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On the Formation and Constitution of Nickel-Ferrite

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Abstract

The authors have studied on the formation, constiution, magnetic properties, and microstructures of Ni-ferrite, and also prepared the single crystals of Ni-ferrite. The intimate mixtures of NiO and Fe_2O_3 powder of various molar ratio were used as raw materials. The samples were heated at various temperature and were investigated by X-ray and magnetic analyses. The main results obtained were as follows. 1) Ni-ferrite is formed from oxides mixture at above 675°C. 2) $NiFe_2O_4$ dissolves excess NiO and Fe_2O_3 at above 1250° and 1200°C respectively. At 1300°, the single spinel phase is obtained in the range of Fe_2O_3 content of from 52% to 86.5% in weight. 3) Ni-ferrite which dissolves excess Fe_2O_3 precipitate free Fe_2O_3 by annealing at 700°C for 3 hours. 4) Ni-ferrite is a ferromagnetic compound and the intensity of magnetization shows a sharp maximum at the 1-2 sample at above 1200°C. The magnetism of the samples containing excess Fe_2O_3 are weakend remarkably by annealing at above 500°C, and this phenomena seems to be connected with precipitation of excess Fe_2O_3. 5) The growth steps are recognized on the crystals which developes on the sintered surface of Ni-ferrite. 6) The lattice constant of Ni-ferrite is about 8.22~8.23 Å, and Curie point is about 588°C. 7) Ni-ferrite single crystal forms regular octahedron.

1. Introduction

There are great many previous works done on Ni-ferrite concerning its electromagnetic properties. At present Ni-ferrite is mainly utilized as soft ferromagnetic materials in the form of solid solution with Zn-ferrite.[9]

In NiO-Fe_2O_3 system, only the compound of equimolar of NiO and Fe_2O_3 such as $NiFe_2O_4$ is well known and the studies on this system itself are comparatively few.[1),2),3)]

The authors have conducted investigations on various ferrites since a few years ago and at this stage we have studied on the formation, constitution, magnetic properties, and micro-structures of Ni-ferrite, and succeeded in the preparation of single crystals of Ni-ferrite. Hence we wish to make a report on the results obtained.

2. Experimental Methods

The formation and constitution of Ni-ferrite were studied with Debye-Scherrer X-ray method and magnetic analyses by ballistic galvanometer method on the mixture of NiO and Fe_2O_3 of various molar ratio.

The samples were sintered to a great extent by heating at high temperatures and, since the fine crystals develop on the surface of sintered samples, we observed the unpolished surface, as sintered, under a microscope.

The single crystal was prepared from the mixture of NiO and Fe_2O_3 by using PbO as solvent.

3. Preparation of the Samples

NiO : NiO was obtained from pure $NiSO_4$, which was prepared by dissolving electrolytic nickel into H_2SO_4 and crystallizing it, by repeating the heating of sulphate at about 900°C for several hours and decomposing it completely.

Fe_2O_3 : As in the cases of the other ferrites, Fe_2O_3 was prepared by heating the ferrous oxalate at 600°~700°C for several hours and completely decomposing and oxidizing it.

Mixed sample : NiO and Fe_2O_3 were mixed so that the molar ratio of NiO : Fe_2O_3 would become 9 : 1, 7 : 1, 5 : 1, 3 : 1, 2 : 1, 3 : 2, 1 : 1, 2 : 3, 1 : 2, 1 : 3, 1 : 5 and 1 : 9. These samples are represented respectively as 9–1, 7–1··· and so on. These mixed samples were pressed in the mold into tablets of 15 mm diameter and about 3 mm wide for X-ray and chemical analyses, or into square bars of 5 $mm^2 \times 50$ mm for magnetic analyses under 100 kg/cm^2 pressure. The pressed samples were heated at 650°, 675°, 700°, 725°, 750°, 775°, 800°, 850°, 900°, 930°, 1000°, 1075°, 1125°, 1150°, 1200°, 1250°, 1300°, 1350° and 1380° for 3 hours or more. After magnetic measurements, some of the bar samples were annealed at 400°, 450°, 500°, 550°, 575°, 600°, 650°, 700°, 750°, 800°, 850°, 900°, 1000° and 1100°C for 3 hours or more until their intensity of magnetization reached an almost constant value for each annealing temperature.

4. Experimental Results and Considerations

1) On the formation of Ni-ferrite

The intensity of magnetization of the samples are shown in Fig. 1. Presumably the temperature, at which the magnetism of the sample appears, will show the beginning of formation of Ni-ferrite. In our experiments, the 1–1 sample begin to show the magnetism at about 675°C and, thereafter, the intensity of magnetization is increased with the rising of heating temperature. By the X-ray analyses, Ni-ferrite could not be seen in the 1–1 sample heated at 675°, and it was uncertain in the case of 700°, but the existence of ferrite was obviously recognized in the case of 750°C. Free NiO

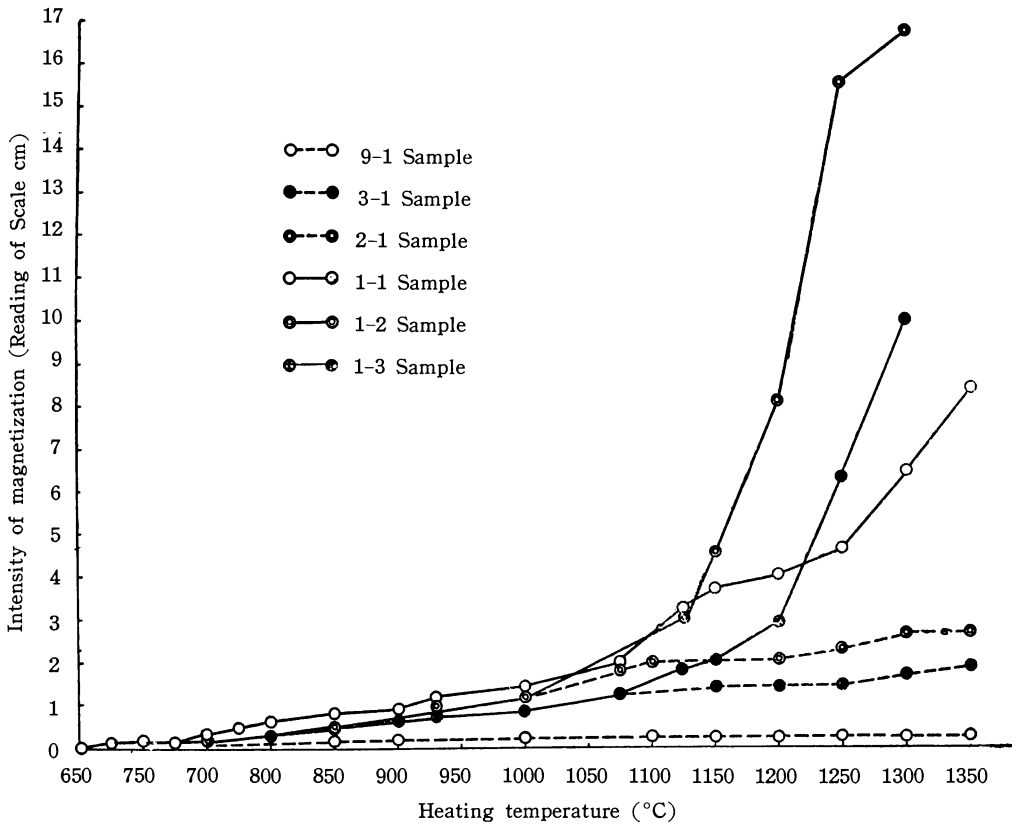


Fig. 1 Effect of the heating temperature on the intensity of magnetization of samples.

