

Technical Report

TR 44.0010
January 4, 1967

IBM Systems Development Division, Boulder Laboratory

MAGNETIC RECORDING
MATERIALS

D. E. SPELIOTIS

BY

D. E. SPELIOTIS

ABSTRACT

The increasing demand for higher storage capacity in magnetic recording media has led to an intensive examination of magnetically hard particles and films, in a search for better magnetic properties and improved storage capabilities than those offered by the traditional particulate dispersions of $\gamma\text{-Fe}_2\text{O}_3$ micropowders.

In this paper, we discuss the effect of the magnetic properties and of the thickness of recording surfaces in high resolution recording applications, and specify design criteria for their optimization.

The properties and the origin of magnetic hardness in oxide and metallic particles and in metallic films are discussed, and their high recording resolution behavior is compared. It is concluded that the greatest potential in particulate coatings is offered by single-domain ferromagnetic metallic particles, while ultimate recording optimization can be achieved in thin metallic surfaces.

LIMITED DISTRIBUTION NOTICE

Paper presented at the ~~Symposium on Plating in the~~ *Magnetics Conference, Washington, D.C.*
~~Electronics Industry sponsored by the American~~
~~Electroplaters Society, December 8-9, 1966. It will~~
~~be published in the Plating journal sponsored by~~
~~A. E. S. Do not disseminate outside IBM until after~~
~~January 1, 1967.~~

INTRODUCTION

Technological advances have created an ever-increasing demand on the information storage capacity of magnetic recording systems and have generated much interest in the characterization and fabrication of optimized magnetic recording materials.

In this paper we discuss the fundamental characteristics of the digital magnetic recording process and the role that the magnetic properties and the thickness of recording media play in the resolution and signal amplitude of recording systems. We are thus led to design criteria for magnetic recording materials which define the direction to optimize their recording performance. Only passing mention is made of the physical characteristics - surface smoothness, flexibility, uniformity, wear, corrosion, etc. of the recording media.

The methods of fabrication, and the effect of the preparation conditions on the ensuing magnetic properties are discussed for magnetically hard oxide and metallic particles and for metallic thin films. Finally, the recording characteristics of the various magnetic recording materials are compared and summarized, and conclusions drawn on their potential for high density storage applications.

THE RECORDING PROCESS

In digital magnetic recording, a bit is defined by a change in the state of magnetization of the recording surface. Such magnetization transitions are introduced by the trailing edge of the writing transducer field, and their gradient $(\frac{dI}{dx})$, where x is in the direction of motion of the recording surface, is primarily determined by the gradient of the writing transducer field $(\frac{dH}{dx})$, and the slope of the hysteresis loop of the recording surface $(\frac{dI}{dH})$. After the surface has moved away from the recording transducer, it has a tendency to demagnetize irreversibly, particularly in the vicinity of the written transition region where the demagnetizing fields can be very large. Consequently, a new, wider magnetization transition results, whose characteristics (specifically the gradient of the magnetization, $\Delta \cdot \vec{I}$) are controlled primarily by the magnetic properties and the thickness of the recording surface; the writing process which determines the initial transition region has only a very minor effect on the extent of the transition region that results after demagnetization has taken its toll.¹ However, the writing process determines the gradient of the magnetization about the center of the transition region which is unaffected by demagnetization, since both the magnetization and the demagnetizing field go through zero at the center of the transition region with odd symmetry. During readback, additional losses are introduced by the read transducer and medium-to-transducer spacing.

Consequently, the width and amplitude of the readback pulse are in general and to a first order a function of the magnetic parameters and the thickness of the recording medium which determine the magnetization transition region, the medium-to-transducer spacing including the effective spacing introduced by the further away portions of thick media, and the characteristics of the read transducer. In general, any one of these parameters can dominate the readback pulse characteristics, depending on their relative magnitudes.

RECORDING SURFACE DESIGN CRITERIA

The resultant magnetization transition region in a recording surface is primarily determined by demagnetization effects. Consequently, it is characterized by a ratio of the form:

$$I_r \delta / H_c^n$$

where I_r is the remanent magnetic dipole moment per unit volume, H_c is the coercivity, and δ is the thickness of the recording surface. The exponent n depends on the I_r/H_c ratio of the material, having a value of approximately 1/2 for small I_r/H_c ratios, and increasing gradually to 1 for large I_r/H_c ratios.

The correlation between the magnetic properties and the recording performance of magnetic recording surfaces is a subject of very active and current interest.²⁻⁵ Our findings,⁶ based on an experimental investigation of the recording characteristics of a large number of thin metallic surfaces with widely different magnetic properties and thicknesses, lead us to the following conclusions regarding the width and amplitude of a pulse read back from an isolated magnetization transition:

$$\text{half pulse width} \propto [\delta / H_c]^{1/2} \quad (1)$$

and

$$\text{pulse amplitude} \propto [\delta I_r H_c]^{1/2} \quad (2)$$

Whereas these relationships were established for thin (up to 1μ) metallic surfaces, there are experimental indications that they are approximately valid for thicker particulate surfaces as well.⁶ The striking fact in these relationships is the absence of the remanent magnetization from relationship (1), which defines the resolution of a recording surface.

The approach to specifying the parameters of recording media for high density applications is clearly indicated by the above relationships:

- a) Increase the coercivity of the recording surface to a maximum

value, consistent with the field capabilities of the writing transducer (somewhere in the vicinity of 600-800 oersteds for contact recording with conventional metal lamination transducers). Any advantages that might be gained by using coercivities higher than 600-800 oersteds, are usually offset by the deterioration of the writing transducer field gradient due to the large write currents. This limitation, however, can be essentially removed by using high saturation magnetic moment laminations in the writing transducer. The optimum value of the coercivity also depends to some degree on the thickness of the recording surface - - it is larger for thinner surfaces. Increasing the coercivity of the recording surface should increase both its signal output and its resolution, according to relationships (1) and (2).

