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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	MGOe	mega-gauss-oersted
cm	centimeter	MPa	megapascal
g	gram	min	minute
h	hour	µm	micrometer
kG	kilogauss	pct	percent
kOe	kilooersted	psi	pounds of force per square inch

MAGNETIC PROPERTIES OF SYNTHETIC MISCHMETAL ALLOYED WITH COBALT, COPPER, IRON, AND MAGNESIUM

By J. W. Walkiewicz,[1] M. M. Wong,[2] and E. Morrice[1]

ABSTRACT

The Bureau of Mines investigated alloys containing lanthanum (La), praseodymium (Pr), neodymium (Nd), cobalt (Co), copper (Cu), iron (Fe), and magnesium (Mg) as possible components of a permanent magnet material utilizing a cerium-free synthetic mischmetal (M) as a substitute for scarce samarium (Sm) metal. Magnets containing M-Co-Cu-Mg and M-Co-Cu-Fe-Mg were fabricated by powder metallurgy techniques and evaluated.

A synthetic mischmetal (M20) containing 20 pct La, 60 Pr, and 20 Nd yielded the best overall magnetic properties. The M20-Co-Cu-Mg alloys had energy products as high as 13.2 MGOe, remanences as high as 7.89 kG, normal coercivities as high as 6.26 kOe, and intrinsic coercivities as high as 13.4 kOe. The best value of intrinsic coercivity, 22.9 kOe, was obtained with an M-Co-Cu-Mg magnet in which the synthetic mischmetal contained 30 pct La, 50 Pr, and 20 Nd. These values compare favorably with those of the Sm-Co magnets fabricated and measured at the Bureau's Reno Research Center, which had energy product of 15.1 MGOe, remanence of 7.8 kG, normal coercivity of 7.5 kOe, and intrinsic coercivity of 27.4 kOe. Iron substitution for part of the cobalt resulted in a decrease of magnetic properties, although several percent iron can be added before a drastic loss of magnetic properties occurs.

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INTRODUCTION

Samarium is a scarce metal which is important for Sm-Co magnets in national defense applications and in energy-efficient electrical devices. The "preferred status" of Sm-Co has created a demand for samarium metal that exceeds production. The need to alleviate the demand for samarium has stimulated research on (MM,Sm)-Co (1, 3, 6, 10-12)[2] and MM-Co (4-5, 8-11) magnets in which natural mischmetal (MM) replaces part or all of the samarium.

The term "natural mischmetal" denotes a mixture of the light rare-earth metals consisting of 23-27 pct La, 4-7 Pr, 10-14 Nd, and 50-55 Ce. This is approximately the same ratio of rare-earth elements found in natural ore. A samarium-free, high-intrinsic-coercivity MM-Co-Cu-Mg magnet was developed by the Bureau of Mines (13-14) and had the following magnetic properties: energy product, $(BH)_{max}$ = 9.2 MGOe; remanence, B_r = 6.23 kG; normal coercivity, $_BH_c$ = 5.89 kOe; intrinsic coercivity, $_MH_c$ = 29.0 kOe. In comparison, the best Sm-Co values obtained at the Reno Research Center (15) were $(BH)_{max}$ = 15.1 MGOe, B_r = 7.8 kG, $_BH_c$ = 7.5 kOe, and $_MH_c$ = 27.4 kOe.

Although the reason for the extremely high intrinsic coercivity that resulted from the copper and magnesium additions to MM-Co alloys was not fully understood, a recent investigation (16) showed that improved coercivity values were not obtained with Ce-Co-Cu-Mg, Pr-Co-Cu-Mg, and Nd-Co-Cu-Mg alloys. A substantial increase in coercivity was obtained only with La-Co-Cu-Mg alloys which had best magnetic properties of $(BH)_{max}$ = 9.8 MGOe, B_r = 6.6 kG, and $_BH_c$ = 6.1 kOe, and $_MH_c$ = 23.2 kOe. These results indicated that La-Co-Cu-Mg was the primary contributor to the high intrinsic and normal coercivity of the MM-Co-Cu-Mg alloys.

[2]Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

Even though the addition of copper and magnesium to MM-Co increased the coercivity, a substantial loss of remanence and energy product occurred. This prompted the Bureau of Mines to conduct an investigation to develop a synthetic mischmetal (M) with values of remanence and energy product comparable to those of Sm-Co alloys: energy product 15.1 MGOe, remanence 7.8 kG, normal coercivity 7.5 kOe, intrinsic coercivity 27.4 kOe. The initial rare-earth mixture of 50 pct La, 30 Pr, and 20 Nd was selected for the following reasons:

1. Cerium was eliminated because Ce-Co had the lowest theoretical value of magnetization (2, 7), which was confirmed by previous Bureau research.

