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Constricted Hysteresis Loop of Nonstoichiometric Polycrystalline $NiFe_2O_4$

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In the course of research on $Ni_{1-x}Co_xFe_2O_4$-Fe_2O_3 and $Ni_{1-x}Co_xFe_2O_4$-$BeO \cdot Fe_2O_3$ systems, it was found that forms of constricted hysteresis loops are affected by CoO and Fe_2O_3 contents. It seems that constricted hysteresis loops of these systems, especially perminvar character, are caused by exolution of magnetic hard materials on {111} plane of nickel ferrite host.

Small content of BeO presses forward to break out constricted hysteresis loops in these system.

The authors have already reported the constricted hysteresis loop found in $Ni_{1-x}Co_xFe_2O_4-Fe_2O_3$ and $Ni_{1-x}Co_xFe_2O_4 - BeO \cdot Fe_2O_3$* systems at higher Fe_2O_3 content[1,2]. This paper deals with the particular variation of microscopic textures with Fe_2O_3 content in these systems which can be related to the change in the form of hysteresis loop.

Experimental Procedure

NiO, $CoCO_3$, $Be(OH)_2$ and Fe_2O_3 were weighed and mixed with water in stainless steel ball-mill jars containing stainless steel balls. They were calcined for 8 hours at 1100°C, pulverized with a wet ball mill and then dried up. Disks and troids were pressed at 1 t/cm^2, kept at 1400°C in stagnant air for 4 hours, and a cooled in a furnance.

To determine the phase of $Ni_{1-x}Co_xFe_2O_4-Fe_2O_3$ and $Ni_{1-x}Co_xFe_2O_4BeO \cdot Fe_2O_3$, X-ray powder diffraction patterns were recorded with Toshiba-automatic *X*-ray spectrometer using Fe-*K* radiation. The amount of hematite was determined from a calibration curve which was obtained from mixtures of various ratios of pure hematite (hem) and $NiFe_2O_4$ (sp) by intensities of reflections from $10\bar{1}4$ hem, $11\bar{2}0$ hem, 220 sp and 331 sp for Fe$K\alpha$ and Fe$K\beta$. *B-H* hysteresis loop measurements were made with Toei-Cioffi type automatic *B-H* recorder with a field strength of 200 oersteds maximum.

Results and Discussion

The form of constricted hysteresis loop (Fig. 1) seems to have a relation with the texture of unique exolution of hematite as proved by Fig. 2.

As to the orientation relation between exoluted hematite and its ferrite host, the following result has already been obtained by J.W. Greig *et al.*[3] and R.E. Carter *et al.*[4]:

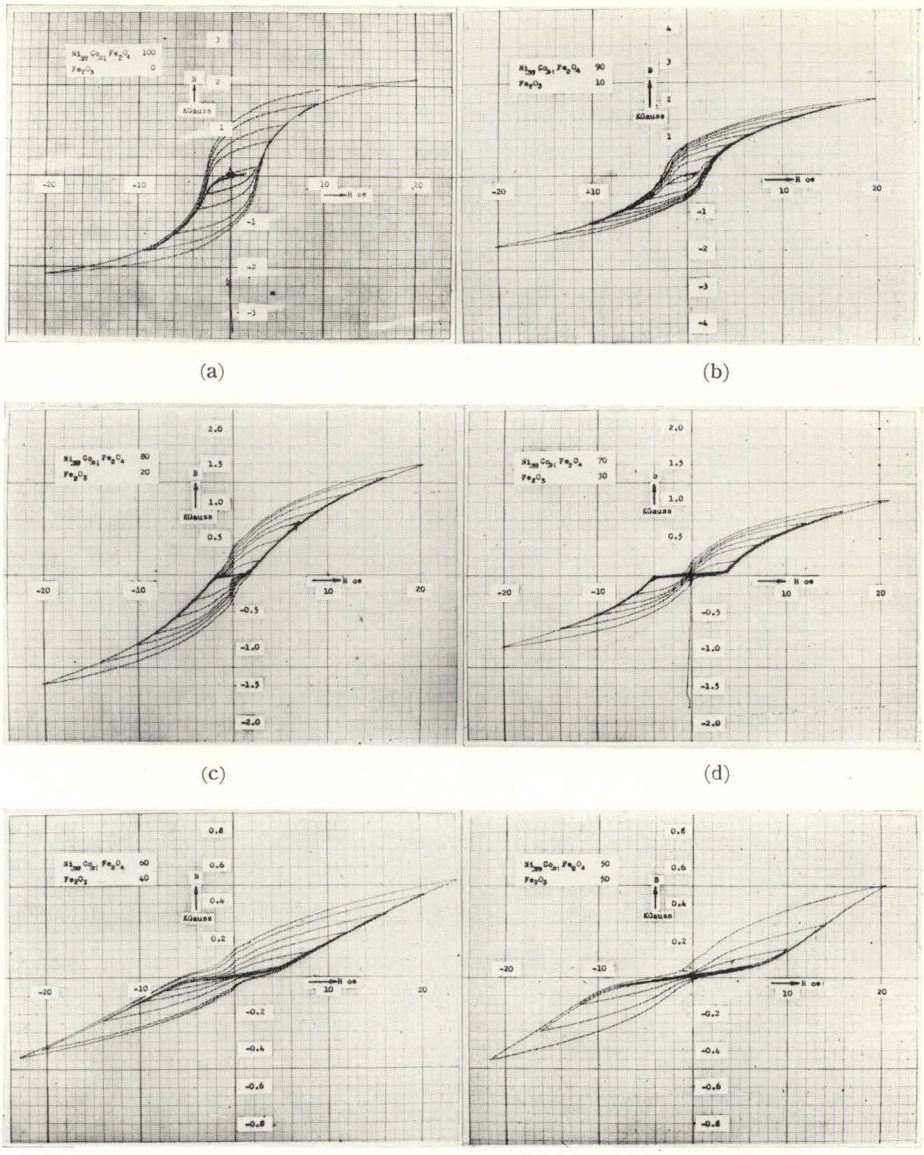
[{111} ferrite//{0001} hematite,
⟨110⟩ ferrite//⟨$10\bar{1}0$⟩ hematite.]

In addition to such an epitaxial exolution, it was found in this research that spherical particles of hematite exolute in case of excess Fe_2O_3 content. If BeO is contained in the system, the 3rd phase may be observed even when its content is rather small.

The variation of electric resistance with Fe_2O_3 content, shown in Fig. 3, is explained as follows: under the firing condition in this experiment, Fe_2O_3 dissolves in $NiFe_2O_4$ at 1400°C but the specimen exolutes magnetite in cooling stage. As a result, the electric resistance of specimen is lowered. With the increase of Fe_2O_3 content, hematite begins to exolute at first epitaxially, and then unepitaxial on {111} plane of $NiFe_2O_4$ (Fig. 4). It results in the steep rise in the electric resistance. The result obtained from x-ray diffraction data does not contradict with this behavior (Fig. 5).

The outbreak of the constricted hysteresis loop does not appear in the region where CoO content is less than 0.01 mol%. Maximum *B* in perminvar region is 100–200 gauss in each specimen. The curvature of *B-H* loops at rising point from perminvar region depends on the composition. If Fe_2O_3 content is about 30 mol% and CoO content is 0.4 mol%, it is

* $BeO \cdot Fe_2O_3$ means an equimol mixture, not compound.