- b) Increase the remanent magnetization of the recording surface to the maximum possible value, which should result in an increase in output without any appreciable deterioration in resolution, particularly for thin recording surfaces.
- c) Decrease the thickness of the recording surface to the minimum possible value, consistent with acceptable output signal, good surface finish, uniformity of coating, and good wear characteristics. The thickness of the recording surface adversely affects its resolution in two primary roles. First, it enters in the demagnetizing factor and broadens the magnetization transition region. This effect is the one mainly reflected in relationship (1), which was established for thin metallic surfaces. In addition to its effect on demagnetization, the thickness plays another very important role in the readback process by introducing an effective spacing between the transducer and the medium, which again adversely affects the resolution. If we consider the recording medium to consist of a number of thin layers parallel to its surface, then we can superpose the contribution of each layer to obtain the total readback pulse. It is then evident that the contributions of the layers further away from the read transducer will be smaller in amplitude and broader in width. This effect becomes the more important with increasing thicknesses. Of the three primary properties of a recording surface - - coercivity, remanence, and thickness - - it is the thickness which allows for true optimization for any given application since it adversely affects the resolution, while it beneficially affects the low density output. However, it is our belief that digital recording surfaces of today, as well as those of the foreseeable future, are primarily limited by resolution and not by output. If this is correct, it would seem that one should strive for the thinnest possible recording surface, while relying on optimized coercivity and remanence to assure acceptable signal output.

In addition, it would appear desirable to strive for high squareness

(I_r/I_s) and steep sided hysteresis loop, but the desirability of magnetic anisotropy in the plane of the recording surface is not apparent. Furthermore, magnetic hardness perpendicular to the recording surface would be desirable in that it eliminates the pulse assymetries introduced by the vertical component of surface magnetization, and this can be achieved by very thin media and by orienting the easy crystallographic or shape axes of the particles or crystallites in the plane of the recording surface.

PARTICULATE MEDIA

Magnetic hardness has been sought and realized in small (sub-micron) particles which exist as ferromagnetic single domains, because the presence of domain walls is energetically unfavorable. Magnetization reversal then proceeds by rotational processes, and magnetic hardness arises from the various anisotropies, which set up very effective energy barriers that must be overcome by the field supplying the energy for reversal. The most common anisotropies present in small particles are crystalline, shape, strain, and exchange, which may be characterized by an anisotropy constant K , resulting in an anisotropy field $H_a \sim K/I_s$.

Predominant among these are the crystalline and shape anisotropies, with respective fields of $H_a \sim K_1/I_s$ and $H_a \sim (N_b - N_a)I_s$, where K_1 is the crystalline anisotropy constant, and N_a, N_b are respectively the long and short axis demagnetizing factors of a prolate spheroid.⁷⁻⁹ The coercivity values that are predicted for coherent magnetization reversals in the presence of these anisotropies are almost invariably too large, because incoherent modes of reversal are in many instances energetically more favorable.

The single domain particle size range is bounded on the upper end by multi-domain, and on the lower end by superparamagnetic behavior, both of which would tend to drastically decrease the coercivity of an assembly of particles with size distribution extending beyond the single domain range. Furthermore, anisotropy variations and particle interactions in compact assemblies can also result in a reduction of their coercivity. These effects explain in part the reason why the coercivities of typical particle assemblies used in recording media are only in order of magnitude agreement with the intrinsic coercivities that are predicted for idealized individual single domain particles.

Magnetically Hard Oxide Particles

The most common magnetic recording media in present use consist of dispersions of single-domain $\gamma\text{-Fe}_2\text{O}_3$ particles immersed in an organic binder and coated on to flexible substrates with a 40 percent by volume loading of particles. The $\gamma\text{-Fe}_2\text{O}_3$ particles are acicular with a typical length-to-width ratio of 6 to 1, and an average length of 0.6μ . They are

usually prepared from hydrated ferric oxide (α -FeO.OH) acicular particles by a sequence of steps involving dehydration to hematite (α -Fe₂O₃), followed by reduction at 300° -400° C in hydrogen to form magnetite (Fe₃O₄) and subsequent re-oxidation at a low temperature (200-250° C) in air to form acicular γ -Fe₂O₃.

Crystallographically, γ -Fe₂O₃ has a defect spinel structure with the lattice vacancies ordered¹⁰ on a superlattice in the octahedral sites. However, epitaxially grown single crystals of γ -Fe₂O₃ show no vacancy ordering, and about twenty percent of the vacancies in tetrahedral sites,¹¹ probably because of the higher growth temperature. Typical particles are polycrystalline, with a [110] needle axis for the acicular crystallites.^{12,13}

The saturation magnetization of commercial γ -Fe₂O₃ powders is about 74 emu/g, and assuming a density of 5.26 g/cm³, we obtain a value for I_s of 390 emu/cm³. The crystalline anisotropy constant is rather small¹¹ ($K_1 = -4.64 \times 10^4$ erg/cm³), giving rise to a maximum anisotropy field of $2 K_1/I_s \sim 240$ oe, whereas the theoretical limit of the shape anisotropy field is $2\pi I_s = 2450$ oe. Observed coercivities are in the range 250-300 oe, which are too large to be explained by crystalline anisotropy, and too small for coherent rotation limited by shape anisotropy. However, the Stoner-Wohlfarth¹⁴ coherent rotation model predicts much larger values for the coercivity than are usually observed, because incoherent rotational processes may be energetically more favorable.^{15,16,17}

It appears most likely that shape is the controlling anisotropy, and magnetization reversal proceeds by incoherent rotation.¹⁸ This conclusion is further supported by the relatively temperature-independent coercivity of acicular γ -Fe₂O₃ particles¹⁹ (corresponding to a somewhat similar temperature dependence of their saturation magnetization), and by a rotational hysteresis integral value²⁰ of 1.6, indicative of incoherent rotational processes.²¹ The observed large variations in the size and shape of the particles would also contribute in reducing the coercivity of such particle assemblies.²²

In the tape coating process, the acicular particles are usually aligned by strong magnetic fields along the long dimension of the tape to increase the remanent magnetization in that direction. Thus, typical ratios of remanence to saturation of 0.7-0.8 are obtained which are much lower than desired and expected from assemblies of highly acicular particles. Imperfect dispersions, particle interactions, and the roughness and irregularity of the particle surfaces are apparently the main causes of imperfect alignment. The alternative approach to higher remanence, that of increasing the particle to binder ratio, conflicts with good particle wettability, resulting in inferior physical properties for the recording media.

