Cobalt-Platinum Permanent Magnets

MODELS FOR STUDY AND TECHNICAL DEVELOPMENT

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The 50 atomic per cent cobalt platinum alloy continues to hold a special place as an outstanding permanent magnet material and to receive considerable scientific study. It is suggested that much remains to be done before its properties can be fully understood and some reasonable models for study are proposed. Technological development could improve its properties still further and the implications of this with respect to specialised applications are discussed.

The equiatomic cobalt-platinum alloy is a fascinating and challenging material. It constitutes, when properly treated, one of the highest quality permanent magnet materials in current use, with special properties which justify its continued application in spite of the obviously substantial cost. For this reason it has undergone a considerable amount of technical development and has also been subjected to careful scientific study. In spite of this it is far from certain that its technical properties could not be improved still further, and absolutely certain that more study will be required before its behaviour is fully understood.

Before discussing the technical properties a brief outline of the relevant magnetic principles may be helpful. An attempt will then be made to decide just which of the principles are the most relevant to this material in its familiar form or in alternative forms in which it might be produced; a certain amount of flexibility seems to be called for in the present situation and if one cannot reach definite conclusions concerning the behaviour of the material in one condition it might well be advisable to consider lines of experimentation which include the preparation of specimens with a simpler structure.

Magnetic Properties

There are two classes of magnetic properties; the technical properties, coercivity H_c, remanent magnetisation M_r or induction $B_r(=4\pi M_r)$, susceptibility M/H, and permeability B/H; and the intrinsic properties including saturation magnetisation M_s, anisotropy coefficient K and exchange coefficient A. These latter are in turn related to quantum mechanical effects at an atomic level, and the intrinsic properties interact with the microstructure of any particular specimen to give rise to the technical properties. Thus we may write, formally:

quantum state→intrinsic properties+microstructure→technical properties.

Clearly the intrinsic properties may be regarded as those of a perfect crystal, while the technical properties can only relate to specimens in a particular form. From this point of view there are no "hard" and "soft" magnetic materials, just magnetically hard and soft specimens. However it will be seen that high values of K indicate the feasibility of preparing good permanent magnets if the appropriate structure can be achieved.

The spinning electrons in the ions of a magnetic material can be represented as

minute current loops which thus have magnetic moments. The spins are coupled within any one ion to give a net ionic magnetic moment, and in a ferromagnetic metal all the ionic moments are coupled together to give a spontaneous magnetisation M_s which is the magnetic moment per unit volume. The strength of this so-called exchange coupling is indicated by a parameter A, such that there is an exchange energy per unit volume of

$$E_A = A\left(\frac{d\theta}{dx}\right)^2$$

where $d\theta/dx$ represents the rate of change of orientation of the spins along a particular axis OX. Clearly $E_A = 0$ if the ionic spins are all parallel and, generally, exchange has the effect of smoothing out any variations in the direction of M_s.

It is relevant to note one very important and almost unique feature of exchange interactions. They have a quantum mechanical derivation which relates them to the direct overlap of the charge clouds representing the orbits of the electrons in the neighbouring ions, and so they have a very short range. This is a major distinction from magnetostatic interactions, which are long-range. A hypothetical slot one atom wide cut through a crystal constitutes a real barrier to exchange.

Exchange alone gives rise to a net magnetisation vector which points in an arbitrary direction, but there are also interactions between the charge clouds or orbitals and the electrostatic fields of neighbouring ions in the crystal lattice which, via the spin-orbit coupling, constrain the spins and thus M_s to lie in a particular direction with respect to the lattice. Thus easy directions arise and the strength with which M_s is coupled to an easy direction is indicated by an anisotropy constant K such that there is an energy per unit volume $E_K = K \sin^2 \theta$, where θ is the angle between M_s and the easy direction.

Suppose that a field is applied at an angle to an easy direction. The energy of interaction of the magnetisation vector with H is

$$E_H = -\mathbf{H}.\mathbf{M}_s = -HM_s \cos(\widehat{\mathbf{HM}_s})$$

and thus $\mathbf{M}_s$ rotates towards $\mathbf{H}$ to minimise E_H ($= -HM_s$ when $\theta = 0$) but is restrained by the anisotropy so that the final orientation balances the two effects. However the magnetic and anisotropy interactions are so much weaker than the exchange interactions that it can generally be assumed that M_s rotates as a whole, or at least remains uniform over small distances.

