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AN INVESTIGATION OF THE COMPOSITION OF AN IRON-RICH NICKEL-ZINC FERRITE

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ABSTRACT

The composition of the system $Ni_aZn_{1-a}Fe_2O_4$ - Fe_2O_3 in equilibrium in air at one atmosphere pressure has been investigated. The composition of the spinel phase can be represented as

$$XNi_aZn_{1-a}Fe_2O_4 \cdot YFe\ Fe_2O_4 \cdot ZFe_2O_3$$

The value of X/Y, which is the solubility of magnetite in the nickel-zinc ferrite, has been found between the temperatures 700° and 1300°C. The spinel phase also contains some Fe_2O_3, which is assumed to be present as γFe_2O_3.

The value of $\frac{Y}{Y+Z}$ at the boundary line between the spinel field and the spinel-hematite field has been found to be independent of the value of X.

AN INVESTIGATION OF THE COMPOSITION OF AN IRON-RICH NICKEL-ZINC FERRITE

I. INTRODUCTION

In recent years, the preparation of ferrites for use in electrical circuits has received a considerable amount of attention. The ferrite $Ni_aZn_{1-a}Fe_2O_4$ is formed when NiO, ZnO and Fe_2O_3 are mixed in stoichiometric proportions and then sintered. At temperatures below about 1300°C, no ferrous iron is formed in an air atmosphere. When excess Fe_2O_3 is added, however, some of the Fe_2O_3 is converted to Fe_3O_4, forming a solid solution with $Ni_aZn_{1-a}Fe_2O_4$. The conditions necessary for the formation of ferrous iron in Ni-Zn ferrites are discussed in Technical Report No. 58[1]. This report is a continuation of work discussed in Technical Report No. 58. The purpose of this work is to determine the composition of the system $Ni_aZn_{1-a}Fe_2O_4$ - Fe_2O_3 as a function of temperature in air at one atmosphere.

Technical Report No. 58 contained references to some of the past work on the system RO-Fe_2O_3, where R is a divalent cation. For the sake of completeness, these will be reviewed again, with references to additional work included.

Kato and Takei[2] attribute the magnetic properties of sintered ZnO and Fe_2O_3 containing a large amount of Fe_2O_3, to either the formation of Fe_3O_4 on solid solution with the $ZnFe_2O_4$ or the formation of Fe_2O_3 as a magnetic second

1. C. F. Jefferson and D. M. Grimes, "A Study of the Preparation of Nickel-Zinc Ferrites," Technical Report No. 58, Electronic Defense Group, Department of Electrical Engineering, University of Michigan, Jan. 1956.

2. Y. Kato and T. Takei, "Studies on Zinc Ferrite: Its Formation, Composition and Chemical and Magnetic Properties," Trans. Amer. Electrochemical Soc., 57, 297-312, (1930).

phase, depending upon the method of preparation. Kushima and Amanuma[1] investigated the same system and concluded that while some Fe_2O_3 is converted to Fe_3O_4, the magnetic properties of the Fe_2O_3-rich material was due to Fe_2O_3 in solid solution with $ZnFe_2O_4$.

Roberts and Merwin[2] investigated the system MgO-FeO-Fe_2O_3 in air at one atmosphere. In the system FeO-Fe_2O_3, above 1386 ∓ 5°C, the stable phase was found to be a magnetite solid solution containing excess oxygen, while below this temperature the stable phase is a hematite solid solution containing less oxygen than Fe_2O_3. The solubility of MgO in $MgFe_2O_4$ was found to be about 1% from 1750°C to 1000°C.

Berger[3] investigated the same system and determined the solubility of Fe_2O_3 in zinc ferrite by measurement of the lattice constant. He found the composition of the stable phase to be 76 mole % Fe_2O_3 at 1400°C, 64 mole % at 1200°C, and about 61 mole % Fe_2O_3 at 1000°C. From density considerations he concluded that the solid solution contained lattice holes, which could be accounted for by assuming the presence of γFe_2O_3.

Smolenski[4] investigated the solid solutions of $(Ni_{.3}Zn_{.7})$ Fe_2O_4-Fe_2O_3 and attempted to explain the magnetic properties on the basis of Neel's theory. He found that with increasing Fe_2O_3 content, the saturation magnetization

1. Kushima and Amanuma, "On the Constitution of Zinc Ferrite," Memoirs of the Faculty of Engineering, Kyoto University, 16, 191-203, (1954).

2. H. S. Roberts and H. E. Merwin, "The System MgO-FeO-Fe_2O_3 in Air at One atmosphere," American Journal of Science, 21, 145-157, (1931).

3. S. V. Berger, "Rontgenunderokningar Av Spinellfasen I System ZnO-Fe_2O_3," Festskrift Tellagnad J. Arvid Hedvall, 31-42, (1948).

