

The Coercivity of Cobalt-Platinum

POSSIBLE MECHANISMS IN RELATION TO MICROSTRUCTURE

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The magnetic properties of the 50 atomic per cent cobalt-platinum alloy are quite exceptional and make it one of the most powerful permanent magnet materials available. In this article the author reviews the accepted mechanisms for high coercivities in an attempt to establish which is the more likely to apply to equiatomic cobalt-platinum in its hard magnetic condition. Some original studies are also presented, and some suggestions are put forward for the further development of this material.

The great technological value of equiatomic cobalt-platinum alloys has long been recognised. Extremely high values of coercivity and energy product, 4500 Oe and 9.5 MGO (mega-gauss-oersted) respectively, can be achieved routinely, so these alloys are particularly suitable for use as high-quality permanent magnets. The purpose of this article is to discuss the extent to which the basic cause of the high coercivities is understood, to present some original observations on the material, and to speculate on the possibilities of further technological developments.

The earlier sections will deal mainly with

coercivity, since this is the parameter which is better understood from a scientific point of view, although energy-product is a good indication of the usefulness of a permanent magnet material.

Nearly all materials with high coercivity are in the form of fine particles or have a finely-divided structure. Exceptions are crystals of substantial size (several mm) of materials such as rare-earth orthoferrites which have exceptionally large values of the ratio K/I_s , (I_s is the saturation magnetisation in e.m.u./cm³ and K the anisotropy constant which indicates the strength of the forces binding the magnetisation to a preferred crystal axis: there is a crystal anisotropy energy $E_K = K\sin^2\theta$ when the magnetisation vector deviates by an angle θ from an easy axis).

In cobalt-platinum the finely-divided structure is known to be formed by the growth of lamellae of ordered material, with tetragonal crystal structure, in an originally disordered phase which has cubic crystal structure. The disordered phase may be retained by quenching from above 1000°C, and such single-phase disordered specimens have low coercivities (~10 Oe). Completely ordered specimens can be produced by prolonged annealing and these also have fairly low coercivities in spite of the high crystal aniso-

Approximate Intrinsic Properties of the Ordered and Disordered Phases of Cobalt-Platinum

	I_s (e.m.u. cm ⁻³)	K (erg cm ⁻³)	$2K/I_s$ (Oe)
Cubic (disordered)	600	6×10^6	2000
Tetragonal (ordered)	500	2×10^7	80,000