Magnetic Behaviour: Coherent Rotation

Suppose a field is applied normal to the easy axis of a spherical crystal (to avoid complications from demagnetising effects) as in Fig. 1a. $\mathbf{M}_s$ rotates through an angle θ, so that the total energy involved is

$$E_K + E_H = K \sin^2\theta - HM_s \cos(90-\theta) = K \sin^2\theta - HM_s \sin\theta$$

and the actual value of θ will be that which minimises $E_K + E_H$:

$$2K \sin\theta \cos\theta - HM_s \cos\theta = 0$$

$$\theta = \sin^{-1}(HM_s/2K)$$

The induced magnetisation, measured as the component along the direction of H is

$$M = M_s \sin\theta = HM_s^2/2K$$

so that the susceptibility $\chi = M/H$ is constant, $\chi = M_s^2/2K$, up to saturation ($M = M_s$) at $H = 2K/M_s$. This gives the magnetisation curve shown in Fig. 1b. The particular value of $H = 2K/M_s$ is called the anisotropy field H_K since it is the field which has an equivalent effect to that of the anisotropy, for small rotations. It is noted that the remanent magnetisation in zero field, and thus the coercivity or field required to cause demagnetisation, are both zero.

Very different results are obtained when fields are applied parallel to the easy axis, opposing the initial direction of $\mathbf{M}_s$ (Fig. 1c). The torque due to the field, which is the rate of change of $-\mathbf{H}.\mathbf{M}_s$ or $HM_s\sin\theta$, is zero when $\theta = 0$ so the situation is at least metastable whatever the value of H. However,

