

New Magnetic Alloys

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Since the turn of the century, a large number of new magnetic materials have been developed to meet growing needs in telecommunications, electric power generation, and information processing. Today the value of the U.S. magnetics market is estimated to exceed \$2 billion, three times more than a decade ago. We are constantly touched by some aspect

when operated at high induction (1.7 teslas); thus they promise greater economy in the transmission of electrical power.

Other new developments in magnetic materials during the past decade include magnetic bubbles and amorphous alloys, which are treated elsewhere in this issue by Giess (1) and Gilman (2), respectively.

Summary. Three notable new developments in magnetic alloys are highlighted. They include rare earth-cobalt permanent magnets with maximum energy products up to 240 kilojoules per cubic meter; chromium-cobalt-iron permanent magnets that have magnetic properties similar to those of the Alnicos, but contain only about half as much cobalt and are sufficiently ductile to be cold-formable; and high-induction grain-oriented silicon steels that exhibit 20 percent less core loss as transformer core materials than conventional oriented grades.

of magnetics—making or receiving a telephone call, switching on a radio or TV set, turning on a washing machine or vacuum cleaner.

In this article three notable developments in magnetic alloys during the past decade are highlighted. These are the rare earth-cobalt and chromium-cobalt-iron permanent magnets and the high-induction, grain-oriented soft magnetic silicon steels. The rare earth-cobalt alloys have intrinsic coercivities more than 20 times and maximum energy products more than four times those of Alnico 5, the most widely used permanent magnet alloy to date. The chromium-cobalt-iron alloys essentially duplicate the magnetic properties of Alnico 5 at less than half the cobalt content of the latter. They also have the advantage of good ductility, which permits them to be cold-rolled, drawn, or stamped into finished shape, whereas most permanent magnets are brittle and must be formed by casting or powder technology. As transformer core materials, the high-induction, grain-oriented silicon steels exhibit a 20 percent decrease in core loss compared with conventional grain-oriented silicon steel

ly. Of course, important advances have also been made in the established magnetic materials; a summary of progress in several areas has recently been given by Jacobs (3).

Rare Earth-Cobalt Permanent Magnets

In the late 1950's and early 1960's, Nesbitt, Wernick, and their co-workers (4) and Wallace and his associates (5) prepared a series of rare earth (R)-transition metal compounds and studied their intrinsic magnetic properties. Among the compounds studied were RCO_2 and R_2Co_{17} , which now form the bases of the most prominent R-Co high-performance permanent magnet systems. Studies by others followed, but it was not until 1966 that R-Co magnet development really took off; in that year Hoffer and Strnat (6) reported on the extremely high magnetocrystalline anisotropy of YCo_5 and emphasized the potential of such compounds as permanent magnets. There are now more than 20 companies worldwide that offer rare earth-cobalt magnets commercially. These alloys are distinguished by their extremely high values of intrinsic coercivity, up to 3 million amperes per meter, and maximum energy

product, $(BH)_{max}$, up to 240 kilojoules per cubic meter. The latter represents the maximum energy storage per unit volume and is the figure of merit most often used for permanent magnet materials. Figure 1 shows the spectacular progress in quality of the rare earth alloys in comparison with other permanent magnet materials over the years.

The RCO_5 compounds have the $CaCu_5$ type of hexagonal crystal structure; the R_2Co_{17} compounds also have a hexagonal crystal structure, with either the Th_2Ni_{17} type or the Th_2Zn_{17} type of modification. Table 1 lists the Curie temperature (T_c) and room-temperature values of the saturation magnetization ($4\pi M_s$) and magnetocrystalline anisotropy constant (K_1) for most of these compounds. The RCO_5 compounds have moderate values of $4\pi M_s$ (~1 T) but extremely large values of K_1 (>1 MJ/m³). The latter property is primarily responsible for the exceptionally large coercivity. In this regard, $SmCo_5$ is the most outstanding of all RCO_5 magnets by virtue of having the largest value of K_1 (17 MJ/m³). The R_2Co_{17} compounds have higher $4\pi M_s$ values than the corresponding RCO_5 series and hence might have greater energy products. However, as Table 1 shows, the magnitude of K_1 for the "2-17" compounds is considerably smaller than that for the corresponding "1-5" series. Furthermore, with the exception of $SmCo_5$ and Tm , all 2-17 binary compounds have $K_1 < 0$ —that is, an easy (0001) plane. For these compounds, magnetization reversal becomes relatively easy and low coercivity is expected. There has been some success at modifying the sign and magnitude of K_1 by partial substitution for Co by other transition metals such as Fe, Cr, and Mn.

The magnetism of the R-Co compounds is due to the interatomic exchange between the spins of the two sublattices plus the spin-orbit coupling within the rare earth atoms. In the lighter rare earth series—Ce, Pr, Nd, and Sm—the spins of the R and Co atoms are aligned parallel. The values of $4\pi M_s$ are thus high. In the others they are aligned antiparallel, and the values of $4\pi M_s$ tend to be low. Yttrium is nonmagnetic and hence the magnetic induction comes from Co alone. The magnetocrystalline anisotropy also comes from two sources, one originating in the itinerant electrons of the Co sublattice and one due to the crystalline electric field of the rare earths. A broad summary ranging from basic magnetism to the technology of the rare earth magnets is given by Mentz et al. (7).