2. La-Co was the primary source of high coercivity in the form of the alloy La-Co-Cu-Mg. The choice of 50 pct La was an arbitrary starting point.

3. Nd-Co had the greatest theoretical value of magnetization. Although Nd-Co showed no promise as a permanent magnet because of low crystal anisotropy (2, 7), Nd-Co-Cu-Mg had no adverse effect on the coercivity of MM-Co-Cu-Mg magnets. A 20-pct Nd content was arbitrarily chosen and kept constant throughout the study.

4. Pr-Co was retained because its theoretical magnetic properties are superior to those of Sm-Co.

5. Lanthanum, cerium, praseodymium, and neodymium are coproduced from the same natural ore. A balanced market for these rare earths would result in a maximum use and lowest cost for these products. Lanthanum and cerium have many commercial uses and are readily marketable. Since praseodymium and neodymium have only a limited market, new applications for these rare earths would be desirable.

EXPERIMENTAL PROCEDURES AND EQUIPMENT

ALLOY PREPARATION

Alloys of the composition R-Co-Cu-Mg (R is La, Pr, or Nd) were prepared in a nonconsumable arc furnace and from metals with a minimum purity of 99.9 pct. Charges of 60 to 100 g were melted, turned over, and remelted to achieve uniformity. To obtain M-Co, M-Co-Cu, and M-Co-Fe the following procedure was employed: Using M-Co-Cu as an example, La-Co-Cu, Pr-Co-Cu, and Nd-Co-Cu were prepared separately. The individual R-Co-Cu alloys were melted a total of four times. The alloy charges were removed from the furnace and crushed to approximately minus 4 mesh. Desired proportions of La-Co-Cu, Pr-Co-Cu, and Nd-Co-Cu were mixed into charges of 70 to 75 g and melted three additional times, again turning over the button between melts to insure homogeneity of the product, M-Co-Cu.

When the alloy was to contain magnesium, as in M-Co-Cu-Mg, the melting procedure was modified. Because magnesium vaporizes at a much lower temperature than the other metals, magnesium was not included in the initial metal charges but was added to the alloy product just before the last two meltings to keep the magnesium vapor loss at a minumum.

To simplify description, the four rare-earth mixtures that were evaluated are abbreviated as M50, M30, M20, and M10, where--

M50 is 50 pct La, 30 Pr, 20 Nd;

M30 is 30 pct La, 50 Pr, 20 Nd;

M20 is 20 pct La, 60 Pr, 20 Nd;

M10 is 10 pct La, 70 Pr, 20 Nd.

Magnets were prepared by a sintering procedure that required blending of a base compound, MCo_5, with a lower melting sintering aid, M_2Co_7. For convenience the base alloy containing 33.5 pct M was denoted as MCo_5, although stoichiometry dictates 32.3 pct M50 and 32.4 pct M10. The sintering aid containing 40.7 pct M was M_2Co_7, where stoichiometry requires 40.6 pct M50 and 40.7 pct M10.

The base alloys and sintering aid compounds containing synthetic mischmetal are listed in table 1. The compositions shown are for all values of M except the alloys containing iron, which were prepared with only M50 and M20. Wet-chemical and X-ray fluorescence analyses were used to determine rare-earth and cobalt concentrations. Copper, iron, and magnesium concentrations were determined by atomic absorption spectroscopy. Oxygen concentrations of the as-melted samples, ranging between 0.02 and 0.20 pct, were determined by neutron activation analysis.

TABLE 1. - Composition of M-Co-Cu-Fe-Mg alloys prepared by arc melting,[1] pct

M	Cu	Mg	Fe	M	Cu	Mg	Fe
BASE COMPOUND				SINTERING AID			
33.5	0	0	0	40.7	0	0	0
33.5	14.0	0	0	40.7	0	0	21.0
33.5	14.0	1.2	0				

[1]Balance Co.