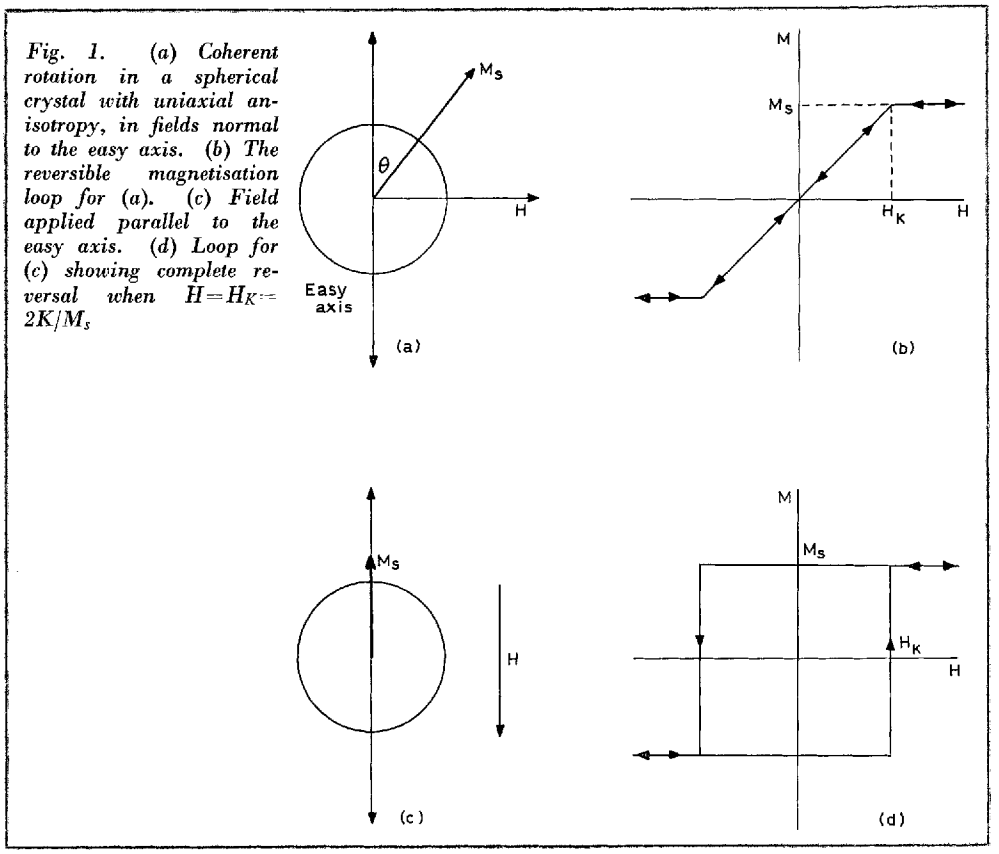

Fig. 1. (a) Coherent rotation in a spherical crystal with uniaxial anisotropy, in fields normal to the easy axis. (b) The reversible magnetisation loop for (a). (c) Field applied parallel to the easy axis. (d) Loop for (c) showing complete reversal when $H=H_K=2K/M_s$

the anisotropy torque, which is $2K\sin\theta\cos\theta$ or $K \sin 2\theta$, has a maximum when $\theta=45°$ and also approaches zero as $\theta\rightarrow 0$, and if one plots out the torques as a function of θ it can be seen that the net torque is always in the field direction so long as $H>2K/M_s$. Thus complete reversal occurs at $H=H_K$, giving the loop shown in Fig. 1d with $M_r=M_s$ and $H_c=H_K$.

Anisotropy fields can be extremely high; specifically for ordered cobalt-platinum $2K/M_s \approx 80{,}000$ Oe, so very large coercivities may be expected whenever magnetisation reversal does occur by coherent rotation. The mode of reversal depends largely on the size of the crystal or crystallites, but coherent rotation should apply below a critical diameter of the order of 10^{-4} cm for this material. (This is well above a second critical size at which reversal is aided by thermal fluctuations to the extent that the remanence decays spontaneously in zero applied field and $H_c\rightarrow 0$).

Partially Ordered Material

When cobalt-platinum is quenched from about 1000°C it has a cubic crystal structure with low crystal anisotropy, and also a low coercivity. After prolonged heating at 600 to 700°C X-ray diffraction shows that there is a tetragonal distortion of the lattice and that this is due to the production of a regular arrangement of the cobalt and platinum atoms, i.e. to ordering. The ordered material has a very high uniaxial anisotropy but since it occurs coherently in the form of large uniform "sub-crystallites" it is not surprising that the coercivity is again low. It is a general observation that relatively low coercivities occur, whatever the anisotropy, in any crystalline regions which are large enough to contain domain

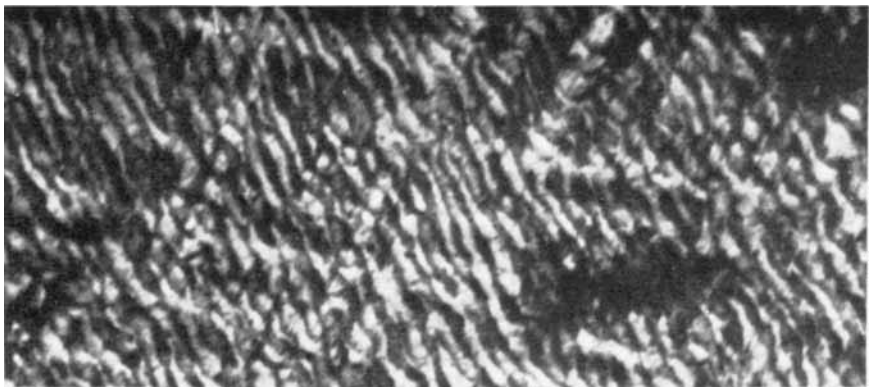

Fig. 2 Transmission electron micrograph of a thin foil of high coercivity material, reduced to the required thickness by ion bombardment (by M. Paulus of C.N.R.S., Bellevue, France). The fine structure indicated, with 100Å spacing, is assumed to be a consequence of the ordering, although a detailed interpretation is not yet possible. $\times 50{,}000$

walls which represent a gradual transition from one direction of magnetisation to the other. These walls have a characteristic width ($\delta \sim \sqrt{A/K}$) and energy ($\gamma \sim \sqrt{AK}$) since within them the ionic moments or spins must be directed out of an easy direction and also there must be an angle between neighbouring spins giving an exchange energy contribution. In a perfect crystal the energy will not be a function of position and thus the walls will move freely in small fields to change the overall state of magnetisation, and demagnetisation is readily achieved. The walls can be caught up on imperfections but this usually gives coercivities far below those expected for coherent rotation.