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There are at present two dominant groups of R-Co alloys in commercial production. One group, the earlier and more established, is based on single-phase R_2Co_{17} ; the other, more recent group is based on precipitation-hardened alloys of the $Sm_2(Co,Cu)_{17}$ type. The best magnetic properties are obtained in Sm alloys, and these are produced in the greatest quantity.

SmCo₅-type single-phase magnets. Table 2 shows some representative magnetic properties of commercial SmCo₅ magnets compared with those of other materials. Typical demagnetization curves are shown in Fig. 2. Although values of $(BH)_{max}$ for laboratory samples as high as 200 kJ/m³ have been reported, typical commercial samples are in the range 130 to 160 kJ/m³.

Detailed studies have shown that the mechanism of coercivity in single-phase SmCo₅ magnets is one of domain nucleation or wall pinning at grain boundaries. Wall motion within the grains is relatively easy. To minimize the existence of domain walls within the grain by spontaneous nucleation, and thus to achieve high coercivity, the alloys must be ground into fine particles (1 to 10 micrometers). The particles are then aligned and compacted in a strong magnetic field and are sintered by powder metallurgical techniques. Plastic-bonded magnets are also in production, either as rigid bodies with thermosetting resins or as flexible parts with thermoplastic resins or rubbers. Energy products are in the range 3 to 10 kJ/m³.

In addition to those containing Sm, other RCo₅ single-phase permanent magnets have been prepared, both in the laboratory and commercially. These include Sm in combination with Ce, Ce-rich misch metal (~55 percent Ce, 25 La, 13 Nd, and 5 Pr), and Gd. The Ce and misch metal additions lower the magnetic properties, but the raw material price is substantially lower than that of Sm. The Gd addition is used to decrease the temperature coefficient of remanence, a useful feature in temperature-stable devices.

Precipitation-hardened Sm₂(Co,Cu)₁₇ type alloys. Not long after the initial development of single-phase SmCo₅-type permanent magnets, Nesbitt *et al.* (8) and Tawara and Senno (9) discovered that partial substitution for Co by Cu in SmCo₅ and CeCo₅ can lead to high coercivity (to 2 MA/m) on suitable heat treatment near 400° to 500°C. Furthermore, the Cu-substituted magnets do not have to be ground into fine particles to develop magnetic hardness. For this reason, these magnets can be prepared as

Table 1. Magnetic properties of RCo₅ and R₂Co₁₇ compounds; $4\pi M_s$ and K_1 values at 25°C are given (31).

| Rare earth | RCo ₅ | | | R ₂ Co ₁₇ | | |
|------------|------------------|------------|----------------------------|---------------------------------|------------|----------------------------|
| | $4\pi M_s$ (T) | T_c (°C) | K_1 (MJ/m ³) | $4\pi M_s$ (T) | T_c (°C) | K_1 (MJ/m ³) |
| Ce | 0.85 | 374 | 5.3 | 1.15 | 800 | -0.6 |
| Pr | 1.12 | 612 | 8.1 | 1.38 | 890 | -0.6 |
| Nd | 1.20 | 630 | 0.7 | 1.39 | 900 | -1.1 |
| Sm | 0.97 | 724 | 17.2 | 1.20 | 920 | 3.3 |
| Gd | 0.19 | 735 | 4.6 | 0.73 | 930 | -0.5 |
| Tb | 0.24 | 707 | | 0.68 | 920 | -3.3 |
| Dy | 0.30 | 693 | | 0.70 | 910 | -2.6 |
| Ho | 0.53 | 727 | 3.6 | 0.83 | 920 | -1.0 |
| Er | 0.63 | 713 | 3.8 | 0.90 | 930 | 0.41 |
| Tm | 0.67 | 747 | | 1.13 | 920 | 0.50 |
| Yb | | | | | | -0.38 |
| Lu | | | | 1.27 | 940 | -0.20 |
| La | 0.91 | 567 | 5.9 | | | |
| Y | 1.06 | 648 | 5.2 | 1.25 | 940 | -0.34 |
| Th | | | 2.6 | | | -0.53 |

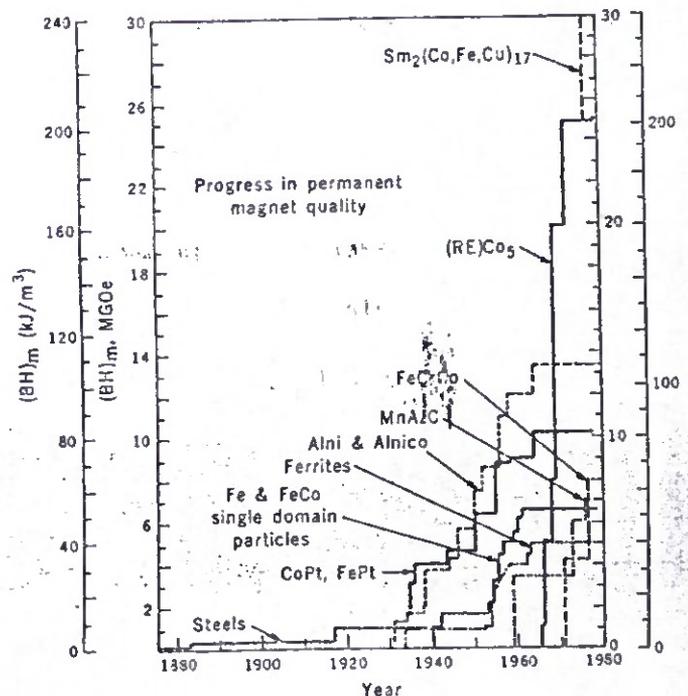
Table 2. Properties of some permanent magnets.

