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To cite this version:

HAL Id: jpa-00217030
https://hal.archives-ouvertes.fr/jpa-00217030
Submitted on 1 Jan 1977

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ANISOTROPY OF COBALT-ADSORBED \(\gamma Fe_2O_3\) PARTICLES

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Résumé. — Les particules aciculaires monocristallines de \(\gamma Fe_2O_3\) traitées à l’hdroxide de cobalt (particules de type cobalt-adsorbé) présentent des propriétés magnétiques plus stables que les particules classiques dopées au cobalt. Leur faible variation thermique du champ coercitif et leurs caractéristiques uniaxiales stables sont comparables à celles des particules de \(\gamma Fe_2O_3\). L’anisotropie effective accompagnant l’accroissement de la coercivité du type de particule cobalt-adsorbé est produite à la surface de la particule, où Co\(^{2+}\) se concentre dans presque une couche adsorbée. On estime que l’anisotropie \(K_u^*\) est de l’ordre d’environ \(10^6\) ergs/cm\(^3\).

Abstract. — Acicular single domain particles of \(\gamma Fe_2O_3\), treated with cobalt hydroxide (cobalt-adsorbed type) have more stable magnetic properties than ordinary cobalt-doped particles of \(\gamma Fe_2O_3\). Their small temperature dependence of coercive force and stable uniaxial characteristic are comparable with those of particles of \(\gamma Fe_2O_3\). The effective anisotropy in increasing coercivity of this adsorbed type is produced at the surface of the particle, in which Co\(^{2+}\) is concentrated with nearly one adsorbed layer. This anisotropy \(K_u^*\) is approximately estimated to be in the order of \(10^6\) erg/cm\(^3\).

1. Introduction. — A newly developed magnetic iron oxide particle for magnetic recording use (cobalt-adsorbed type) is made of an acicular particle of \(\gamma Fe_2O_3\) treated with cobalt hydroxide, and is characterized by the following magnetic properties such as higher coercitivity than that of an ordinary particle of \(\gamma Fe_2O_3\), small temperature dependence of coercive force and stable uniaxial characteristic of the particle.

These magnetic features which are not found all together in a cobalt-doped particle of \(\gamma Fe_2O_3\), are supposed to be due to the surface anisotropy originated from the cobalt concentrated at the surface of the particle.

Some chemical observations on this adsorbed type lead us to look into the state of the adsorption of cobalt and to estimate the magnitude of the anisotropy of this adsorbed cobalt.

2. Preparation and magnetic properties of the particle. — The adsorbed type particles were prepared in the following way. Acicular particles of \(\gamma Fe_2O_3\) which contained different amounts of cobalt hydroxide by an adsorption were dispersed in NaOH solution and heated to boiling. The average size of the starting \(\gamma Fe_2O_3\) was 0.46 \(\mu\)m in length and 0.05 \(\mu\)m in width.

In figure 1, boiling effect is shown. The coercive force increases rapidly before the temperature reaches to boiling and nearly levels off with continued boiling.

The magnetic properties were measured with a vibrating sample magnetometer in fields of 5 kOe on a sample of randomly assembled particles.

As a function of cobalt content (Fig. 2), the coercive force of the particles boiled for an hour, levels off at nearly more than 2 % cobalt of the weight of the particles, while the saturation magnetization decreases with increasing cobalt content as the same slope as that of a calculated curve of a mixture of \(\gamma Fe_2O_3\) and Co(OH)\(_2\) at more than 2 wt % cobalt. From above results, the excess cobalt seems to exist in a particle as cobalt hydroxide in the range of more than 2 wt % cobalt.
3. Chemical treatment. — Each sample in figure 2 (No. 1 ~ No. 4), was treated with a large amount of HCl solution of different pH 0 ~ 7 for 30 minutes at room temperature and the amounts of dissolved ions are plotted against pH as shown in figure 3, in which coercive force of the HCl treated particles are also shown.

In the case of pH ≈ 0, small amounts of cobalt (0.5 ~ 1 wt % of the particles) still remain in each sample. Since these remained cobalts have no effect on the coercivity, most of them may possibly exist in cavities or in sub-boundaries penetrating from the surface. A maximum depth of the penetration is estimated about 40 Å from the surface, from the fact that about 30 wt % iron of total iron was necessary to dissolve to remove all cobalt from the particle.

On the other hand, at pH higher than 4, coercive force does not change and the pH at which coercive force begins to decrease, shifts to lower value with an increase of the attached cobalt hydroxide in the sample as in the case of No 4, since the cobalt hydroxide preferentially dissolves at first.

Thus, from the above observations, it is roughly estimated that the maximum amount of the really effective Co$^{2+}$ contributed to the coercivity at the surface is a little more than 1 wt %.

