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

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Electronic Defense Group
Department of Electrical Engineering

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ABSTRACT

The composition of the system Ni$_a$Zn$_{1-a}$Fe$_2$O$_4$ - Fe$_2$O$_3$ in equilibrium in air at one atmosphere pressure has been investigated. The composition of the spinel phase can be represented as

$$X\text{Ni}_a\text{Zn}_{1-a}\text{Fe}_2\text{O}_4 \cdot Y\text{Fe}\text{Fe}_2\text{O}_4 \cdot Z\text{Fe}_2\text{O}_3$$

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$_2$O$_3$, which is assumed to be present as γFe$_2$O$_3$.

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
$\text{Ni}_a \text{Zn}_{1-a} \text{Fe}_2 \text{O}_4$ is formed when NiO, ZnO and Fe$_2$O$_3$ 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$_2$O$_3$ is added, however, some
of the Fe$_2$O$_3$ is converted to Fe$_3$O$_4$, forming a solid solution with $\text{Ni}_a \text{Zn}_{1-a} \text{Fe}_2 \text{O}_4$.
The conditions necessary for the formation of ferrous iron in Ni-Zn ferrites are
discussed in Technical Report No. 58\textsuperscript{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 $\text{Ni}_a \text{Zn}_{1-a} \text{Fe}_2 \text{O}_4 - \text{Fe}_2 \text{O}_3$ 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 R0-Fe$_2$O$_3$, 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\textsuperscript{2} attribute the magnetic properties of sintered ZnO and
Fe$_2$O$_3$ containing a large amount of Fe$_2$O$_3$, to either the formation of Fe$_3$O$_4$ on
solid solution with the ZnFe$_2$O$_4$ or the formation of Fe$_2$O$_3$ 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\textsuperscript{1} investigated the same system and concluded that while some Fe\textsubscript{2}O\textsubscript{3} is converted to Fe\textsubscript{3}O\textsubscript{4}, the magnetic properties of the Fe\textsubscript{2}O\textsubscript{3}-rich material was due to Fe\textsubscript{2}O\textsubscript{3} in solid solution with ZnFe\textsubscript{2}O\textsubscript{4}.

Roberts and Merwin\textsuperscript{2} investigated the system MgO-FeO-Fe\textsubscript{2}O\textsubscript{3} in air at one atmosphere. In the system FeO-Fe\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{3}. The solubility of MgO in MgFe\textsubscript{2}O\textsubscript{4} was found to be about 1% from 1750°C to 1000°C.

Berger\textsuperscript{3} investigated the same system and determined the solubility of Fe\textsubscript{2}O\textsubscript{3} in zinc ferrite by measurement of the lattice constant. He found the composition of the stable phase to be 76 mole % Fe\textsubscript{2}O\textsubscript{3} at 1400°C, 64 mole % at 1200°C, and about 61 mole % Fe\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{3}.

Smolenski\textsuperscript{4} investigated the solid solutions of (Ni\textsubscript{.3}Zn\textsubscript{.7}) Fe\textsubscript{2}O\textsubscript{4}-Fe\textsubscript{2}O\textsubscript{3} and attempted to explain the magnetic properties on the basis of Neel's theory. He found that with increasing Fe\textsubscript{2}O\textsubscript{3} content, the saturation magnetization

\begin{enumerate}
\item H. S. Roberts and H. E. Merwin, "The System MgO-FeO-Fe\textsubscript{2}O\textsubscript{3} in Air at One atmosphere," American Journal of Science, 21, 145-157, (1931).
\item S. V. Berger, "Rontgenunderokningar Av Spinellfaser I System ZnO-Fe\textsubscript{2}O\textsubscript{3}," Festskrift Tellagnad J. Arvid Hedvall, 31-42, (1948).
\end{enumerate}
increased for a time and then decreased. The Curie temperature increased and
the magnetic permeability decreased. The $\text{Fe}_2\text{O}_3$ in solid solution with
$\text{Ni}_3\text{Zn}_7\text{Fe}_2\text{O}_4$ is given to be $\gamma\text{Fe}_2\text{O}_3$. The basis for this conclusion is not given.

