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METAL-OXIDES COMPOSITES FOR $\text{BaFe}_{12}\text{O}_{19}$ PERMANENT MAGNETS

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Résumé. — Des composés métal-ferrite pour aimants permanents ont été obtenus par traitement chimique en solution aqueuse. Une attention particulière a été apportée à la caractérisation des couches minces de cobalt ainsi déposées. Des effets intéressants ont été relevés en étudiant le comportement magnétique des poudres après dépôt. On a mis ainsi en évidence la possibilité d'obtenir des produits frittés présentant un bon compromis entre les valeurs des différentes propriétés magnétiques et mécaniques.

Abstract. — Metal-ferrite composites for permanent magnets have been obtained by chemical treatment in aqueous solutions. Special care has been given to the structural characterization of cobalt films deposited. Interesting effects have been revealed by studying the magnetic behaviour of as-plated powders. The possibility of realizing sintered products with a good compromise between mechanical and magnetic properties is pointed out.

1. Introduction. — Ceramic permanent magnets based on $\text{BaFe}_{12}\text{O}_{19}$ are widely used because of their high coercivity and low cost. They are also very stable and have high electrical resistivity. Ba ferrite powders are also utilized for making plastic magnets by imbedding them in rubber. Metal-ferrite composites have been studied with the aim of improving the mechanical properties of the magnets, their reliability, shrinkage control and orientation in a magnetic field. We have examined the magnetic properties of powders and sintered products, pointing out the influence of the coupling of $\text{BaFe}_{12}\text{O}_{19}$ or $\text{SrFe}_{12}\text{O}_{19}$ with a nonmagnetic metal, such as Cu or Ni-P, or with a hard magnetic metal, such as Co-P or Co-Ni-P.

The composite powder has been obtained by chemical treatment. By these methods it is possible to avoid wetting problems [1], because of the close contact between the metal and the ferrite. Experiments with slurry electrodes [2] have shown the possibility of producing composites of Ba ferrite with various metals such as cobalt, nickel, iron, copper and zinc by electrodeposition. Chemical reduction with hypophosphite gives uniform deposits and is easily carried out, because no special equipment is needed. With this method it is possible to obtain well resolved structures of different preferred orientation. Figure 1 shows the different aspects of a Co deposit with preferential orientation obtained by chemical reduction and electrodeposition.

2. Co-P and Co-Ni-P films. — We have studied with particular care the coupling of ferrites with hard

magnetic films of chemically reduced Co-P and Co-Ni-P films. The magnetic properties of these films are influenced by thickness, morphology, crystallographic structure and chemical composition (P and Ni content) [3, 4]. Changing the operation parameters permits us to obtain different preferential orientations (p. o.) Well-textured deposits are obtained with the baths given in table I. Hydrolysis phenomena have been shown to have a determining influence on chemical plating [5, 6] and the structures obtained [7]. The development of the structure during the deposition has been the object of a careful study, and growth twinning along $\{10.1\}$ rhombohedral planes has been shown to occur due to stacking faults at a certain thickness in deposits from bath A and B [8, 9]. Figure 1b and 1c show the typical morphology of deposits from these baths.

The magnetic characteristics of the films deposited onto mylar have been studied with a vibrating sample magnetometer. Deposits from bath A have a high coercivity, 0.9 to 1 kOe, and a low B_r/B_s ratio, 0.4, whilst those from bath B have a lower coercivity, 0.7 to 0.8 kOe, and a higher B_r/B_s ratio, 0.5, although in any case low with respect to the films commonly employed for information storage. Nickel addition to the bath gives deposits of high coercivity but lower saturation magnetization. Nickel addition decreases the thickness at which twinning takes place. When nickel becomes the main constituent of the alloy, deposits are amorphous and have soft magnetic behaviour. The structure of the film is responsible for an effective reduction, by a factor 0.6 of the demagnetizing field $H_d = 4\pi I$,