| Material | Remanent induction, B_r (T) | Coercive force, H_c (kA/m) | Maximum energy product, $(BH)_{max}$ (kJ/m ³) | Reference |
|---|-------------------------------|------------------------------|---|-----------|
| Alnico 5 (8Al-14Ni-24Co-3Cu-Fe)* | 1.28 | 50 | 44 | (32) |
| Alnico 9 (7Al-15Ni-35Co-4Cu-5Ti-Fe) | 0.82 | 130 | 72 | (32) |
| Ceramic 5 [(Ba,Sr)Fe ₁₂ O ₁₉] | 0.38 | 190 | 27 | (32) |
| SmCo ₅ | 0.87 | 640/1600† | 144 | (32) |
| Sm(Co _{0.76} Fe _{0.10} Cu _{0.11}) _{5.3} | 1.04 | 430/500† | 210 | (10) |
| Sm(Co _{0.66} Cu _{0.16} Fe _{0.21} Zr _{0.01}) _{7.4} | 1.10 | 510/520† | 240 | (11) |
| 23Co-28Cr-1Si-Fe | 1.30 | 46 | 42 | (14) |
| 15Co-23Cr-3V-2Ti-Fe | 1.35 | 44 | 44 | (17) |
| 11.5Co-33Cr-Fe | 1.20 | 60 | 42 | (16) |
| 5Co-30Cr-Fe | 1.33 | 42 | 42 | (28) |
| 70Mn-29.5Al-0.5C | 0.56 | 180 | 44 | (29) |

*In the composition, numbers are percentages and the balance is Fe.

†Intrinsic coercive force, H_{ci} .

Fig. 1. Progress in permanent magnet quality since 1880 as indicated by the value of the maximum energy product achieved for various material systems. [Adapted from (3)]



cast. However, current commercial practice is still based on powder metallurgy, as magnets so prepared are mechanically stronger and have better magnetic alignment.

Electron microscopy studies have revealed that low-temperature heat treatment of the Cu-substituted magnets leads to homogeneous fine-scale precipitation (~15 nanometers) of a second phase coherent with the RCo_5 structure. Magnetic hardening results from pinning of domain walls at these particles. Hence the coercivity is independent of the sample dimensions.

The $Sm(Co,Cu)_5$ magnets have low values of saturation magnetization because of the copper replacing cobalt. Nesbitt *et al.* (8) were able to increase the saturation magnetization by the addition of Fe. In recent years, further increases in saturation magnetization have been made possible by increasing the ratio of (Co,Cu,Fe) to Sm toward the value 17:2 at the sacrifice of coercivity. A $Sm(Co_{0.76}Fe_{0.10}Cu_{0.14})_{6.8}$ alloy, with values $B_r = 1.04$ T, $H_{c2} = 500$ kA/m, and $(BH)_{max} = 210$ kJ/m³ (Table 2), is representative of this class (10). Very recently, the addition of small amounts of Zr (11) or Hf (12) has enabled a further increase in saturation magnetization

with an additional increase in the (Co,Cu,Fe):Sm ratio toward the value 17:2 and a further increase in the Fe content. The addition of Zr or Hf stabilizes the coercivity that would otherwise be degraded. As a result, additional increases in energy product were achieved. As shown in Table 2, this class includes a $Sm(Co_{0.68}Cu_{0.10}Fe_{0.21}Zr_{0.01})_{7.4}$ alloy with $B_r = 1.10$ T, $H_{c2} = 520$ kA/m, and $(BH)_{max} = 240$ kJ/m³ (11). The alloy containing Zr has the highest energy product of all permanent magnet alloys offered commercially to date.

Applications. The exceptionally large maximum energy products and coercivities of the rare earth magnets permit their use in devices where small size and superior performance are desired. Magnets for electronic wrist watches and for traveling wave tubes—once the domain of expensive platinum-cobalt magnets—are now largely made of rare earth alloys. Rare earth magnets have been used for a number of medical devices, ranging from thin motors in implantable pumps and valves to holding magnets for artificial teeth and for aiding eyelid motion. Direct-current and synchronous motors and generators have been designed with rare earth magnets with an overall reduction in size. A very succinct summary

has been given by Strnat (13). The use of rare earth magnets in automotive accessory motors was recently considered as a means of reducing the size of the motors and the mass of cars and achieving greater fuel economy. If this were done there would be huge demands for such magnets. However, this effort was dealt a serious blow when, in addition to the high cost of samarium, the price of cobalt jumped drastically in 1978 as a result of political instability in Zaire, which supplies 70 percent of the free world's cobalt. The general prognosis is that the price of the rare earth magnets will always be relatively high; however, because of their exceptional magnetic properties, they will be used in a large number of low-volume specialized applications.

