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**THE RECENT DEVELOPMENT OF PERMANENT
MAGNET MATERIALS CONTAINING
RARE EARTH METALS**

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University of Dayton

TECHNICAL REPORT AFML-TR-69-299

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FOREWORD

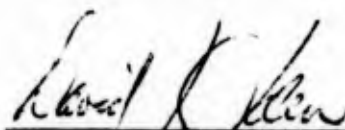
This report deals with a group of new permanent magnet materials which are superior in many respects to conventional magnets and which are potentially of great importance for the Air Force. The paper reviews results obtained before the fall of 1969 in a development effort that began in 1965 with the discovery of the large crystal anisotropy of YCo_5 and the realization of the great practical potential of this and some related compounds in the course of a rather basic research investigation in the AF Materials Laboratory. The effort has since then become worldwide, with a growing number of industrial, governmental and university laboratories participating with remarkable success. The author's group at the University of Dayton, in close cooperation with the Physics Division, AF Materials Laboratory has also continued experimental and analytical work. Results of this are incorporated in the report which is, however, a broad review of the general development effort.

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The report manuscript served as the basis of a review paper presented at the 2nd European Conference on Hardmagnetic Materials which will be printed in the IEEE Transactions on Magnetics in 1970. The manuscript was released by the author in November 1969 for publication as a technical report.

The author acknowledges gratefully the continuing support by Dr. A. E. Ray and the experimental assistance of the Messrs. D. Walsh, H. Mildrum and A. Kleman, all of the University of Dayton. Rare earths and alloys were donated by the Ronson Corp. and the Th. Goldschmidt Comp. Data compilations and some unpublished experimental results by Mr. G. I. Hoffer, formerly of the Air Force Materials Laboratory, have been used.

This technical report has been reviewed and is approved for publication.



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ABSTRACT

The prospect that permanent magnets with previously unattainable coercivities and energy products might be made from cobalt-rare earth alloys has caused intense research efforts in the last three years. Alternative ways of preparing magnets from powders and by casting were demonstrated in several laboratories. $(BH)_{\max} \approx 20 \text{ MGOe}$ and $M_H > 25000 \text{ Oe}$ have been achieved with SmCo_5 , and the development of manufacturing processes for magnets made from this alloy has begun.

This paper reviews the basic concepts, properties of the alloys of interest and the physical factors influencing the coercive force. Approaches to alloy, powder and magnet fabrication are discussed, with their merits and drawbacks; also problems incurred in the materials development and their possible solutions. Application areas are reviewed and some economic factors considered.

It is concluded that the RCO_5 magnets are indeed beginning to live up to their promise, but that more materials research, process development and circuit redesign are needed if their potential is to be fully utilized.

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SECTION I

INTRODUCTION

Research work aimed at discovering new permanent magnet materials in the period after World War II has been strongly influenced by predictions based on the theoretical model of single-domain particles¹ and the evolution of micromagnetic concepts. The latter took place as an interplay of theoretical analysis and new experimental findings about the magnetic behavior of fine ferromagnetic powders. Following a decade of intense work on shape-anisotropic particles, which resulted in the commercial magnets of the ESD-type² but also revealed the limitations inherent in this approach,³ researchers turned their attention to magnetic substances with high magnetocrystalline anisotropy. Two previously discovered ferrimagnetic oxides which are in this category, the barium and strontium ferrites have, of course, achieved outstanding commercial significance. PtCo, known since 1936 as a material of very desirable properties that is much too expensive for widespread application, has found increased use in recent years. Of the many other compounds studied more recently,^{4, 5} MnBi and a Mn-Al phase seemed especially promising. A considerable amount of development work was done on them, but because of various serious problems encountered, the materials have not yet found technological application.

In the meantime, many of the so-called rare earth metals, (abbreviated below as R), i. e., the fifteen elements No. 57, lanthanum, through 71, lutetium, and their close chemical kins, yttrium (39) and scandium (21), became available individually and in quantity.

This stimulated basic research into the properties of the rare earth elements and their alloys. (For a recent review of this work see e. g. reference 6.) While most of these substances have magnetic properties that are of considerable but so far strictly academic interest, some of the intermetallic phases of the rare earths with transition metals of the iron group have sufficiently high saturation magnetization and Curie temperature to make them appear possible candidates for use in magnetic devices at room temperature. Notable for this reason are especially the rare earth compounds with cobalt, but some of the iron and manganese intermetallics are also of interest. For recent reviews of the basic properties of these groups of compounds, the reader is referred to the papers by Lemaire et al.,^{6, 7} Velge and Buschow,⁸ Ray,⁹ Kirchmayr,¹⁰ Strnat et al.^{11, 12} and to the references cited there.

A survey of such intermetallic phases for those that may be useful in permanent magnets restricts the choice essentially to the cobalt-rich R-Co alloys of the light rare earths and yttrium.^{12, 13} Investigations of the magnetocrystalline anisotropy of several R-Co intermetallic

compounds were performed on this premise. They showed that the compound YCo_5 ,^{14,15} and most of the other isostructural RCo_5 phases,^{16,17} have extremely high anisotropy constants, the hexagonal c-axis usually being the direction preferred by the magnetization vector. These findings were quickly interpreted to mean that the RCo_5 phases where $\text{R} = \text{Ce}, \text{Pr}, \text{Sm}$, or a mixture of several rare-earth metals have outstanding potential as new permanent magnet materials,^{14,16,18} and first attempts were made to realize this promise in the laboratory. LaCo_5 and ThCo_5 were added to the list of candidate materials by Buschow et al.^{8,17} Lattice parameters,¹⁹ saturation values^{20,21} and Curie temperatures²¹ for most RCo_5 phases had been previously reported. Earlier reports of a high crystal anisotropy and high coercivity of powders for GdCo_5 ²² and neutron diffraction results for YCo_5 ²³ could have suggested the utility of the RCo_5 phases for magnets, but these clues were generally overlooked at the time.

SECTION II

PROPERTIES OF THE RCo_5 COMPOUNDS THAT MAKE THEM USEFUL FOR PERMANENT MAGNETS

Before preceeding to a discussion of the magnet development work to date, we shall briefly summarize the present knowledge of the pertinent basic properties of several RCo_5 phases and review the reasons why these alloys are so highly desirable as the active component of permanent magnets.

Table I lists what the author believes to be the most reliable reported data for the Curie temperature, T_c ; the room temperature values of the saturation magnetization, $4\pi M_s = B_s$; the anisotropy field, H_A ; an anisotropy constant, $K = H_A M_s / 2$; the X-ray density, d_x ; and the melting temperatures, t_l and t_p . In some cases where newer and better results are now available, there are discrepancies with previously published figures. Our new, lower Curie temperatures for the Y, Ce, Pr and Sm compounds were determined from 1kHz initial permeability measurements²⁴ ("anisotropy Curie points") and are believed to be accurate to within a few degrees. For H_A of CeCo_5 , PrCo_5 and SmCo_5 , where different numbers of equal credibility have been measured on different samples, the range covered by them is given. Such a range may be expected for all the properties listed, since the RCo_5 phases show finite - if as yet poorly established - homogeneity regions in the phase diagrams. This composition dependence has not been systematically studied for any of the phases or parameters. H_A may be affected strongly by a minor change in composition, because it depends sensitively on the lattice parameters.