Magnetite (Fe₃O₄) has a higher saturation magnetization by approximately 20% than γ -Fe₂O₃, and a higher (by about 15%) coercivity than that of the same shape and size γ -Fe₂O₃ particles, due apparently to its higher magnetization and the competing effect of its larger crystalline

anisotropy. It should, therefore, be distinctly superior to $\gamma\text{-Fe}_2\text{O}_3$, except that it exhibits a strong tendency to oxidize and magnetic accommodation effects.

Magnetite particles can also be precipitated from a solution of ferrous sulfate by sodium hydroxide or oxalic acid, and by subsequent oxidation converted to $\gamma\text{-Fe}_2\text{O}_3$. The particles are cubic in shape (non-acicular) with a coercivity of about 100 oe and a size range of 300-3000 Å controllable by the precipitation parameters. Such particles, while not in themselves very useful for recording media because of their low coercivity, can easily be doped by suitable cations such as cobalt, by adding appropriate amounts of cobalt sulphate in the precipitating solution. The coercivity increases sharply with increasing cobalt content²³ reaching values as high as 1000 oe at room temperature for 10% Co, because of the strong coupling of the unquenched orbital moment of the cobaltous ion to the trigonal axis of the crystalline field and to the spin system.²⁴ However, because the coercivity of these particles is primarily controlled by crystalline anisotropy, it exhibits a large temperature dependence,²⁵ whereas their saturation magnetization is essentially temperature independent in the range 200-450° K. Consequently, their superior recording properties resulting from their higher coercivity are offset in some applications by loss of remanence and demagnetization at elevated temperatures.

In addition to cobalt substitutions, a large number of other metallic divalent ions may be substituted for the ferrous ions in magnetite to derive a large class of magnetically hard ferrite micropowders.^{9,27} Such materials have very high coercivities, but their saturation magnetization is usually considerably lower than that of Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$.

A very interesting ferromagnetic oxide, CrO_2 , has been prepared in highly acicular micropowder form^{28,29} by hydrothermal decomposition of CrO_3 at high pressure and in the presence of metal oxide catalysts (Sb_2O_3), or by vapor deposition from CrO_2Cl_2 . The particles have lengths in the range 0.2-1.5 μ and axial ratios as high as 20:1. Their saturation magnetization is in the range 90-100 emu/g, depending on the catalyst concentration, with a coercivity as high as 600 oe, and a Curie temperature of 126° C. The smaller particles are single crystals with a rutile structure, and with the tetragonal axis along the particle axis, which apparently coincides with the magnetocrystalline easy axis.³⁰ Even though the uniaxial crystalline anisotropy is quite large ($K_1 = 3 \times 10^5 \text{ erg/cm}^3$), the temperature dependence of the coercivity favors shape as the dominant anisotropy.²⁹

The high acicularity of the CrO_2 particles, their single crystal nature and coincidence of shape and magnetocrystalline easy axis, their smooth surface resulting from their crystallinity, and their superior magnetic properties compared to iron oxides, should combine to produce superior recording surfaces. Their low Curie point should not be cause for serious concern in most applications, because the demagnetizing field of recorded transitions decreases along with the magnetization as the temperature increases.

Magnetically Hard Metallic Particles

Metallic particles offer the greatest flexibility in the variation of the magnetic properties of particulate recording surfaces because of their high intrinsic magnetization and the possibility of realizing any desirable coercivity. It is, in fact, their high intensity of magnetization which in many instances gives rise to high coercivity in the presence of relatively small shape anisotropies. Single domain metallic micropowders can be prepared by numerous methods and have been studied extensively because of their permanent magnet applications.

An obvious method is to reduce the fine particle oxides of the ferromagnetic metals. Reduction is done in hydrogen at the highest efficient temperature ($\sim 400^\circ\text{C}$) which avoids sintering of the particles and the adverse consequences on their coercivity and remanence.

Fine metallic particles can also be prepared from an aqueous solution of the salts of ferromagnetic elements by hydroxide precipitation, followed by reduction to the metal.³¹ Similar methods use ammonium oxalate³² or oxalic acid³³ to precipitate the oxalates of iron cobalt and nickel to any desired composition, with subsequent thermal decomposition to the oxides and hydrogen reduction to the metal. Very small ($< 1000 \text{ \AA}$) metallic particles can thus be prepared with some acicularity and high coercivities (700-900 oe). In addition to the composition, resultant magnetic properties depend on the precipitation conditions, as well as on the oxidation and reduction temperature and time, which determine particle size and shape. Recording surfaces made from aligned dispersions of such particles have ratios of remanence to saturation quite similar to those of oriented $\gamma\text{-Fe}_2\text{O}_3$ media ($\sim .75$), but much larger remanent inductions (~ 3500 gauss) for the same particle-to-binder ratios.

Very acicular single domain particles of iron and iron cobalt have also been precipitated from their salts by reduction with aqueous potassium borohydride.³⁴ Furthermore, the acicularity and the coercivity of these particles can be greatly enhanced by the presence of strong external magnetic fields during the reaction.

An alternative approach involves the electrodeposition of iron or iron cobalt into a mercury cathode from an aqueous electrolyte, followed by thermal growth of the particles to eliminate their dendritic branches.³⁵ Particles with length-to-diameter ratios greater than 10:1, and average diameters of $\sim 225 \text{ \AA}$ can be prepared by this method. They have coercivities in the range 700-1000 oe, resulting from shape anisotropy, and best explained by a chain-of-spheres fanning model of incoherent rotational magnetization reversal.