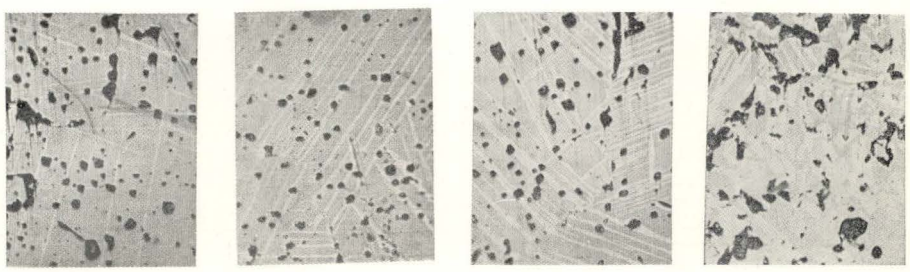


(a) (b)

(c) (d)

(e) (f)

Fig. 1. Constricted hysteresis loops of $Ni_{0.99}Co_{0.01}Fe_2O_4$—$Fe_2O_3$ system. Fe_2O_3 contents are (a) 0 mol%, (b) 10 mol%, (c) 20 mol%, (d) 30 mol%, (e) 40 mol%, (f) 50 mol%.



(a) (b) (c) (d)

Fig. 2. Photomicrographs of $Ni_{0.99}Co_{0.01}Fe_2O_4$—$Fe_2O_3$ system. Fe_2O_3 contents are (a) 20 mol%, (b) 30 mol%, (c) 40 mol%, (d) 50 mol%.

convex, but if CoO content is increased to 1 mol% it changes to concave. When CoO/NiO is kept in 1/99, the specimen changing its curvature from convex to concave has so much Fe_2O_3 content as Fe_2O_3 which must be exoluted unepitaxially in its texture. It is observed that the existence of BeO makes the curvature concave even in the case of small content of Fe_2O_3 (Fig. 6)

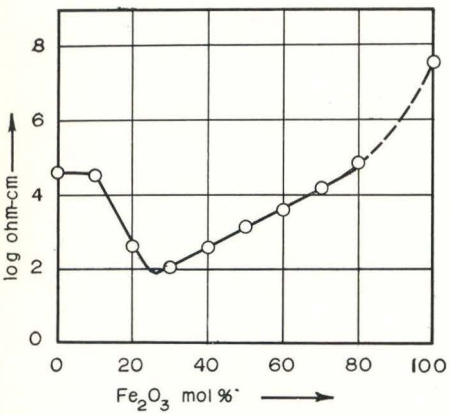


Fig. 3. log ρ *vs* Fe_2O_3 content.

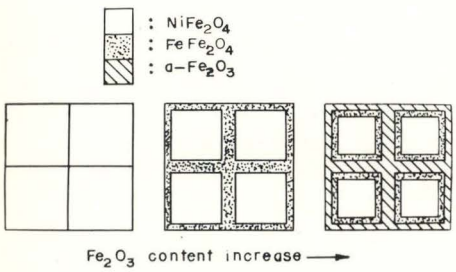


Fig. 4. Schematic diagram of electric resistance for variation of Fe_2O_3 contents.

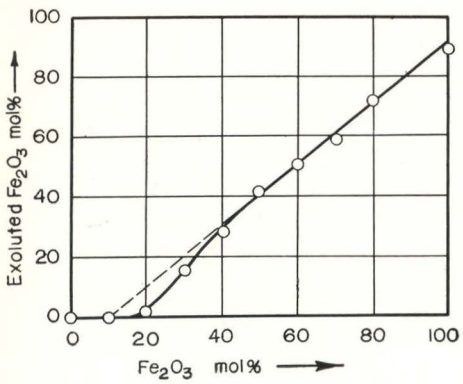
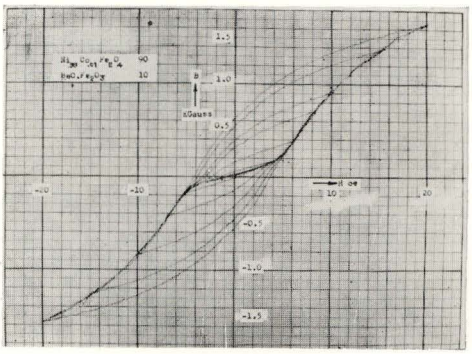
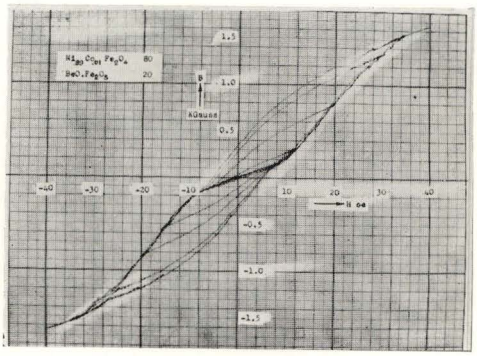


