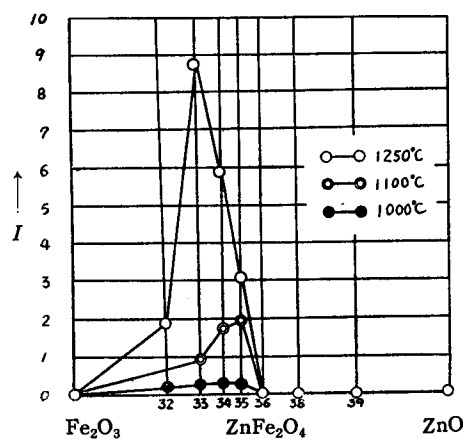


Fig. 5. Intensity of magnetization of various samples.

original ferrite which is heated in the air. This point will be discussed in the latter part of this treatise. Fig. 5 shows the intensity of magnetization of samples of various components under the same magnetic field. The heat treatment has a great effect on the intensity of magnetization of ferrites of the same components. For example, in the 2-3 sample (No. 34), the intensity of magnetization varies decidedly by its heat treatments such as quenching, slow cooling or annealing. As is shown in Table 4, in the case of cooling in the air, the intensity of magnetiza-

tion of the sample is the strongest, which is followed by the case of quenching, and when the sample is cooled slowly or annealed in the furnace, it becomes very weak or non-magnetic. It seems that, in the case of quenching, the sample becomes of more porous structure as compared with the case of air cooling.

Table 4. Intensity of Magnetization of the 2-3 Sample (No. 34) for various heat treatment.

Heating Temp.	Heating Time	Heat Treatment	Intensity of Magnetization
1000°C.	3 hours	air cool	0.2
1100°C.	"	"	1.7
1250°C.	"	"	5.9
"	"	quench	4.3
"	"	slow cool	0.1
"	"	annealed at 800°C. for 2 hours	0.0

The samples with higher ZnO contents does not possess ferro-magnetism by heating them at 1250°C.

From the results obtained, it is surmised that the zinc-ferrite becomes ferro-magnetic when it forms a solid solution with the Fe_2O_3 , and presumably this dissolved Fe_2O_3 is not ferro-magnetic but is non-magnetic. And the fact that the samples having high Fe_2O_3 contents becomes non-magnetic in the case of slow cooling or annealing is due to the eduction of Fe_2O_3 from the solid solution. Of course, when the zinc ferrites having high Fe_2O_3 contents are heated at a high temperature, a part of Fe_2O_3 contained in the sample becomes magnetite and this Fe_3O_4 is retransformed into non-magnetic Fe_2O_3 in the process of air cooling, and it is

almost non-magnetic Fe_2O_3 , not Fe_3O_4 , that is dissolved in the solid solution.

D. The formation of magnetite.

From the X-ray studies and chemical analyses, it became clear that the pure Fe_2O_3 is dissociated only few quantities by heating it at 1250°C . But the degree of dissociation of Fe_2O_3 by heating varies not only with the temperature, duration of heating and the atmosphere, but also with the presence of other oxides. This is what often occurs in ferrospinels containing excess Fe_2O_3 over the stoichiometric (equimolar) amount. On this point, we studied the ratio of formation of magnetite in various kinds of zinc-ferrite. In case of quenching from high temperature, the magnetite formed by dissociation of Fe_2O_3 cannot be re-oxidized to Fe_2O_3 and the Fe_3O_4 content

Table 5. Formation ratio of Magnetite (%)

Sample No.	31	32	33	34	35	36	38	39
ZnO : Fe_2O_3	—	1 : 3	1 : 2	2 : 3	4 : 5	1 : 1	3 : 2	3.5 : 1
Heating temp.								
1100°C.	0	—	0	0	2	—	—	—
1250°C.	1.5	—	—	14	4.5	2	0.3	0
1350°C.	6.6	24.2	21.6	18.2	—	4.4	4.4	0.9
1440°C.	9.1	26	—	21.6	—	6.3	3.0	—

becomes higher than that in the case of air cooling. The dissociation becomes more vigorous when the samples are heated in vacuum.