A different chemical deposition method involves the spontaneous autocatalytic reduction of metal ions by hypophosphite in solutions similar to those used for electroless deposition of metal films. Instead of a controlled catalytic surface, fine particles of catalyst are introduced in the solution and the solu-

tion is then heated to initiate spontaneous decomposition. The metallic particles thus prepared are of sub-micron size with a platelet shape, and have coercivities up to 1000 oe, depending on the solution composition and the deposition parameters.³⁶

In addition to the methods discussed above, many other routes have been followed for the preparation of high coercivity metallic micro-powders, most notable of which are the decomposition of metal carbonyls,³⁷ and the vacuum deposition of iron and cobalt whiskers.^{38,39} Finally, there is the very large class of magnetically hard alloys used in permanent magnets.^{7,9}

Sub-micron metallic particles are usually pyrophoric because of their large surface-to-volume ratio. This is particularly true of the highly acicular and porous particles, and of those containing mostly iron. Consequently, they must either be kept in a non-oxidizing atmosphere, overcoated with appropriate plastics, or exposed to controlled oxidation (by immersion, for example, in benzene, toluene, or water) which allows them to form a protective oxide coating that inhibits further oxidation. With appropriate treatment the oxide shell can be a ferrite, giving rise to exchange anisotropy and different magnetic properties, particularly high remanence to saturation ratios.⁴⁰

METALLIC FILM MEDIA

The properties and the mechanism of magnetization reversal in uni-axial permalloy films with small crystalline anisotropy and negligible magnetostriction are fairly well understood.⁴¹ This is not the case, however, with high coercivity ($H_c > 150$ oe) films, such as chemically deposited Co-Ni-P, which have high random anisotropy. Such films are usually isotropic in the film plane, and show high remanence and essentially rectangular hysteresis loops. Furthermore, no domain structure is observable for any state of magnetization reversal by any of the customary techniques (Bitter, Kerr, Lorentz). On the other hand, such films cannot be viewed as continuous, because they contain a large number of non-ferromagnetic inclusions, imperfections, and crystallographic faults. Their properties can be best understood on the basis of fine particle behavior, with very strong magnetostatic interactions between the crystallites. Such a magneto-statically coupled aggregate of high random anisotropy particles has been shown to exhibit rectangular hysteresis behavior,⁴² and the observed thickness dependence of the coercivity and rotational hysteresis integrals (which are usually in the range 1.2 to 2.2), are in support of a single-domain model involving incoherent magnetization reversal, probably magnetization buckling or fanning in the plane of the film.^{43,44}

Magnetically hard thin metallic films, having a very wide range of magnetic properties, and with recording characteristics far surpassing those of thicker particulate media, have been prepared by a variety of methods.

a) Electrochemical deposition

Electrodeposition has been used to prepare ferromagnetic coatings for metallic drums and disks, and more recently for non-conducting substrates previously metallized with electroless nickel.⁴⁵

Typical electroplating solutions contain the sulphates or chlorides of the ferromagnetic elements,⁴⁶ sodium hypophosphite for coercivity control,⁴⁷ ammonium chloride for magnetic uniformity, and are operated at a pH of 3-5, a temperature of $\sim 50^\circ\text{C}$, and a current density of 20-100 mA/cm². Films deposited from such solutions contain small amounts of phosphorus (0-3 percent by weight, depending on the hypophosphite concentration), which profoundly influences their coercivity and magnetic moment density.

The coercivity increases monotonically^{48,49} and the magnetization intensity decreases logarithmically⁵⁰ with increasing hypophosphite concentration in the plating solution. The composition of the films depends not only on the corresponding ion concentration in the solution, but also on the temperature, current density, and pH. Thin films ($< 1\ \mu$) of Co-Ni-P exhibit a coercivity peak at approximately 20-30 percent Ni⁵¹ (coinciding with a maximum faulting density of the fcc and hcp phases) at a thickness range of 500-1000 Å,⁵² small unoriented crystallites ($< 100\ \text{Å}$), magnetic isotropy in the film plane, and good hysteresis loop squareness (0.8-1.0).

Lamellar and rod structures have been observed in thicker films^{53,54} ($> 1\ \mu$) along with a thickness independent coercivity, smaller ratios of remanence to saturation, and the hexagonal c-axes randomly arranged in the plane of the films.

The magnetic characteristics of these films imply a semi-particulate nature with strong magnetostatic interactions between the particles. The large values of the observed rotational hysteresis integral⁵² (2-4), and the absence of any domain structure, suggest incoherent rotational processes for magnetization reversal, dominated by crystalline anisotropy, while shape⁵⁴ and stress⁵⁵ may play a significant role in certain special cases.

b) Autocatalytic Deposition

Chemical or electroless deposition of cobalt, nickel, and iron can be initiated by the presence of a catalytic substrate in an aqueous solution of the metallic ions and in the presence of a reducing agent.⁵⁶ The deposition, once started is autocatalytically sustained provided that a controlled concentration of metal ions and reductant are maintained. The metal ions are usually introduced through their chlorides or sulfates with hypophosphite or borohydride ions employed as reductants. To control the concentration of the free metal ions, it becomes necessary to use complexing agents (such as citrate, tartrate or malonate) to which the metal ions are attached by ligand substitution, and

from which a small equilibrium amount of metal ions is freed by dissociation. Typically, solutions are operated at a pH \sim 8.5 and at a temperature of \sim 80° C.

The magnetic properties of films prepared by autocatalytic deposition are critically dependent on the conditions of preparation and are a complicated function of the codeposited phosphorus content, crystallite size, orientation of the deposits and thickness, which in turn are controlled by the deposition variables, primarily solution composition, pH, and temperature.^{43,44,57-60} The coercivities of these films can be varied from a few oersteds to greater than 2000 oe, and the saturation magnetization, σ_s , can vary from zero (thin nickel films are paramagnetic) to the magnetization of the corresponding bulk alloy, depending on the composition, the conditions of deposition, the complexing agent, and the amount of codeposited phosphorus. With the tartrate solution, the saturation magnetization is about 40 emu/g lower than bulk values due to co-deposited phosphorus, while the rate of deposition and the coercivity exhibit a peak at $\text{Co}^{2+}/\text{Ni}^{2+}=4$. It is of interest to note that at this composition the maximum mixing of the hcp and fcc phases occurs. With the malonate solution, no detectable phosphorus is deposited, resulting in films with saturation magnetization approximately equal to that of the bulk alloys, while the coercivity again exhibits a peak at 20%Ni-80%Co. The citrate solution produces the highest rates and highest coercivities (>2000 oe at 15%Ni), but the saturation magnetization values are generally 30 emu/g lower than bulk values, again due to codeposited phosphorus.⁶¹