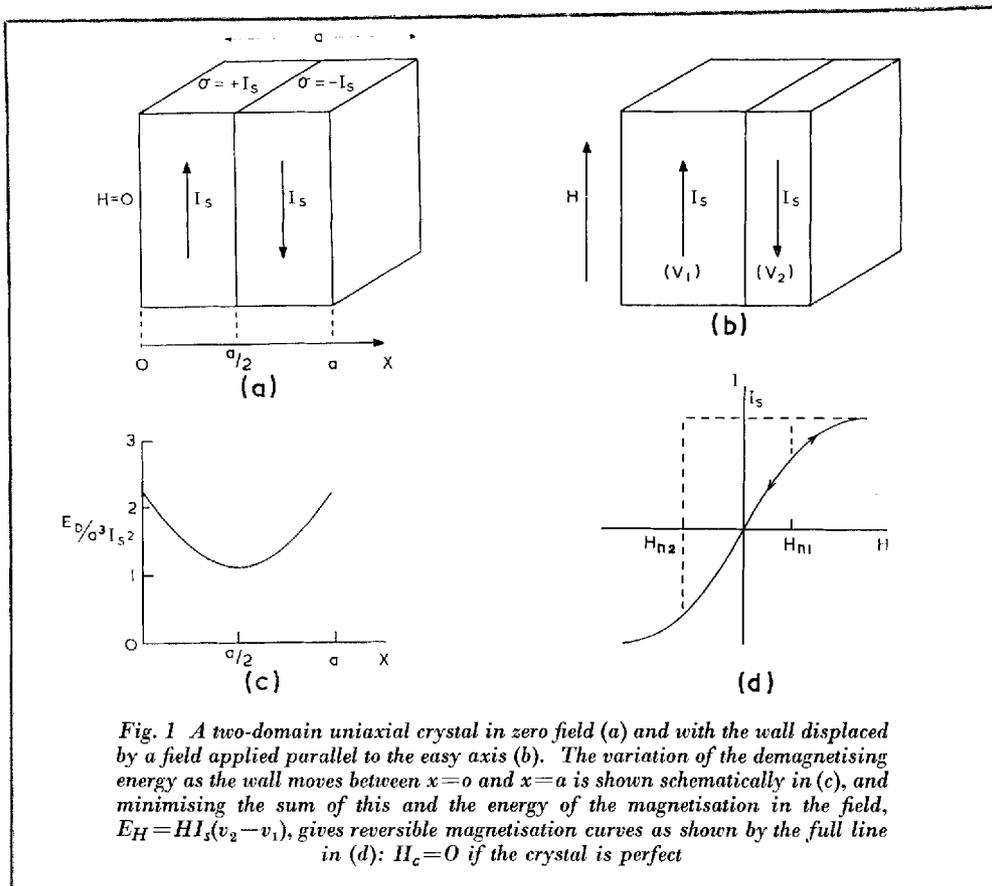


Fig. 1 A two-domain uniaxial crystal in zero field (a) and with the wall displaced by a field applied parallel to the easy axis (b). The variation of the demagnetising energy as the wall moves between $x=0$ and $x=a$ is shown schematically in (c), and minimising the sum of this and the energy of the magnetisation in the field, $E_H = HI_s(v_2 - v_1)$, gives reversible magnetisation curves as shown by the full line in (d): $H_c = 0$ if the crystal is perfect

tropy of the ordered phase. (The intrinsic properties are summarised in the table: note that the saturation magnetisation is little changed by the ordering, the principal effect being the great increase in anisotropy.) It is when about half the material is ordered, by controlled annealing, that the coercivity reaches high values, plots of coercivity vs. annealing time at 500 to 600°C showing a broad maximum (1). It has been indicated by field ion microscopy (2) that in the hard magnetic state the ordered regions have dimensions of around 200Å, and the high coercivities would appear to be associated in some way with this fine structure.

Theories of Coercivity

A perfect crystal which is subdivided into domains should have a vanishingly small coercivity. The situation is illustrated by

Fig. 1, for a two-domain crystal. Assuming that the magnetisation always follows an easy direction the anisotropy energy is zero except in the domain wall. This also involves the exchange energy constant A , since in a ferromagnetic crystal there is an energy term which depends on the rate of change of direction of the magnetisation vector and is given by $E_A = A(d\theta/dx)^2$, where θ is the angle between the magnetisation and any arbitrary direction and OX the direction along which the rotation occurs.

The calculated domain wall energy density is $\gamma = \sqrt{AK}$ erg cm^{-2} , and when neither A , K , nor the total wall area vary, as in the figure, the total wall energy is independent of the position of the wall during magnetisation.

The only energy terms which vary when a field is applied, causing the domain wall to move, are the energy of interaction of the

magnetisation with the field, $E_H = -H.I = -HI_s(v_1 - v_2)$ in Fig. 1b and zero in Fig. 1a, and the demagnetising energy E_D . This may be calculated by treating the surfaces of the crystal as sheets of uniform charge density equal to the normal component of the magnetisation across the surfaces: E_D is then found by integrating the product of the elementary charge at any point and the magnetic potential produced by the remainder of the surface charges (3).

E_D is a function of the position of the wall (x), as shown in Fig. 1c. It is minimum when the wall is central and the specimen is thus demagnetised (1a). If a field is applied the wall will take up a position for which the sum ($E_D + E_H$) is a minimum (1b) and the entire magnetisation curve can be derived as in Fig. 1d.

For the perfect crystal the curve is reversible and anhysteretic, with zero remanence and coercivity, because in the absence of a field the total variable energy is just E_D . Finite coercivities arise in three different ways.