TABLE I. Selected Magnetic and Physical Properties of Some RCo₅ Phases¹

	YCo ₅	LaCo ₅	CeCo ₅	PrCo ₅	SmCo ₅	(MM)Co ₅ (2)
T _C [°C]	648	567	374	612	724	495, 541 (3)
4πM _S [G]	10600	9090	7700	12000	9650	~8900
H _A [kOe]	~130	~175	170 - 210	145 - 210	210 - 290	180 - 195 (4)
K [10 ⁷ erg/cm ³]	~5.5	~6.3	5.2 - 6.4	6.9 - 10.0	8.1 - 11.2	6.4 - 6.9 (5)
d _x [g/cm ³]	7.60	8.03	8.55	8.34	8.60	~8.35 (6)
t _i [°C]	~1360	~1220	~1205	~1245	~1325	(7)
t _p [°C]	1352	1090	1196	1232	1320	~1185 (8)

- (1) This table is based on a critical review of available literature data and on unpublished results obtained at the University of Dayton and the US Air Force Materials Laboratory.
- (2) T_C = 495° and the other properties are for MM = Ceralloy 100X of the Ronson Metals Corp. (54.5% Ce, 26% La, 13% Nd, 5% Pr).
- (3) T_C of LaCo₅ from Reference 8, other values from Reference 24. The two values for (MM)Co₅ are for alloys made with mischmetal from two producers.
- (4) H_A is the field strength needed to saturate normal to the c-axis direction. Values estimated by extrapolation of hard-axis magnetization curves measured on single crystals (Y, Sm) or crystal-oriented powders at fields up to 45-65 kOe.
- (5) Anisotropy constant calculated as K = H_AM_S/2
- (6) Average densities. Reported values cover a range, but with no correlation to composition.
- (7) Liquidus temperature (8) Temperature of peritectic reaction by which RCo₅ is formed.

The variation of M_s should be much less; in fact, all recently reported saturation values deviate very little from those listed in Table I. M_s is expected to rise toward the Co-rich side of the homogeneity region, proportional to the increase in the cobalt content of the alloy.

The saturation magnetization determines the absolute theoretical upper limit of the energy product possible for magnets made from a given ferromagnetic substance, which is $(BH)_{\max} = 4\pi^2 M_s^2$. The theoretical limit for the intrinsic coercive force is H_A . It is thus important to know the temperature dependence of these two quantities in the range of temperatures to which magnets may be exposed in use, but very few such measurements have been reported. The data known to the author is summarized in Figure 1. For the reasons mentioned above, values for other alloys may well deviate from those measured on individual samples whose exact composition within the homogeneity region was not specified. However, the trends seen should be generally valid. For comparison, curves for two "classic" high-anisotropy materials, barium ferrite and MnBi, are shown. It can be seen that the anisotropy of the R-Co phases is approximately one order of magnitude higher than that of the ferrites and does not exhibit the sharp decrease with temperature which is one of the serious problems of MnBi. NdCo_5 (not shown) is an exception. Its anisotropy has a low minimum near the ice point which makes the compound unsuited for magnet use. The magnetic moment per unit mass for the RCo_5 at room temperature is greater than that of the ferrites, the magnetization per unit volume even more so, and the temperature coefficient of σ is much more favorable.

From the saturation induction values were calculated theoretical energy product values for magnets based on the RCo_5 phases which are far in excess of those of present-date commercial magnets,^{12,16,18} and because of the extreme anisotropy there was reason to hope that they could be approached in practice. The theoretical energies, based on the newer saturation data of Table I, are recapitulated in Table II. Energy products per unit volume and unit weight are calculated for a density of 100% (which can be approached by sintering,²⁵ or with extreme pressures,²⁶ or in massive two-phase alloys²⁷), and for a 70% effective packing fraction of the magnetic phase which can be obtained by conventional pressing with a binder.²⁸ These values are contrasted with the best energy products, coercive forces and packing densities that have so far been experimentally achieved. In addition to the "pure" RCo_5 phases, two alloys are included in the Table in which a part of the cobalt is replaced by copper and iron. They are only examples of many possible magnet alloys in this category.

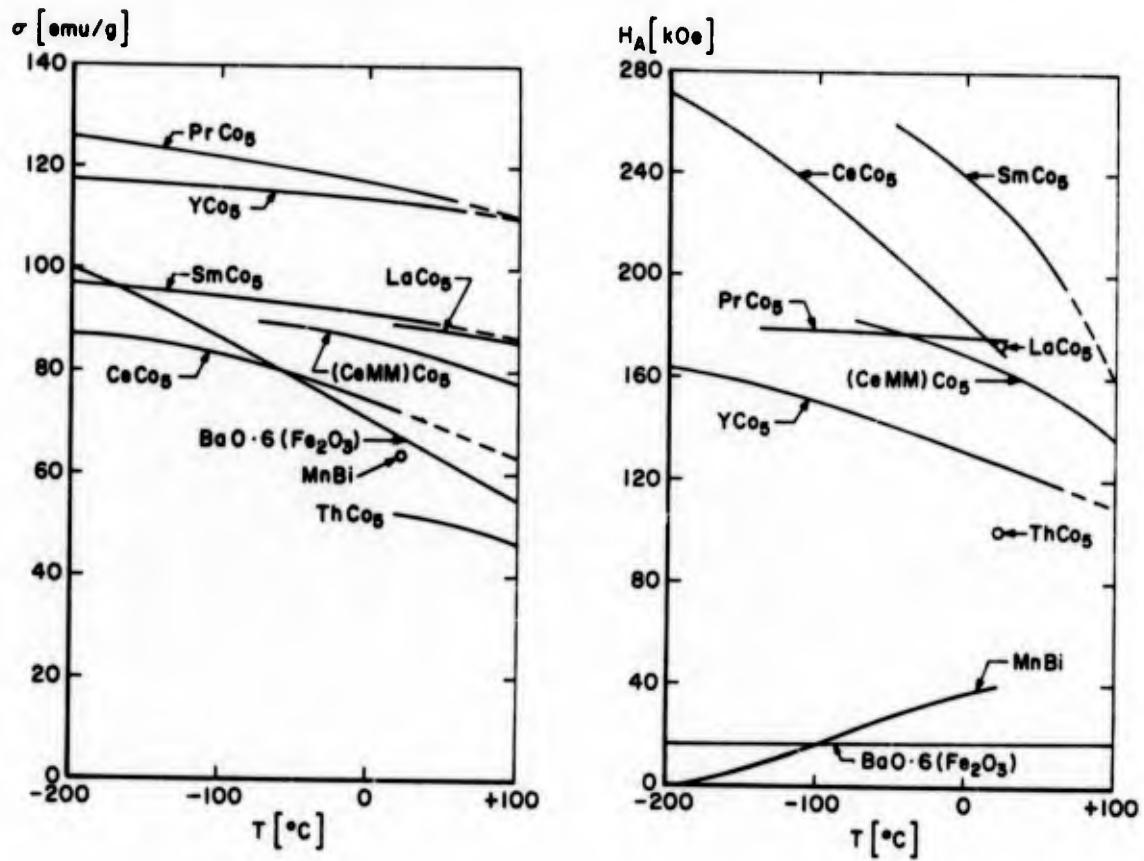


Figure 1. Temperature dependence of the magnetic saturation moment per unit mass and of the crystal anisotropy field.