Crystallographically, the Co-P films exhibit only the hcp phase, with crystallite sizes in the range 200-700 Å. The low coercivity films (300 oe) showed a preferred orientation of the hexagonal c-axes perpendicular to the film plane. The intermediate coercivity films (400-700 oe) showed random distribution of c-axes. The high coercivity films (1000 oe) have the c-axes in the film plane, randomly distributed. As nickel is introduced, there appears an increasing orientation of the hexagonal (002) and the cubic (111) axes perpendicular to the substrate. Crystallite size varies directly with the rate of deposition, exceeding 1000 Å for the maximum rate composition of 25%Ni-73%Co. Nickel plates out preferentially, so that the percent nickel in the deposits is 1.4 times the percent nickel in the solution.⁵⁹

By contrast to Co-Ni-P films, where the coercivity and the rate of deposition attain a maximum at approximately 20-25%Ni, the coercivity and rate of deposition of Co-Fe-P films decrease continuously with increasing iron content.⁶²

High coercivity films prepared by autocatalytic deposition are magnetically isotropic in the film plane, and exhibit very respectable values of hysteretic squareness ($I_r/I_s \sim .75-.95$).

c) Vacuum Deposition

High coercivity thin films of Fe, Co, and Ni have been prepared by evaporation in a vacuum at a high angle of incidence of the vapor flux with respect to the substrate normal.^{63,64,65} The coercivity of these films increases monotonically with increasing angle of incidence, attaining values of 1000 oe or higher for iron and cobalt, and 400 oe for nickel, at angles of incidence exceeding 80° .

Vacuum deposited oblique-incidence films are composed of small crystallites (20\AA - 100\AA) when deposited at small angles of incidence, which increase in size as the angle of incidence increases (1000\AA at 75°). The crystallites do not exhibit any particular crystallographic orientation; however, replication electron microscopy revealed a textured structure, with particles being somewhat elongated in the plane of incidence due to a shadowing effect, which becomes more pronounced at very large angles of incidence. This would account for the observed magnetic anisotropy of the films which have their easy axis in the plane of incidence, and a decreasing hard axis remanence with increasing angle of deposition. It is also characteristic that the observed coercivities for iron, cobalt, and nickel are proportional to their magnetizations, and, therefore, to the values one would calculate assuming shape is the predominant anisotropy,⁶⁵ even though the maximum observed coercivities are almost an order of magnitude smaller than those calculated for acicular single domain particles with coherent rotation reversal.⁶⁶ This discrepancy is most likely due to the small acicularity of the particles and the large local anisotropy variations (particularly crystalline), resulting in incoherent rotation magnetization reversal modes.

An alternative approach in producing vacuum deposited high coercivity films would be to destroy magnetic homogeneity by incorporating non-ferromagnetic inclusions during deposition, which should impede the formation and propagation of walls.

d) Sputtering

The homogeneity and uniformity of multi-component vacuum deposited films is difficult to control if the elements involved have different vapor pressures. Sputtering avoids such difficulties if cathodes of the desired composition can be made, because the composition of sputtered films replicates that of the cathode from which they derive. Thus, we have produced films of various compositions by sputtering from cathodes produced by autocatalytic deposition or electrodeposition of suitable compounds. Using this method, magnetic films have been deposited at a rate of $50\text{\AA}/\text{min.}$ to about $500\text{\AA}/\text{min.}$ By varying the thickness and composition, as well as the rate of deposition, coercivities ranging from 3 oe to about 500 oe with I_r/I_s ratios of unity were observed. In a prior work,⁶⁷ iron films with coercivities in excess of 200 oe have been reported.

PARTICULATE COATINGS VERSUS METALLIC FILMS

The chief limitation of particulate coatings is their thickness. The very large and adverse effect of thickness on the resolution of $\gamma\text{-Fe}_2\text{O}_3$ media is shown in figure 1. The theoretical bit density ("all ones") response curves were calculated using a theoretical model simulation of the recording process based on harmonic analysis.⁶⁸ The transducer used for both the experimental and the theoretical results had a write gap of 4μ and a read gap of 1μ . Contact recording and magnetic saturation of the recording surfaces for all bit densities were assumed, and the response curves were normalized to their own maxima. It is evident from figure 1, that as the thickness of the recording surface decreases, its response over a range of densities (dynamic range) becomes flatter, and the signal amplitude at high bit densities can be considerably larger than for thicker surfaces. To minimize the effect of thickness it is necessary to strive for as thin coatings as possible, or resort to non-saturation recording by effectively penetrating only a thin top layer of a thick recording medium. However, the latter technique is critically dependent on write current and spacing fluctuations between the medium and the transducer.