Structural Imperfections

Whenever imperfections of the crystal structure exist the domain wall energy (more strictly the energy of the wall and its immediate environment) ceases to be independent of its position. The effect is most simply illustrated by Fig. 2, which shows a crystal including a spherical cavity. When the wall does not intersect the cavity its energy is $a^2\gamma$, and the cavity itself has a demagnetising energy equal to $(1/2)(4\pi/3)I_s^2$ per unit volume since the charge distribution at its surface is equivalent to that for a uniformly magnetised sphere, i.e., $(1/2)NI_s^2$ where the demagnetising factor, N , is just $4\pi/3$. When the wall intersects the cavity a part of the energy equivalent to the area of intersection $\times \gamma$ is abolished ("surface tension effect") and also the demagnetising energy of the cavity is reduced. Adding these two effects to give the total energy associated with the wall (E_w) one obtains a variation with position as shown in Fig. 2b, which also gives the

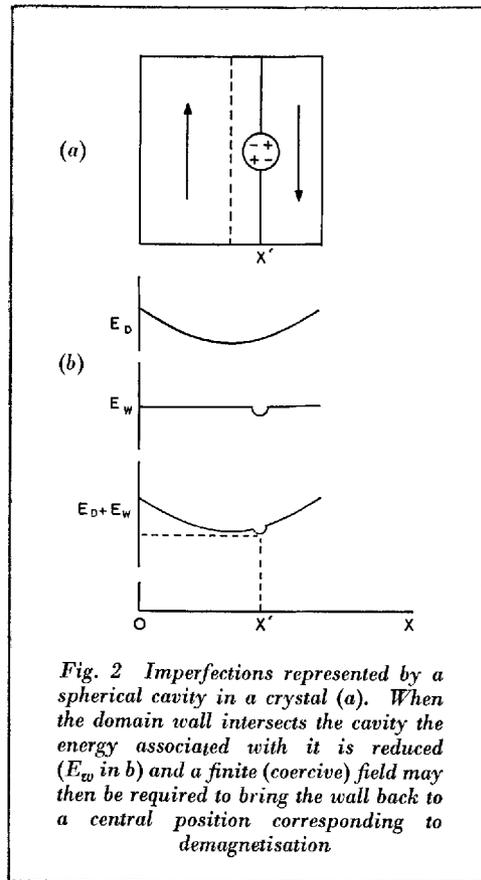


Fig. 2 Imperfections represented by a spherical cavity in a crystal (a). When the domain wall intersects the cavity the energy associated with it is reduced (E_w in b) and a finite (coercive) field may then be required to bring the wall back to a central position corresponding to demagnetisation

total energy of the system, $E_D + E_w$. A new position of minimum energy may be formed; the wall is thus impeded and a finite field is required to drive the wall away from the cavity and thus effect demagnetisation. (A little consideration will show that the nature of the slope of $(E_D + E_w)$ is of more importance than the actual positions of the minima).

This model is amenable to precise analysis. It was pointed out by Néel (4) that the changes of demagnetising energy of the inclusions are usually much more important than the reduction in wall energy itself.

The same reasoning applies to a sphere of one magnetic material (magnetisation I_{s1}) embedded in a sphere of another material (I_{s2}). If the magnetisation vectors of the two materials are parallel, however, the effectiveness will be reduced because the equivalent surface charge density will be only $(I_{s1} - I_{s2})$

resolved normal to the interface. This is discussed further in a later section.

Domain Wall Nucleation

A feature omitted from the discussion of Fig. 1 was the consequence of driving the wall right out of the crystal, i.e., it was tacitly assumed that saturation was only closely approached. It was also implied that the energy of the two-domain state was less than that of the single-domain or saturated state, but even if this is so it does not follow that, on the removal of a saturating field, the domain wall will form spontaneously. The "nucleation" of a domain of reverse magnetisation requires the rotation of the magnetisation vector in some region of the specimen, and this should require a field at least equal to that required to overcome the crystal anisotropy. This can be calculated as the crystal anisotropy field, and is equal to $2K/I_s$. The observations that nucleation fields are generally very much lower than this, in any but very small and perfect crystals such as iron "whiskers", and are affected by grinding the surfaces of a crystal, for example, indicate that nucleation barriers can be greatly reduced by the presence of structural imperfections.