and Fe_2O_3 still existed in the sample heated at 900°C. Although it is said by H. Forestier and N, Perbet[2),4)] that when the absorbed water is present, the reaction begins at 415°, but it is considerable from our results that the formation of Ni-ferrite begins at above 650°C by solid reaction between NiO and Fe_2O_3; and this reaction proceeds rapidly with increasing temperature and continues up to a considerably high temperature. The reaction was completed at about 1100°C.

2) On the constitution of Ni-ferrite.

According to the studies on NiO–Fe_2O_3 system by N. A. Toropov and A. I. Borisenko,[1)] the compound $NiOFe_2O_3$ forms at 950°, and a little Fe_2O_3 dissolves in $NiOFe_2O_3$ at 1050°, and a solid solution whose ratio of $NiO : Fe_2O_3$ is up to 3 : 7 is formed at 1300°C (see Table 2).

The authors investigated systematically on the above mentioned samples for this system, and recognized that both NiO and Fe_2O_3 are dissolved in solid $NiOFe_2O_3$ to some extent at high temperature.

i) X-ray analyses

"d" values of main samples are shown in Table 1. As is shown in this table or Photo. 1~24, the 2-3, 1-2 and 1-3 samples show the single spinel phase at above 1200°, 1250° and 1300°C. When the solid solution was annealed at 600°, excess Fe_2O_3 did not precipitated after 2 hours, free Fe_2O_3 is barely recognized after 5.5 hours, and

Table 1. "d" values of several samples.

Sample	Fe_2O_3		NiO		Fe_3O_4		$NiFe_2O_4$		2-1 Ni-f 1300		1-1 Ni-f 700		1-2 Ni-f 1250		1-3 Ni-f 1200		1-3 Ni-f 1250		1-2 Ni-f 1250, 750*	
	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I
							4.116	w							4.10	vw	4.11	vw		
	3.67	w									3.69	vw			3.62	vw				
	2.95	w					2.96	m												
							2.83	w	2.88	w			2.88	w	2.89	w	2.89	w	2.86	w
	2.68	s					2.69	w	2.72	w			2.72	w	2.73	w	2.72	w	2.693	w
			2.608	vw					2.603	vw	2.61	w								
					2.56	vw	2.57	vw	2.55	vw			2.535	w			2.535	w		
	2.49	s			2.484	s	2.478	s	2.47	s	2.45	w	2.47	vs	2.48	vs	2.47	vs	2.45	s
			2.37	m			2.39	w	2.37	w	2.35	m	2.367	vw	2.38	vw	2.367	vw	2.35	vw
			2.366	w			2.28	w	2.27	w	2.25	w			2.26	vw	2.261	vw	2.24	vw
	2.192	w																		
			2.11	w							2.14	vw							2.151	vw
					2.06	w	2.065	m	2.06	s			2.052	m	2.06	m	2.052	m	2.038	m
			2.056	s							2.04	s								
	1.854	w																		
	1.845	m													1.82	w			1.83	vw
							1.745	vw	1.747	w	1.75	vw	1.751	vw	1.753	w	1.751	vw	1.739	w
	1.686	m			1.695	w	1.68	vw	1.683	w	1.66	vw	1.683	w	1.677	m	1.683	w	1.668	m
			1.635	w																
	1.629	vw			1.628	w	1.614	w	1.610	w			1.612	vw			1.612	vw	1.603	vw
					1.595	s	1.595	m	1.59	m	1.605	w	1.59	m	1.588	s	1.588	m	1.582	s
	1.536	w																		
			1.513	vw																
	1.492	m																		
			1.466	s	1.460	vs	1.455	vs	1.463	vs	1.456	m	1.463	s	1.462	vs	1.463	s	1.457	s
	1.448	m									1.44	w			1.44	w			1.437	w
			1.380	w							1.375	vw							1.379	vw
			1.323	w	1.315	w	1.310	vw	1.309	vw	1.300	vw	1.311	vw					1.307	w
	1.290	w									1.273	w							1.295	vw
	1.257	w	1.256	m	1.27	m	1.264	vw	1.264	w	1.249	s	1.266	w	1.267	w	1.266	w	1.261	w
							1.25	w	1.25	w			1.253	vw	1.250	w	1.253	vw	1.247	w
			1.205	m	1.204	w	1.20	vw	1.197	w					1.20	vw			1.220	vw
	1.188	w									1.184	vw			1.183	vw			11.84	vw
	1.162	w									1.157	vw			1.159	vw			1.159	vw
	1.130	w									1.135	vw	1.132	vw	1.138	vw	1.132	vw	1.135	vw
							1.115	w	1.110	w			1.111	w	1.112	vw	1.111	w	1.199	vw
					1.089	vs	1.085	s	1.082	s			1.085	s	1.083	s	1.085	s	1.082	s
					1.068	w														
	1.055	m	1.054	w							1.052	m	1.05	vw	1.054	w	1.059	vw	1.051	w
			1.046	s	1.047	m														
							1.042	m	1.041	m	1.042	m	1.042	m	1.042	m	1.042	m	1.037	m
			1.032	w																
							1.028	vw	1.027	w	1.027	m			1.027	vw				
Exist. Form	Fe_2O_3		NiO		Fe_3O_4		Ni-f		Ni-f		NiO, Fi_2O_3 Ni-f		Ni-f		Ni-f Fe_2O_3		Ni-f		Ni-f Fe_2O_3	