Chromium-Cobalt-Iron Permanent Magnets

Overshadowed by the impressive progress made with the rare earth alloys has been the development of another new family of permanent magnet alloys. In 1971 Kaneko and his colleagues at Tohoku University announced the discovery of ductile permanent magnet alloys in the Cr-Co-Fe system (14). Since then, continued progress has been made in the development of these alloys, by the Tohoku group and more recently at Bell Laboratories. The magnetic properties of the Cr-Co-Fe alloys are remarkably similar to those of the Alnicos, with values in the ranges $B_r = 1.0$ to 1.3 T, $H_c = 15$ to 60 kA/m, and $(BH)_{max} = 10$ to 45 kJ/m³. Unlike the brittle Alnicos, which must be cast and ground to finished shape or shaped by powder metallurgy techniques, these new alloys are cold-formable at room temperature. Hence normal metal-forming operations such as rolling, wire drawing, and stamping can be done relatively easily. In addition, equivalent magnetic properties can be attained with much less of the expensive constituent cobalt.

Metallurgy and magnetic behavior. The Cr-Co-Fe alloys of interest as permanent magnets are in the range 25 to 35 percent Cr and up to about 25 percent Co. At temperatures exceeding about 1200°C, depending on composition, the alloys exist in the ferromagnetic body-centered cubic (α) phase. In the intermediate temperature range of about 700°C to 1200°C, again depending on composition, the α phase tends to coexist with a nonmagnetic face-centered cubic phase, γ . At high-Cr end a brittle σ phase may

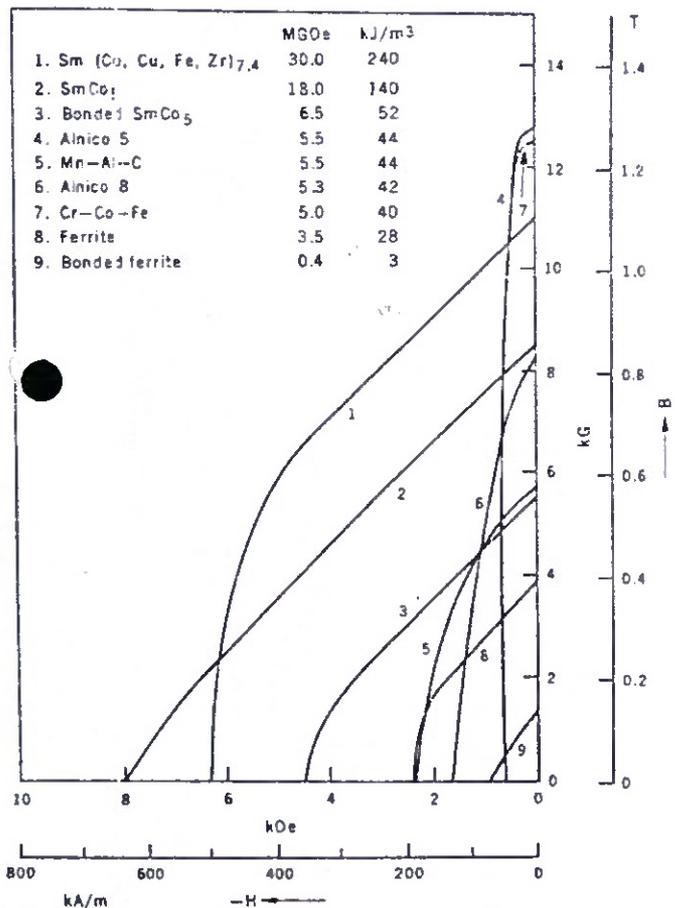


Fig. 2. Demagnetization curves of selected permanent magnet materials. Values of the maximum energy product are tabulated above the curves. [From (31)]

also appear in this temperature range. The α phase is retained when the alloy is rapidly cooled from a high temperature. It then undergoes spinodal decomposition at a lower temperature to a highly ferromagnetic Fe-rich α_1 phase and a less magnetic Cr-rich α_2 phase, both of which maintain the body-centered cubic structure. This decomposition temperature is about 550°C for the Fe-30Cr binary (Fe with 30 percent Cr) and increases to about 650°C for the Fe-30Cr-20Co ternary alloy. Thus a very important function of the addition of cobalt is to raise the decomposition temperature so that decomposition can proceed within practical heat-treating time intervals, since it is the decomposition product that yields the optimum permanent magnet properties.