4. A. Smolenski, "Non-Metallic Ferromagnetics-Ferrites," Izvestigy Akademii Nauk SSSR Seriya Fizicheskaya, 26, 728-738, (1952).

increased for a time and then decreased. The Curie temperature increased and the magnetic permeability decreased. The Fe_2O_3 in solid solution with $Ni_{.3}Zn_{.7}Fe_2O_4$ is given to be γFe_2O_3. The basis for this conclusion is not given.

Toropov, Rabkin, Freingenfeld, and Epstein[1] investigated the system NiO-ZnO-Fe_2O_3 and attempted to correlate the phase composition with the magnetic properties. They plotted a triaxial diagram of the system NiO-ZnO-Fe_2O_3 showing the area of solid solutions. The firing temperature is given as 1350-1400°C. The statement is made that the effect of changing the temperature is to change the amount of Fe_3O_4 and to change the area of solid solutions. The temperature effect on the compositions is not adequately investigated.

Geisler[2] found that $CoFe_2O_4$ would dissolve Fe_2O_3 above 1000°C and that it could be precipitated again by ageing at temperatures below 800°C. The compositions investigated are not given. He speculates that the first-formed Fe_2O_3 is γFe_2O_3, but, due to the similarity of structure between $CoFe_2O_4$ and γFe_2O_3, it cannot be detected by x-ray analysis.

II. PREPARATION AND MEASUREMENT OF SAMPLES

The procedure followed in the preparation of the samples is given in Technical Report No. 58 and will not be repeated here. Methods used to identify the composition of the sintered oxides were (1) chemical analysis, (2) microscopic examination, (3) Curie temperature measurements, and (4) X-ray analysis.

1. N. A. Toropov, L. I. Rabkin, E.ZH. Freigenfeld and B. Sh. Epstein, "The Influence of Several Technological Factors on Phase Composition and Magnetic Properties of Nickel-Zinc Ferrites," Journal of Technical Physics, Vol. 23, Issue 9, (1941).

2. A. H. Geisler, "Structure of Permanent Magnetic Alloys," Transactions of Amer. Soc. for Metals, 43, 70-99, (1951).

The procedure used to determine the amount of ferrous iron is also given in Technical Report No. 58. Microscopic examination of the material was accomplished by mounting the samples in a bakelite mount and polishing according to standard metallographic techniques.

The Curie temperatures were obtained by measuring the fall-off of $\sqrt{\mu_1^2 + \mu_2^2}$ with temperature, where μ_1 is the real part and μ_2 the imaginary part of the initial permeability. This is nearly equal to μ_1 except in the tail of the curve. The Curie temperature is defined here as the temperature at which $\sqrt{\mu_1^2 + \mu_2^2}$ starts to drop. The circuit diagram for the measurements is given in Fig. 1.

X-ray powder photographs were taken using a Debye-Scherrer camera. The pictures were taken with CoK_α radiation.

III. RESULTS AND DISCUSSION

Table 1 contains data for the moles of Fe_3O_4 per mole Ni-Zn ferrite sintered at various temperatures and water quenched. The method of calculating these data from the results of ferrous iron analyses is given in Technical Report No. 58. The value of Y/X (see composition I) increases with temperature for any given composition and approaches the value indicated as the theoretical limit, which is the value the material would have if the excess Fe_2O_3 were completely converted to Fe_3O_4.

The Curie temperature of the material investigated is given in Table 2. The material used in the measurement of the Curie temperature was fired for lengths of time varying from three hours for the material fired at 1400°C. to five days for the material fired at 1000°C. The material fired at 900°C was prefired at 1150°C for four hours, and then refired at 900°C for 24 hours. The