* annealing temperature

vs, very strong. s, strong. m, medium. w, weak. vw, very weak

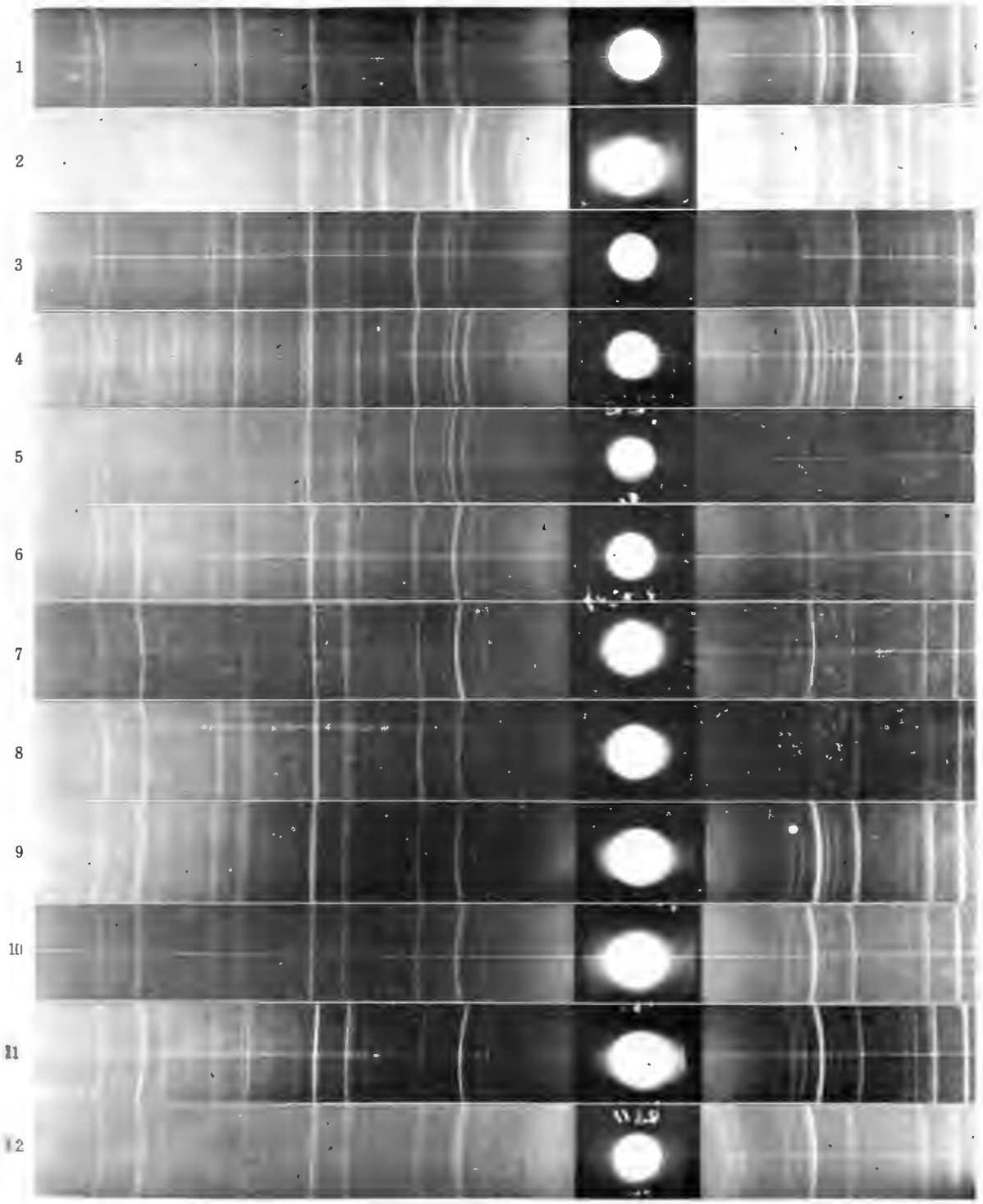


Photo. 1 NiO
Photo. 2 Fe_2O_3
Photo. 3 1-1 Sample heated at 700°C.
Photo. 4 1-1 Sample heated at 750°C.
Photo. 5 1-1 Sample heated at 800°C.
Photo. 6 1-1 Sample heated at 950°C.
Photo. 7 1-1 Sampe helated at 1100°C.
Photo. 8 3-1 Sample heated at 1350°C.
Photo. 9 2-1 Sample heated at 1250°C.
Photo. 10 3-2 Sample heated at 1200°C.
Photo. 11 1-1 Sample heated at 1300°C.
Photh. 12 1-1 Sample heated at 1150°C.