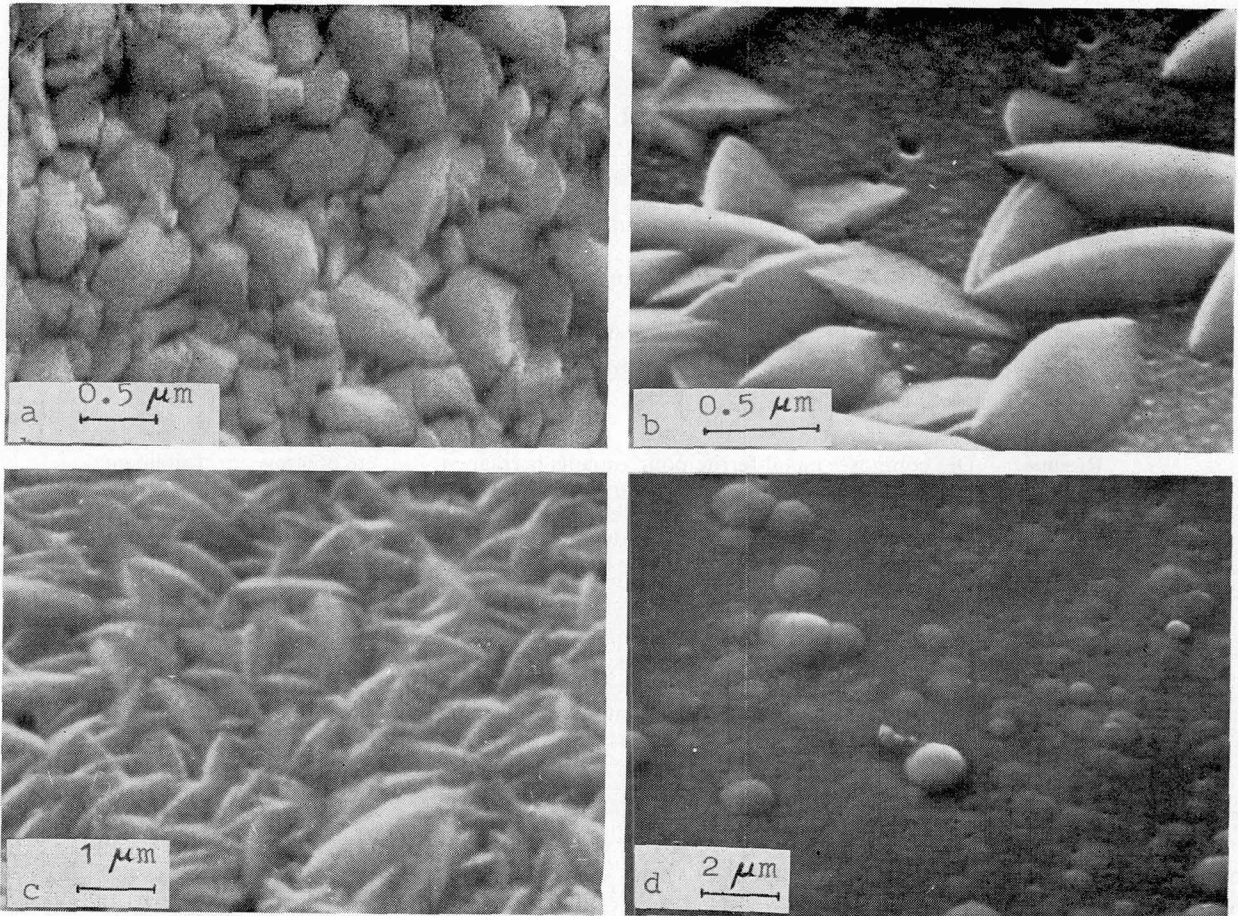


FIG. 1. — SEM micrographs of deposits on (111) Ni single crystals : a) Co, electrodeposit, 1.5 μm ; b) Co-P, chemical bath A, 1 μm ; c) Co-P, chemical bath B, 0.8 μm ; d) Co-Ni-P, chemical deposit, $Co^{2+}/Ni^{2+} = 2.14$ μm.