POWDER PREPARATION

The as-melted alloys were crushed and passed through a 35-mesh sieve. Thirty-gram charges were prepared by blending MCo_5, M_2Co_7, $M_2(Co,Fe)_7$, $M(Co,Cu)_5$, and $M(Co,Cu,Mg)_5$ in the desired proportions. The minus 35-mesh blends were ground in toluene with a Spex[5] shatterbox. The temperature of grinding was controlled at approximately minus 60° C by surrounding the shatterbox container with Dry Ice. Grinding periods ranged from 30 to 135 min. Products with average Fisher Sub-Sieve Sizer measurements ranging between 3.4 and 2.0 µm were obtained. The powders were vacuum-dried and stored under helium to minimize oxidation.

[5]Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

ALINEMENT AND COMPACTION

The powder was alined in a magnetic field of 8 kG and compacted in air. The alinement apparatus consisted of a 1,200-turn coil wound with No. 10 AWG magnet wire and an iron core 2.5 cm in diameter and 15.2 cm long. Pressing was done in a single-action cylindrical die with a magnetic base and a nonmagnetic body and plunger. The die base and body rested on the iron core within the coil. The coil was energized, and the powder was introduced into the die. After the die was tapped and vibrated to enhance alinement of the particles, the plunger was inserted, and a pressure of approximately 6.9 MPa (1,000 psi) was applied. The die was removed from the alinement apparatus, and the powder was compacted with a hydraulic press at 310 MPa (45,000 psi). The green compacts obtained were 1.1 cm in diameter and 0.5 cm in height and had a density of approximately 60 pct of the theoretical. The density of the green compacts was determined by direct measurements of the mass and volume.

SINTERING

Eight compacts were enclosed in stainless steel sheaths welded at one end and fitted with a removable plug at the other end. Extra compacts were placed at each end to serve as getters for gaseous contaminants. The sheaths were evacuated and filled with helium. This arrangement provided a uniform temperature distribution and protected the compacts from oxidation. The compacts were sintered in a tube furnace swept with helium. Sintering was conducted for 2 h at temperatures between 975° and 1,020° C which depended primarily on the rare-earth content of the synthetic mischmetal.

The sintered magnets were cooled to ambient temperature by a slow cooling method referred to as furnace cooling. The samples remained in the heat zone of the furnace and the temperature was slowly decreased to approximately 600° C, after which the samples were removed from the heat zone and cooled quickly to room temperature. To prevent oxidation, the samples remained in the furnace tube under a protective helium flow throughout the entire cooling process. The density of the sintered magnets, which ranged between 90 and 98 pct of the theoretical, was determined by immersion in isopropyl alcohol.

MAGNETIC PROPERTY MEASUREMENTS

The magnetic properties were measured with an O. S. Walker hysteresisgraph, which was designed to plot B versus H hysteresis loops. The magnetic induction (B) was obtained by integrating the voltage change in a search coil closely fitted around two sample magnets. The sintered magnets were approximately 0.5 cm in length and ranged between 0.98 and 1.02 cm in diameter. A number of search coils of different diameters and 0.64 cm in length were made to accommodate the sintered magnets. Each pair of magnets, stacked and wrapped with cellophane tape, was in contact with the pole faces of the electromagnet to minimize any self-demagnetizing effect. The exciting field (H) was measured with a Hall-effect probe centered between the pole faces and adjacent to the search coil. The peak magnetizing field was 30 kOe at a pole gap of 0.94 cm. The hysteresisgraph was calibrated against standard samples obtained from the Magnetics Laboratory, University of Dayton, Ohio. A pair of Pt-Co permanent magnets was used as a secondary standard each time magnetic measurements were made.

RESULTS AND DISCUSSION

The primary purpose of this research was to develop a synthetic mischmetal, M_s, with improved remanence and energy product values over those of natural mischmetal, MM, when alloyed with Co, Cu, and Mg. Because of the many possible combinations of these metals, the study was limited to selected combinations. Copper contents of 5 and 6 pct and a magnesium content of 0.24 pct were chosen because these values were near optimum in recent investigations of alloys containing natural mischmetal and lanthanum (14, 16). The choice of a constant 20 pct Nd was arbitrary, although this value approximates the neodymium content of natural mischmetal after the cerium is removed.

MAGNETIC PROPERTIES OF M50-Co-Cu-Mg

Effect of Mischmetal Content

The initial composition for optimizing a rare-earth mixture was a synthetic mischmetal, M50, containing 50 pct La, 30 Pr, and 20 Nd. Studies were made to determine the effect of the mischmetal content on the magnetic properties of M50-Co-Cu-Mg alloys. The rare-earth content of the magnets was varied between 35 and 37.5 pct. The alloys contained 5 and 6 pct Cu, 0.24 Mg, and balance Co. The minus 35-mesh blends were shatterbox-ground for 60 min and sintered at 1,000° C.