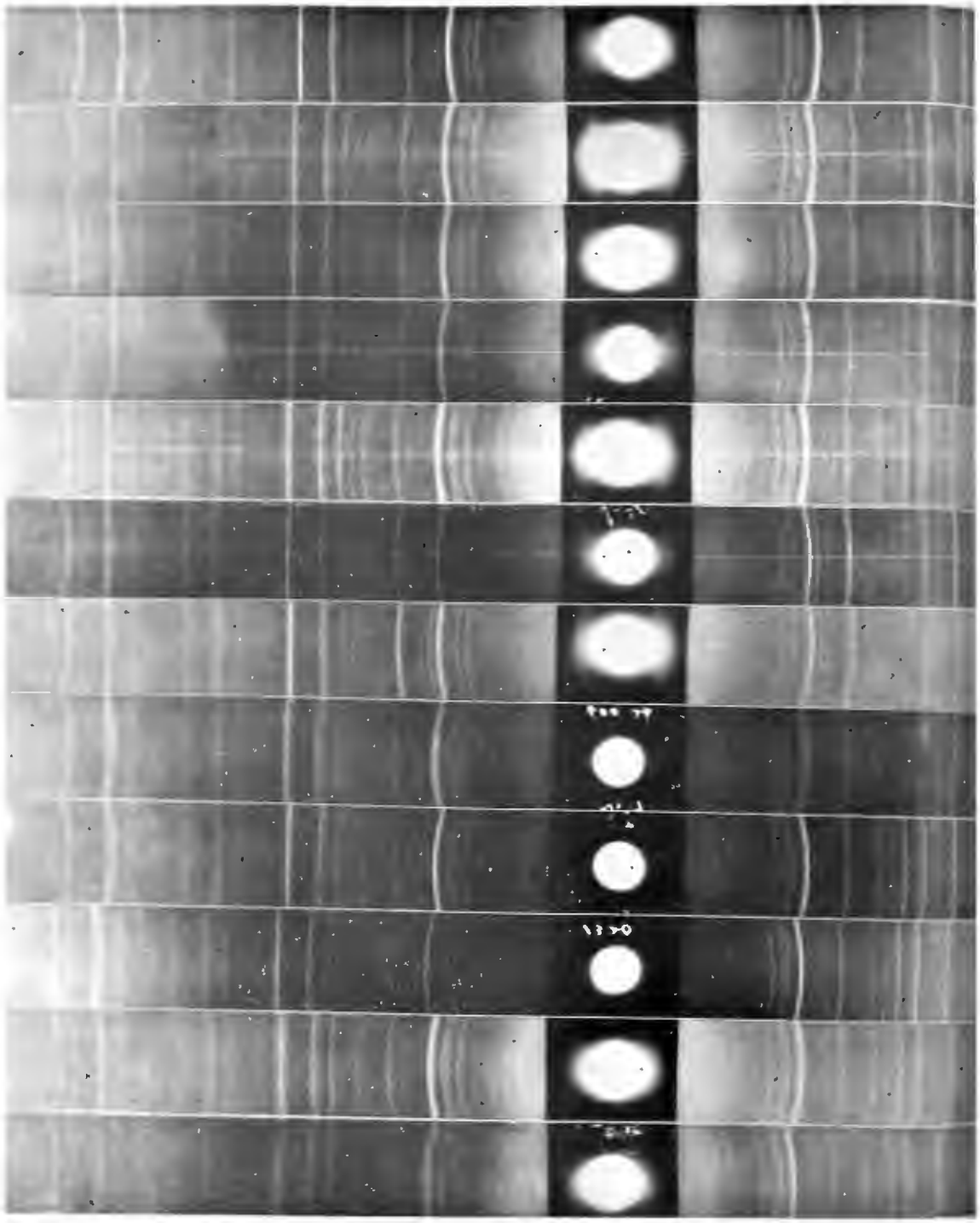


Photo. 13 2-3 Sample heated at 1200°C.
Photo. 14 2-3 Sample heated at 1150°C.
Photo. 15 1-2 Sample heated at 1200°C.
Photo. 16 1-3 Sample heated at 1250°C.
Photo. 17 1-3 Sample heated at 1200°C.
Photo. 18 1-5 Sample heated at 1300°C.
Photo. 19 2-1 Sample heated at 1300°C and annealed at 800°C.
Peoto. 20 1-2 Sample heated at 1320°C and annealed at 600°C for 2 hrs.
Photh. 21 1-2 Sample heated at 1320°C and annealed at 600°C for 5.5 hrs.
Photo. 22 1-2 Sample heated at 1320°C and annealed at 700°C for 3 hrs.
Photo. 23 1-2 Sample heated at 1320°C and annealed at 800°C for 2 hrs.
Photo. 24 1-3 Sample heated at 1250°C and annealed at 800°C for 2 hrs.

the precipitated Fe_2O_3 is definitely recognized at above 700°C for 3 hours. (see Photo. 20~24).

In the samples which contain excess NiO, the 3-2 and 2-1 samples show the single spinel phase only and free NiO cannot be obserbed at 1250° and 1300°C respectively. In the case of Ni-ferrite which contains excess NiO, it is difficult to find the precipitation of NiO by annealing, and free NiO in the case of annealed sample at 800°C for 3 hours is uncertain under X-ray examination (see Photo. 19).

In the samples heated above 1150°C the existence of magnetite was found to a little extent.

It seems that the dissociation from Fe_2O_3 to Fe_3O_4 is accelerated by the existence of NiO and it begins to occur by heating over 1150°C.

From the results obtained by X-ray analyeses of various samples, we could summarize the form of compound in the system as is shown in Table 2. The results obtained by Toropov and Borisenko is shown by the dotted line in this Table. It is certain that the Ni-ferrite dissolves considerable amount of Fe_2O_3 at high temperatures and it seems, also, that NiO is dissolved at above 1250°C within certain range.

Table 2. Results of X-ray Analyses.

Heating Temp. \ Sample	9-1	7-1	5-1	3-1	2-1	3-2	1-1	2-3	1-2	1-3	1-5	1-9
1350	N+f			N+f						f	f+F	F+f
1300	N+f	N+f	N+f	N+f	f	f	f	f	f	f	f+F	
1250					N+f	f		f	f	f+F?		
1200						N+f	f	f	f+F	f+F		
1150							f	f+F				
1100							f					
1050												

N: NiO, f: Ni-ferrite, F: Fe_2O_3

ii) Magnetic analyses

The intensity of magnetization of the 2-3 and 1-2 samples is stronger than that of the 1-1 sample over 1150°, and that of the 1-2 and 1-3 samples grows rapidly over 1100° and 1200°C respectively (see Fig. 3).

Summarizing the results of X-ray and magnetic analyses, it is shown that $NiFe_2O_4$ begins to dissolve excess Fe_2O_3 at above 1150°C and for that reason the magnetic intensity of Ni-ferrite which has dissolved Fe_2O_3, increases sharply above this temperature. On the other hand, in the samples which are richer in NiO, the magnetic intensity increases linearly with increase in heating temperature. Any sharp increase

in magnetism cannot be observed in the sample which has dissolved excess NiO.

3) On the magnetic property of Ni-ferrite

The H–I curves of Ni-ferrite of various molar ratios are shown in Fig. 2, and for the comparison with of the magnetic property in other ferrites, the H–I curves of several ferrites are shown in the same figure. The intensity of magnetization of NiO–Fe_2O_3 system for some heating temperatures under about 120 Oersted magnetic field

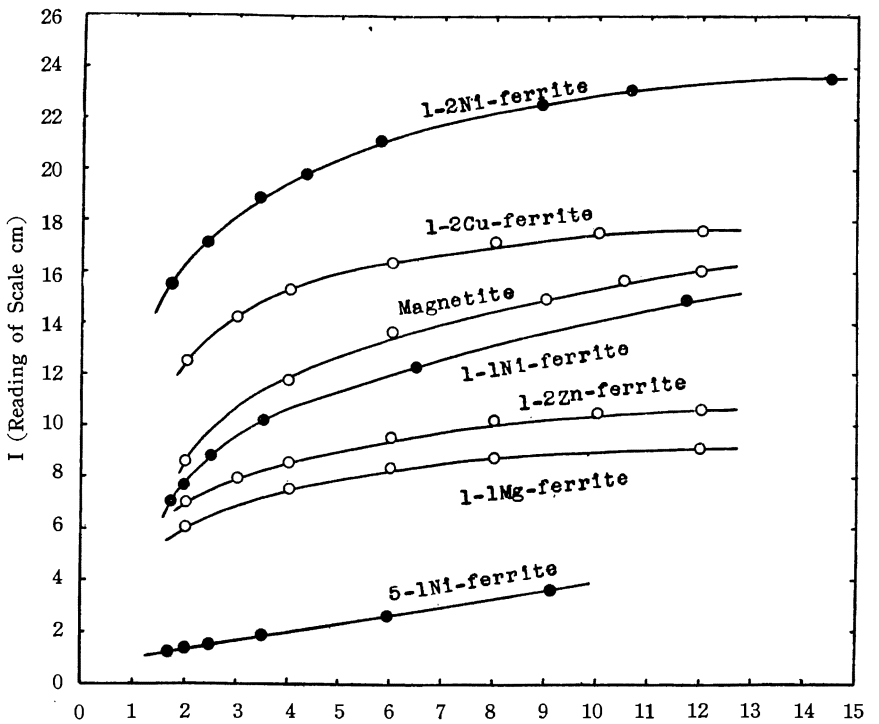


Fig. 2 H–I Curves of Ni-ferrite and various other ferrite.

shown in Fig. 3. Over 1200°C, a sharp maximum is shown in the 1–2 sample (namely, at 66 mol % Fe_2O_3). Beyond the maximum, the curve falls off sharply with further increase of Fe_2O_3. This results coincides with that of Ya. I. Gerasimon and others.[5]

The hysteresis curves of Ni-ferrite measured with an A.C. magnetic field of under about 1400 Oersted are shown in Photo 25. The hysteresis curve rises gradually with the decreasing NiO contents.