TABLE I

BATH	A	B	C
CoSo ₄ (+ NiSO ₄)	0.3 M	0.3 M	0.3 M
Ammonium citrate or tartrate	0.3 M	0.3 M	0.3 M
Glycine	0.3 M	0.3 M	0.3 M
Sodium hypophosphite	1.2 M	0.6 M	0.4 M
pH (at 25 °C with NaOH)	10.5	10.5	11.5
T(°C)	80	80	80
p. o.	<11.0>	<10.0>	<00.1>
Deposition rate (mg/cm ² .h)	12.5	10.7	10
P content (% by weight)	4.8	4.2	2.0

in direction perpendicular to the film plane, whilst high local demagnetizing effects are observed when magnetizing in the film plane ; this explains why the same H_c is observed in both directions.

3. Magnetic characteristics of the treated powders. — The powders were chemically plated after a sensitiza-

tion-activation treatment with SnCl₄-SnCl₂-PdCl₂ solutions. For details on the operation procedure and on the characteristics of the powder see [10]. Table II reports characteristic magnetic properties of some treated powders. The B_r/B_s ratio was always a little

TABLE II

Starting powder	Chemical treatment (t)	σ_s at 20 kOe (emu/g)	μH_c (kOe)
BaFe ₁₂ O ₁₉	—	66.4	4.34
BaFe ₁₂ O ₁₉	Ni-P(0.5')	65.2	4.47
BaFe ₁₂ O ₁₉	Co-P(A ; 1') + Cu(1')	65.0	4.27
BaFe ₁₂ O ₁₉	Co-P(A ; 1') + Ni-P(1')	67.3	4.53
SrFe ₁₂ O ₁₉	—	65.1	5.35
SrFe ₁₂ O ₁₉	Ni-P(0.5')	61.8	5.55
BaFe ₁₂ O ₁₉	Co-P(B ; 0.5') + Cu(1')	64.0	4.40
BaFe ₁₂ O ₁₉	Gr (*)+Co-P(A ; 5')(**)	66.2	3.79
BaFe ₁₂ O ₁₉	Gr(*)+Co-P(B ; 0.5')(**)	67.4	3.69
BaFe ₁₂ O ₁₉	Gr(*)+Co-P(C ; 0.5')(**)	67.1	3.65
BaFe ₁₂ O ₁₉	Co-Ni-P(A ; Co/Ni 2 ; 1') + Ni-P(0.5')	65.0	4.47
BaFe ₁₂ O ₁₉	Co-Ni-P(B ; Co/Ni 2 ; 1') + Ni + P(0.5')	61.9	4.50

(1) Numbers in parenthesis refer to the time in minutes.
 (*) Gr = Ground for 3 h in SnCl₄ solution with a ball mill
 (**) Tartrate bath.