As revealed by transmission electron microscopy, the mechanism for coercivity in the Cr-Co-Fe alloys is pinning of domain walls by the spinodally decomposed particles. Two very important structural parameters in this case are differences in saturation magnetization as a result of composition differences between the two decomposed phases, and particle size. Both are affected by heat-treatment temperature and time. Jin *et al.* (15) recently developed a two-step aging technique that optimizes both these parameters. The technique consists of initial rapid cooling from above the decomposition temperature to a suitable lower temperature to establish an optimum particle size for the decomposed phase of ~50 nm, followed by slower cooling to maximize the composition difference between the two phases.

Elongated and aligned particles are extremely important in increasing the energy product by increasing values of B_r and H_c , and by "squaring up" the shape of the demagnetization curve. The elongation and alignment can be affected by heat treatment in a magnetic field (14)—a well-known technique in the production of anisotropic Alnicos. On the other hand, Jin (16) took advantage of the ductility of the Cr-Co-Fe alloys to uniaxially deform an alloy that had been deliberately overaged. In this way, he was able to mechanically elongate and align the particles without magnetic field treatment (Fig. 3). As a result, values of $B_r = 1.2$ T, $H_c = 60$ kA/m, and $(BH)_{max} = 42$ kJ/m³—comparable to those of Alnico 5 and several times better than those without the deformation—have been achieved in an Fe-33Cr-11.5Co alloy. Figure 4 shows the improvement in magnetic properties of this alloy through "deformation-aging" and

compares them with those of Alnico 5.

Some representative properties of commercially available materials and laboratory specimens are listed in Table 2. One group is concentrated in the high-Co regime with a typical composition of 23Co-28Cr-1Si-Fe, along the lines of Kaneko's early studies. A small amount of Si (~1 percent) is said to improve the ductility, since formability decreases with Co content. Later, attention shifted to a medium Co content of ~15 percent, often with small additions such as Nb, Al, V, Ti, and Zr—so-called α -formers—to suppress the formation of the undesirable nonmagnetic γ phase. A typical alloy in this range is 23Cr-15Co-3V-2Ti-Fe (17). More recently, very favorable permanent magnet properties have been ob-

tained near 10 percent Co (16). Unlike some 10 percent Co commercial alloys that were developed earlier and contained additions of a fourth element such as Si and Ti (18), the more recent alloys are pure ternaries.

Applications. One major application of the Cr-Co-Fe alloys is in ring armature-type telephone receivers. The current design for this type of receiver, which is produced at the rate of about 10 million annually for all general-purpose handsets, makes use of a cup-shaped permanent magnet to provide the required d-c bias magnetic field. Up to now the permanent magnet has been 20 Remalloy (20Mo-12Co-Fe), which has nominal values of $B_r = 0.95$ T, $H_c = 28$ kA/m, and $(BH)_{max} = 10$ kJ/m³. Remalloy is semi-