Toropov, Rabkin, Freingenfeld, and Epstein\(^1\) investigated the system
$\text{NiO-ZnO-Fe}_2\text{O}_3$ and attempted to correlate the phase composition with the magnetic
properties. They plotted a triaxial diagram of the system $\text{NiO-ZnO-Fe}_2\text{O}_3$ 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 $\text{Fe}_3\text{O}_4$ and to change the area of solid solutions. The temperature effect
on the compositions is not adequately investigated.

Geisler\(^2\) found that $\text{CoFe}_2\text{O}_4$ would dissolve $\text{Fe}_2\text{O}_3$ above 1000°C and that
it could be precipitated again by ageing at temperatures below 800°C. The compo-
sitions investigated are not given. He speculates that the first-formed $\text{Fe}_2\text{O}_3$
is $\gamma\text{Fe}_2\text{O}_3$, but due to the similarity of structure between $\text{CoFe}_2\text{O}_4$ and $\gamma\text{Fe}_2\text{O}_3$,
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. Freingenfeld 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).

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 $\mu_1$ is the real part and $\mu_2$ the imaginary part of the initial permeability. This is nearly equal to $\mu_1$ 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 CoKα radiation.

III. RESULTS AND DISCUSSION

Table 1 contains data for the moles of Fe$_3$O$_4$ 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$_2$O$_3$ were completely converted to Fe$_3$O$_4$.

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
FIG 1. 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 Ni0.474 Zn0.526 Fe$_2$O$_4$ + BFe$_2$O$_3$

<table>
<thead>
<tr>
<th>Temp.</th>
<th>$B = 0.135$</th>
<th>$B = 0.294$</th>
<th>$B = 0.938$</th>
<th>$B = 2.00$</th>
<th>$B = 3.00$</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>0.004</td>
<td>0.004</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>0.015</td>
<td>0.012</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>0.035</td>
<td>0.028</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>0.06</td>
<td>0.050</td>
<td>0.054</td>
<td>0.051</td>
<td></td>
</tr>
<tr>
<td>1050</td>
<td></td>
<td>0.083</td>
<td>0.079</td>
<td>0.090</td>
<td></td>
</tr>
<tr>
<td>1100</td>
<td>0.085</td>
<td>0.143</td>
<td>0.142</td>
<td>0.149</td>
<td></td>
</tr>
<tr>
<td>1150</td>
<td></td>
<td>0.159</td>
<td>0.237</td>
<td>0.247</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td></td>
<td>0.175</td>
<td>0.412</td>
<td>0.431</td>
<td></td>
</tr>
<tr>
<td>1250</td>
<td></td>
<td>0.180</td>
<td>0.509</td>
<td>0.688</td>
<td></td>
</tr>
<tr>
<td>1300</td>
<td></td>
<td>0.187</td>
<td>0.542</td>
<td>1.07</td>
<td>1.27</td>
</tr>
<tr>
<td>1350</td>
<td></td>
<td>0.190</td>
<td>0.570</td>
<td>1.15</td>
<td></td>
</tr>
<tr>
<td>1400</td>
<td></td>
<td>0.194</td>
<td>0.585</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td>Theoretical Limit</td>
<td>0.09</td>
<td>0.196</td>
<td>0.625</td>
<td>1.33</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE (2)