Curie point of Ni-ferrite was measured by several investigators[6], according to R. Rautenet, it is 575°C and from C. Guilland is 650°C. We obtained Curie point in the 5–1 sample as shown in Fig. 4, which shows that Ni-ferrite losses its ferromagnetism at 588°C.

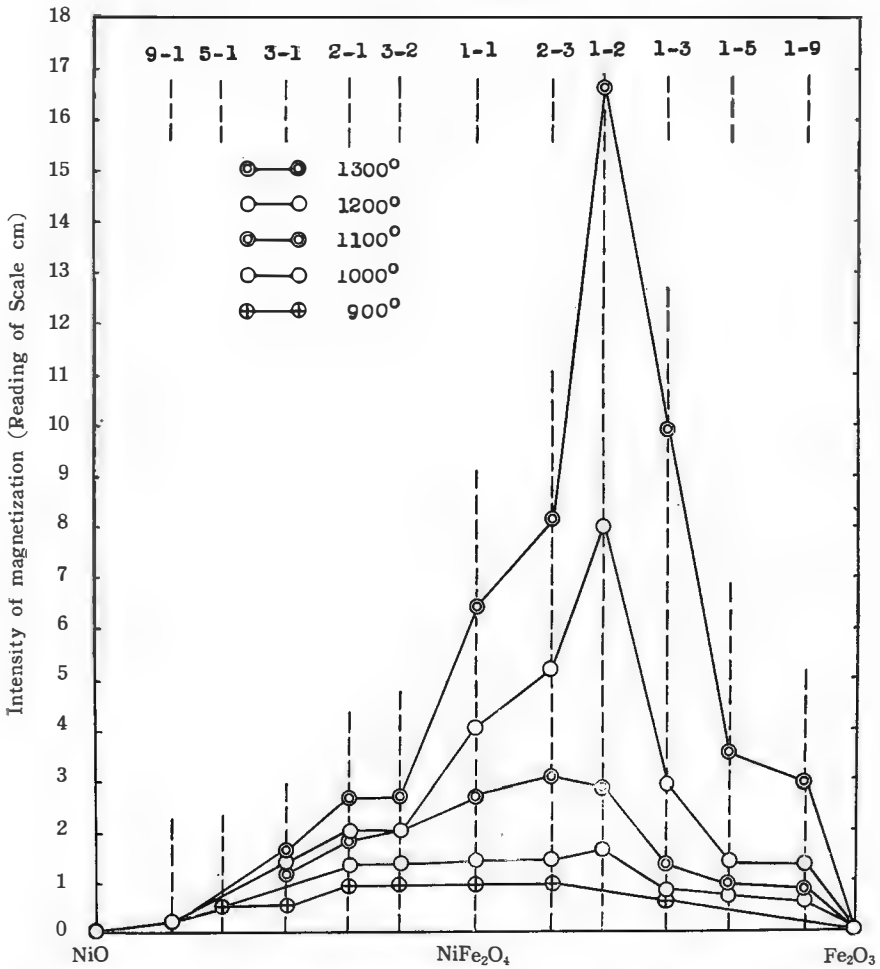
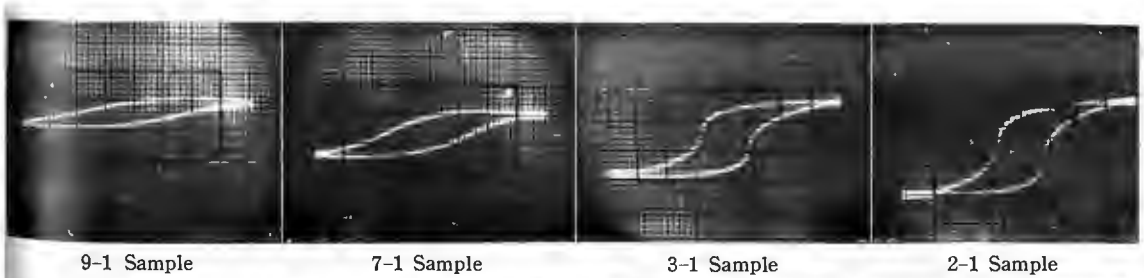
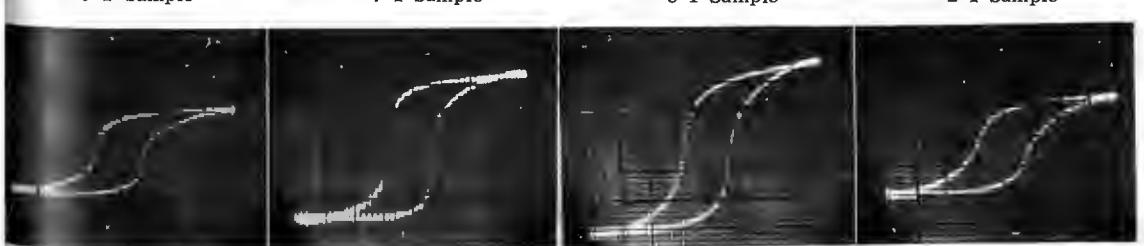


Fig. 3 Intensity of magnetization at various temperature



9-1 Sample 7-1 Sample 3-1 Sample 2-1 Sample



3-2 Sample 1-1 Sample 1-3 Sample 1-9 Sample

Peoto. 25 Hysteresis curves of various Ni-ferrite.

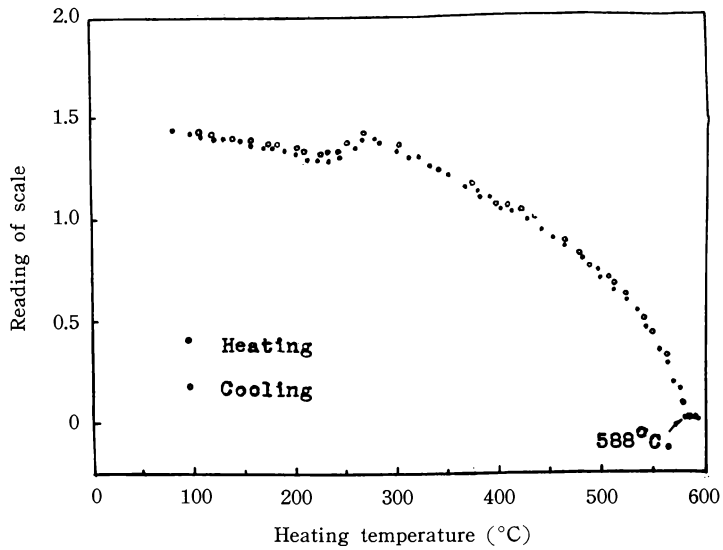


Fig. 4 Measurement of curie point of Ni-ferrite.