It is generally only for an intermediate state of order between the two extremes, which can be achieved by controlled heat treatment, that the highest coercivities of 5000 Oe or more occur. It seems quite natural to suggest that in this condition the ordering has occurred in such a way as to give very small tetragonal regions, which are too small to contain domain walls and thus have very high coercivities or switching fields. Naturally there is great interest in the exact manner in which the ordering occurs, and in this state in particular. Much excellent work has been done, by Southworth for example, using advanced techniques such as field-ion microscopy. The author has taken a different approach, and Fig. 2 shows what is thought to be the first straightforward transmission electron micrograph of optimum cobalt-platinum to be published.

This was only obtained with the kind assistance of Max Paulus, in charge of microstructural and synthesis studies at C.N.R.S., Bellevue. The difficulty is mainly one of preparing specimens which are transparent to the electron beam, i.e. ~100 Å thick, since this material is difficult to thin by electropolishing: the specimen illustrated was prepared by the ion polishing technique pioneered by Paulus, and it is hoped that it marks the beginning of a systematic study using these techniques.

So far it can only be said that the micrographs give direct visual confirmation of an extremely finely-divided structure in the partially ordered material, with an oriented texture which occurs systematically throughout certain regions within each grain. At the same time it is readily demonstrated that domains on a relatively enormous scale exist in this material, by simple powder patterns such as that in Fig. 3, and this has led some workers to introduce simple models for the impedance of domain walls which pass through both the "disordered matrix" and the "ordered precipitate particles".

Fig. 3 (a) Electron micrograph of a magnetic powder pattern replica, produced by the author's method, showing extensive domain walls at low magnification in high coercivity material. It is also clear that M_s is not uniform within each domain but that some fine magnetic structure exists. ×5,000

These could be relevant, but since the period of the structures shown in Fig. 2 is similar to the predicted domain wall widths the following alternative "micromagnetic" approach is suggested.

This is basically to start with non-interacting particle assemblies and then to see how the interactions depend upon the dimensions of the system. The simplest situation is a pair of non-interacting discs of the two phases, as shown in Fig. 4a. Particle 1 (softer phase) switches in a field of $2K_1/M_{s_1}$ and particle 2 then switches at $H = 2K_2/M_{s_2}$. Introducing magnetostatic interactions we see that 1 switches at

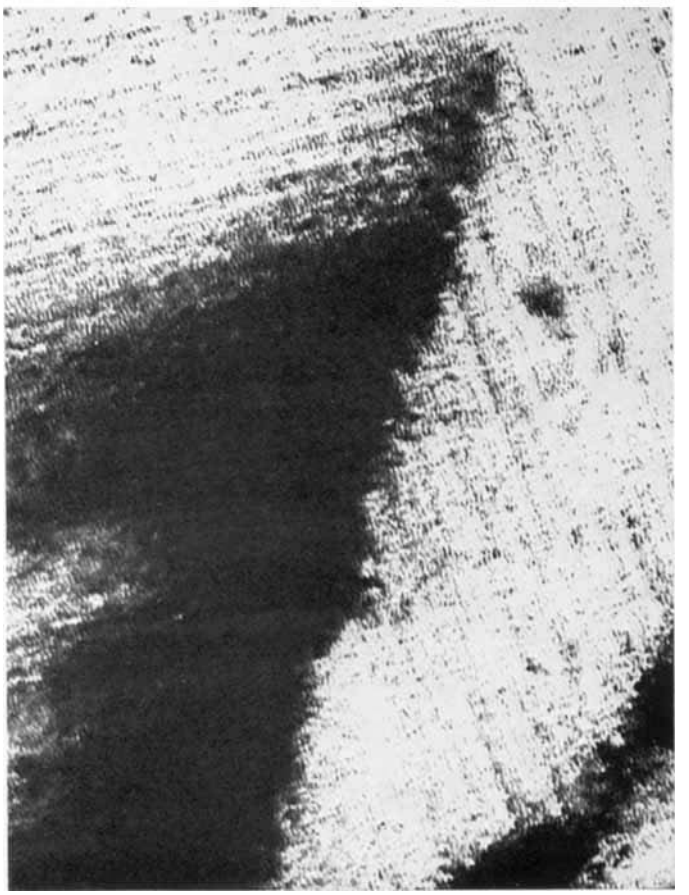

Fig. 3 (b) As (a) at very high magnification, indicating that the striations shown within the domains have themselves an ultra-fine structure with a spacing of about 100Å which it is tempting to associate directly with the ordering structures shown in Fig. 2. ×32,000