If the nucleation field happens to be less than the demagnetising field of the saturated crystal (H_{n1} in Fig. 1d) this will not give a finite coercivity. It is only when $H_n (= H_{n2}$ in Fig. 1d) is greater than the demagnetising fields that it constitutes the coercive field.

Fine-particle Theory

Referring again to Fig. 1, the assumption that the multi-domain energy is lower than the single-domain energy may be questioned. The demagnetising energy of the whole crystal is the energy per unit volume $\times a^3$; for the saturated cube just $\left(\frac{1}{2}\right)(4\pi/3)I_s^2 a^3$, as for a sphere. This energy is approximately halved by the division into two domains (Fig. 1c), but a domain wall energy of (γa^2) must be introduced to effect this reduction. As a is reduced the diminution in demag-

netising energy falls off more rapidly than the increase in domain wall energy, and below a value of $a = a_{os}$ given by

$$\left(\frac{1}{2}\right)\left\{\left(\frac{1}{2}\right)(4\pi/3)I_s^2\right\}a^3 = \gamma a^2$$

$$\text{i.e. } a_{os} = 3\gamma/\pi I_s^2$$

one would not expect domains to form at all in the absence of an applied field. This gives the critical size for the single-domain state in a static sense, and in itself has no relation to coercivity at all.

However, the application of applied fields, antiparallel to the magnetisation of an initially single-domain crystal ($a < a_{os}$), changes the energy balance. For any value of a it is possible to calculate a field for which the two-domain state does have the lower energy. The magnetisation reverses completely in this field, which thus constitutes the coercivity, and so a size-dependence of the coercivity can be calculated (5). When this rises above $H_K = 2K/I_s$ domains will cease to form, and the magnetisation will rotate coherently, the upper limit of coercivity thus being H_K .

This theory is not completely satisfactory, since it ignores the possibility that the nucleation fields may be size-dependent, but one arrives at a similar upper limit corresponding to coherent rotation in either case, for sufficiently small crystals.

Applicability to Cobalt-Platinum

Fine particle theory has the appeal of simplicity, and the ordered lamellae are indeed very small (well below a_{os} in diameter).

There are two apparent difficulties concerning its direct application. First, assuming that coherent rotation does occur, the coercivity should be:

$$H_c = H_K = 4 \times 10^7 / 500 = 80,000 \text{ Oe.}$$

The problem, then is to explain the *low* values of the observed coercivities.

The second difficulty arises from the observation, which can be very easily made, that domain structures of quite common form exist in cobalt-platinum in a magnetically hard condition. They can be made visible by the ordinary powder pattern technique,

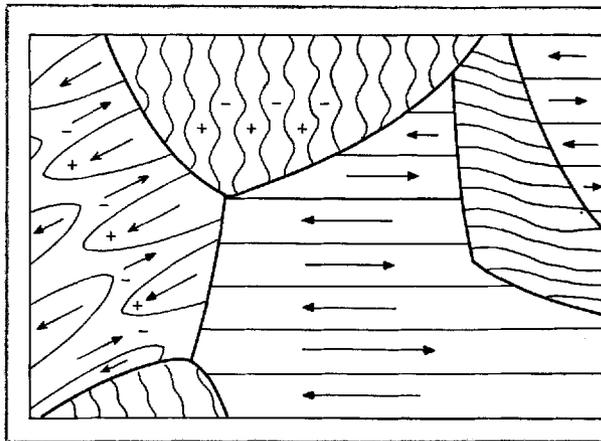


Fig. 3 A tracing of a powder pattern showing the large-scale domain structure in equi-atomic cobalt-platinum alloy in its magnetically hard condition, with the directions of magnetisation indicated. In any one region the structures are typical of a single-phase homogeneous uniaxial material, but there may be more than one such region in any one crystallite, with differently-oriented easy axes. The grain boundaries are indicated by heavy lines

and have the characteristic appearance of 180° domains in homogeneous materials with low I_s and high K , such as barium ferrite: a tracing of such a pattern for the demagnetised state is shown in Fig. 3.