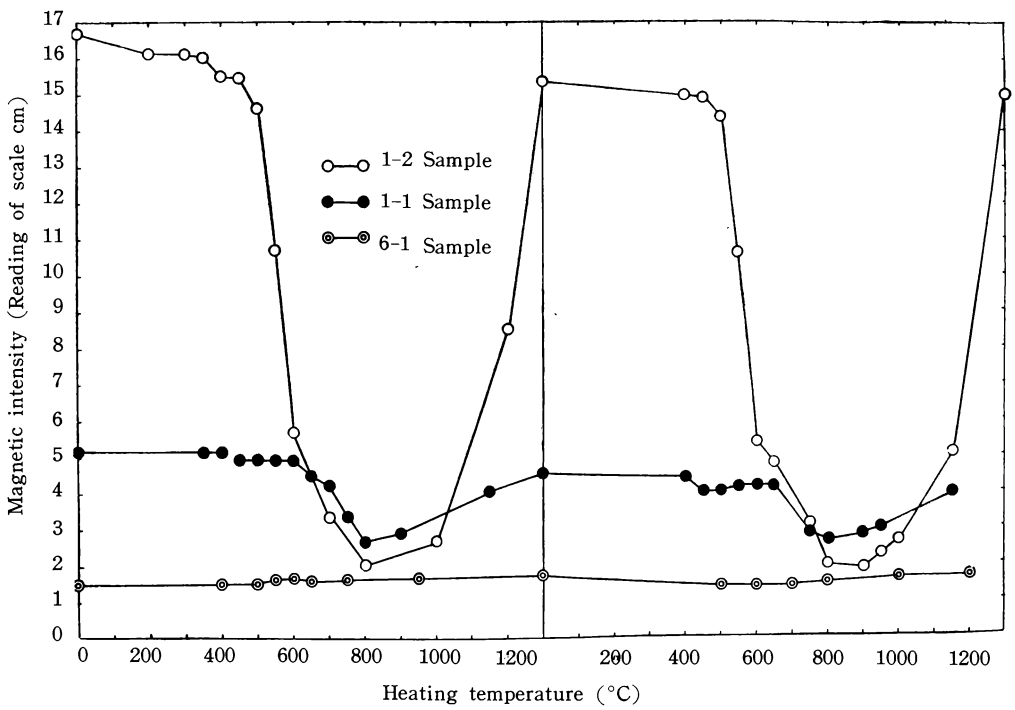


Fig. 5 Changes of the magnetic properties of Ni-ferrite affected by annealing temperature.

We also studied on the changes of magnetism affected by annealing on several sintered samples. Fig. 5 shows the changes of magnetism when the several samples are heated at 200°~1300°C for 2 or more hours and when this treatment is repeated. It is shown that the decrease and increase of magnetism of the 1-1 or 1-2 sample repeat almost regularly. The changes of the magnetism of the annealed sample was plotted for annealing time at some constant temperature, and from this experiment it was shown that the magnetism of the sample reaches an almost constant value after 10 hours of annealing. Plotting the changes of the magnetism versus annealing temperature in the case of 10 hours annealing, we obtained Fig. 6. Fig. 5 and 6 show that the magnetism of the sample containing excess Fe_2O_3 sharply decreases over 500° or 550°, but that

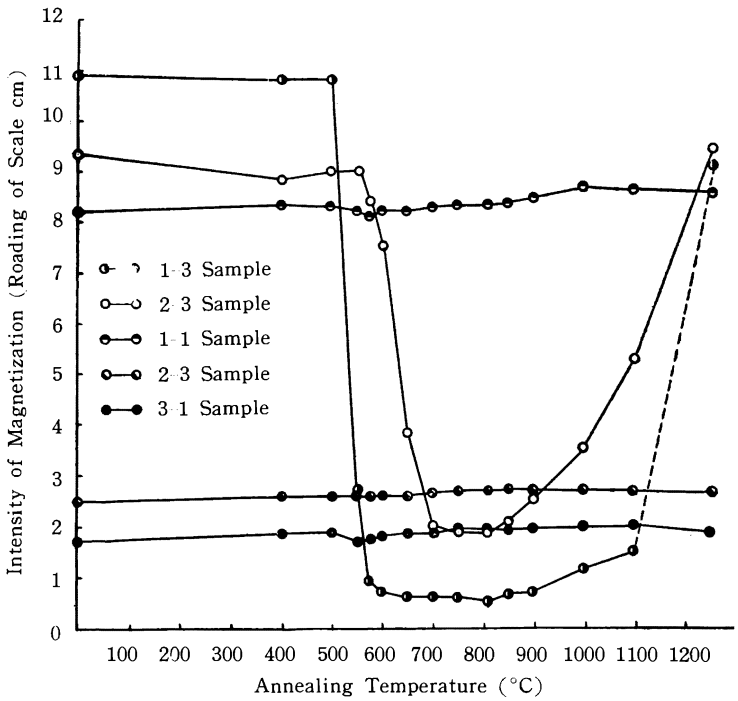


Fig. 6 Changes of magnetic properties after 10 hrs annealing.

of the 1-1 sample is constant or slightly decreses over 650° or 700°C, further, that of the sample containing excess NiO remain almost unchanged. The magnetism of sample becomes minimum at about 800° or 900°C, and thereafter it increases again. The magnetism of the 2-3, 1-2 or 1-3 sample is weaker than that of the 1-1 sample over

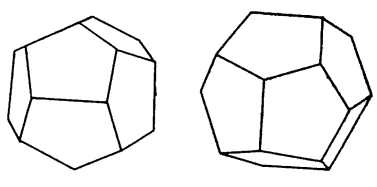


Fig. 7 Pentagonal dodecahedron

550° or 600°, and becomes stronger again over 900°~1000°C. Presumably, these facts show that the precipitation of Fe_2O_3 from solid solution begins to occur over 500° or 550°C, and this free Fe_2O_3 dissolves into Ni-ferrite again over 1000°C. However, as abovementioned, the precipitation of Fe_2O_3 is obviously seen over 700°C by X-ray analyses. There is a temperature gap between the temperature at which magnetism changes suddenly and the precipitation of Fe_2O_3 begin obviously, and it is considered that in this gap, namely, in the temperature range of from 500° to 700°C, Ni-ferrite is presumably in unstable, transitional state.