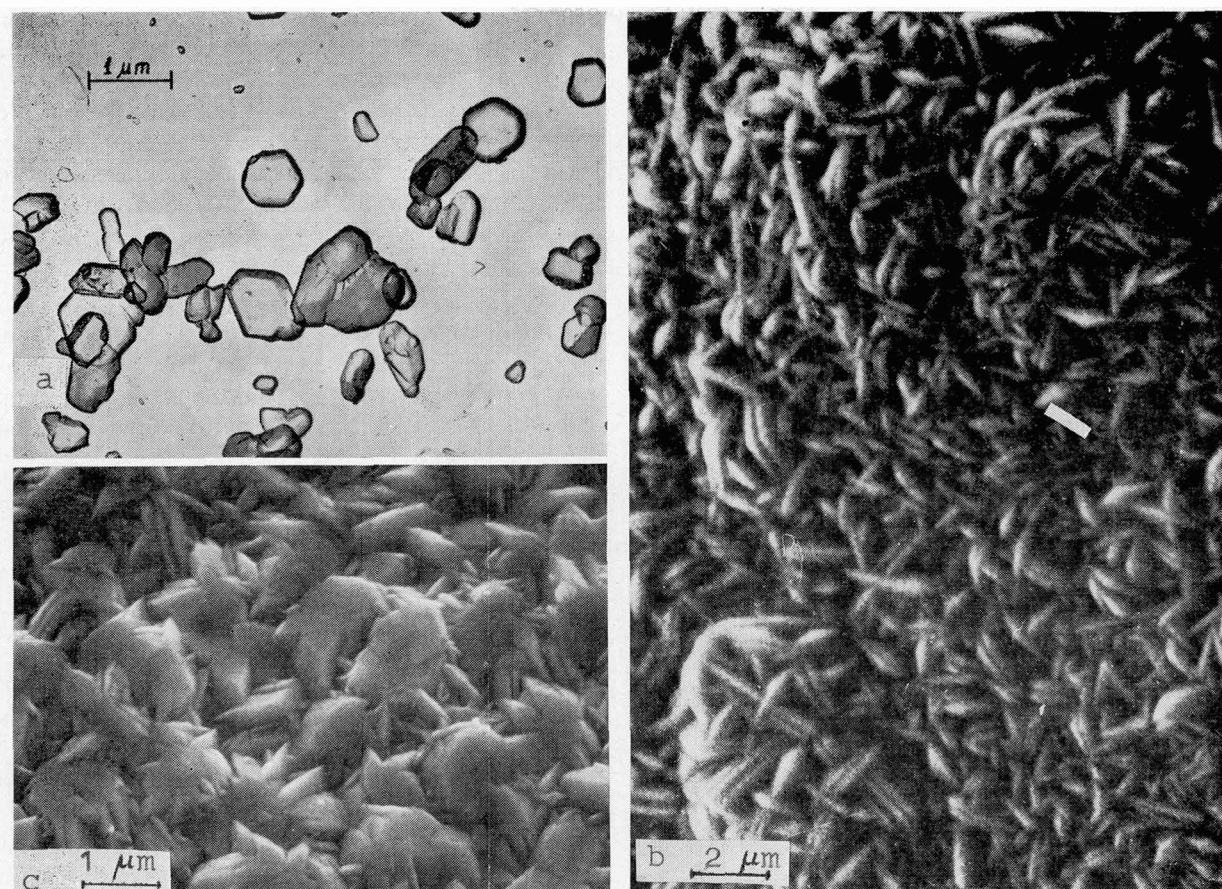


FIG. 2. — Micrographs of $\text{BaFe}_{12}\text{O}_{19}$ plated with CoP: *a*) TEM of a powder, bath A, 1'; *b*) SEM on a (00.1) face, bath A, 20'; *c*) SEM on a (00.1) face; bath B, 20'.

less than 0.5, except for the grinded powders where it was 0.5. Figure 2 gives some micrographs of the treated powder and of Co-P deposits on (00.1) faces of $\text{BaFe}_{12}\text{O}_{19}$ single crystals, where the influence of the bath composition on the deposit morphology is shown.

Powder plated in bath A had greater saturation magnetization than those deposited in bath B and C, although always lower than expected, if we assume that the CoP deposit has to contribute with a

$\sigma_s \approx 130$ emu/g. A negative effect is probably due to partial Co-oxidation and reduction of ferrite by the action of phosphorus. The presence of Ni either by codeposition or subsequent plating seems to cause a slight increase in coercive force.