Fig. 5. Exoluted Fe_2O_3 *vs* total Fe_2O_3 content determined by x-ray diffraction method.

The above mentioned experiment may be explained by the assumption that CoO would be dissolved into magnetite (a_0=8.40Å) rather than in $NiFe_2O_4$ (a_0=8.34Å). If this is proved true, reversible magnetization process



(a)



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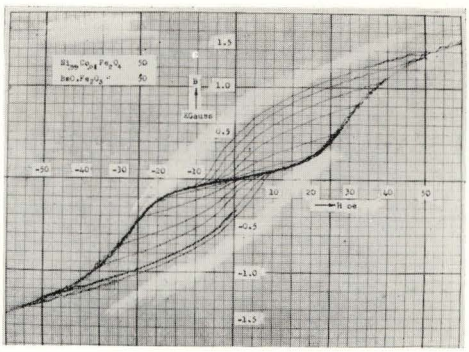

(c)

Fig. 6. Constricted hysteresis loops of $Ni_{0.99}Co_{0.01}Fe_2O_4$—$BeOFe_2O_3$ system. $BeOFe_2O_3$ contents are (a) 10 mol%, (b) 20 mol%, (c) 30 mol%.

occurs, because some magnetic hard material which is precipitated parallel to the {111} plane of $NiFe_2O_4$ hinders the magnetic domains from their free displacement and rotation in $NiFe_2O_4$. Then the domain movement becomes irreversible when the magnetic field strength is exceeded over H_c of the material, and finally the bulk reaches saturation. Thermal treatment only makes the specimen bring its virgin state, rather than initial state.

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Domain Structure and Magnetic Properties of Mn_5Ge_3

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Domain structure in the intermetallic compound Mn_5Ge_3 was investigated by the method of powder patterns, and the coercivity and anisotropy of this alloy were measured.

The surface of Mn_5Ge_3 samples (crystallographic type $D8_8$)[1], was carefully polished mechanically; on spreading a magnetic suspension thereon[2], powder patterns could be observed microscopically. Identical ones were observed on non-polished small crystals. This shows that mechanical processing introduces no deformations appreciably affecting the patterns.

Fig. 1 shows patterns on a surface approximately parallel to the esay axis (denoted by ***e***), whence intentionally not all scratches had been removed in order to gain insight into the changes in concentration of the colloid grains as dependent on the external magnetic field ***H***. Photo (a) is at $\boldsymbol{H}=0$. ***H*** applied parallel to ***e*** gives rise to a pattern of alternately lighter and darker areas. Reversion of ***H*** by 180° causes the darker areas to become light, and inversely. Thus, the direction of magnetisation of a single domain can be determined in a simple manner. The ***H*** values were insufficient here for producing a noticeable broadening of the one domains and narrowing of the remaining ones.

Reduction of the intense scattered fields on the surface perpendicular to ***e*** occurs through formation of dagger-like sub-domains reaching into the bulk of the basic domains. The cross sections (perpendicular to ***e***) of the Bloch walls of these sub-domains form chains of single small circles (Fig. 2a) or of wreaths of circles (Figs. 2b and 3), according to the basic domain width. At very small thickness of the crystal dagger-like domains no longer arise.

Experimentally, the basic domains can be inferred to have the shape of plates (Fig. 4a)