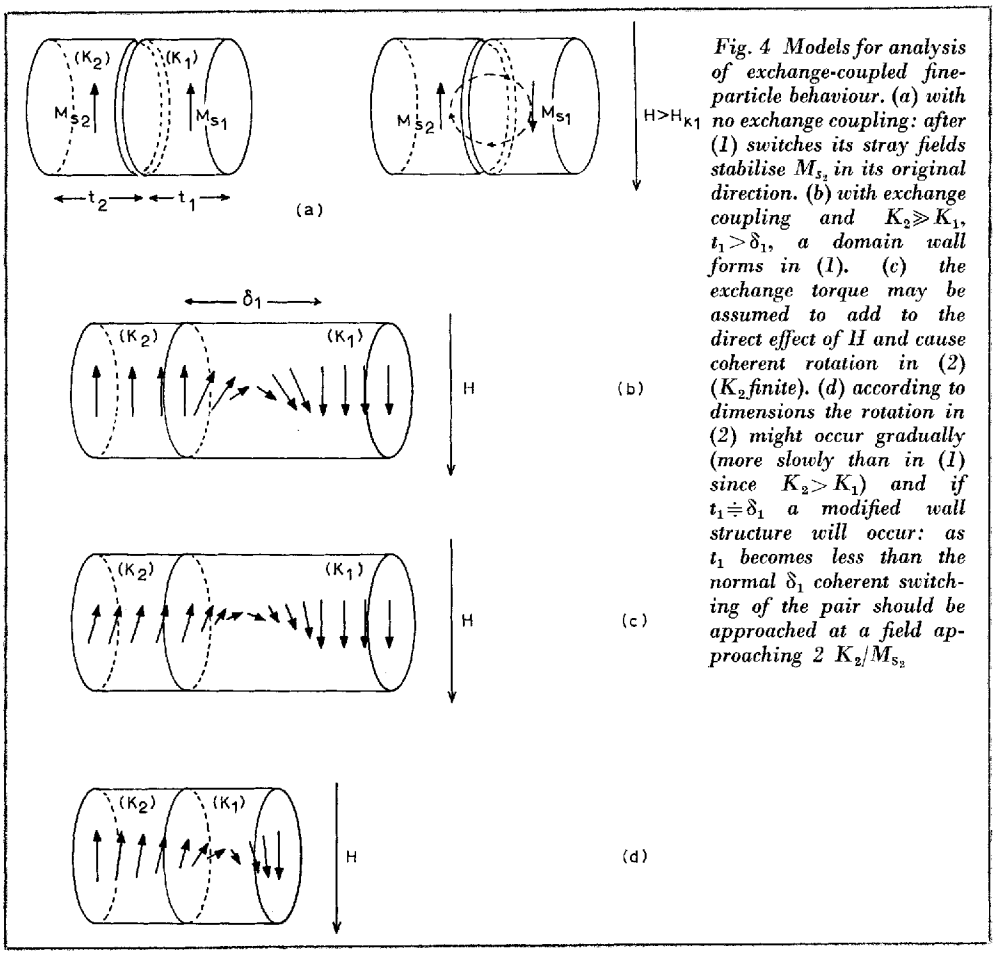

Fig. 4 Models for analysis of exchange-coupled fine-particle behaviour. (a) with no exchange coupling: after (1) switches its stray fields stabilise M_{s_2} in its original direction. (b) with exchange coupling and $K_2 \gg K_1$, $t_1 > \delta_1$, a domain wall forms in (1). (c) the exchange torque may be assumed to add to the direct effect of H and cause coherent rotation in (2) (K_2 finite). (d) according to dimensions the rotation in (2) might occur gradually (more slowly than in (1) since $K_2 > K_1$) and if $t_1 \doteqdot \delta_1$ a modified wall structure will occur: as t_1 becomes less than the normal δ_1 coherent switching of the pair should be approached at a field approaching $2\ K_2/M_{s_2}$