4. **Sintered products.** — Some preliminary experiments have been made by compaction and sintering of the powders. These experiments have shown a great

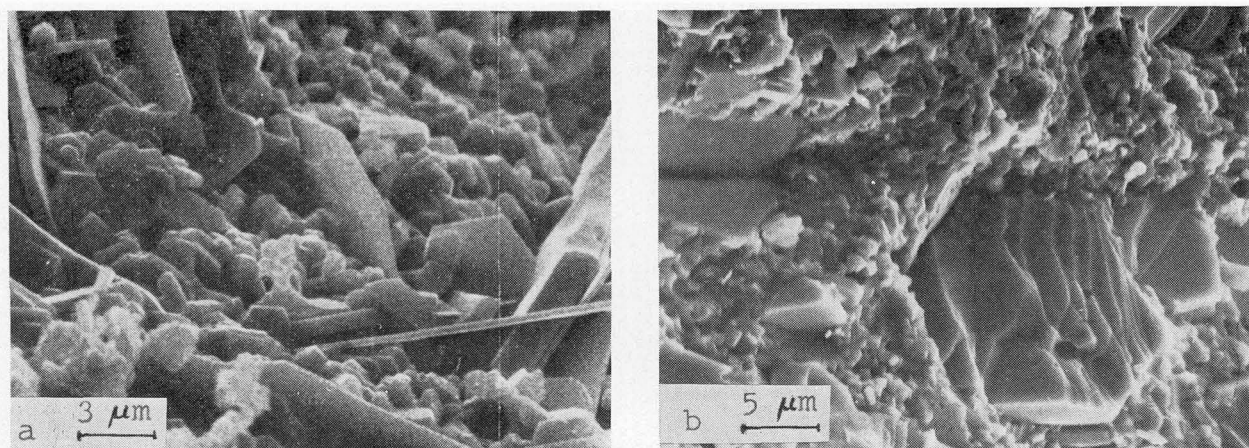
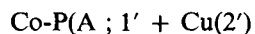


FIG. 3. — SEM micrographs of fracture surfaces of sintered composites. *a*) Co-Ni-P, 30'; $T_{\text{sin}} = 1\,200$ °C, 30'; *b*) Co-Ni-P, 1'; $T_{\text{sint}} = 1\,250$ °C, 30'.

deal of recrystallization at 1250 °C with a neat decrease of the magnetic properties ($JH_C = 1.35$ kOe, $B_r = 1.4$ kG); great platelets are formed (see Fig. 3). At 1200 °C the mechanical properties of the sintered specimens becomes noticeable. To increase the mechanical properties without decreasing the magnetic ones we have made some hot pressed specimens at 900 °C with a pressure of 45 kg/cm². Already at this temperature a certain sintering and shrinkage of the powder is observed without losing the magnetic properties. A sample from powder treated with



where the numbers in parenthesis refer to the time in minutes of the chemical treatment and hot pressed at

850 °C exhibits relatively high magnetization and coercive field ($\sigma_s = 68$ emu/g, $H_C = 3950$). This is the case where we observe the lowest decrease of H_C moving from the powder to the compact. The effect of copper is here probably to maintain a good separation between particles while allowing the dispersion of surface charges at the twinned structure of the Co film, which is capable, as we have seen before, of reducing the local demagnetizing field.

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References

- [1] PASSERONE, A., BIAGINI, E., LORENZELLI, V., *Ceramurgia Int.* **1** (1975) 23.
- [2] CAVALLOTTI, P., DUCATI, V., ROBERTI, R., *Ceramurgia* **6** (1976) 17.
- [3] MORRAL, F. R., *Plating*, **60** (1972) 131.
- [4] SAFRANCK, W. H., *The Properties of Electrodeposited Metals and Alloys*, Elsevier N. Y. (1974) Ch. 21.
- [5] CAVALLOTTI, P., SALVAGO, G., *Eelectrochim. Met.* **3** (1968) 329.
- [6] SALVAGO, G., CAVALLOTTI, P., *Plating* **60** (1972) 665.
- [7] CAVALLOTTI, P., SALVAGO, E., *Electrochem.* **116** (1969) 819.
- [8] CAVALLOTTI, P., NOER, S. J., *Mater. Sci* **11** (1976) 645.
- [9] CAVALLOTTI, P., NOER, S., CAIRONI, G., *J. Mater. Sci.* **11** (1976) 1.
- [10] ASTI, G., CAVALLOTTI, P., ROBERTI, P., *Ceramurgia Int.* (in press).