4) On the micro-structures of Ni-ferrite

The fine crystals are observed under microscope on the sintered surfaces of NiO–Fe_2O_3 system, but they cannot be observed in the case where only NiO or Fe_2O_3 is contained. In the 9–1 sample, the sintered surface is crystallized and a part of it developes step by step. In the 3–1 or 1–1 sample, both the fine and comparatively coarse crystals are found. In the samples containing excess Fe_2O_3, the crystals develope considerably great. In the 1–2 sample, as shown in Photo 29~31, either the triangular or hexagonal crystals develop step by step or, as shown in Photo 32 and 33, the crystals

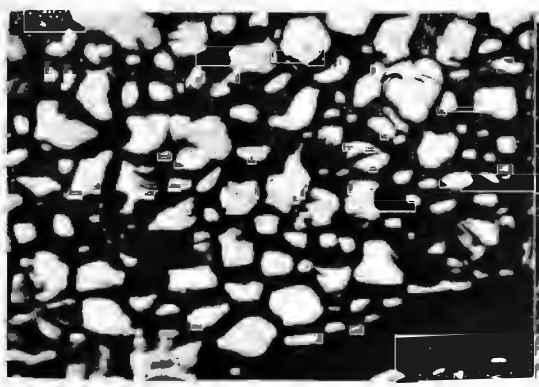


Photo. 26 9–1 Sample ×400

Photo. 27 3–1 Sample ×400

Photo. 28 1–1 Sample ×400

Photo. 29 1–2 Sample ×400

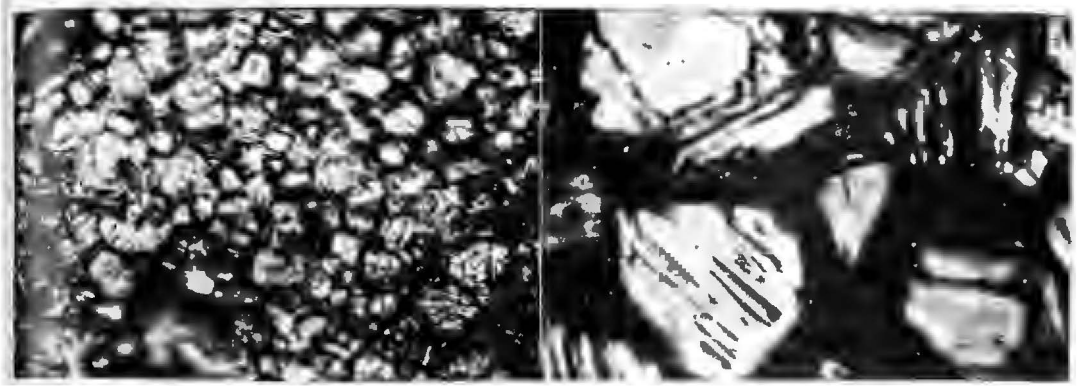


Photo. 30 1-2 Sample annealed at 900° ×400

Photo. 31 1-2 Sample annealed at 900° enlarged. ×400

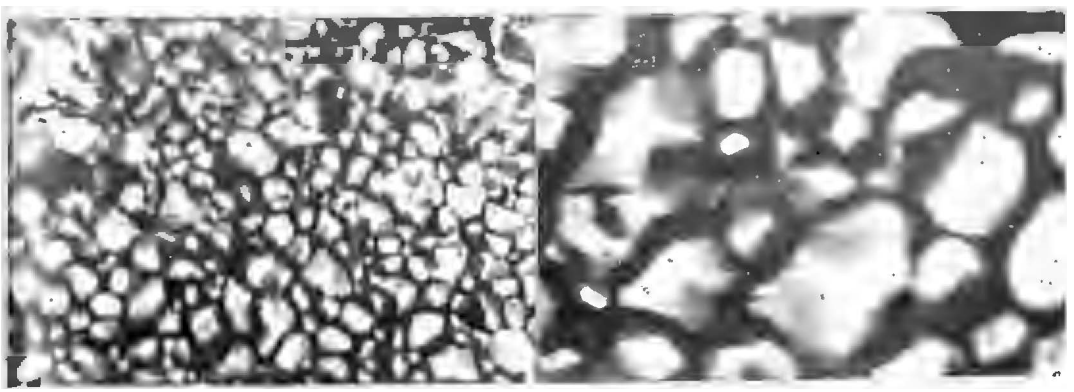


Photo. 32 1-2 Sample ×400

Photo. 33. 1-2 Sample Enlarged

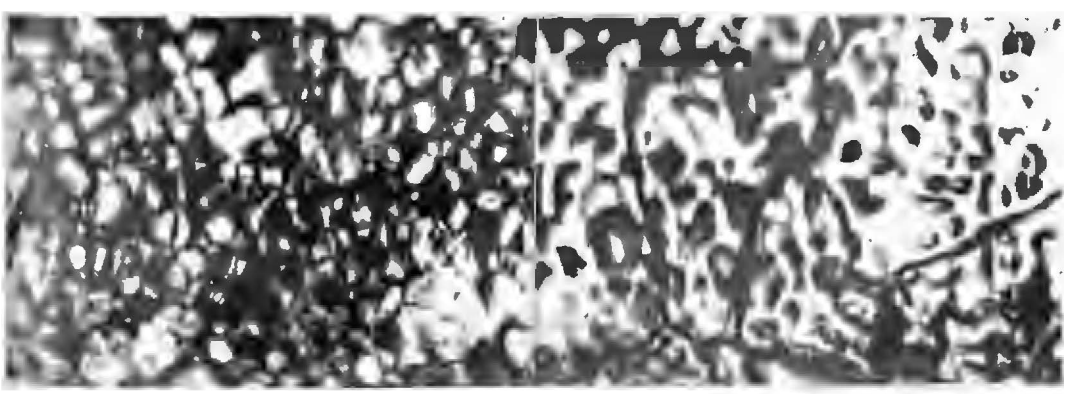


Photo. 34 1-9 Sample ×400

Photo. 35 Fe_2O_3

develope to form pentagonal or hexagonal dodecahedron without growth steps as shown in Fig. 7. The crystals with or without growth steps are found in the 5–1, 1–3 or 1–9 sample also.

5) On the preparation of Ni-ferrite single crystals

As J. P. Remeika[7] reported on the preparation of the single crystals of rare earth orthoferrite and others. We also attempted to prepare Ni-ferrite single crystals by using molten lead oxide as a solvent.

The equimolar mixture of NiO and Fe_2O_3 were mixed with PbO of sixfold in weight. In Pt crucible, the mixture of the three was heated to 1300° and that temperature was held for 2 hours, then it was cooled to 850° at the rate of 30°C per hour.

After rapidly cooling it to room temperature from 850°C, PbO was leached in dil hot HNO_3, and the single crystals of Ni-ferrite of pyramidal form were taken out.

The single crystals of Ni-ferrite take a regular octahedron shape and its length of edge is about 1.3~2.2 mm, and its faces take regular triangle forms as shown in Photo 36 and 37. The microstructure of this face is shown in Photo 38 and 39.