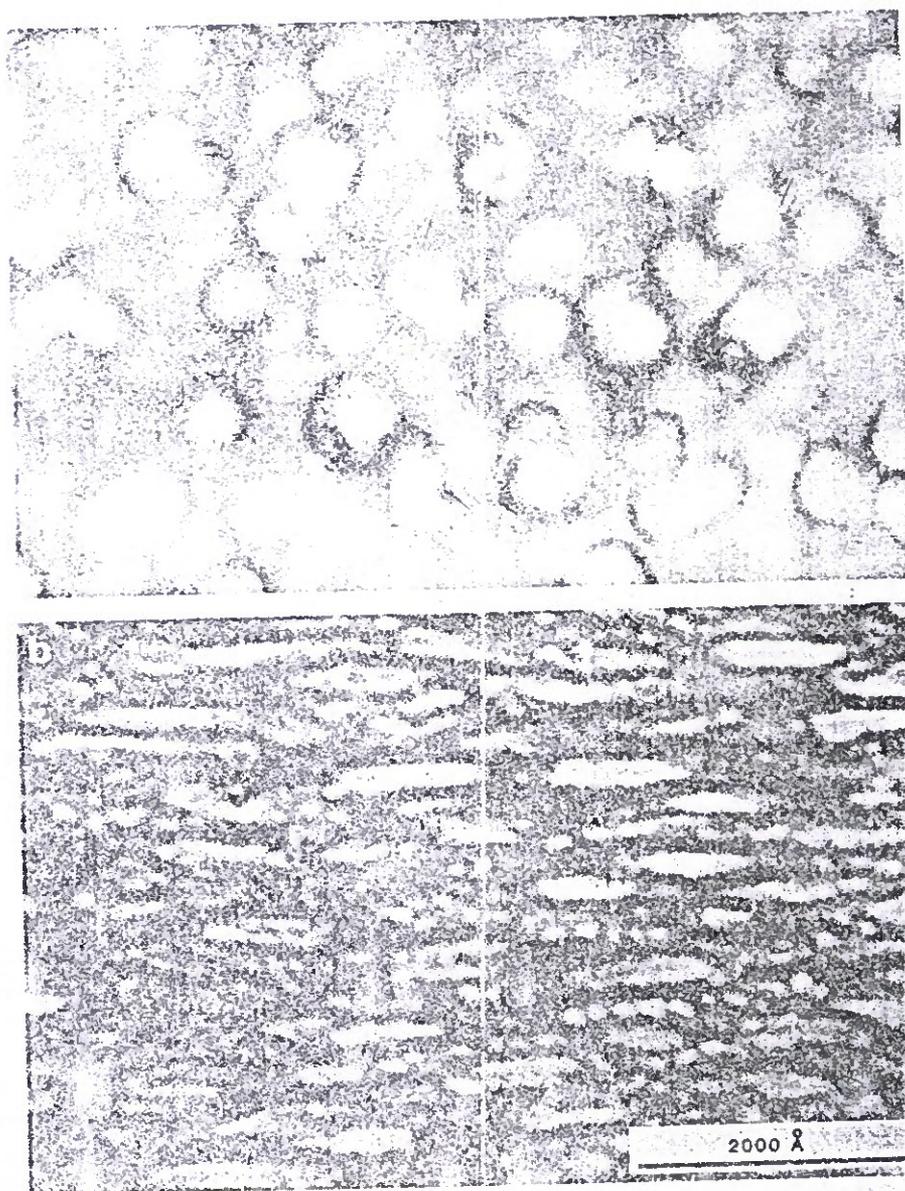


Fig. 3. Transmission electron micrographs of a Fe-33Cr-11.5Co alloy. (a) Spherical particles obtained by continuous cooling from solution-treated state. (b) Elongated structure obtained after uniaxial deformation by wire drawing of (a); such a structure is conducive to superior permanent magnet properties (see Fig. 4). [Micrographs by S. Mahajan from (16)]

Table 3. Core loss of grain-oriented silicon steels at 50 Hz and 1.7 T, in watts per kilogram.

| Type | Grade | Thickness (mm) | | |
|----------------|-------|----------------|------|------|
| | | 0.27 | 0.30 | 0.35 |
| High-induction | M0H | 0.99 | 1.05 | |
| | M1H | 1.04 | 1.11 | 1.15 |
| | M2H | 1.11 | 1.17 | 1.22 |
| Conventional | M4 | 1.27 | | |
| | M5 | | 1.39 | |
| | M6 | | | 1.57 |

Table 4. Comparison of manufacturing processes for grain-oriented silicon steel.

| Conventional | Nippon Steel |
|---|-----------------------------------|
| Steelmaking (MnS) | Steelmaking (AlN + MnS) |
| Hot rolling (1370°C) | Hot rolling |
| Annealing (800° to 1000°C) | Annealing (950° to 1200°C) |
| Cold rolling (70 percent) | Cold rolling (85 percent) |
| Annealing | |
| Cold rolling (50 percent) | |
| Decarburizing (800°C, wet H ₂ + N ₂) | Decarburizing |
| Box annealing (1200°C, dry H ₂) | Box annealing |
| Kawasaki Steel | General Electric-Allegheny Ludlum |
| Steelmaking (Sb + MnSe or MnS) | Steelmaking (B + N + S or Se) |
| Hot rolling | Hot rolling (1250°C) |
| Annealing | Annealing |
| Cold rolling | Cold rolling (> 80 percent) |
| Annealing | |
| Cold rolling (65 percent) | |
| Decarburizing | Decarburizing |
| Box annealing (820° to 900°C, then 1200°C, dry H ₂) | Box annealing |

Table 5. Energy products of some Co-bearing permanent magnets (28).

| Alloy | Co (%) | (BH) _{max} (kJ/m ³) | (BH) _{max} per unit Co (based on Alnico 5) |
|--|--------|--|---|
| Alnico 5 | 24 | 44 | 1.0 |
| Alnico 9 | 35 | 72 | 1.1 |
| SmCo ₅ | 63 | 144 | 1.3 |
| Sm ₂ (Co,Cu,Fe) ₁₇ | 50 | 240 | 2.7 |
| 5Co-30Cr-Fe | 5 | 42 | 4.7 |
| 3Co-32Cr-Fe | 3 | 33 | 6.0 |

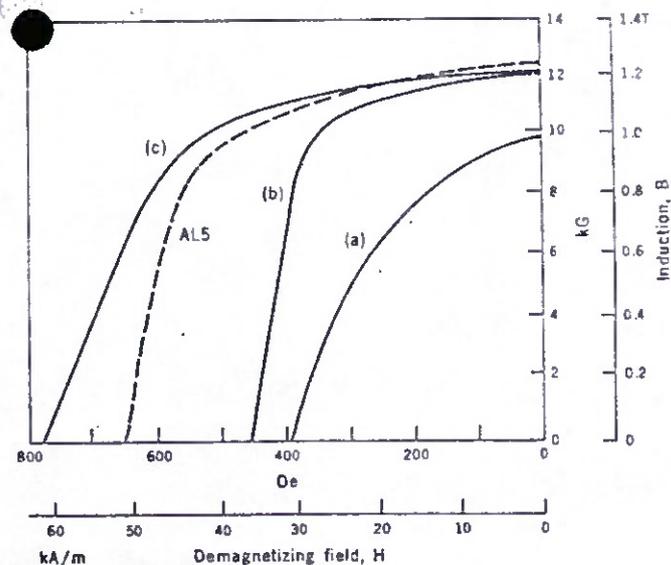


Fig. 4. Demagnetization curves of a Fe-33Cr-11.5Co alloy showing the improvement in permanent magnet properties obtained with the deformation-aging technique (16): (a) aged without intervening deformation step, (b) aged with intervening rolling step, and (c) aged with intervening wire-drawing step. AL5 refers to commercial Alnico 5.