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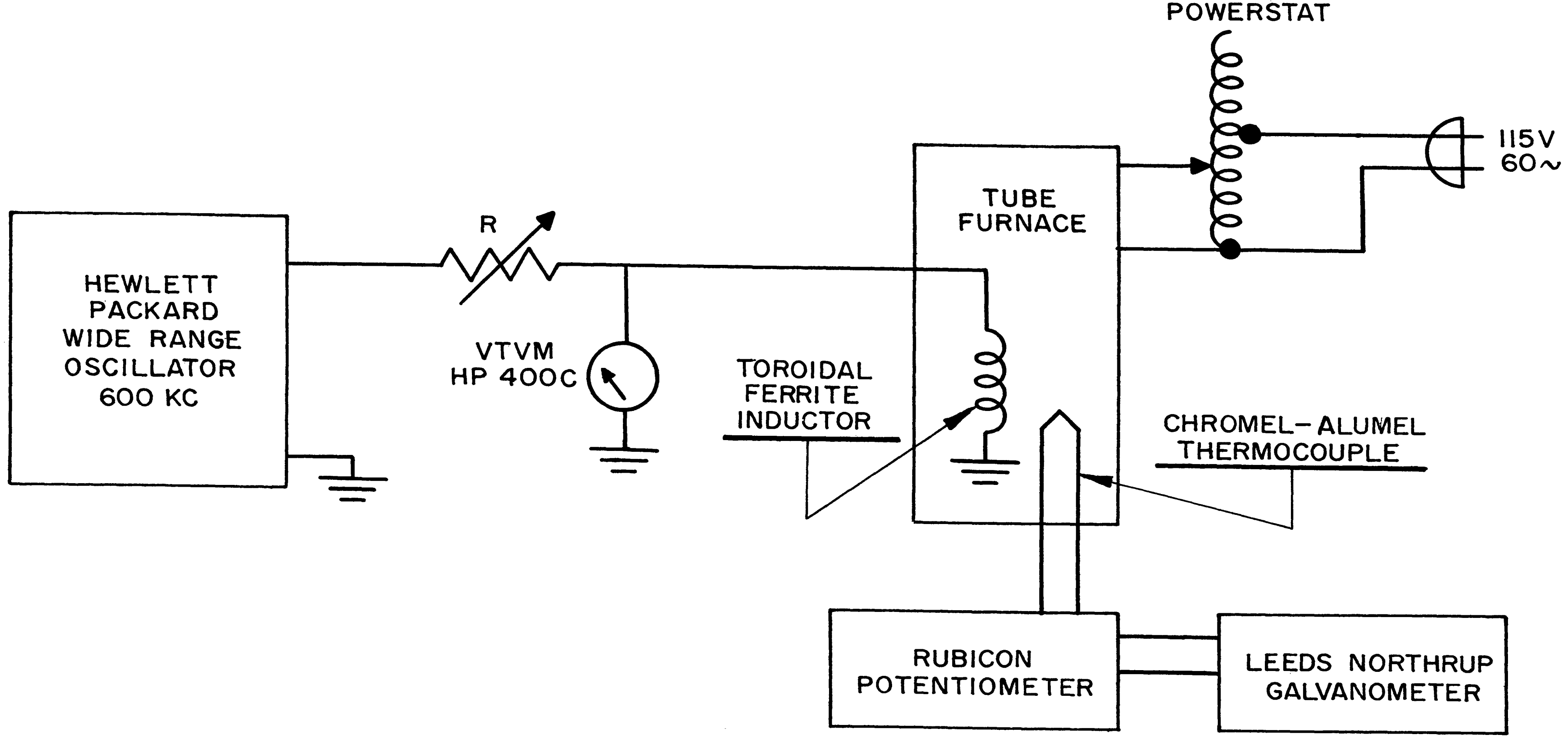

FIG I. CIRCUIT FOR MEASUREMENT OF $\sqrt{\mu_1^2+\mu_2^2}$ VS TEMPERATURE

TABLE (1)

Value of $\frac{Y}{X}$ of Equation (1) for Initial

Material $Ni_{.474}Zn_{.526}Fe_2O_4 + BFe_2O_3$

Temp.	B = .135	B = .294	B = .938	B = 2.00	B = 3.00
700	.004	.004			
800	.015	.012			
900	.035	.028			
1000	.06	.050	.054	.051	
1050		.083	.079	.090	
1100	.085	.143	.142	.149	
1150		.159	.237	.247	
1200		.175	.412	.431	
1250		.180	.509	.688	
1300		.187	.542	1.07	1.27
1350		.190	.570	1.15	
1400		.194	.585	1.20	
Theoretical Limit	.09	.196	.625	1.33	

TABLE (2)

Curie Temperature of Material Having an Initial Composition

of $Ni_{.474}Zn_{.526}Fe_2O_4 + BFe_2O_3$

B	900°C.	1000°C.	1100°C.	1200°C.	1300°C.	1400°C.
0		230	259	256	261	268
.135	276	280	293	280	280	298
.294	272	280	322	327	328	325
.570	267	286	328	380	368	374
.938	260	284	330	418	424	416
2.000				421	477	465
3.000				418	486	498
4.000					474	
5.667					474	
Pure Fe_2O_3						577 *

* Fired at 1425°C.

Curie temperature of Fe_3O_4 was obtained from material prepared by firing Fe_2O_3 at 1425°C. All material was water quenched. A comparison of Curie temperatures measured in a nitrogen atmosphere, an oxygen atmosphere, and an air atmosphere showed that the measurements were not sensitive to the atmosphere used. All measurements were subsequently made in an air atmosphere. A plot of $\sqrt{\mu_1^2 + \mu_2^2}$ versus temperature for a typical material is given in Fig. 2. Some of the material exhibited a behavior as shown in Fig. 3. While the explanation for this behavior is not known, it did not interfere with the determination of the Curie temperatures.