TABLE II. Permanent Magnet Properties of Some RCo₅ Phases and Related Alloys

Material		YCo ₅	LaCo ₅	CeCo ₅	PrCo ₅	SmCo ₅	(MM)Co ₅	SmCo _{3.5} Cu _{1.35} Fe _{0.4}	Ce _{1.05} Co _{4.25} Cu _{0.75}
Theoretical Limits	(BH) _{max} { [MGOe] { p=100% p=70%	28.1	20.6	14.8	36.0	23.4	19.8	~11.5	~10.5
	(BH) _{max} /4πd { [10 ⁴ erg/g] { p=100% p=70%	13.8	10.1	7.2	17.6	11.4	9.7	~5.6	~5.1
	(BH) _{max} /4πd { [10 ⁴ erg/g] { p=100% p=70%	29.4	20.4	13.8	34.3	21.6	18.8	~10.6	~9.8
Best Reported Magnet Properties	Record values of M _{Hc} [Oe]	(1) 20.6	14.3	9.6	24.0	15.1	13.2	~7.4	~6.9
	(2) 6700		3600	2800	5750	25000	4750	28700	10500
	M _{Hc} [Oe]	(3) 2650	LaSmCo ₁₀	--	3500	25000	2010	5500	3750
	B _{Hc} [Oe]	1600	3350	--	2680	9000	1620	4000	3250
	4πM _r [G]	3000	5195	--	4910	9000	4060	6400	6000
	d [g/cm ³]	(4) 4.85	--	--	5.3	8.5	5.1	~8.5	~8.5
	p [%]	(5) 64	--	--	63.5	>98	61.4	~100	~100
	(BH) _{max} [MGOe]	1.5	5.81	--	4.35	20	2.34	8.8	8.0
	(BH) _{max} /4πd [10 ⁴ erg/g]	(6) 1.87	--	--	6.5	18.7	3.64	8.2	7.5

- (1) In calculating the energy per unit weight, the d_x-values of Table I were used for p=100%, 0.7d_x for a packing density of p=70%, i. e., 30% void is assumed. If a heavy binder is used, the energy figures for p=70% are lower.
- (2) These are the highest values measured on powders of the RCo₅ components, or on massive pieces of R(Co, Cu, Fe)₅ alloys similar to, but not identical with, the compositions given at the top of the table.
- (3) These M_{Hc} values and the properties below are all for one sample reported to have the highest energy product achieved so far with the alloy composition given at the top of the table.
- (4) Pycnometric densities of pressed or sintered samples made without a binder. Estimated values for the massive, two-phase alloys for the last two materials.
- (5) p = 100 d/dx.
- (6) The pycnometric density, p, was used in calculating these numbers.

SECTION III

UNIQUE CHARACTERISTICS AND POTENTIAL DEVICE USES OF RCO_5 MAGNETS

Of the two commercially important types of permanent magnets, the Alnicos offer high remanent flux density (8-13kG) combined with relatively low coercive force (500-2000 Oe), with an inverse relationship between these two properties (see Figure 2). The low coercivity keeps the energy product far below $4\pi^2 M_s^2$. It also imposes geometrical design restrictions and causes a poor recoil behavior which brings with it severe disadvantages for dynamic applications such as in permanent-magnet motors. The ferrites have considerably higher coercive forces, but the remanence is confined to the range 3.5-4.75kG, consequently the energy product to < 5.7 MGOe, and the Curie point is low ($T_c = 460^\circ\text{C}$).

The RCO_5 alloys combine the advantages of both types: they have saturation values and (with the exception of CeCo_5) Curie temperatures not much below those of the Alnicos. The coercive forces can be far in excess of those of the ferrites. As a consequence, previously impossible values of the energy product may be achieved, and excellent dynamic behavior and stability against demagnetization should result. Until recently, the only magnet material which showed this favorable combination of properties (although to a lesser degree) was PtCo. This alloy contains 75 weight % platinum which makes it prohibitively expensive for most applications. The above comparison is illustrated in Figure 2 with demagnetization curves for the best commercial magnets, the ideal lines for four of the RCO_5 alloys, and curves for the best experimental cobalt-rare earth-based magnets of three different varieties. In the left half of the bar graph, Figure 3, the static energy products of RCO_5 magnets are compared with the best of commercially available magnets. The markers indicate the results of various attempts to prepare R-Co magnets. Here, the copper-containing modifications are included with the "parent alloy," CeCo_5 or SmCo_5 .

In many applications of magnets, a high static energy product is not sufficient to insure good performance, and a very high coercive force is needed,²⁹ ideally $BH_c \approx 4\pi M_r$ and consequently $MH_c > 4\pi M_r$. In the strongly demagnetizing geometry of traveling-wave tube focussing magnets, BH_c directly determines the usable field, and in permanent-magnet motors equally high coercivities are very desirable. The straight-line demagnetization curve which is the consequence of a high H_c and of good crystal alignment permits greater freedom in design and a high useful recoil energy product,^{29,30} $(BH)_u$, which can become equal to the static $(BH)_{\text{max}}$. The comparison of $(BH)_u$ values made in the right half of Figure 3 shows that the RCO_5 magnets have an overwhelming advantage over conventional materials in dynamic applications.