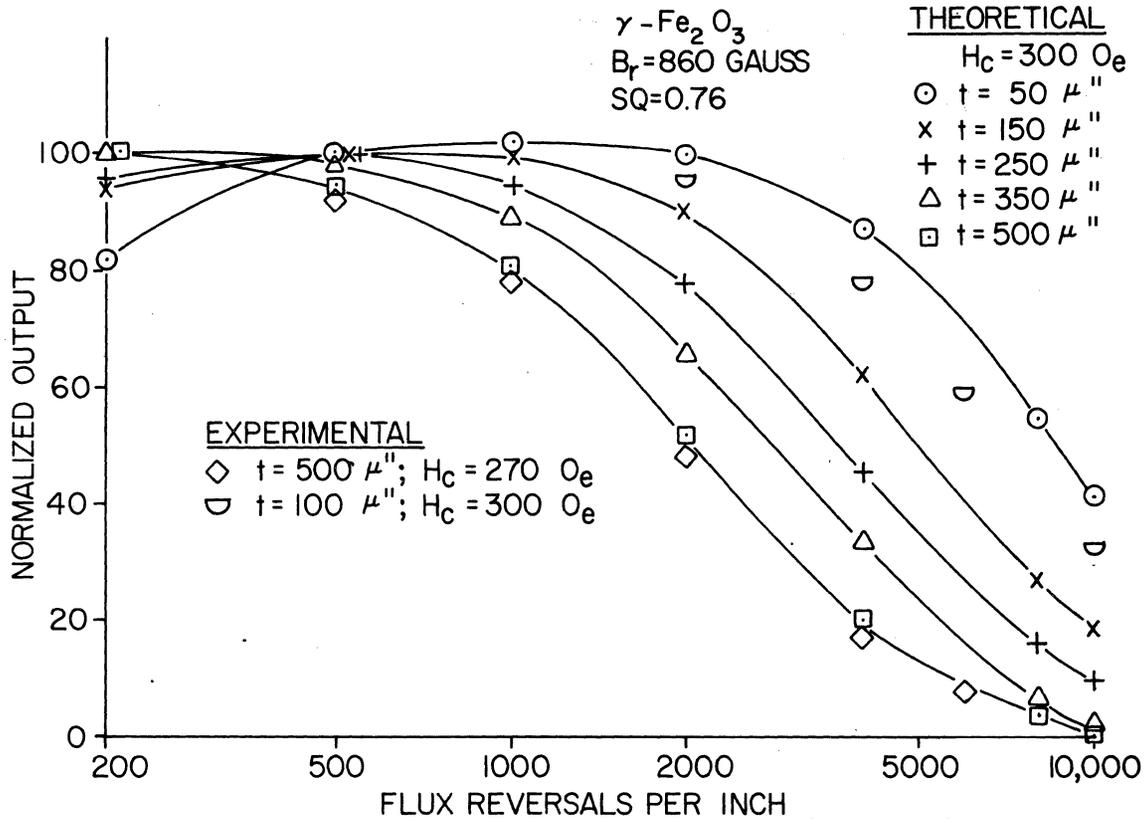


FIGURE 1
 NORMALIZED BIT DENSITY RESPONSE CURVES FOR
 $\gamma\text{-Fe}_2\text{O}_3$ MEDIA OF VARIOUS THICKNESSES

A comparison of theoretical and experimental bit density response curves for a number of particulate media with thicknesses of 12.5μ and 2.5μ and metallic film media with thicknesses of 0.13μ and 0.25μ is shown in figures 2 and 3. The superiority of the thin metallic media at very high bit densities is evident. That this superiority results primarily from their thinness is evident in figure 3, where a significant improvement in bit density response is realized by decreasing the thickness of a metallic film from 0.25μ to 0.13μ .