The Curie temperature is plotted against the initial composition in Fig. 4. From this plot the composition of the material on the boundary line between the one phase and two phase area at 1000°, 1100°, 1200°, and 1300° can be obtained. With these data and the additional information obtained by microscopic examination of the material, the phase diagram in Fig. 5 was obtained. X-ray diffraction pictures identified the second phase as $\alpha\ Fe_2O_3$. (Hematite).

The data in Table 1 indicate that the composition of the spinel phase in the one phase area consists of a solid solution of $Ni_aZn_{1-a}Fe_2O_4$, Fe_3O_4 and γFe_2O_3. This is in agreement with the findings of H. S. Roberts and H. E. Merwin[1] in the system $MgO\text{-}FeO\text{-}Fe_2O_3$. The composition of the spinel phase might best be represented as:[2]

$$XNi_aZn_{1-a}Fe_2O_4 \cdot YFeFe_2O_4 \cdot ZFe_2O_3 \qquad (1)$$

1. op. cit., page 2, footnote 2.

2. The Fe_2O_3 in the spinel phase might also be written so as to show the relationship between γFe_2O_3 and Fe_3O_4 as follows:

$$Fe_{2/3}\square_{1/3}Fe_2O_4$$

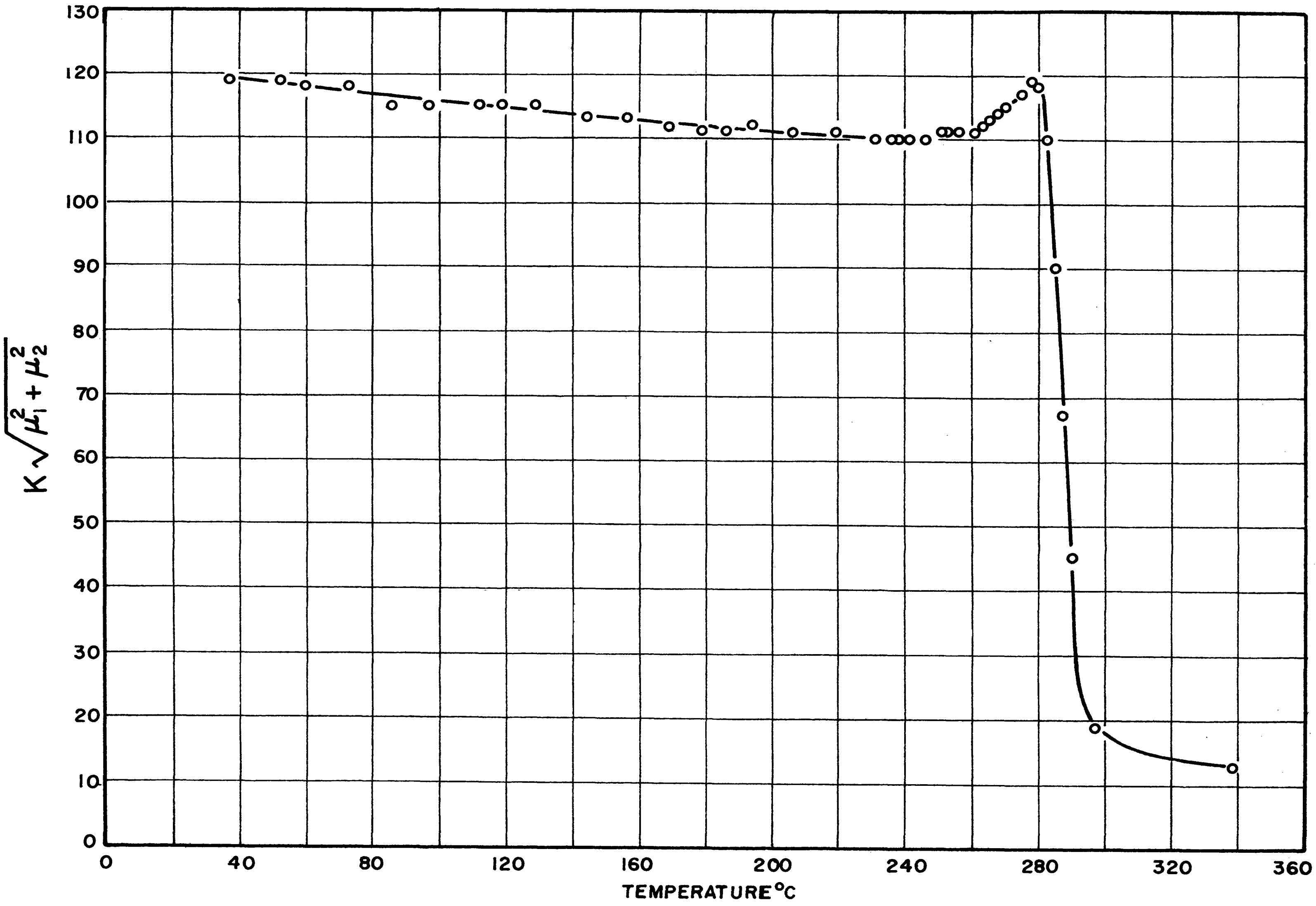

FIG 2 $K\sqrt{\mu_1^2+\mu_2^2}$ VS TEMPERATURE FOR $Ni_{.474}Zn_{.526}Fe_2O_4 + .294Fe_2O_3$ FIRED AT 1000°C