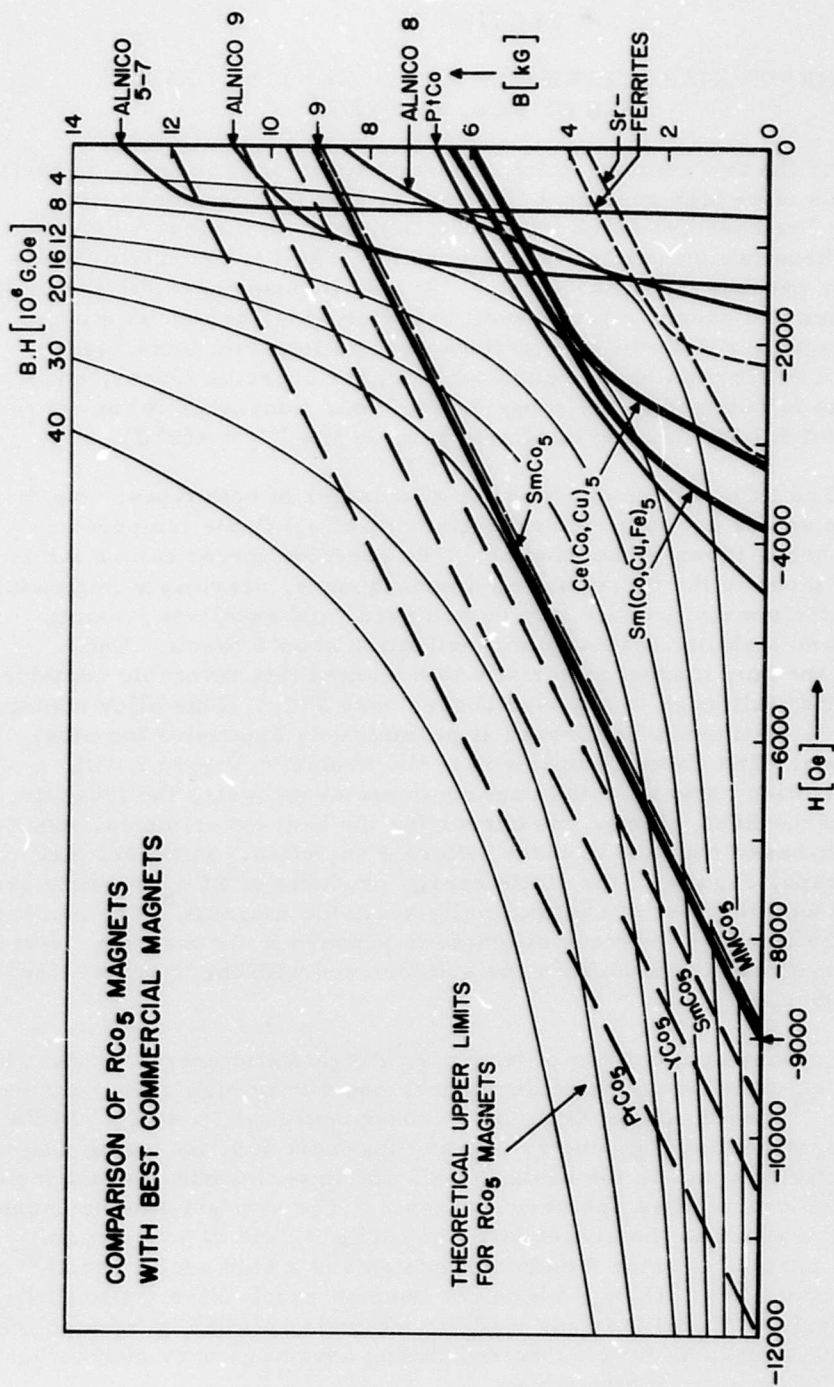


Figure 2. Demagnetization curves for selected commercial magnet types, theoretical curves for four RCO_5 materials, and the best reported experimental results for three kinds of cobalt-rare earth-based magnets.

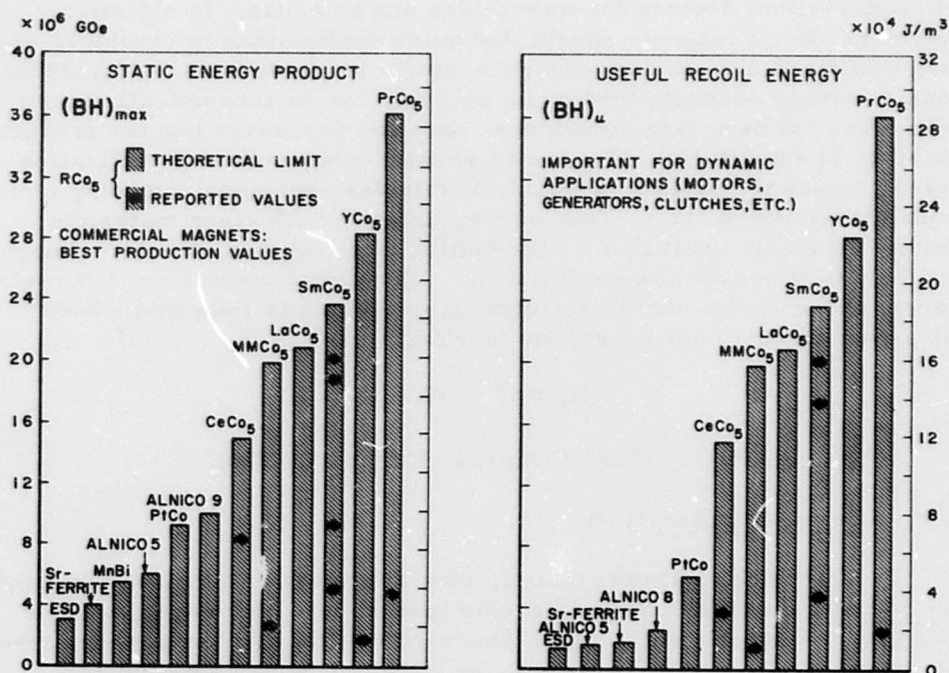


Figure 3. Comparison of static and dynamic energy products for the best commercial magnets and cobalt-rare earth-based magnets. Most of the experimental values of $(BH)_u$ were estimated from published static demagnetization curves.

If we try to predict in which technological fields the R-Co magnets could become commercially significant, we have to keep in mind that they are made from relatively expensive materials. Thus they will never be able to compete with the ferrites and lower-grade Alnicos for use in such cheap, mass-produced items where a low price is most important and performance demands are minimal. Natural areas of initial application are those where even PtCo has been used in spite of its extreme price, or where it would be used if it were a factor ten cheaper: traveling-wave tube focussing stacks, electric wrist watches, and ferrite-biasing magnets in Faraday-effect devices for waveguides and antennas. In electrical machinery, R-Co magnets should find quick applications in brushless and other miniature d. c. motors and generators; but in view of the favorable dynamic energy products they could well become an economically sound choice even for very large machines, once the necessary magnet production capability is established. There are several other potential application areas: microwave tubes in general, frictionless bearings, stepping motors, torque transmitters, etc. And, as was the case with other materials offering a hitherto unavailable combination of properties, the RCo_5 magnets are likely to generate new applications. These may come from a pursuit of some of the device and design concepts put forth in Polgreen's book³¹ with a view toward high-coercivity ferrites.

SECTION IV

APPROACHES TO MAGNET FABRICATION

A. Basic Considerations

According to simple theory, small crystals of a high-anisotropy material with a single easy axis should have an intrinsic coercive force equal to H_A . Experimentally it is observed that the $M H_c$ of powders rises with decreasing particle size to maximum values between 15 and 30% of H_A . By analogy with other materials, one might therefore expect $M H_c = 20$ to 90 kOe for the RCo_5 phases. Even the lower value would be far more than is practically needed. Thus, one approach to making magnets from such materials is to prepare them in the form of small crystal particles and pack these densely, with good parallel alignment of their easy axes.