brittle and fabrication in the cup shape requires blanking and drawing at 1250°C, a slow and energy-intensive process. The search for a low-cost cold-formable, ductile magnet led Chin *et al.* (19) to develop a 15Co-28Cr-1Al-1/4Zr-Fe alloy called Chromindur I. Subsequently, J. *et al.* (15) developed a low-cobalt ternary (Chromindur II; 10.5Co-28Cr-Fe) with simplified melting and fabrication practices. A team from Bell Laboratories and Western Electric has now successfully introduced Chromindur II in the commercial production of receiver magnets at a projected annual savings of 10,000 kilograms of cobalt. Other uses of Cr-Co-Fe alloys in telephone apparatus as potential substitutes for Alnicos are outlined in (20).

Because of their similarity in magnetic properties to the Alnicos, particularly Alnico 5, and their added advantages of ductility and lower Co contents, the Cr-Co-Fe alloys are possible substitutes for Alnicos in a number of situations. In addition, because their properties are superior to those of other available ductile alloys, such as Cunife (60Cu-20Ni-Fe) and Vicalloy (10V-52Co-Fe), the Cr-Co-Fe alloys may replace some of these as well.

High-Induction Grain-Oriented Silicon Steel

Unlike the R-Co and Cr-Co-Fe alloys, silicon steel is not a new product that has been around since the turn of the century. However, since on a tonnage basis silicon steel is used far more than other magnetic materials, any breakthrough in improvement must be applauded.

Silicon steel containing up to about 4 percent Si is divided into two grades, nonoriented and oriented, according to whether the steel is processed to exhibit a substantial preferred crystallographic orientation, or texture. Since the steel is used as the core in motors, generators, and transformers operating at standard low frequencies such as 50 or 60 hertz, the so-called core loss has been the single material parameter of utmost concern. This loss is related to the generation of eddy currents induced by the moving magnetic domain walls in response to the a-c excitation and represents precious energy that is wasted as heat. For silicon steel the optimum domain structure for minimum loss is in the <100> direction, and one major breakthrough occurred in 1935, when Goss (21) developed a technique for producing low-loss silicon steel sheet with a {110}<001> oriented texture, with {110}

planes predominantly parallel to the sheet surface and an $\langle 001 \rangle$ direction in the rolling direction. This is the so-called cube-on-edge texture. Today, U.S. consumption of silicon steel is split between oriented and nonoriented grades, amounting to about 310 million kilograms each. The oriented grade, containing about 3 percent Si, is used almost exclusively in large power and distribution transformers, where low loss is particularly important. Until recently, the typical oriented grade had a core loss of about 1.15 watts per kilogram. Even at a low estimate of \sim \$1000 per kilowatt in capitalized value, which includes the capital outlay to generate and deliver extra power and the cost of power plant fuel and operation, the core loss amounts to nearly \$400 million annually. Therefore there is a large incentive to cut down losses, even by a small percentage.

Historically, with each improvement in core loss the steel tends to be used at a higher level of magnetic flux density, since this means a reduced amount of steel and hence transformer size for the same transformer core loss. Core loss level increases with flux density. Thus, for a number of years, oriented silicon steel has been operated at 1.5 T, in comparison with 1.0 T for the lossier nonoriented grade. In 1968 another breakthrough came with the commercial introduction by Nippon Steel (22) of new grades of oriented steel that had an exceptionally sharp cube-on-edge texture and low loss at high flux densities. As a result, operating core levels are now quoted at 1.7 T for these steels. Table 3 lists values of core loss of the new grades, often referred to as high-induction grain-oriented silicon steel, along with conventional oriented grades. The decrease in core loss is about 20 percent, a truly remarkable development. New grades of high-induction steel were also developed by Kawasaki Steel in 1974 (23) and by Allegheny Ludlum in 1977 (24). The latter effort was based on laboratory processes developed at General Electric (25).

In the conventional commercial process for making oriented steel, outlined in Table 4, the cast ingot is hot-rolled near 1370°C to a thickness of about 2 millimeters, annealed at 800° to 1000°C , and then cold-rolled to the finished thickness of 0.27 to 0.35 mm in two steps of about 3 and 50 percent, respectively. A recrystallization anneal is sandwiched between the two cold-rolling steps. The cold-rolled strip is first decarburized near 800°C as carbon is detrimental to the magnetic properties. This step also

results in a primary recrystallized structure containing some grains of the desired cube-on-edge orientation. A final step involves box annealing at $> 1200^\circ\text{C}$ to form an essentially all cube-on-edge texture by secondary recrystallization as these grains cannibalize their neighbors.