Curie Temperature of Material Having an Initial Composition

of Ni${}_{0.474}$Zn${}_{0.526}$Fe$_2$O$_4$ + BFe$_2$O$_3$

<table>
<thead>
<tr>
<th>B</th>
<th>900°C</th>
<th>1000°C</th>
<th>1100°C</th>
<th>1200°C</th>
<th>1300°C</th>
<th>1400°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>230</td>
<td>259</td>
<td>256</td>
<td>261</td>
<td>268</td>
<td></td>
</tr>
<tr>
<td>.135</td>
<td>276</td>
<td>280</td>
<td>293</td>
<td>280</td>
<td>280</td>
<td>298</td>
</tr>
<tr>
<td>.294</td>
<td>272</td>
<td>280</td>
<td>322</td>
<td>327</td>
<td>328</td>
<td>325</td>
</tr>
<tr>
<td>.570</td>
<td>267</td>
<td>286</td>
<td>328</td>
<td>380</td>
<td>368</td>
<td>374</td>
</tr>
<tr>
<td>.938</td>
<td>260</td>
<td>284</td>
<td>330</td>
<td>418</td>
<td>424</td>
<td>416</td>
</tr>
<tr>
<td>2.000</td>
<td></td>
<td></td>
<td></td>
<td>421</td>
<td>477</td>
<td>465</td>
</tr>
<tr>
<td>3.000</td>
<td></td>
<td></td>
<td></td>
<td>418</td>
<td>486</td>
<td>498</td>
</tr>
<tr>
<td>4.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>474</td>
<td></td>
</tr>
<tr>
<td>5.667</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>474</td>
<td></td>
</tr>
<tr>
<td>Pure Fe$_2$O$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>577 *</td>
<td></td>
</tr>
</tbody>
</table>

* Fired at 1425°C.
Curie temperature of Fe$_3$O$_4$ was obtained from material prepared by firing Fe$_2$O$_3$ 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 α Fe$_2$O$_3$. (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$_a$Zn$_{1-a}$Fe$_2$O$_4$, Fe$_3$O$_4$ and γFe$_2$O$_3$. This is in agreement with the findings of H. S. Roberts and H. E. Merwin in the system MgO-FeO-Fe$_2$O$_3$. The composition of the spinel phase might best be represented as:

$$X_{Ni_aZn_{1-a}Fe_2O_4} \cdot Y_{Fe_3O_4} \cdot Z_{Fe_2O_3}$$

(1)

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

2. The Fe$_2$O$_3$ in the spinel phase might also be written so as to show the relationship between γFe$_2$O$_3$ and Fe$_3$O$_4$ as follows:

$$\text{Fe}_{2/3} \square \text{1/3Fe}_2\text{O}_4$$
FIG 3. $K\sqrt{\mu_1^2 + \mu_2^2}$ VS TEMPERATURE FOR Ni$_{.474}$Zn$_{.526}$Fe$_2$O$_4$ + .938Fe$_2$O$_3$ FIRED AT 1400°C.
Fig 5. The phase diagram for $\text{Ni}_{0.474}\text{Zn}_{0.526}\text{Fe}_2\text{O}_4 - \text{Fe}_2\text{O}_3$.
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 \( \text{Fe}_2\text{O}_3 \) 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-\( \text{Fe}_2\text{O}_3 \) field can be done as follows. In the two phase area the compositions can be given as:

\[
X\text{Ni}_{1-a}\text{Zn}_1-a\text{Fe}_2\text{O}_4 \cdot Y\text{Fe}_2\text{O}_4 \cdot Z\text{Fe}_2\text{O}_3 + B\text{Fe}_2\text{O}_3
\]  

(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\(^\circ\)C, the composition of the magnetite in terms of the components \( \text{Fe}_3\text{O}_4 \) and \( \text{Fe}_2\text{O}_3 \) was found to be .7 mole \% \( \text{Fe}_3\text{O}_4 \). Written in terms of composition (1) this is:

\[
Y\text{Fe}_2\text{O}_4 \cdot Z\text{Fe}_2\text{O}_3
\]  

(3)

where they found that \( N\text{Fe}_3\text{O}_4 = \frac{Y}{Y+Z} = .7 \). 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).

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

The author wishes to thank Professor Edgar F. Westrum of the Chemistry Department for his helpful discussions during the course of this work and Hsien Wu Chang for his part in measuring Curie temperatures.
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