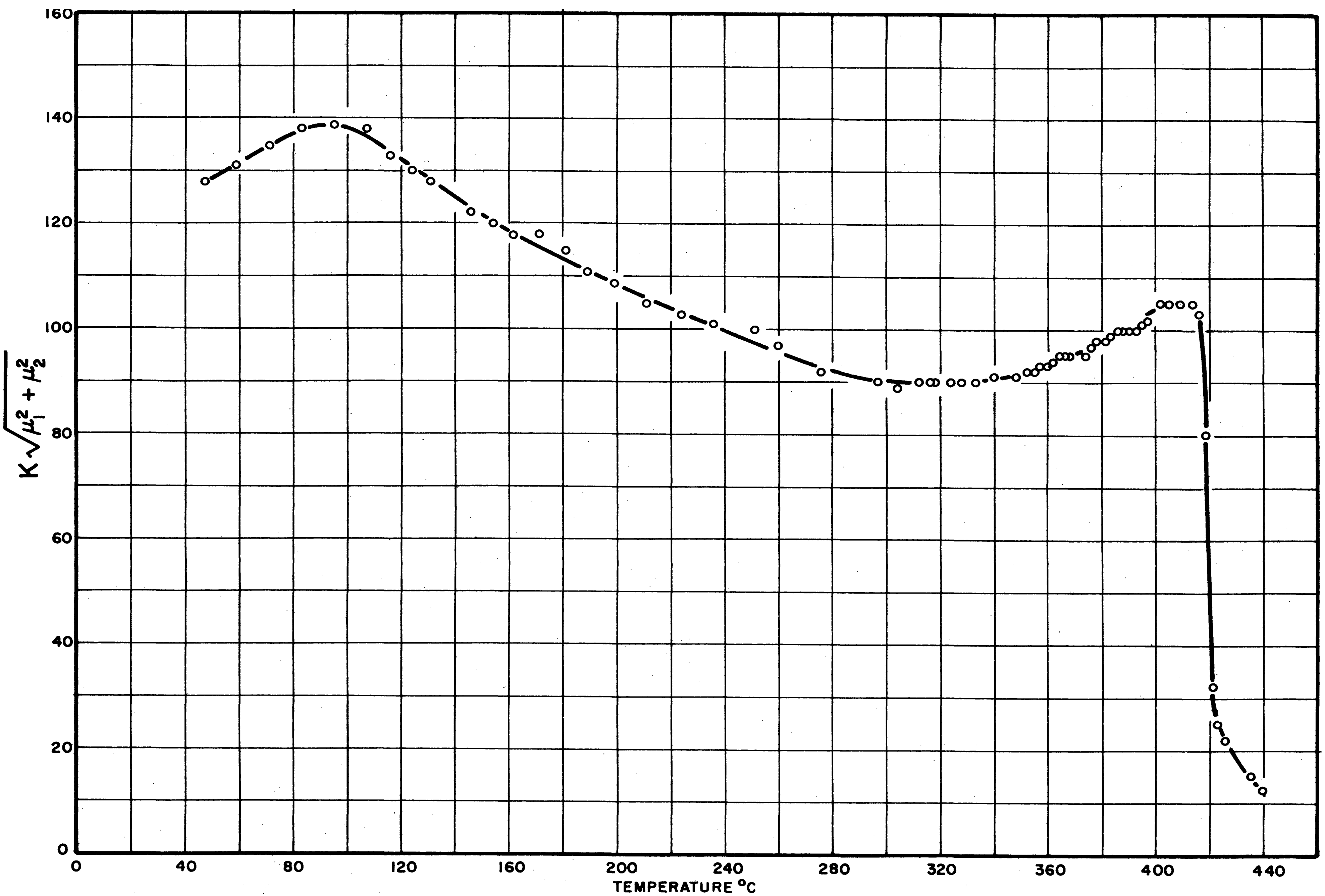

FIG 3. $K\sqrt{\mu_1^2+\mu_2^2}$ VS TEMPERATURE FOR $Ni_{.474}Zn_{.526}Fe_2O_4 + .938\,Fe_2O_3$ FIRED AT 1400°C