As shown in figure 1, the best magnetic properties were obtained at 36.5 pct M50 for both copper contents. The samples containing 6 pct Cu had better magnetic properties than the corresponding alloys with 5 pct Cu. The shapes of the curves were unaffected by the difference in copper.

Effect of Copper Content

The effect of copper content on the magnetic properties of a M50-Co-Cu-Mg alloy also was determined. The copper content was varied between 3 and 7 pct in increments of 1 pct. The alloy contained 36.5 pct M50, 0.24 Mg, and balance Co. Each charge was ground for 60 min and sintered at 1,000° C.

Figure 2 shows the magnetic properties of the M50-Co-Cu-Mg alloy as a function of copper concentration. All properties showed more dependence on copper than was observed in alloys containing natural mischmetal. Remanence exhibited the greatest variation in comparison to a nearly constant value for samples containing natural mischmetal. Peak values were obtained at 6 pct Cu and were $(BH)_{max}$ = 11.6 MGOe, B_r = 7.12 kG, $_BH_c$ = 6.62 kOe, and $_MH_c$ = 21.4 kOe.

Effect of Magnesium Content

Tests were conducted to show the effects of magnesium on the magnetic properties of alloys containing 36.5 pct M50, 5 and 6 pct Cu, and balance Co. The magnesium content was varied by blending a base alloy, $M(Co,Cu,Mg)_5$, containing 1.2 pct Mg with MCo_5, M_2Co_7, and $M(Co,Cu)_5$. Each charge was ground for 60 min and sintered at 1,000° C.

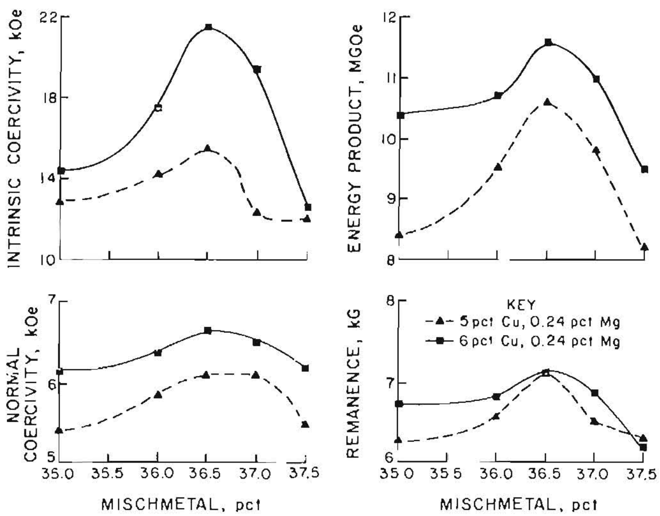

FIGURE 1. - Effect of mischmetal content on the magnetic properties of M50-Co-Cu-Mg alloys.

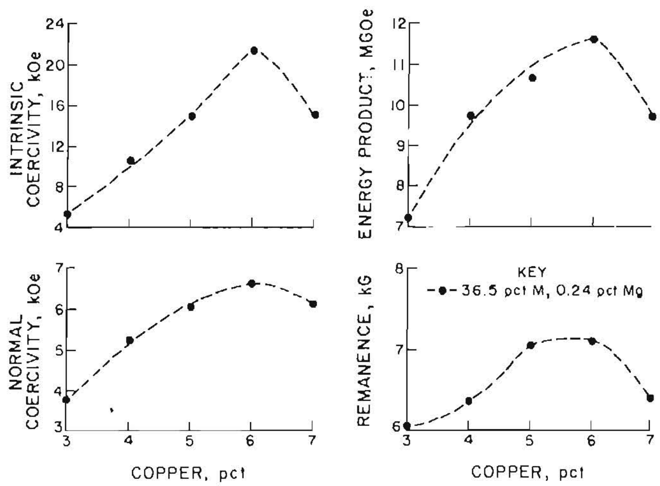

FIGURE 2. Effect of copper content on the magnetic properties of M50-Co-Cu-Mg alloys.

Figure 3 shows the magnetic properties as a function of magnesium concentration in the M50-Co-Cu-Mg alloys. The coercivities and energy product exhibited peak values and a definite dependence on the magnesium content. The remanence values were fairly constant and showed no peak values. All magnetic properties were maximum at 0.24±0.04 pct Mg. The alloy containing 6 pct Cu had the best magnetic properties.