$H < 2K_1/M_{s_1}$ and 2 at $H > 2K_2/M_{s_2}$ and so these are "decoupling" interactions which have the reverse of the desired effect. (One object of the analysis is to show why reversal of the whole assembly occurs in a fairly narrow field range and certainly in fields $< 2K_2/M_{s_2}$.) We now introduce exchange coupling across the interface and initially consider that $K_2/M_{s_2} \gg K_1/M_{s_1}$ and that $t_1 > \delta_1$. Particle 1 now switches at $H \doteqdot 2K_1/M_{s_1}$ over most of its volume but a domain wall must form towards the interface with 2. This exerts an exchange torque on 2 which thus switches at $H < 2K_2/M_{s_2}$; in effect a transitory domain wall may sweep across particle 2 even if $t_2 \doteqdot \delta_2$. Thus it is clear that exchange interactions bring the two switching fields closer together and reduce the overall switching field to below $2K_2/M_{s_2}$. It should then be quite feasible to relax the above conditions, permitting a partial rotation in 2 due to the switching of 1 (Fig. 4d) and studying the increasing effects of the coupling as $t_1 \to \delta_1$ or becomes less than δ_1.

The main points to be made are that even formulating the problem leads to some sensible conclusions and, more important, one can see how the full analysis of the model could in fact be carried out (even if the final energy minimisation has to be done numerically). The negative effect of the magnetostatic interaction is, to a certain extent, overcome by the presence of the domains which are now recognised as assemblies of interacting single-domain particles. It is clear that a connection between the type of fine particle

theory proposed and the observed domain structures must be made when extending the theory to encompass many particles or interacting pairs of particles.

It should be stressed that the computations themselves would require a considerable effort and also that much more structural work is required by a variety of methods to determine whether the model is in fact appropriate or whether one should be dealing with regions differing in their degree of order or indeed equally ordered but, as suggested previously by the author, still having an identity as fine particles from the magnetic point of view due to the variation of the easy directions created.

Applications and Scope for Development

Following the speculation on the origins of the coercivity of conventional cobalt-platinum, it is no less interesting to speculate on the possibilities of further development of this material. This type of undertaking has a serious purpose, because development is generally quite costly and any possible outcome must be evaluated with care.

It may well be possible to achieve further improvements in the properties of tempered alloys, but since their behaviour is not fully understood it seems advisable for the moment to consider an ideal microstructure and then to ask whether this could be approached in practice. From a scientific point of view a truly flexible approach implies a readiness to fabricate an alternative type of specimen which might respond more readily to study and analysis than existing ones. Any results, or conclusions drawn, might then help to elucidate the behaviour of the original specimens.

Perhaps the only conclusion to be drawn with any confidence, from the preceding section, is that with mixed phases the presence of a low-H_k phase is always likely to reduce the overall coercivity. Since M_s only falls from 696 to 687 on ordering it would appear advisable to consider the properties of fully ordered specimens. There is indeed evidence that the coercivity of fully ordered specimens *can* remain high, although this is certainly not inevitably the case. This retention of coercivity is presumably associated with the persistence of a finely-divided structure due to the distribution of the tetragonal axes of the ordered regions among the different cube axes of the disordered crystal structure. However, this distribution of easy directions implies that the remanence cannot be optimum.

Thus it seems that an entirely different structure, and method of preparation, is called for: i.e. an oriented compact of wholly ordered material in the form of particles apparently, but not perhaps necessarily, below the critical single-domain size. It is readily admitted that this rather obvious suggestion is only made seriously because there seems now to be indirect evidence at least that it should be feasible, stemming from recent studies on rare-earth cobalt alloys. Furthermore it would be very short-sighted in general to ignore these latter studies in any account of any permanent magnet material.