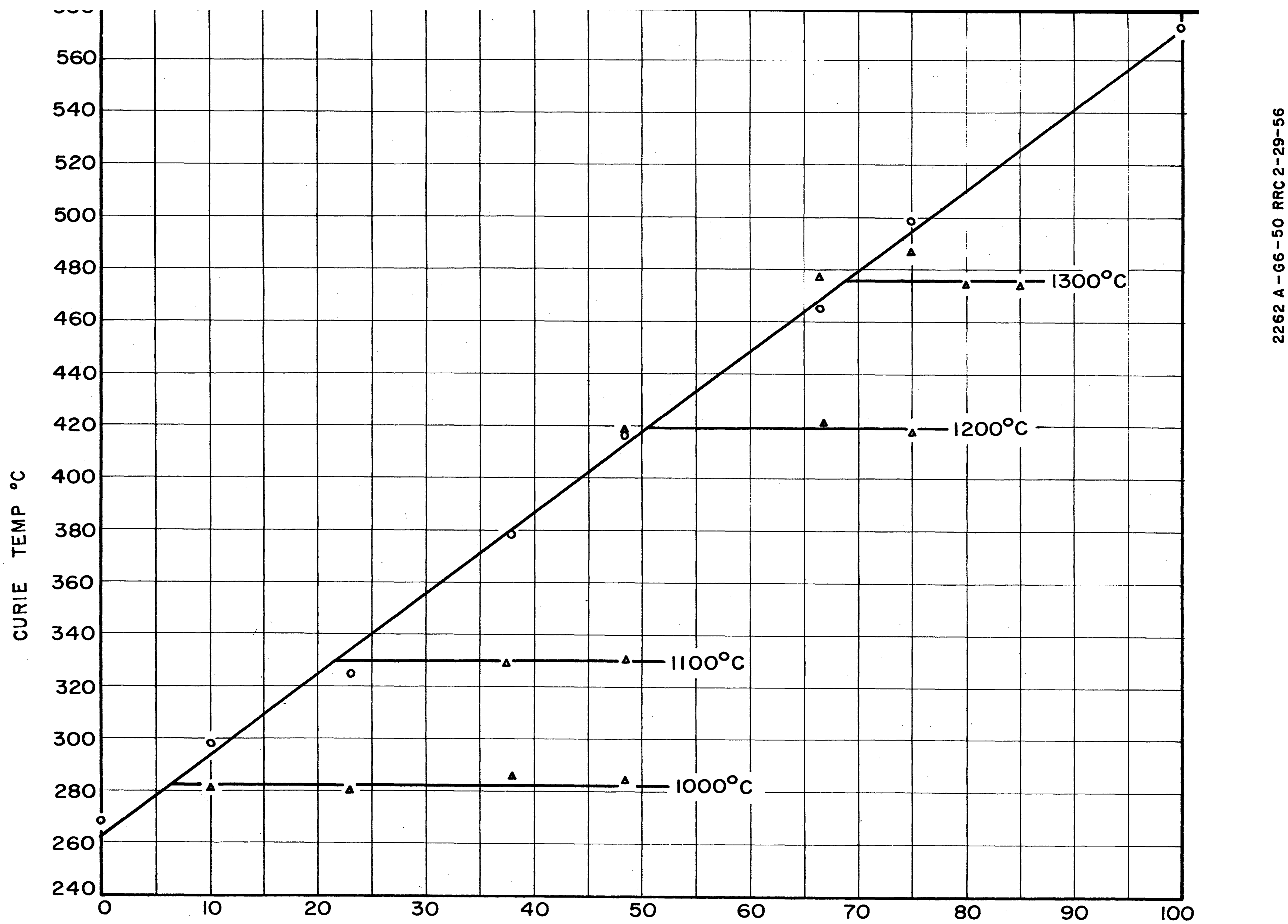

FIG 4
CURIE TEMPERATURE VS INITIAL COMPOSITION

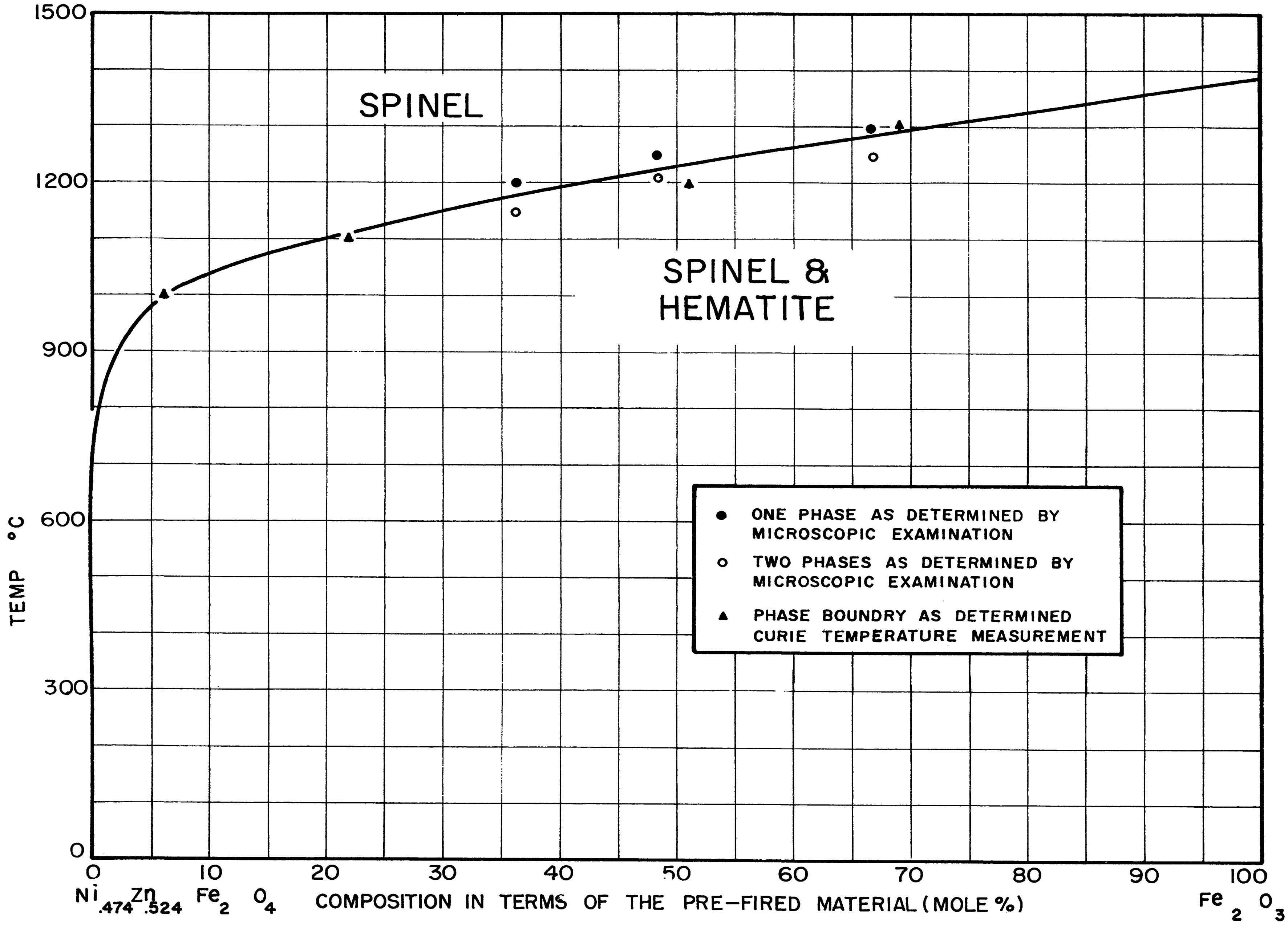

FIG 5 THE PHASE DIAGRAM FOR $Ni_{.474}Zn_{.526}Fe_2O_4 - Fe_2O_3$

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In this notation the data in Table 1 are Y/X. This ratio can be interpreted as the solubility of magnetite in the Ni-Zn ferrite when the spinel phase is in equilibrium with the Fe_2O_3 phase, as is the case in the two phase area. It can be seen that in this region the ratio Y/X is a constant at a given temperature. The value of $\frac{Y}{Z+Y}$ can be thought of as a measure of the amount of excess oxygen in the spinel phase. The calculation of this ratio at the boundary line between the spinel field and the spinel-Fe_2O_3 field can be done as follows. In the two phase area the compositions can be given as:

$$XNi_aZn_{1-a}Fe_2O_4 \cdot YFeFe_2O_4 \cdot ZFe_2O_3 + BFe_2O_3 \qquad (2)$$

The ratio $\frac{Y}{Y+Z+B}$ can be calculated from a knowledge of the initial composition and the ferrous iron content. In the one phase area B=0 and the ratio becomes $\frac{Y}{Y+Z}$. As the temperature is increased further, Z approaches zero and the ratio approaches 1. The value of $\frac{Y}{Y+Z+B}$ has been plotted in Fig. 6 for three compositions. The composition at which the second phase disappears has been marked. It can be seen that the value of $\frac{Y}{Y+Z}$ at this temperature is .7 for all compositions.