The existence of large-scale domains suggests the applicability of theories based on domain wall impedance. Since the magnetisation of the two phases of cobalt-platinum are quite similar, 500 and 600 e.m.u. for the tetragonal (ordered) and cubic (disordered) material respectively, this would not at first sight seem very promising; particularly since wall impedance is usually considered to give only moderate coercivities. However, McCurrie and Gaunt (6) made two important points illustrated by Fig. 4.

Due to the orientation of the tetragonal lamellae in the cubic matrix, and the directions imposed on the magnetisation vectors by the crystal anisotropies as indicated in the figure, there will be substantial pole densities at the interfaces. The field required to move the domain wall away, i.e., H_c , will be effectively that required to magnetise the lamella shown to saturation. Also, due to the extreme shape of the lamellae, which are taken to be flat discs, these fields can be quite high: they are given by

$$H_c \cos 54^\circ 44' = 4\pi I_s \cos^2 45^\circ$$

for fields applied // $\langle 111 \rangle$ directions as indicated, and simply

$$H_c = 4\pi I_s \cos^2 45^\circ$$

for fields // $\langle 011 \rangle$ of the matrix. Presum-

ably these are obtained by equating the component of the field parallel to I_s in the lamella to the demagnetising field, taking the lamellae to be sheets with the maximum possible demagnetising factors, 4π . (It is not easy to see why the square of the cosine appears, since the pole density at the interface is $I_s \cos 45^\circ$.) The numerical values obtained for H_c are about 5000 Oe.

It is noticeable that the crystal anisotropies of the phases do not enter the expression

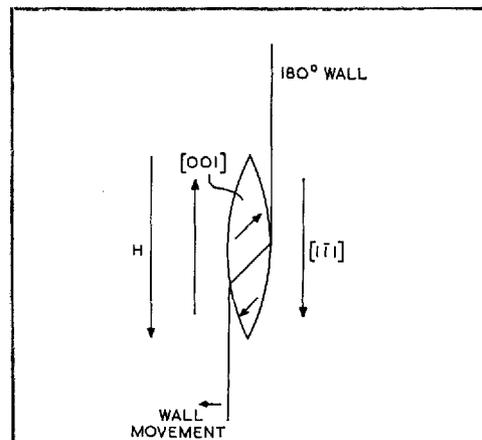


Fig. 4 A model for the orientation of the magnetisation vectors and domain walls in an ordered (uniaxial) lamella and the surrounding disordered (cubic) matrix which has been shown to give very high coercivity due to the anchoring of the domain wall. This is one of two similar possibilities proposed by McCurrie and Gaunt

for the coercivity, but the high anisotropy of the tetragonal material is a prerequisite of the model.

An alternative to this mechanism was suggested later by Gaunt (7). It is still a domain wall impedance model, but takes into account the increased domain wall energy in the tetragonal material (γ_t) with respect to that in the cubic material. To move a domain wall past a sheet of lamellae it was assumed that the wall energy would be increased in proportion to the area intersected by the lamellae. This gave, for spherical inclusions, radius r :

$$H_c = 3\gamma_t/2\pi rI$$

of the correct order of magnitude.

Structural Observations

Fig. 5 shows a powder pattern, obtained by the author using an electron microscope technique, which corresponds remarkably well with Fig. 4. It must be appreciated that this technique does not indicate the domain walls in the cubic material, since such walls are wide, due to the low anisotropy (width $\sim \sqrt{A/K}$) and give low field gradients at the surface. The presumed position of the wall in the matrix is indicated by the broken line. However, this pattern was obtained on material which had been heat-treated to a stage beyond that corresponding to the coercivity peak, as was Fig. 6 which shows very complex arrangements of multi-domain lamellae.