We will first survey the potential properties of this ideal material. By comparison with the anisotropy field of 80,000 Oe it will be assumed that a coercivity of 8,600 ($=4\pi M_s$) can be achieved. Assuming, also, perfect orientation and 100 per cent packing the remanent induction will also be equal to $4\pi M_s$, giving an exceptionally simple and symmetrical demagnetising curve as shown in Fig. 5. This is compared with the demagnetising curve for a similarly idealised $SmCo_5$ specimen, and the similarity in properties is notable by contrast with the broken line for a typical alloy magnet of Alnico type and the dotted line for an oxide magnet.

There are several major features of such idealised magnets. First a negligible recoil effect is implied since there is no change in the magnetisation until H_c is reached, i.e. such a magnet would be extremely stable in dynamic conditions with the flux returning to its

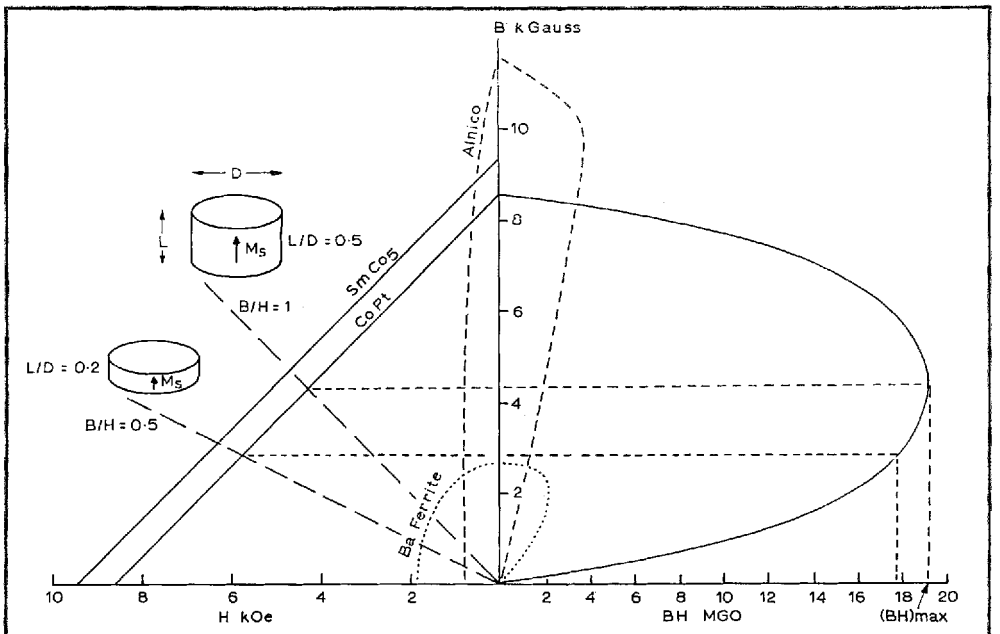

Fig. 5 Idealised demagnetisation curves, for single domain behaviour, for CoPt and $SmCo_5$, with the energy product curve for the CoPt. Typical curves for Alnico and barium ferrite are shown for comparison. The load lines drawn for the two shapes illustrated indicate that with such shapes large energy products are still obtained for the high K materials although they have fallen substantially for the other materials

equilibrium value after application of fields below H_c. Secondly, it should be possible to work at the theoretical $(BH)_{max}$ point and also to obtain a large energy product* with what would generally be considered as very unfavourable geometries. It is recalled that the demagnetising curve may be considered as the response of a block of material which is in a complete magnetic circuit, with no demagnetising effects or zero demagnetising factor, to reverse fields of external origin, or as the response of the material in the form of an isolated block to its own demagnetising fields. The first situation is that in which the curve would be measured while the second is that in which the magnet is actually used to produce fields. The working point of a magnet may be represented by a load line construction, i.e. by drawing a line from the origin with a slope B/H which indicates the relative magnitude of the reverse fields (self demagnetising fields and possibly additional reverse fields of external origin).