Darken and Gurry[1] found that magnetite prepared in air contained excess oxygen. At the boundary between the magnetite-hematite and the magnetite field which occurs at 1390°, the composition of the magnetite in terms of the components Fe_3O_4 and Fe_2O_3 was found to be .7 mole % Fe_3O_4. Written in terms of composition (1) this is:

$$YFeFe_2O_4 \cdot ZFe_2O_3 \qquad (3)$$

where they found that $NFe_3O_4 = \frac{Y}{Y+Z} = .7$. Since composition (3) is identical to composition (1) where x = 0, it appears that this ratio is independent of the value of x of composition (1).

1. L. S. Darken and R. W. Gurry, "The System Iron-Oxygen II. Equilibrium and Thermodynamics of Liquid Oxide and Other Phases," J. Amer. Chem. Soc., 68, 798-816, (1946).

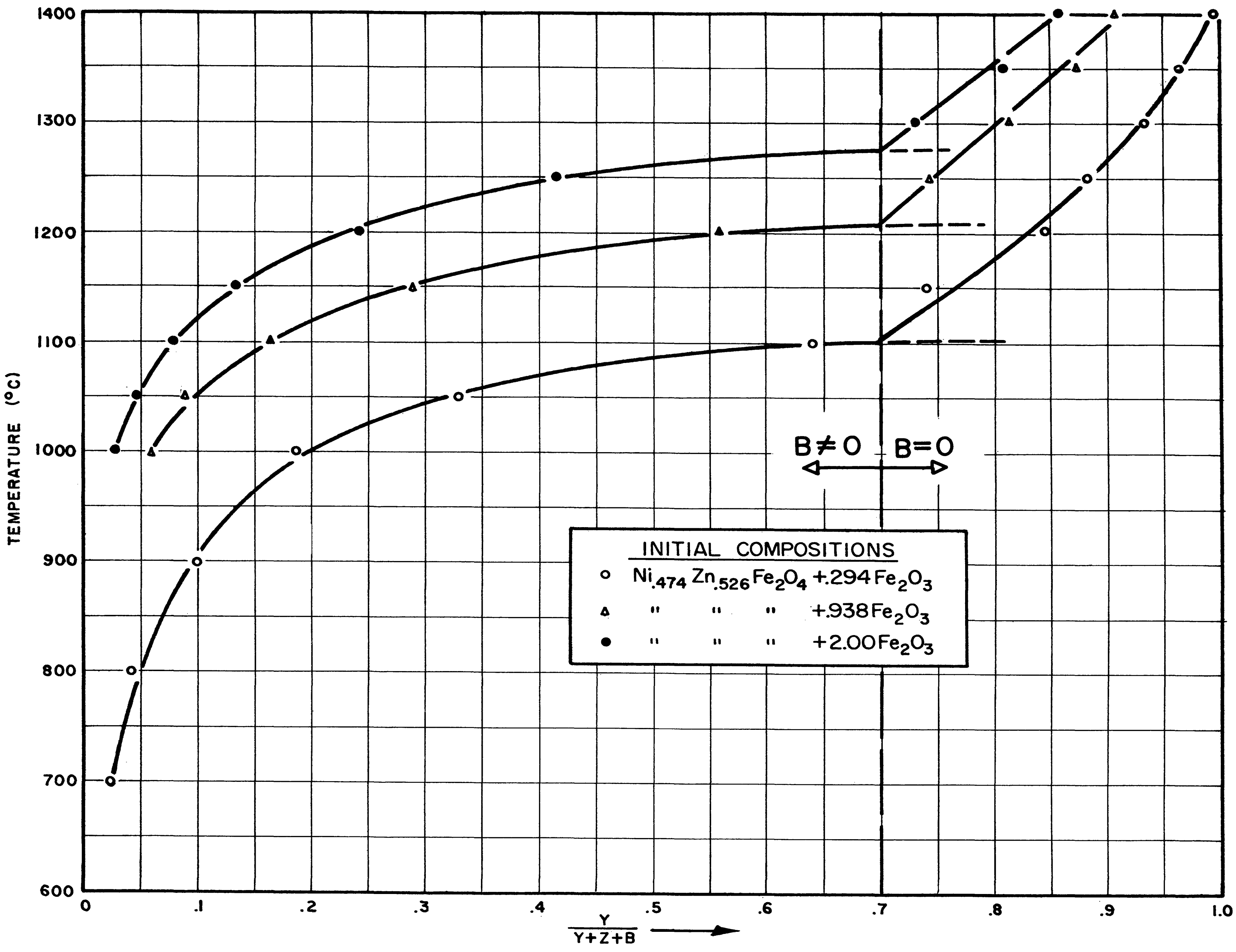

FIG 6. $\left(\frac{Y}{Y+Z+B}\right)$ OF EQUATION 2 VS TEMPERATURE FOR 3 COMPOSITIONS

ACKNOWLEDGMENTS

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