The classical mechanism for the magnetic hardening of massive materials is to create obstacles to domain wall motion. While it was long believed that this could only bring about H_c values of several hundred oersteds, this is not true. If the crystal anisotropy is uniaxial and as high as in the RCo_5 alloys, wall motion coercive forces of many thousand

oersted may be achieved in this manner. Thus, a second principal way to make permanent magnets from the new substances is to harden them in the bulk, for instance by precipitating out a finely distributed, nonmagnetic second phase within the crystals.

Two successful, practical approaches have been used to prepare R-Co magnets in the laboratory. One is to make a powder of the alloy and build up a magnet from it; the other is to cause a two-phase structure in the massive material by proper alloying additions and heat treatment. We shall discuss these in some detail below and interpret them in terms of the two basic magnetic hardening mechanisms.

B. Alloy Preparation

In most experiments to date, the alloys to be powdered or cast were prepared by fusing the elemental metals together in the desired ratio. The R.E. metals are highly reactive when hot, so the melting must be done in vacuum or a protective atmosphere. Small samples were made by levitation melting, arc melting, or in alumina crucibles of high density and extreme purity. As larger quantities of the alloys are produced, crucible and atmosphere requirements become less stringent. All RCo_5 alloys form by a peritectic reaction, but, except for LaCo_5 , the liquidus and solidus temperatures are very close together. Consequently, most can be prepared as single-phase alloys directly from the melt when the proper cooling rates are observed. Sometimes - for LaCo_5 always - a homogenization heat treatment just below the peritectic temperature is required. The binary R-Co phase diagrams of interest are now reasonably well established³²⁻³⁷. An electrolytic process of producing a R-Co master alloy of near-eutectic composition, developed by Henrie and co-workers,³⁸ may become commercially important. By eliminating several production steps, it could help reduce the material cost. The alloy must be remelted and cobalt added, but this presents no new problems.

C. Preparation of Powders

The R-Co alloys are brittle, so it is feasible to prepare fine powders by mechanical grinding. This has been done with varying success on all the RCo_5 phases, using several grinding techniques and mills.^{5, 8, 12, 16, 22, 28} The coercive force obtainable by grinding is limited by a phenomenon previously observed on other substances: H_c increases with decreasing particle size to a maximum and then drops again. Simultaneously it becomes more and more difficult to align the particles in a field. This is attributed to a progressive disruption of the crystal lattice by deformation during grinding which locally lowers the anisotropy.^{5, 16, 17, 39} The H_c -maxima thus obtained are between 2000 and 6000 Oe for most RCo_5 , with

coercivity and alignability of the powder depending on the grinding method²⁸ as well as on the material. These values are not quite high enough for outstanding magnets. Annealing to heal the plastic deformation damage to the crystals, which works well for the ferrites,⁴⁰ so far brought only insignificant improvement of the magnetic properties.^{5, 41} Grinding of the materials in a more brittle state below room temperature is beneficial, but little has been reported of such work.^{39, 41} Several alternative methods of producing powders without excessive grinding have been tried, and appreciably improved powders of YCo_5 and MnCo_5 were prepared by chemical comminution,⁵ and by an amalgam process which combines alloying and pulverization.⁴²

SmCo_5 exhibits the detrimental effects of cold work to a much lesser degree.⁵ MH_c -peaks of 10 to 16 kOe are obtained by grinding,^{16, 17} H_c can be raised up to 25 kOe by subsequent measures,^{5, 25} and excellent SmCo_5 magnets can be made.^{16, 25, 26, 43} This different behavior has been attributed to optimum lattice dimensions for SmCo_5 and GdCo_5 which cause the high anisotropy and a low sensitivity of the latter to plastic deformation.¹⁷ Also, SmCo_5 appears to be more brittle than other R-Co phases. The coercivity of SmCo_5 powders depends in a rather unusual manner on the magnetizing field.^{5, 12} H_c increases strongly with the field up to at least 50 kOe.⁵ Unfortunately, the highest coercivities are not stable. With SmCo_5 ,⁵ and to a lesser degree for the other substances as well,⁴⁴ a drastic reduction of H_c occurs when powders or compacts are aged in air at and above room temperature (see Figure 4). This aging is caused by a very slight superficial corrosion of the particles. This instability problem, although it is much less severe than e. g., with MnBi , must be solved. Fortunately, various ways of coating the particles or the magnets show promise, and the densification of SmCo_5 to near 100% by sintering or pressing is said to stabilize the magnets rather well,⁴³ even to temperatures of 250°C.²⁵

D. Physical Concept of the Magnetization Reversal

Becker⁴⁵ and Zijlstra⁴⁶ have developed a model that explains the dependence of the coercivity of SmCo_5 and other high-anisotropy powders upon the magnetizing field, lattice perfection, and particle surface conditions in terms of domain-wall motion, pinning and nucleation. This model, for which convincing direct evidence has been offered,⁴⁷ supersedes the concept of single-domain particles reversing by coherent spin rotation. Particles full of crystal imperfections from the grinding reverse by wall motion impeded by the stress fields associated with the deformation. Coercivities of several thousand oersted are possible this way which are independent of the magnetizing field above 10-20 kOe and of the surface condition. In the