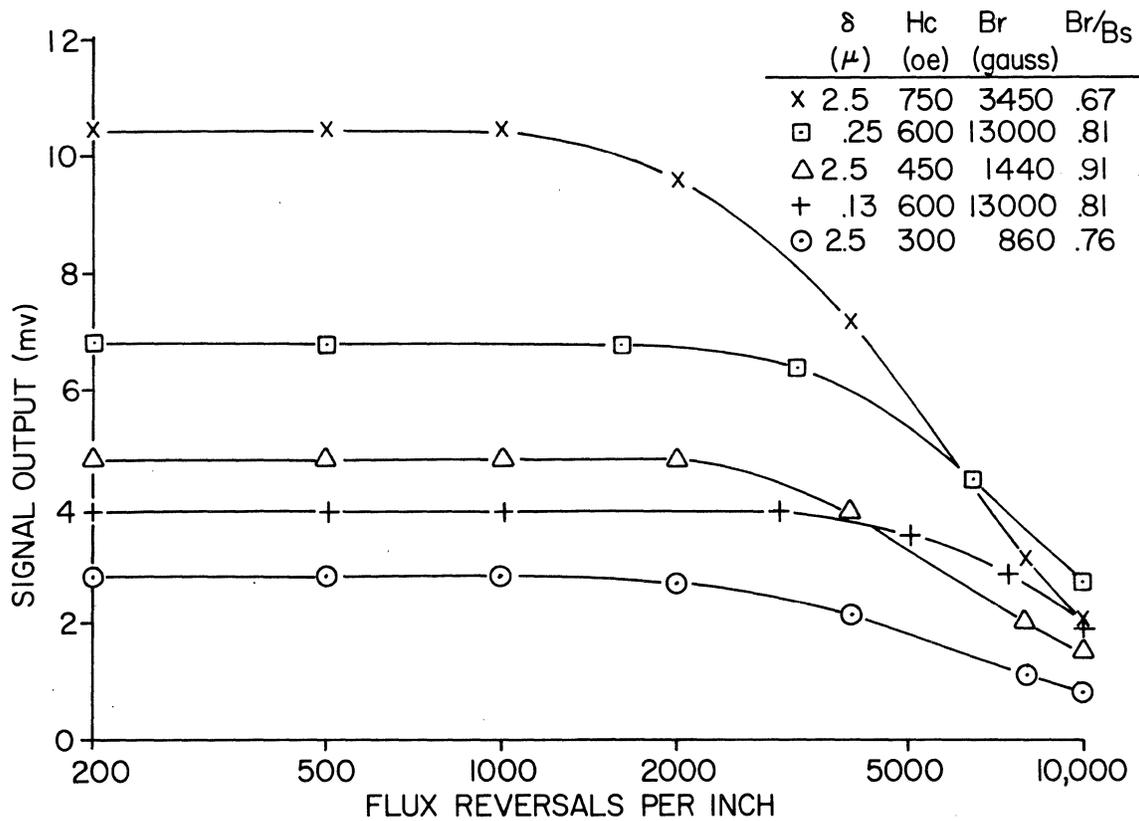


FIGURE 2.
OUTPUT VS. BIT DENSITY FOR TYPICAL PARTICULATE
AND METALLIC FILM RECORDING SURFACES

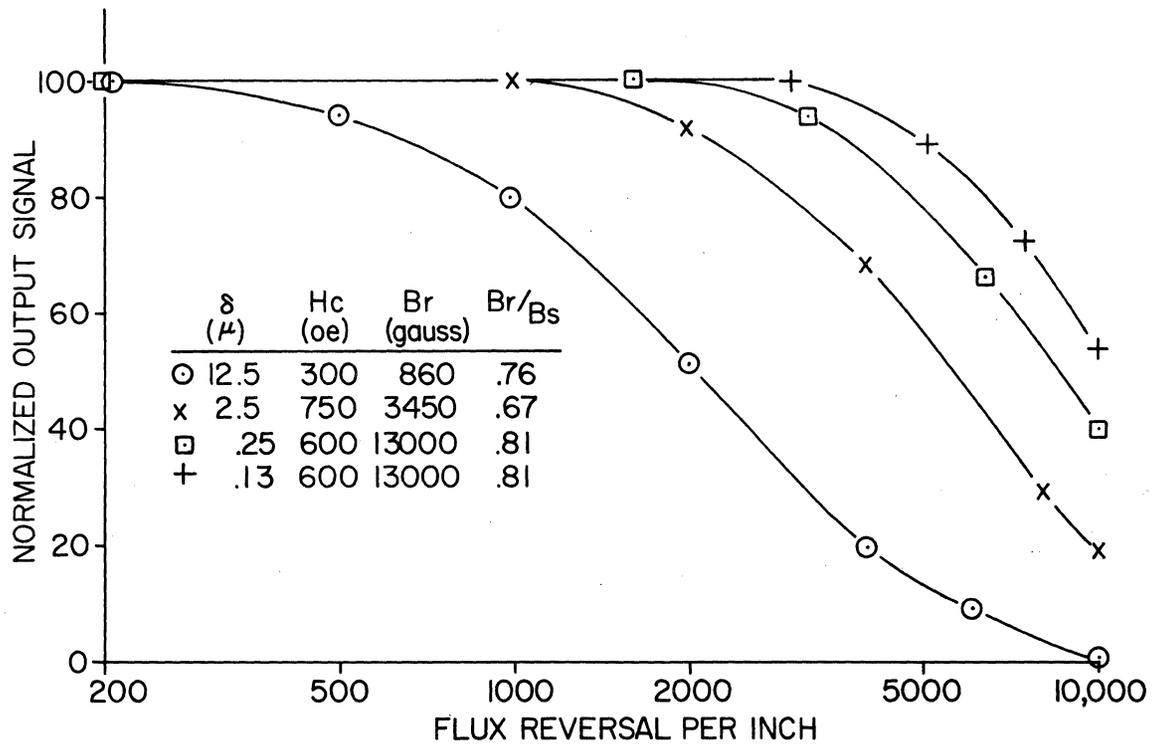


FIGURE 3
 NORMALIZED BIT DENSITY RESPONSE CURVES
 FOR TYPICAL PARTICULATE AND METALLIC FILM MEDIA

Very thin metallic films of high coercivity have information storage capabilities far in excess of what can be read out by conventional methods which scan the flux at some distance above the surface. We have applied the technique of transmission electron microscopy (Lorentz microscopy) to recorded patterns and have observed very sharply defined regions of opposite magnetization at densities of 8000 magnetization reversals per cm. Furthermore, by the same technique, we have observed magnetization transition regions which confirm our theoretical predictions,¹ and indicate that very thin films of very high coercivity can support densities in excess of 40,000 magnetization reversals per cm.

CONCLUSIONS

The most important properties of the various magnetic recording materials are summarized in Table I. The range of values shown indicates what has already been achieved or what should be possible to achieve without major breakthroughs. In particular, the remanent induction shown represents approximately the upper limit that is presently realizable, at least in the laboratory. The thickness shown, which is the most important parameter, represents what is believed to be the lower limit achievable by today's technology. The coercivity is assumed to be bound on the high end to a value of about 1000 oe imposed by writing and erasing efficiency.

A very significant improvement in signal amplitude and resolution is offered by increasing the coercivity and the remanence and decreasing the thickness of digital recording surfaces used for high density storage. The major limitation is one of resolution, manifested mainly in the shift between pulse peaks and pulse asymmetries of coded patterns, and imposed primarily by the thickness of the recording media (in out-of-contact recording applications the medium-to-transducer spacing may impose an equal or even greater limitation on high density).

The greatest flexibility and potential among particulate coatings is offered by metallic particles, while ultimate high density recording optimization can be achieved in thin metallic surfaces.

TABLE I. PARAMETERS OF MAGNETIC RECORDING MATERIALS

MATERIAL	COERCIVITY (oe)	REMANENT INDUCTION (GAUSS)	THICKNESS (μ)	COMMENTS —
IRON OXIDES	250-390	1000	1.25	"THE OLD RELIABLE"
COBALT SUBSTITUTED IRON OXIDES	ANY	1000	1.25	TEMPERATURE INSTABILITY
CHROME OXIDE	300-600	1500	1.25	A SUPERIOR PAR- TICULATE SURFACE
METALLIC PARTICLES	ANY	5000	1.25	OFFERS THE HIGHEST POTENTIAL AMONG PARTICULATE MEDIA
METALLIC THIN FILMS	ANY	24,000	ANY	THE ULTIMATE RECORDING SURFACE

ACKNOWLEDGEMENT

It is a pleasure to acknowledge the many contributions of my colleagues, J. R. Morrison and J. S. Judge, and the helpful discussions with G. Bate and J. H. Judy.

REFERENCES

1. D. E. Speliotis and J. R. Morrison, IBM Jour. Res. and Dev. 10, 233 (1966).
2. R. D. Fisher, Proc. INTERMAG Conf. (1963), p. 4-5-1.
3. A. Aharoni and R. D. Fisher, Proc. INTERMAG Conf. (1965), p. 12. 3-1.
4. A. V. Davies, B. K. Middleton and A. C. Tickle, IEEE Trans. Mag., MAG-1, 344 (1965).
5. D. E. Speliotis, J. R. Morrison and J. S. Judge, IEEE Trans. Mag., MAG-1, 348 (1965).
6. D. E. Speliotis, J. R. Morrison and J. S. Judge, IEEE Trans. Mag., MAG-2, 208 (1966).
7. E. P. Wohlfarth, Advances in Physics, 8, 87 (1959).
8. T. O. Paine, "Magnetic Properties of Metals and Alloys", p. 146. American Society for Metals, Cleveland, Ohio, 1959.
9. E. P. Wohlfarth, "Magnetism", Vol. III, p. 351. Academic Press, New York, 1963.
10. G. W. van Oosterhout and C. J. M. Rooijmans, Nature 181, 44 (1958).
11. H. Takei and S. Chiba, J. Phys. Soc. Japan 21, 1255 (1966).
12. J. Hurt, A. Amendola, and R. E. Smith, J. Appl. Phys. 37, 1170 (1966).
13. G. W. van Oosterhout, Acta Cryst. 13, 932 (1960).
14. E. C. Stoner and E. P. Wohlfarth, Phil Trans. Roy. Soc. A240, 599 (1948).
15. I. S. Jacobs and C. P. Bean, Phys. Rev. 100, 1060 (1955).
16. W. F. Brown, Phys. Rev. 105, 1479 (1957).
17. E. H. Frei, S. Shtrikman, and D. Treves, Phys. Rev. 106, 446 (1957).
18. C. E. Johnson and W. F. Brown, J. Appl. Phys. 29, 1699 (1958).
19. A. H. Morrish and L. A. K. Watt, J. Appl. Phys. 29, 1029 (1958).