In general it seems only possible to observe

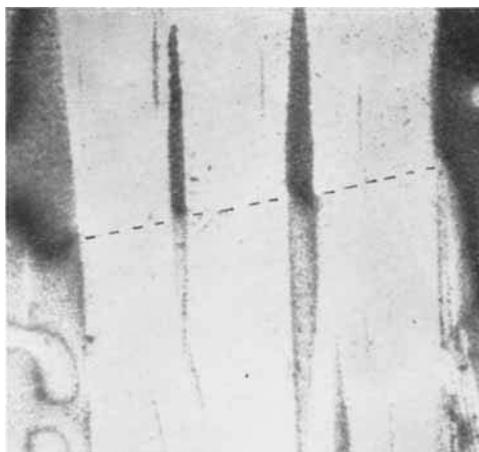
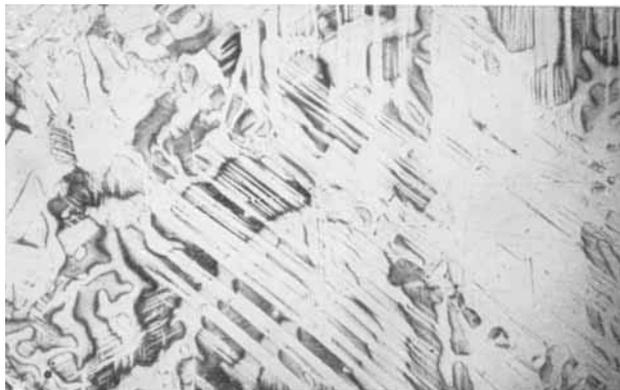


Fig. 5 Electron micrograph of a powder pattern showing two-domain lamellae of ordered material, the smaller one being $(0.2 \times 6) 10^{-4}$ cm in section. The presumed position of the wall in the matrix is indicated by the broken line

two-domain or multi-domain lamellae in cobalt-platinum which has been ordered to an excessive extent compared with the state of maximum coercivity. In fully ordered material the structure is one of uniform 180° domains (8), and in the optimum conditions one again observes very little fine structure within the 180° domains although they must clearly be different in nature.

The observations, in short, appear to favour the second of the domain wall impedance mechanisms, because this does not involve the spontaneous formation of domains within the ordered lamellae: walls only appear in the lamellae, for this mechanism, when they are forced to do so as the co-operative walls

Fig. 6 Electron micrograph showing extremely complex arrays of multi-domain lamellae of ordered material, with consistent orientations. Note (a) the pronounced interaction between the structure in neighbouring lamellae (b) no structures portrayed in the matrix due to the limitations of the technique, not necessarily to the absence of such structures. Figures 5 and 6 are for material which has been heat-treated beyond the highest coercivity condition; $H_c \sim 1000e$



in the matrix sweep past and in the absence of a field one should not find domain walls within the lamellae at all. It is clearly indicated that the observation of multi-domain lamellae corresponds to a relatively low coercivity.

A further relevant observation is that only 180° domains, presumably encompassing large numbers of ordered lamellae, are formed in the optimum material, whereas according to the first model the magnetisation should follow the four easy axes which are typical of the cubic crystal structure and thus give more complex domain structures. In the second model the directions of magnetisation are considered to be controlled by the overriding effects of the high uniaxial anisotropy of the tetragonal material.

Further Developments

Speculation about the principles controlling the coercivity in cobalt-platinum specimens of a certain type should not preclude the consideration that quite different principles might apply to the same material in an alternative physical form. Such thoughts are prompted particularly by a number of recent reports of exceptional coercivities in rare earth-cobalt alloys such as Co_3Sm (9). When prepared in a fine-particle form these high-anisotropy alloys have coercivities exceeding 20,000 Oe. But their anisotropy fields are only comparable to that of tetragonal cobalt-platinum, and it is hardly appropriate to think of them as a startling new discovery from the point of view of the potential coercivity. One very apparent distinction of the rare earth alloys is their brittleness, which permits the ready preparation of fine powders by processes such as grinding.