Chemical analyses of the air cooling samples containing various ratio of ZnO and Fe_2O_3 show that it is not all the excess Fe_2O_3 that is dissociated at 1250°C ., 1350°C ., or even at 1440°C ., and the sample presumably becomes a solid solution of ZnFe_2O_4 , Fe_2O_3 and a part of Fe_3O_4 . In samples containing excess ZnO, only a small portion of Fe_2O_3 is dissociated to Fe_3O_4 by heating it over 1350°C . The results of these are shown in Table 5.

F. Phase diagrams for the systems

ZnO- Fe_2O_3 and ZnO-FeO- Fe_2O_3 .

By summarizing the above results,

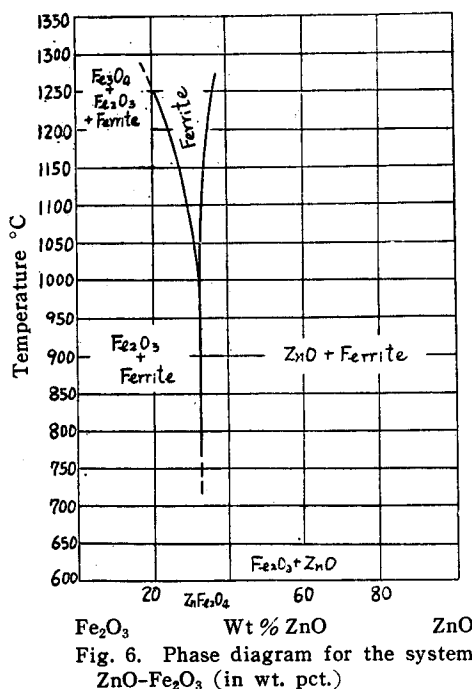


Fig. 6. Phase diagram for the system ZnO- Fe_2O_3 (in wt. pct.)

the phase diagrams for the systems $\text{ZnO-Fe}_2\text{O}_3$ and $\text{ZnO-FeO-Fe}_2\text{O}_3$ are obtained as shown in Fig. 6 and 7.

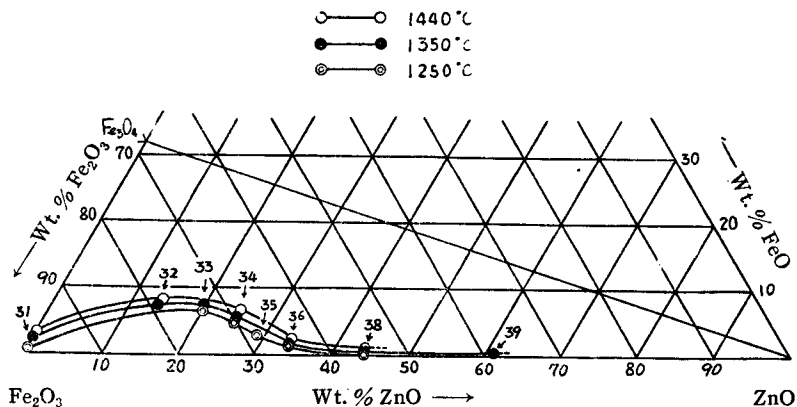


Fig. 7. Phase Diagram for the System $\text{ZnO-Fe}_2\text{O}_3\text{-FeO}$ (in wt. pct.)

4. Consideration

In zinc-ferrite containing excess Fe_2O_3 over the equimolar amount, a part of the excess Fe_2O_3 is apt to be dissociated to Fe_3O_4 . These Fe_3O_4 presumably dissolve in zinc-ferrite, and can be considered that the ferro-magnetism of the zinc-ferrite having a high Fe_2O_3 contents is due to formation of the solid solution of zinc-

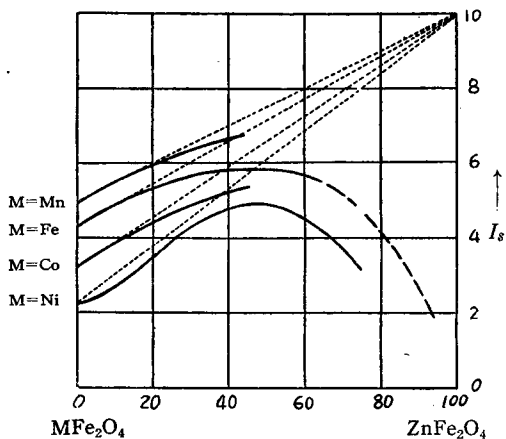


Fig. 8. I_s curves of various solid solution of ferrites.