4. State of Co$^{2+}$ Adsorption. — The authors tried to look into the state of the adsorption. As well known, an acicular particle of γFe$_2$O$_3$ obtained from an acicular FeOOH by a topotactical reaction [2], is composed of many crystallites of γFe$_2$O$_3$, which are oriented to the same direction. Most of the surfaces of these crystallites are considered to be fabricated with (111) plane because of its high atomic density. That is, the surface of the whole particle consists of (111) planes in which O$^{2-}$ is in a close-packed array. When Co$^{2+}$ ions are adsorbed to such surface, they would occupy the B site of lattice point due to their preference for octahedral site. From the stacking sequence of spinel lattice to $<111>$ direction, there are two arrangements of B site on (111) plane, as shown in figure 4. In a case (1), an area per one B site is about 10 Å$^2$, while in a case (b), it is about 30 Å$^2$. Thus, an average area corresponded to one Co$^{2+}$ is estimated to be about 20 Å$^2$, assuming that the chances of appearance of both cases are equal and all B sites are occupied by only Co$^{2+}$ with one layer.
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As the surface area of the particle is measured to be $18 \text{ m}^2/\text{g}$ by BET method, the wt % of Co$^{2+}$ needed to cover the entire surface of the particle with one adsorption layer is calculated as

$$\frac{18 \times 10^4}{20 \times (10^{-9})^2} \times \frac{58.9}{6 \times 10^{23}} \times 100 \approx 1 \text{ (wt %)}.$$  

This result is in a fairly good agreement with our observation. Therefore, the surface of the particle is considered to be covered with one Co$^{2+}$ adsorbed layer as a mean, which plays an important role for the increase of the coercive force in the Co$^{2+}$ adsorbed particle.

5. Anisotropy. — In figure 5, magnetic torques of the adsorbed type particles (No. 3 in Fig. 3) which are coated on a tape oriented along the long axis of the particle, are shown as a function of an angle from the oriented direction of the particles. The observed curves in the form of $\sin 2\theta$ function show an uniaxial characteristic of an anisotropy with easy direction parallel to the alignment of the particles. Thus, the anisotropy produced at the surface is thought to be superposed on the shape anisotropy of the particle by the exchange interaction.

From the electron configuration of Co$^{2+}$, if it occupies on B site at the surface as assumed before, a large surface anisotropy may be produced. If the coercive force of $\gamma$Fe$_2$O$_3$ of randomly assembled particles is assumed approximately equal to $Ku/Is$, where $Ku$ and $Is$ are the shape anisotropy and the saturation magnetization of the particles respectively, the surface anisotropy ($Ku^*$) is estimated from the relation,

$$H^*_c \approx \frac{Ku^* x + Ku(1 - x)}{Is},$$

where $H^*_c$ and $x$ are the coercive force of the adsorbed type particles and a volume ratio of Co$^{2+}$ adsorbed layer. If we put $Ku/Is = 425 \text{ Oe}$, $H^*_c = 525 \text{ Oe}$, $Is = 400 \text{ G}$ and $x = 0.03$, $Ku^*$ is calculated as $1.5 \times 10^6 \text{ erg/cm}^3$ which is the same order of magnitude as the cubic crystalline anisotropy of $K_1$ of Co$^{2+}$ in the spinel ferrite.

6. Comparison between adsorbed type and doped type. — Particles of an adsorbed type (No. 3 in Fig. 2) were annealed at temperatures of 300 $^\circ\text{C}$ and 400 $^\circ\text{C}$ in air for an hour. Since cobalt concentrated at the surface diffuses into the inner part of the particles by the annealing, surface anisotropy disappears and cubic crystalline anisotropy increases. The resultant differences between before and after annealing appear remarkably in their temperature dependences of coercive force and of squareness ratio, as shown in figure 6.

In the case of not-annealed sample, that is the adsorbed type, temperature dependences of both coercive force and squareness ratio are almost comparable with those of $\gamma$Fe$_2$O$_3$. In contrast, in the annealed samples
at 300 °C and 400 °C, the pronounced temperature dependences appear. These strong temperature dependences are due to a cubic crystalline anisotropy and are the typical characteristics found in cobalt-doped \( \gamma Fe_2O_3 \) [3].

Thus, it has been made clear that the adsorbed type changes gradually to the cobalt-doped type by such annealing.

Acknowledgments. — The authors wish to express their sincere thanks to Professor T. Takei for his valuable suggestion and discussion throughout this work and for his helpful comment and review of the manuscript, to Professor Y. Hoshino for his continuous encouragement, to Professor S. Iida for his helpful suggestion concerning theoretical aspects and to Doctor T. Hiraga for his support of this work.

References