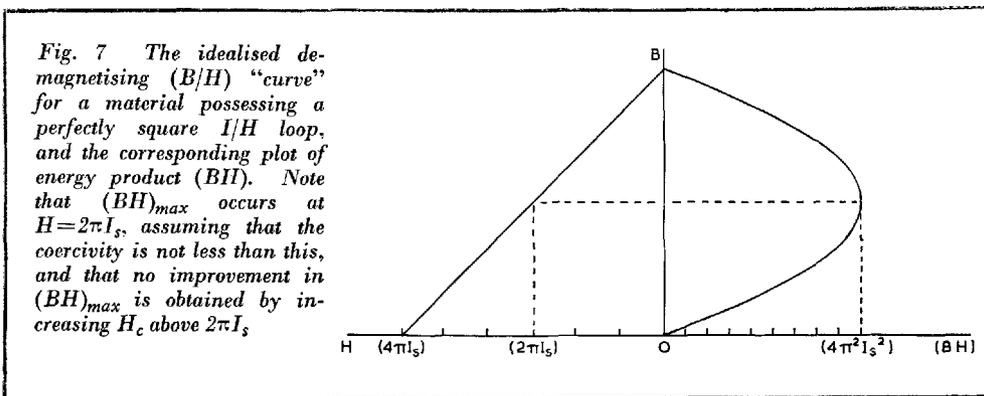
If fully ordered cobalt-platinum could be prepared in the form of sufficiently fine particles it is to be expected that the coercivity should rise towards the limit of $2K/I_s \approx 80,000$ Oe. (This assumes that the particles could be oriented, by compaction or embedding in a strong magnetic field, with their easy axes parallel: if the orientation were random the maximum value of H_c would be

K/I_s .) At the very smallest particle diameters the coercivity might be reduced by the effects of thermally-activated magnetisation reversals, but the comparison with the results so far obtained for the rare earth alloys itself indicates that the coercivities could be much higher than those for the bulk alloys. Interaction effects appear to be negligible when the coercivity is controlled by crystal anisotropy rather than shape anisotropy.

Two questions arise. First, how may such fine particles be prepared? and second, what would be the value of increased coercivities?

It does not appear that grinding would be appropriate, and in any case this is a very crude method of preparing fine particles since it strains and deforms the crystal lattice with a consequent loss of coercivity (which may be partially restored by annealing the rare earth alloys). There are at least two alternatives. One is the evaporation of the alloy in a considerable pressure of inert gas such as argon. This has been shown to give particles of iron, cobalt, nickel, etc., with particle sizes which range down to the order of 100\AA and can be controlled to a certain extent. These particles could be simultaneously collected and aligned by applying strong and non-uniform magnetic fields, and further densification and particle-size control achieved by controlled sintering. It would be necessary to check for changes in the ratio of the components during evaporation; in fact there would clearly be a number of factors to study and control. If the particles were originally formed in a disordered state this could be rectified by further annealing.

The second possible method of preparation suggested would consist of preparing mixed salts of cobalt and platinum, decomposing these to give finely-divided oxides, and finally reducing the oxides to give the finely-divided alloy. In order to maintain the very low particle sizes it might be necessary to utilise an inert diluting solid such as silica, with a consequent loss of magnet power. Only experiments would show how serious a drawback this would be. It is certainly



possible to prepare mixed oxides of 3d transition metals with very low particle size at 50 per cent concentration, and also to prepare particles of platinum metal, diluted with silica, with particle sizes of the order of 100Å; these are commonly used as catalysts.

To estimate the possible usefulness of extremely high coercivities, the effect on the maximum energy product $(BH)_{max}$ may first be considered in relation to the idealised demagnetisation curve in Fig. 7. It is supposed that the particles are aligned so that the magnetisation remains at its saturation value until abrupt reversal occurs in the coercive field. In this case the equation of the "curve" is

$$B = 4\pi I_s - H$$

with intercepts $4\pi I_s$ on both axes, as shown. The product $(BH)_{max}$ is commonly used as an indication of the "power" of a permanent magnet, since it indicates how much magnetic energy can be produced in a gap in a ring of the material. In the ideal case:

$$BH = 4\pi I_s H - H^2$$

$$\frac{\delta (BH)}{\delta H} = 4\pi I_s - 2H$$

and this product is maximum when

$$4\pi I_s = 2H \text{ and } H = 2\pi I_s$$

as might have been guessed by considering the symmetry of Fig. 7.