A very important concept in the secondary recrystallization process involves so-called grain-growth inhibitors. In the conventional process, the manganese and sulfur that are normally present in steelmaking form MnS inclusions, which restrict grain growth during primary recrystallization. Then during secondary recrystallization the inclusions are dissolved, permitting the preferential growth of the cube-on-edge grains. In the Nippon process, AlN as well as MnS is used as a grain-growth inhibitor. A more potent inhibitor, the AlN permits the adoption of a one-stage cold reduction of large deformation (85 percent), resulting in a sharper grain orientation in the final steel. Without the AlN, such a large deformation would also have enhanced the undesirable growth of the primary recrystallized grains.

In the Kawasaki process, antimony, added along with MnSe or MnS, acts as an extra grain-growth inhibitor by segregating to the grain boundaries. Additional grain orientation sharpening also comes from the use of a two-step box anneal—a low-temperature, long-time anneal (820° to 900°C for 5 to 50 hours) followed by the usual high-temperature (1200°C) treatment. Similarly, boron and nitrogen together with sulfur or selenium are adopted in the General Electric-Allegheny Ludlum process for extra grain-growth inhibition. It is thought that the B, N, and S (or Se) segregate to the grain boundaries, as does the Sb in the Kawasaki process. One advantage claimed for the Allegheny steel process is that since the Mn and S levels are lower than the others, the MnS solubility temperature is lower and hence the initial hot-working temperature can be decreased to below 1300°C . This is advantageous in terms of lower fuel costs and added mill life.

It is somewhat disappointing that the anticipated widespread use of these new high-induction oriented Si steels has not yet occurred, even though the price premium is slight, generally less than 10 percent. Because substantial cost penalties are associated with lossy transformers, the recent trend of designers has been to reduce loss by returning to a design with lower flux densities at the expense of a larger unit. At flux densities of 1.5 T and lower, there is hardly any difference in core loss between the new high-induc-

tion steel and the conventional oriented steel. For this reason, a great deal of current interest has focused on the amorphous soft magnetic alloys. Although their highest value of saturation induction is only about 1.7 T, considerably below the 2.0 T for 3 percent Si steel, these amorphous alloys, prepared in continuous ribbon form by rapid quenching from the melt, exhibit less than half the core loss of oriented Si steel. These new alloys are discussed in detail by Gilman (2).

Future Prospects

Since the developments described in this article are relatively new, further improvements are expected. In the area of rare earth-cobalt alloys, attention is clearly focusing on the Cu-substituted R_2Co_{17} precipitation-hardened alloys, as these have exhibited the highest values of $(BH)_{\text{max}}$ thus far achieved on a commercial scale. Although equally high values of $(BH)_{\text{max}}$ have been achieved in single-phase Cu-free R_2Co_{17} alloys in the laboratory (26), reduction to commercial practice has proved difficult, apparently because of the need for critical control of processing variables. As noted earlier, because of the high cost of both cobalt and rare earths, the rare earth alloys will mainly be used in special applications.

The Cr-Co-Fe alloys are attractive both because of their ductility and because of their similarity to the popular Alnicos in magnetics. Values of $(BH)_{\text{max}} \sim 80 \text{ kJ/m}^3$ have been achieved in a 23 percent Co alloy (27). This is the highest value so far reported in Cr-Co-Fe-based alloys and already surpasses that of Alnico 9 ($\sim 72 \text{ kJ/m}^3$), the best of the commercial Alnicos. In addition, the steep rise in Co price has spurred intense research in very low Co or Co-free alloys. This search recently culminated in the attainment of $(BH)_{\text{max}} \sim 42 \text{ kJ/m}^3$ in several 5 percent Co ternary and quaternary Cr-Co-Fe alloys (28). As shown in Table 5, these alloys represent the highest values of $(BH)_{\text{max}}$ per unit of cobalt to date in Co-bearing alloys, far exceeding even those of the precipitation-hardened R_2Co_{17} types. It should be recognized, of course, that $(BH)_{\text{max}}$ is only one of several design criteria for a magnetic component.

In the past 2 years there has been a substantial switch from Alnicos to ceramics in motor and loudspeaker designs because of the instability of the Co price and supply (20). Since the Cr-Co-Fe alloys are similar to the Alnicos in many

respects, particularly the attractive features of high B_r and good temperature stability, they may offer a third alternative in material selection.

Similarly, very attractive Co-free Mn-Al-C magnets with $(BH)_{\max} \sim 45 \text{ kJ/m}^3$ have been developed (29). These magnets have the coercivities of the ceramic magnets but have substantially higher values of B_r (Table 2). It is thus conceivable that the Mn-Al-C magnets could replace some ceramics as well as Alnicos. However, although cheap in raw material price, these magnets are expensive to process at present, requiring the use of hot extrusion. In addition, they have low Curie temperatures ($\sim 320^\circ\text{C}$); therefore their temperature stability, while better than that of the ceramics, is substantially below those of the Alnicos and Cr-Co-Fe alloys.

As for the high-induction oriented silicon steel, further progress may depend on the willingness of designers to emphasize designs with small volume and high flux density, and perhaps on the progress in the competing development

of low-loss amorphous alloys. On the basis of the estimate given by Taguchi *et al.* (30), it appears that a further 50 percent decrease in core loss from the present low values might be achievable in the high-induction silicon steels.

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