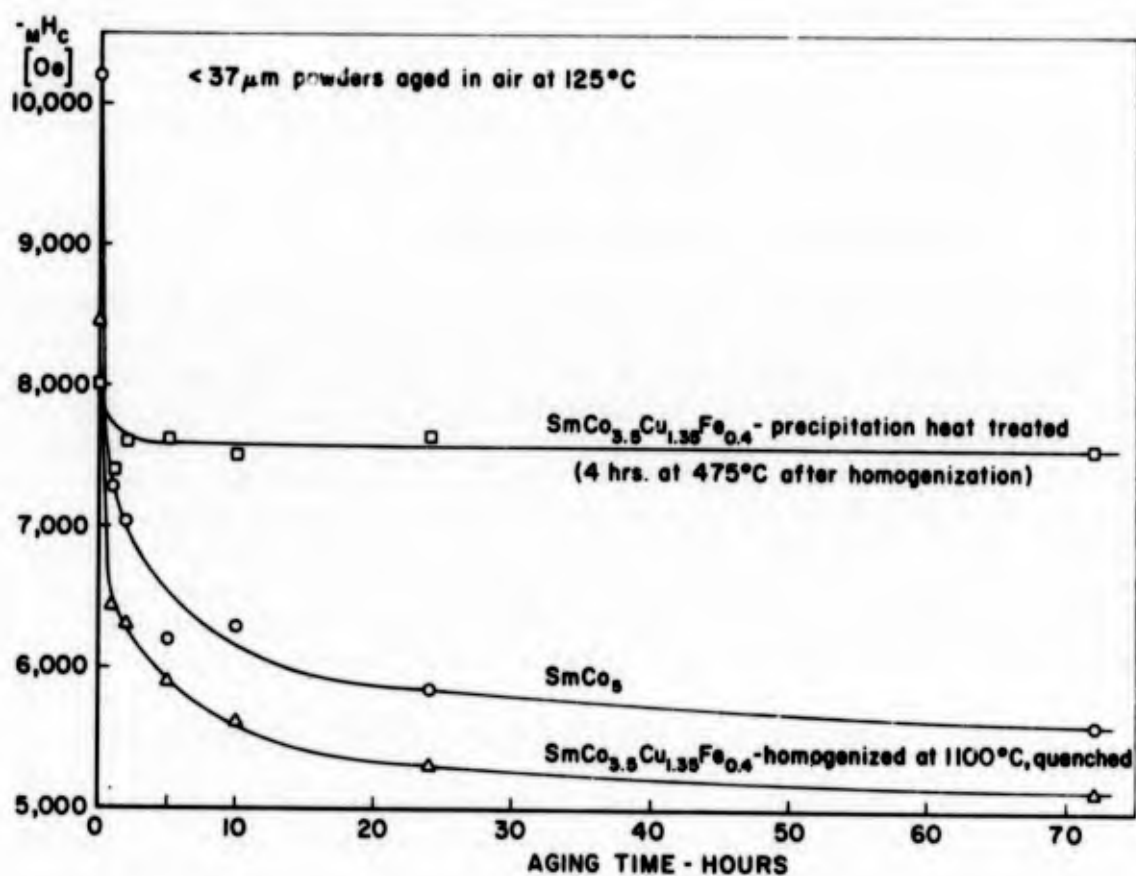


Figure 4. Reduction of the coercive force of several Sm-Co-based magnet alloy powders during aging in air at 125°C. Samples magnetized in 22.4kOe.

other extreme case of nearly perfect single-crystal particles, wall-motion coercivity is very low, but high magnetizing fields can effectively remove or pin walls which must then be renucleated or unpinned by rather high reverse fields whose upper limit can be H_A . The loss of H_C on aging can then be understood as the formation of low-energy domain nucleation sites on an initially perfect particle surface which may eventually reduce H_C to H_{wall} . Removal of the sites by chemical polishing of the surface restores the high H_C .⁴⁷ Even the initial properties of $SmCo_5$ powders can be improved by chemical means.^{47, 48} Powders of other RCo_5 compounds made by milling are normally too heavily deformed to ever reach the stage of reversal by nucleation. It is encouraging, though, that we have seen sensitivity to surface condition and drastic improvement of H_C by chemical polishing even on $MMCo_5$ powders (Figure 5).

E. Consolidation of Powders Into Magnets

Initial attempts to make magnets by compacting ground powders in relatively low fields and under moderate pressures resulted in packing densities of the RCo_5 phase near 60-70% and magnets which had only modest properties.^{12, 16, 28} During early sintering experiments, high densities could be achieved but a severe loss of H_C occurred. Recently, however, magnets with densities over 95% of the theoretical and with excellent crystal alignment having energy products near 20 MGOe were produced by isostatic pressing^{26, 43, 49} as well as by sintering²⁵ from $SmCo_5$. These processing methods now being developed should apply to other RCo_5 alloys as well. The properties of the best R-Co magnets reported to date are summarized in Table II and Figures 2 and 3.

F. Magnetic Hardening of Modified RCo_5 Alloys in Bulk Form

In 1968, Nesbitt et al.²⁷ and Tawara and Senno⁵⁰ announced almost simultaneously that they had achieved extraordinarily high coercive forces with massive Sm-Co and Ce-Co alloys in which a two-phase microstructure was created by substituting Cu for a part of the Co. Selected small pieces had energy products of 4-7 MGOe²⁷ and 8 MGOe,⁵⁰ respectively, and the value for the Sm alloy has since been raised to 8.8 MGOe by also adding a small amount of iron.⁵¹ With 30-50% of the Co replaced by Cu, $M_H H_C$ values near 10 kOe were measured on as-cast samples, and a heat treatment at 400°C raised H_C to almost 30 kOe. It was surmised that a way has been found to create strain-free particles of a modified $SmCo_5$ phase in a nonmagnetic, Cu-rich matrix,⁵¹ and that precipitation may also play a role in the property enhancement by annealing.⁵² We have seen clear evidence⁵³ of a highly ordered, needle-like precipitate in $SmCo_{3.5}Cu_{1.35}Fe_{0.4}$, and F. Hofer⁵⁴ now reports that spinodal decomposition occurs in the $SmCo_{5-x}Cu_x$ system for $x = 1.5$ and 2.

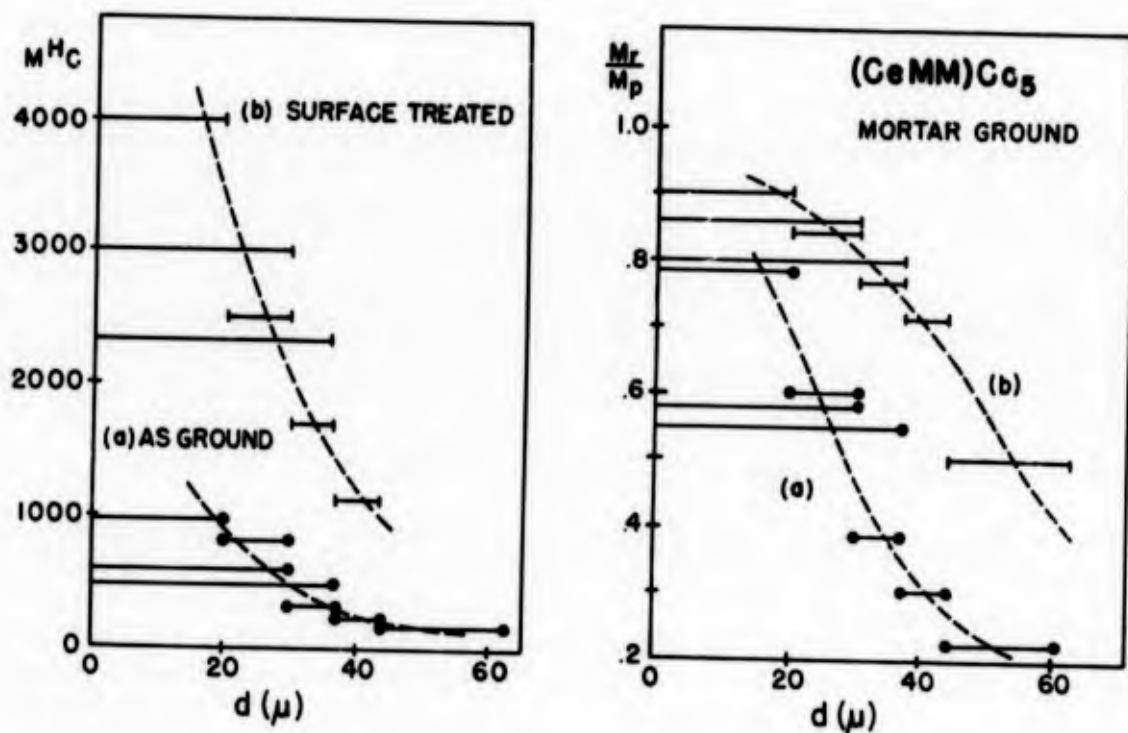


Figure 5. Particle size dependence of coercivity and loop squareness of mortar ground and sifted MMCo_5 powders before and after chemical polishing of the particle surface. (Magnetized with 17.6kOe.)