Assuming that $H_c \geq 2\pi I_s$:

$$(BH)_{max} = 4\pi^2 I_s^2 \doteq 10 \text{ MGO}$$

and since $2\pi I_s \doteq 3000$ the condition is met

by moderate coercivities (for this material) and no improvement in the maximum energy product would be achieved by special measures to increase the coercivity.

However, the value of $(BH)_{max}$ is not all-important, and there are two situations in which the coercivity itself is of primary importance. One is in designs for which it is essential that the magnet shape is that of a flat, thin disc, with the magnetisation directed across the broad surface, so that the demagnetising factor approaches 4π and thus the demagnetising fields to which the magnet is exposed approach $4\pi I_s$. (In the limit, of course, no external fields are produced and $BH=0$). The other situation is that in which the magnet may be exposed to large fields of external origin: it is usually only when the coercivity is far in excess of such fields that the magnetisation remains unchanged and that the induction charges are reversible, corresponding to complete magnet stability.

Returning, finally, to the continuous alloy there is still apparent scope for improvement in the energy product, with a similar coercivity, by considering the directional properties. The effective anisotropy of the magnetically hard material is very complex, and does not appear to have been adequately studied. It is a combination of a uniaxial anisotropy in any one region (not necessarily in any one crystallite), due to the overriding effect of the tetragonal lamellae which are aligned within that region, and a cubic anisotropy arising from the variation of the

common easy axes of tetragonal lamellae from one region to another.

If some means of controlling the ordering process could be devised, such that *all* the tetragonal lamellae formed with the same crystallographic orientation with respect to the original disordered cubic lattice, then a single crystal or grain-oriented polycrystal should have properties which approximate closely to those represented by Fig. 7. The $(BH)_{\max}$ values should then be considerably raised. This might be achieved by the application of stress during the heat treatment, with due regard to the changes in lattice constants during ordering.

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Platinised Titanium Anodes in Chlorate Production

Since the initial announcement in 1958 by J. B. Cotton, of I.C.I., (1) of the advantages and potential usefulness of a titanium anode having a thin coating of platinum, a great deal of experimental and developmental work has been carried out in many quarters. Although the first application proposed was in cathodic protection, it was very soon apparent that the most important area in which anodes of this type could find a major use was in the electrolysis of brine to produce chlorine or sodium chlorate.

In this field graphite anodes have become established over many years, but they have several disadvantages, including poor conductivity (and therefore massive construction) and gradual corrosion, involving periodic adjustment of anode spacing and operation at fairly low temperatures. Metallic anodes thus offered considerable advantages if they could be shown to perform satisfactorily and economically.

Unfortunately, platinum-faced titanium anodes are susceptible to attack by mercury, and they have not therefore been adopted in mercury cathode cells, but in diaphragm cells this problem does not arise and the use of titanium anodes having a thin coating of platinum – or more recently of a 30 per cent iridium-platinum alloy – is likely to become commercial practice in chlorine production in the near future.

In the production of sodium chlorate, however, progress in this direction is rather more rapid. For example, a recent paper from Olin Mathieson (2) describes some earlier development work in the design and operation of first a pilot scale cell and then of a commercial cell using platinum-plated titanium anodes. The thickness of the platinum deposit was 0.00017 inch, and the loss of platinum was 5.3 grams per ton of sodium chlorate, with the expectation that this loss could be reduced with greater control and experience.

A commercial installation recently designed by Krebs et Cie SA for the Finnish manufacturer of paper pulp Oulu Osakeyhtio to produce 10,000 tons a year of sodium chlorate by the beginning of 1970 is to be equipped with titanium anodes having a 30 per cent iridium-platinum coating. This will permit the use of higher current densities and of a higher working temperature than hitherto, while a very low figure for platinum consumption is expected. Preliminary trials with the Krebs cell showed a loss of 500 mg of alloy per ton of chlorate produced, but experience of two years' operation has led to an estimate of only some 200 mg per ton.

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