Demagnetising fields can only be estimated for uniformly magnetised specimens, and generally uniform magnetisation is only obtained for specimens which have the form of ellipsoids of revolution. Thus it is very difficult to estimate the demagnetising effects and thus the load lines for cylindrical or square section blocks of a material such as Alnico with relatively low coercivity or anisotropy. However, for cobalt-platinum the anisotropy fields are so much higher than the largest demagnetising fields ($4\pi M_s$) that the magnetisation can be treated as uniform even in non-ellipsoidal specimens. The demagnetising *fields* are not uniform but at least one can now use an approximate demagnetising factor which gives a mean demagnetising field, and thus associate a

*Energy product BH, measured in mega-gauss-oersted or MGO, is an indication of the ability of a particular magnet to produce a useful field. It clearly depends upon the shape of the magnet and is zero for an infinitely long cylinder (demagnetising H = zero) and for a thin sheet (H = $4\pi M_s$ and B = zero) and in the idealised case has its maximum value $(BH)_{max}$ at $H = 2M\pi_s$; $BH = 4\pi^2 M_s^2 = (BH)_{max}$.

particular shape of specimen with a particular load line or working point on the demagnetising curve.

For example, take a cylinder magnetised along its cylindrical axis of length L, and with cross-sectional diameter D. It happens that for $D=2L$ the demagnetising factor is approximately 2π and the demagnetising field is $2\pi M_s$. The load line has a slope $B/H=(4\pi M_s-2\pi M_s)/2\pi M_s=1$ and this clearly puts the magnet at its point of highest efficiency, $(BH)=(BH)_{max}=(2\pi M_s)^2=4\pi^2M_s^2$. The predicted value for the ideal specimen is 18.7 MGO, and nearly all other materials would give a much lower value because (a) the value of $(BH)_{max}$ is much lower and (b) for this geometry the specimens would be far from their maximum energy product condition, i.e. much more elongated specimens would be required to work at $(BH)_{max}$.

Now take a second example: a disc five times as wide as it is deep: i.e. $L/D=0.2$. The demagnetising factor is nearly $2/3(4\pi)$ and the demagnetising field $(8/3)\pi M_s$. Thus $B=4\pi M_s-(8/3)\pi M_s=(4/3)\pi M_s$; the load line has a slope of $B/H=0.5$ and the energy product is $(32/9)\pi^2M_s^2$. Thus (BH) is only reduced by a factor of (8/9) below its maximum value by this strongly demagnetising geometry, but this stresses the value of achieving a really high H_c and not being obsessed by the $(BH)_{max}$ requirement itself.

It is noted that load lines with slopes of as little as 0.5 are involved in such specialised designs as focusing magnets in travelling wave tubes, which are in fact placed face to face so that each is subject to stray fields from neighbours as well as self-demagnetising fields. Also, the advantages with regard to flexibility of design, where miniaturisation is concerned as in the production of bias fields for microwave components, are very obvious; with such a material the shape is almost immaterial and great economy results from the use of flat geometries in such applications as miniature microphones, and wrist watches.

Faced with these indications of the possibilities of real improvements the question of their realisation has a genuine interest. The encouraging factor is that specimens approaching such an ideal have in fact been achieved for other materials, by carefully controlled grinding, orienting a powder compact in a strong applied field and sintering. Whether the same could be achieved for fully ordered cobalt-platinum remains to be seen. It may be that the response to grinding would not be quite the same and that special procedures would have to be developed, perhaps leading to a lower particle size and true single-domain behaviour. It may not even be possible to grind cobalt-platinum since $SmCo_5$ is particularly brittle, and after all the mechanical properties are a substantial factor favouring cobalt-platinum. Yet again one must balance the possibility that this feature would be impaired in a specimen produced by powder metallurgy. (In the comparison of these two outstanding materials, note that they represent extremes of chemical reactivity so far as permanent magnets are concerned, cobalt-platinum being extremely passive while the properties of $SmCo_5$ are very responsive to the atmosphere, particularly while it is finely divided, and its stability remains a matter for study.)

Conclusions

In its usual form cobalt-platinum continues to present scientific problems, the solutions of which may well lead to a fuller understanding of magnetic behaviour generally and possibly suggest principles for the synthesis of new materials. It is also of considerable scientific and technological interest to speculate on the properties and behaviour of specimens with a classical fine-particle structure which could in principle have such outstanding properties as energy products of 16–17 MGO in strongly demagnetising configurations. However, as is so often the case, a true estimate of the chances of success for further development can only be made with difficulty, although one gains encouragement from the advances made with materials with similar intrinsic properties.