A concept emerges from this work which has room for all these different findings and suggests that two distinct mechanisms can be used in such alloy systems to cause permanent magnet behavior. Large amounts of copper (perhaps up to $x = 5$) are soluble in the "RCo₅" lattice just below the solidus, but a miscibility gap exists at lower temperatures. Alloys in this immiscibility region can be homogenized by annealing near the solidus and rapid quenching, and in this condition they behave much like the copper-free RCo₅ alloy.⁵³ For compositions near the center of the spinodal curve, reheating (or slow initial cooling) will cause a decomposition into Co- and Cu-rich crystals in an extremely fine-grained distribution, creating magnetic particles of only several hundred Å diameter that have extremely high coercivities.⁵⁴ At the steep part of the solvus line on the Co side, low temperature annealing will produce an intragranular, non-magnetic precipitate in the magnetic matrix that can impede wall motion but does not give fine-particle behavior.⁵³ Moderate bulk coercivity in the range of 4000-8000 Oe results which cannot be increased by magnetizing fields substantially higher than MH_c and which depends very little on particle size above 20-40 μ when the alloys are pulverized. The initially reported procedure⁵⁰⁻⁵¹ produces a relatively coarse two-phase microstructure and severe macro-segregation into Co-rich regions of high remanence but moderate MH_c , and Cu-rich parts that have record values of H_c but low remanent flux. The primary grains of the non-equilibrium phases can be further decomposed, and H_c increased by annealing at 300 to 600°C. The two hardening mechanisms discussed thus appear together in this case.

G. Practical Aspects of Bulk-Hardened Magnets

Small, grain-oriented pieces of such alloys have very square hysteresis loops because of the absence of deformation effects. For practical magnets one will have to learn how to produce the proper texture in large volumes, or process the alloys by powder metallurgical methods after all, thus abandoning the initially-claimed advantage that such magnets could be cast. It is also likely that the great brittleness of the alloys will prevent the use of casting in production except for very small magnets of simple shape.

The price one pays for high H_c and squareness is a severe reduction of the remanence due to the dilution by nonmagnetic copper. The samples with 8-9 MGOe were compromise cases where a low Cu-substitution allowed high remanence, but where $H_c < B_r$, and the demagnetization curve has a knee causing poor dynamic properties (see Figure 2). B_r and $(BH)_{max}$ were very near the best values possible for the respective chemical composition. It seems that the most useful magnets of this type may result from an optimization of the precipitation hardening procedure in alloys having a minimum of Cu and as much Fe as the lattice can accommodate.

After proper heat treatment for precipitation, the alloys are not subject to detrimental aging effects, even as moderately fine powders. (The same is presumably true for the spinodally-decomposed alloys.) However, the solution-annealed and quenched alloy behaves like SmCo_5 because here nucleation processes control the magnetization reversal of the powder grains (Figure 4). Powders of $\text{SmCo}_{3.5}\text{Cu}_{1.5}$ made without the homogenization step contain a fraction which suffers an H_C -reduction by oxidation.⁵³ A pronounced magnetic aftereffect, first observed by J. J. Becker, is present in the Cu-containing alloys, but not in single-phase RCo_5 . Figure 6 illustrates this undesirable phenomenon, which is apparently caused by domain-wall creeping.

SECTION V

ECONOMIC CONSIDERATIONS

RCo_5 magnets are made from expensive raw materials. Cobalt, at \$2.20/lb, constitutes 2/3 to 3/4 of the alloy weight, so that this figure is an absolute lower limit for the alloy cost. On the present rare-earth market, only the price of mischmetal is comparable to that of Co, so that MMCo_5 can indeed be produced for nearly \$3-5/lb. Sm is the most expensive of the group (\$50/lb of SmCo_5). However, the prices of the individual R. E. can drop radically if new markets are developed. The most optimistic estimates of the industry⁵⁵ put future lb-prices for the RCo_5 alloys at \$10 for Sm, and at \$4-5 for La, Y and Pr. Estimates of possible selling prices for RCo_5 magnets have been made, all based on many assumptions. It appears realistic, though, that MMCo_5 magnets could sell for 1 to 1.5 times the present average price per lb of finished Alnico 8, while SmCo_5 may cost 4 to 5 times as much. A comparison of the RCo_5 magnets with others on a basis of price per unit magnetic energy suggests that they could offer appreciably higher energy/\$ than the high-grade Alnicos or even oriented ferrites in dynamic applications. SmCo_5 is indeed least favorable, while MMCo_5 would offer the most if 70-80% of its theoretical energy product can be achieved in practice. But even SmCo_5 is vastly cheaper than PtCo.

Some other factors concerning the rare-earth metals may not be generally known. In spite of the misleading group name, the R. E. are rather abundant, and neither ore supply nor present production capability would impose any limits. The R. E. occur together in the ores, and at present it is the cost of separation that makes the individual metals so expensive. If mixtures, such as mischmetal, or low-purity individual R. E. are used, the materials cost is much reduced. Either appears permissible in magnets if the content of heavy lanthanides is kept low. Nor is the use of highly pure Co essential. Several % of Fe and Ni can be tolerated, Fe may even be desirable.