20. G. Bate, J. Appl. Phys. 33, 2263 (1962).
21. I. S. Jacobs and F. E. Luborsky, J. Appl. Phys. 28, 467 (1957).
22. W. P. Osmond, Proc. Phys. Soc. 67, 875 (1954).
23. F. Kroner, Technik der Magnetspeicher (Berlin: Springer-Verlag), p. 479 (1960).
24. J. C. Slonczewski, Phys. Rev. 110, 1341 (1960).
25. D. E. Speliotis, J. R. Morrison and G. Bate, Proc. Int'l. Conf. Magnetism, Nottingham, England, p. 623 (1965).
26. J. R. Morrison and D. E. Speliotis, IEEE Trans. Elec. Comput. EC - 15, No. 5, October (1966).
27. C. D. Mee, Proc. INTERMAG Conf. (1963), p. 4-11.
28. T. J. Swoboda, P. Arthur Jr., N. L. Cox, J. N. Ingraham, A. L. Opegaard, and M. S. Sadler, J. Appl. Phys. 32, 374S (1961).
29. F. J. Darnell, J. Appl. Phys. 32, 1269 (1961).
30. D. S. Rodbell, J. Phys. Soc. Japan 21, 1224 (1966).
31. G. C. Marcot, W. J. C. Cauwenberg, and S. A. Lamanna, U. S. Patent 2,558,302. June 26 (1951).
32. W. J. Schuele, J. Phys. Chem. 63, 83 (1959).
33. S. Iwasaki and K. Nagai, Rep. Res. Inst. Elect. Commun. Tohoku Univ. B15, 85 (1963).
34. A. L. Opegaard, F. J. Darnell, and H. C. Miller, J. Appl. Phys. 32, 184S (1961).
35. F. E. Luborsky, J. Appl. Phys. 32, 171S (1961).
36. J. S. Judge, J. R. Morrison, and D. E. Speliotis, IBM Tech. Discl. Bull. 9 No. 3, p. 320 August (1966).
37. R. W. Fabian and J. L. Sienczyk, U. S. Patent No. 2,884,319, April 28 (1959).
38. C. R. Morelock, Acta Met. 10, 161 (1962).
39. F. E. Luborsky and C. R. Morelock, J. Appl. Phys. 35, 2055 (1964).
40. R. B. Falk and G. D. Hooper, J. Appl. Phys. 32, 190S (1961).

41. D. O. Smith, "Magnetism" Vol. III, p. 465, Academic Press, New York, 1963.
42. L. Reimer, Z. Angew, Phys. 17, 196 (1964).
43. D. E. Speliotis, J. S. Judge, and J. R. Morrison, J. Appl. Phys. 37, 1158 (1966).
44. J. S. Judge, J. R. Morrison and D. E. Speliotis, J. Electrochem. Soc. 113, 547 (1966).
45. J. W. Wenner, U. S. Patent 3,150,939. September 29, 1964.
46. P. P. Zapponi, U. S. Patent 2,619,454. November 25, 1952.
47. T. H. Bonn and D. C. Wendell, Jr., U. S. Patent 2,644,787. July 7, 1953.
48. H. Koretzky, Proc. First Australian Conf. on Electrochemistry, Pergamon: New York 1964, p. 417.
49. J. S. Sallo and J. M. Carr, J. Electrochemical Society 109, 1040 (1962).
50. J. S. Judge, J. R. Morrison and D. E. Speliotis, Plating 53, 441 (1966).
51. J. H. Kefalas, J. Appl. Phys. 37, 1160 (1966).
52. G. Bate and D. E. Speliotis, J. Appl. Phys. 34, 1073 (1963).
53. J. S. Sallo and K. H. Olsen, J. Appl. Phys. 32, 203S (1961).
54. J. S. Sallo and J. M. Carr, J. Appl. Phys. 33, 1316 (1962).
55. R. D. Fisher, J. Electrochem. Soc. 109, 479 (1962).
56. A. Brenner and G. E. Ridell, J. Res. Nat'l. Bur. Stds. 37, 1 (1946).
57. R. D. Fisher and W. H. Chilton, J. Electrochem. Soc. 109, 485 (1962)
58. J. S. Judge, J. R. Morrison, D. E. Speliotis, and G. Bate, J. Electrochem. Soc. 112, 681 (1965).
59. J. S. Judge, J. R. Morrison, and D. E. Speliotis, J. Appl. Phys. 36, 948 (1965).
60. Y. Moradzadeh, J. Electrochem. Soc. 112, 891 (1965).

61. D. E. Speliotis, J. S. Judge, and J. R. Morrison, to be published.
62. J. R. DePew, and D. E. Speliotis, Proc. Symp. Plating in Electronics Industry, Newark, N. J. (1966).
63. W. J. Schuele, J. Appl. Phys. 35, 2558 (1964).
64. G. Bate, D. E. Speliotis, J. K. Alstad, and J. R. Morrison, Proc. Intn'l. Conf. on Magnetism, Nottingham, (The Institute of Physics and the Physical Society, London, 1965), p. 816
65. D. E. Speliotis, G. Bate, J. K. Alstad, and J. R. Morrison, J. Appl. Phys. 36, 972 (1965).
66. C. Kittel, Rev. Mod. Phys. 21, 541 (1949).
67. E. Kay, J. Appl. Phys. 32, 99S (1961).
68. B. Kostyshyn, IEEE Trans. Mag., MAG-2, 236 (1966).