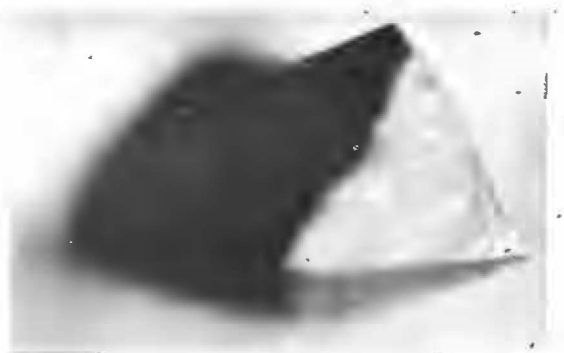


Photo. 36. Ni-ferrite single crystal ×50

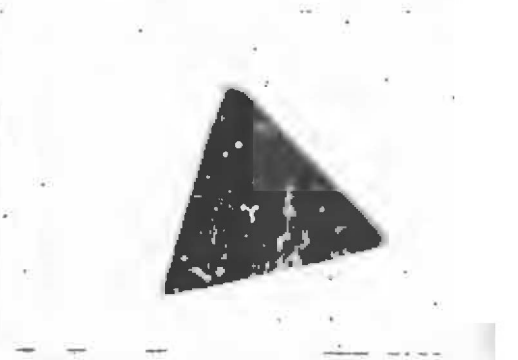


Photo. 37 One of faces of Ni-ferrite single crystal ×50

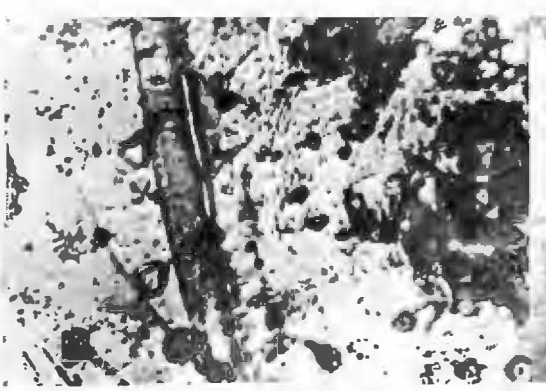


Photo. 38 Surface of Ni-ferrite single crystal ×400

Photo. 39 Surface of Ni-ferrite single crystal ×400

Many small regular triangles which look like etching figures caused by HNO_3 are shown in these photographs. These tiny triangles have a size of about $4\sim12\mu$ and each edge is facing the similar direction. The Laue spots of this crystal show that it consists of single crystal. This single crystal is attracted strongly by magnet and is chemically stable, and it is not dissolved by alkali fusion over 10 hours. The sample consisted of about 27.1% NiO, 68.7% Fe_2O_3 and 3.4% PbO, and molar ratio of NiO : Fe_2O_3 is about 1.0 : 1.2. The inclusion of Pt is spectrographically negligible.

6) On the crystal structure of Ni-ferrite

It was considered from the results of microscopic observation, that Ni-ferrite crystal would form rhombic dodecahedron as Zn- or Cu-ferrite. The single crystal of Ni-ferrite forms regular octahedron. At any rate, Ni-ferrite crystal belongs to the face centered cubic lattice, and its lattice constant "a" calculated from X-ray analyses is about 8.22~8.23Å.

7) On NiO–Fe_2O_3 system

Summarizing the results mentioned above, we obtained Fig. 8, which shows the existing form in NiO–Fe_2O_3 system high temperatures.

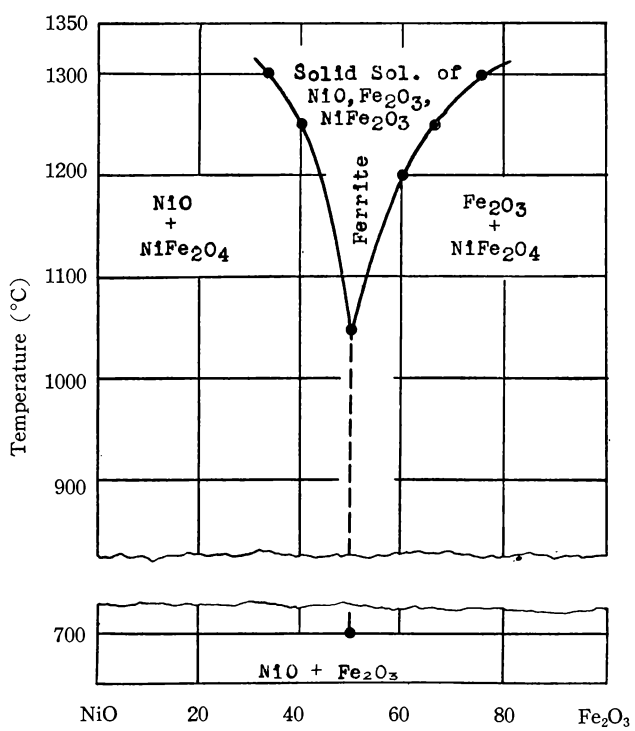


Fig. 8 Existence form in NiO–Fe_2O_3 system at high temperature

5. Conclusions

A systematic investigations were performed on NiO and Fe_2O_3 mixtures of various molar ratio and the following results were obtained.

1) Ni-ferrite is formed from NiO and Fe_2O_3 mixture at above 675°C.

2) Ni-ferrite ($NiFe_2O_4$) dissolves excess NiO and Fe_2O_3 over 1 : 1 ratio at above 1250° and 1200°C respectively. At 1300°C, the single spinel phase is observed up to 2 : 1 and 1 : 3 ratio; namely, this system forms a solid solution in the range of Fe_2O_3 content of from 33.3% to 75% in mol. (from 52% to 86.5% in weight).

3) Ni-ferrite which dissolves excess Fe_2O_3 precipitates free Fe_2O_3 by annealing at 700°C for 3 hours.

4) Ni-ferrite is a ferromagnetic compound and the intensity of magnetization is strongest of the 1–2 sample. The intensity of magnetization of the 1–1 or more NiO samples are not remarkably affeced by annealing. On the contrary, the samples containing excess Fe_2O_3 are affected remarkably by annealing on their magnetic property over 550°C.

5) The growth steps are recognized on the crystals which are formed on the sintered surfaces of Ni-ferrite.

6) The lattice constant of Ni-ferrite is about 8.22~8.23Å, and Curie point is about 588°C.

7) The Ni-ferrite single crystals are obtained and their shape is regular octahedron.

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References

1) N. A. Toropov and A. I. Borisenko: Doklady Akad. Nauk. S.S.S.R. **63**, No. 6 (1948) 485.
2) H. Forestier and N. Perbet: Compt. rend. **223**, (1946) 575; C. A. **41** (1947) 4658[a].
3) T. Okamura and J. Simoizaka: Science Reports of the Research Institutes, Tôhoku University. **2** (1950) 673.
4) H. Forestier and C. Haasser: Compt. rend. **225** (1947) 188.
5) Ya. Z. Gerasimon, T. I. Bulgakoria and Yu. P. Simanov: Zhur. Obschchei Khim. (J. Gen. Chem.) **19**, (1949) 219.; C. A. **44** (1950) 5354[i].
6) R. Pauthenet: Compt. rend. **230**, (1950) 1842.; C. A. **44** (1950) 7601[c].
7) J. P. Remeika: J.A.C.S. **78**, (1956) 4259.
8) M. L. Weil: Compt. rend. **231**, N° 2, (1950) 122.
9) H. Kedesdy and G. Katz: Chemical Age. July (1953), 29.