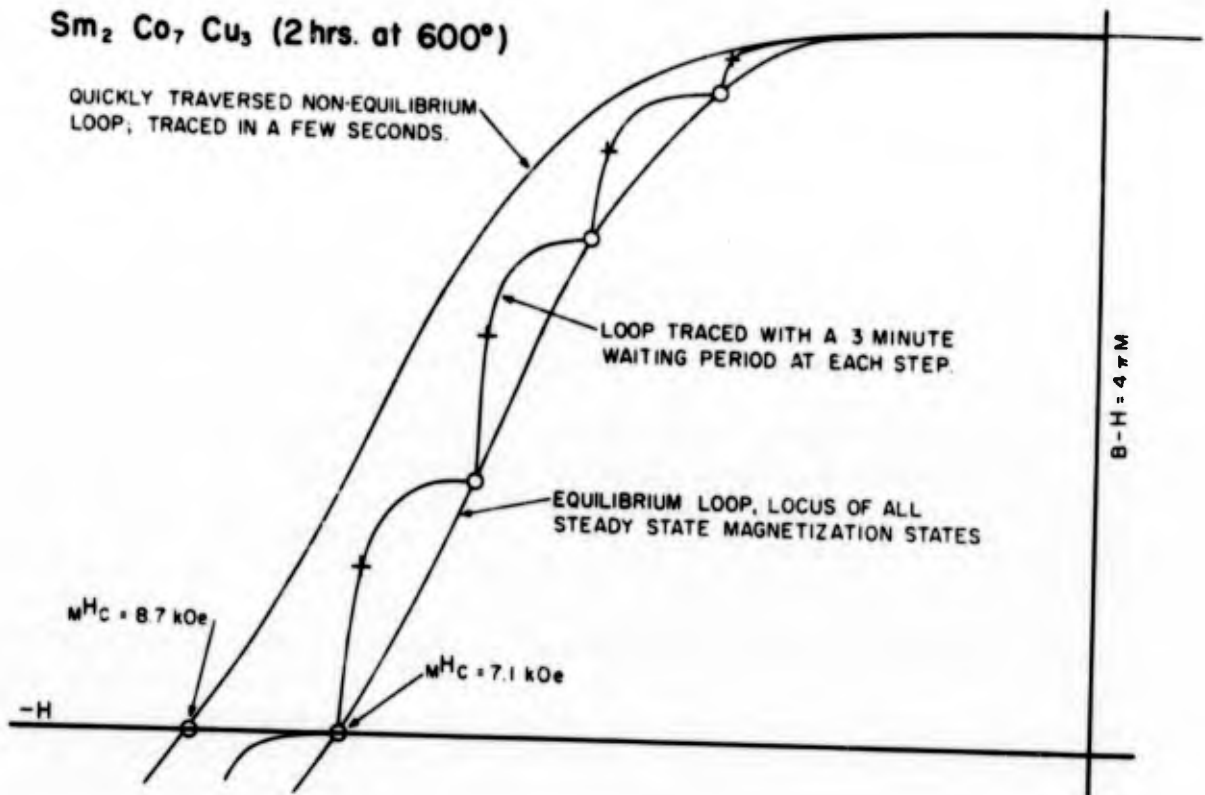


Figure 6. Magnetic aftereffect in a compact of $<37\mu$ $\text{Sm}_2\text{Co}_7\text{Cu}_3$ powder after magnetization in 17.6 kOe. The alloy was quenched in the arc melting furnace and heat treated 2 hrs. at 600°C .

SECTION VI

SUMMARY AND OUTLOOK

In little more than three years of laboratory work, the technical possibility of magnets vastly superior to the best conventional ones was demonstrated on SmCo_5 , and magnets equivalent to PtCo were made of two other alloys. In the history of permanent magnets, this is an impressive accomplishment (see Figure 7). Difficulties were incurred with these and other RCo_5 alloys, but their causes are now well enough understood that there is hope for the development of even better magnets based on YCo_5 and PrCo_5 , and much cheaper ones using mischmetal. Process development for the production of alloys and magnets is in progress. The reader is referred to the original literature cited and to recent review articles 5, 12, 13, 17, 29, 51, 56 for more details. The industrial interest in R-Co magnets is now widespread and intense, and it seems certain that SmCo_5 will soon be in production for special applications. However, much more materials research, manufacturing methods development and, last but not least, an open-minded new approach on the part of circuit designers, especially in the field of rotating electrical machinery, will be required if the potential of these new magnet materials is to be fully utilized.

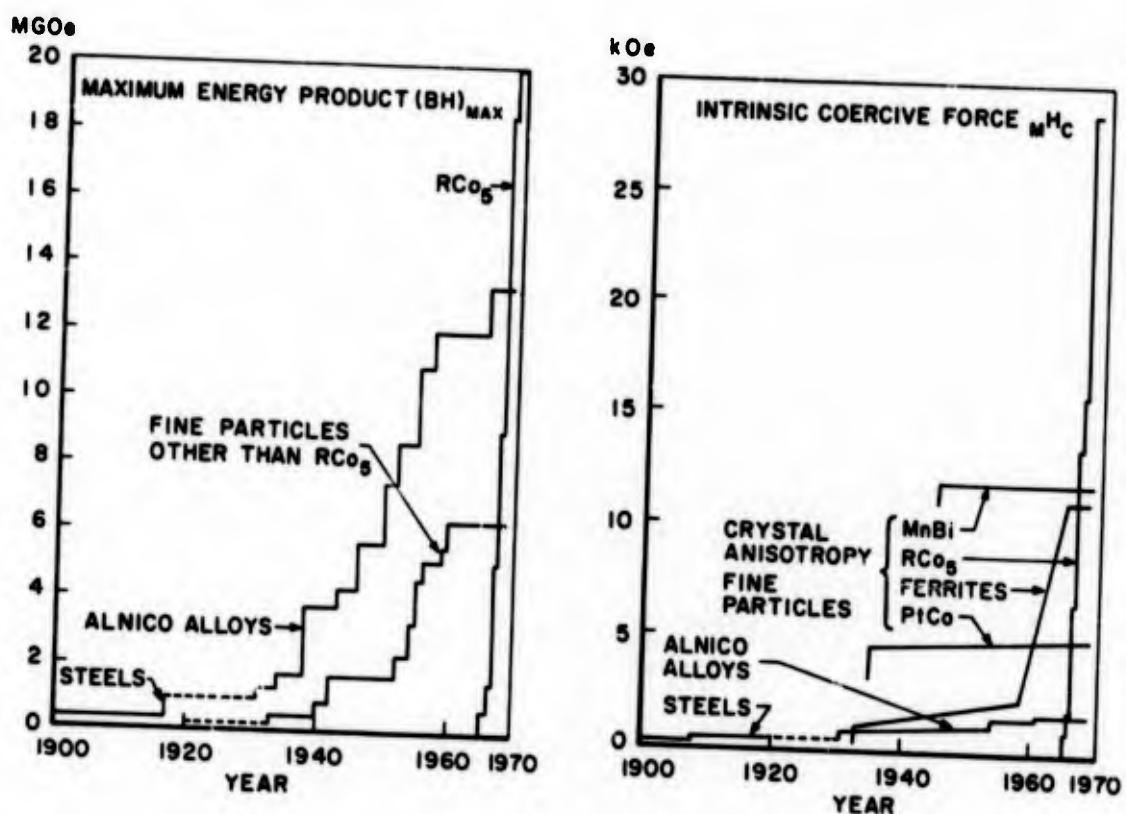


Figure 7. Progress in RCo_5 magnet development to date compared to the history of other materials. The figure is based on an older one compiled by F. Luborsky and presents best reported laboratory values of $(BH)_{max}$ and MH_c .

SECTION VII

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13. ABSTRACT The prospect that permanent magnets with previously unattainable coercivities and energy products might be made from cobalt-rare earth alloys has caused intense research efforts in the last three years. Alternative ways of preparing magnets from powders and by casting were demonstrated in several laboratories. (BH) _{max} ≈ 20MG0e and $M_H C > 25000$ Oe have been achieved with $SmCo_5$, and the development of manufacturing processes for magnets made from this alloy has begun. This paper reviews the basic concepts, properties of the alloys of interest and the physical factors influencing the coercive force. Approaches to alloy, powder and magnet fabrication are discussed, with their merits and drawbacks; also problems incurred in the materials development and their possible solutions. Application areas are reviewed and some economic factors considered. It is concluded that the RCo_5 magnets are indeed beginning to live up to their promise, but that more materials research, process development and circuit redesign are needed if their potential is to be fully utilized.			

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