ferrite and magnetite. Fig. 8 shows the changes of the intensities of the magnetism when the solid solutions are formed by various proportions of zinc-ferrite and various kinds of ferrite such as Mn-, Fe-, Co-, and Ni-ferrite. From the theory of "Ferri-magnetism" it is expected that the intensity of the magnetization of these solid solutions in each case increases along the dotted lines. According to a literature⁹⁾, the magnetism intensifies at first as Zn Fe_2O_4 is increased and attains the maximum value near the equimolar compound (solid solution). Although it lacks the value on the side of ZnFe_2O_4 , it is considered that the I_s curve concerning $\text{Fe}_3\text{O}_4\text{-ZnFe}_2\text{O}_4$ solid solution proceeds as designated by the broken line in Fig. 8.

In our experiments, the 2-3, and 4-5 samples (No. 34 and 35) contained a small

volume of Fe_3O_4 (about 3~4%) in case of air cooling, and when these samples were reheated in vacuum at 800°C . for 2 hours, they increased the Fe_3O_4 content (10~12%). But, in spite of the increase of Fe_3O_4 in these samples, the intensities of the magnetization decreased remarkably from 5.8 to 0.4 as shown in Table 6. On the other hand, the intensities of magnetization of the magnetite and the solid

Table 6. Intensity of Magnetization and the Content of Fe_3O_4 for various Samples.

Sample	Heated at 1250°C . for 3 hrs. in air.		Annealed at 800°C . for 2 hrs. in vacuum.	
	Intensity of Magnetization	Content of Fe_3O_4 (%)	Intensity of Magnetization	Content of Fe_3O_4 (%)
2-3 (No. 34)	5.8	4.2	0.6	12.3
4-5 (No. 35)	2.8	3.6	0.4	9.4
Sample	Heated at 1250°C . for 3 hrs. in vacuum.		Annealed at 800°C . for 2 hrs. in vacuum.	
	Intensity of Magnetization	Content of Fe_3O_4 (%)	Intensity of Magnetization	Content of Fe_3O_4 (%)
Magnetite	9.3	94	9.6	95
Solid Solution of Zinc-Ferrite and Magnetite	3.85	34	3.6	40~41.5

solution of ZnFe_2O_4 and Fe_3O_4 (content of Fe_3O_4 is about 34%) were not decreased after the same heat treatment (annealing). These results are shown in Table 6. From these results, we ought to consider that the decrease of magnetization of annealed samples having a high Fe_2O_3 content is ascribed to the eduction of the dissolved Fe_2O_3 . On these facts, as has been previously mentioned, the authors consider that the ferro-magnetism of zinc-ferrite having a high Fe_2O_3 contents is due to the dissolved Fe_2O_3 .

5. Summary

Nearly 80 kinds of specimens were prepared and measurements of the electrical resistance and magnetic properties, X-ray examinations, and chemical analyses were carried out, and the following results were obtained.

1) Zinc-ferrite at a high temperature dissolves Fe_2O_3 which is contained in excess over the stoichiometric amount. The maximum content of Fe_2O_3 in the solid solution is about 67 mol. pct. (81.5 wt. pct.) at 1250°C . The compound such as $2\text{ZnO}\cdot 3\text{Fe}_2\text{O}_3$ is nothing but a solid solution of zinc-ferrite and ferric oxide.

2) Fe_2O_3 dissolved in zinc-ferrite is precipitated again by annealing.

3) It seems that the zinc-ferrite dissolves a little quantities of ZnO containing excess over the equimolar amount in the sample at high temperature.

4) Zinc-ferrite that dissolved Fe_2O_3 is ferromagnetic. After annealing it is non-magnetic.

5) When zinc-ferrite contains excess Fe_2O_3 , a part of Fe_2O_3 is converted to Fe_3O_4 by heating over 1100°C . in the air. On the contrary, a very limited quantity of pure Fe_2O_3 is dissociated at 1250°C .

6) The phase diagrams for the systems $\text{ZnO}-\text{Fe}_2\text{O}_3$ and $\text{ZnO}-\text{FeO}-\text{Fe}_2\text{O}_3$ have been obtained by summarizing these results.

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