Effect of Grinding

Comminution of the bulk alloy to a fine powder was a critical step in the fabrication of M50-Co-Cu-Mg magnets because reproducibility of shatterbox grinding was difficult to control. Thirty-gram charges were ground in toluene at minus 60° C. Grinding at this low temperature improved magnetic properties and minimized oxidation.

The oxygen content of the as-melted alloys was typically 0.09 pct and ranged from 0.02 to 0.2 pct. The oxygen content of powders ranged between 0.3 and 0.9 pct and had a typical value of 0.6 pct for powder ground for 60 and 90 min. The oxygen value increased slightly (less than 0.1 pct) with increasing amounts of lanthanum in the alloy. The oxygen values reported are representative for the M50 through M10 rare-earth mixtures evaluated.

To evaluate the effects of comminution time on the magnetic properties, M50-Co-Cu-Mg alloys containing 36.5 and 37 pct M50, 6 Cu, 0.24 Mg, and balance Co were ground 30 to 120 min. The green compacts were sintered at 1,000° C. The results are shown in figure 4. Except for the intrinsic coercivity of the alloy containing 37.0 pct M50, all maximum values were obtained with alloys ground for 60 min. For alloys containing 36.5 pct M50, the average Fisher Sub-Sieve particle size was 3.0, 2.9, and 2.5 µm for grinding times of 30, 60, and 120 min, respectively. For alloys containing 37 pct M50, the average particle size was 3.4, 2.7, and 2.5 µm for grinding times of 30, 60, and 120 min, respectively.

MAGNETIC PROPERTIES OF M30-Co-Cu-Mg

Effect of Mischmetal Content

Using synthetic mischmetal M30, containing 30 pct La, 50 Pr, and 20 Nd, the effect of the mischmetal content on the magnetic properties of M-Co-Cu-Mg was determined. The rare-earth content of the magnets was varied between 36 and 37.5

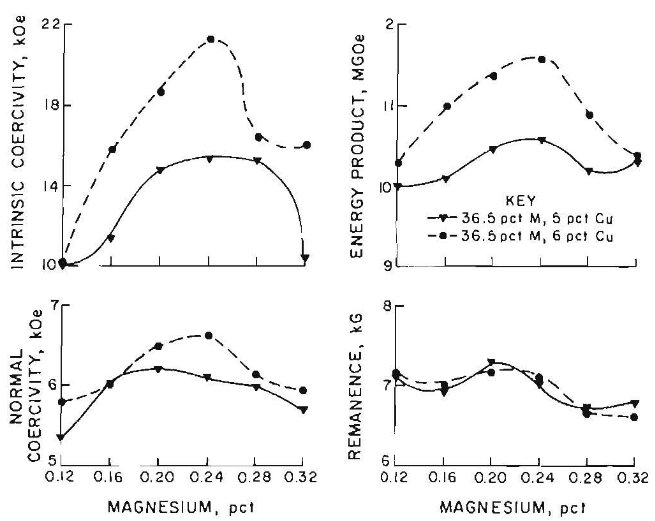

FIGURE 3. - Effect of magnesium content on the magnetic properties of M50-Co-Cu-Mg alloys.

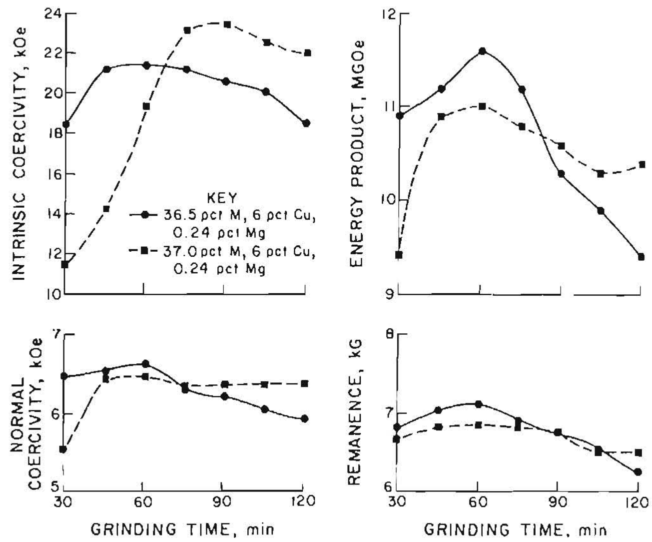

FIGURE 4. - Dependence of magnetic properties on the comminution time of M50-Co-Cu-Mg alloys.

pct. The alloys contained 5 and 6 pct Cu, 0.24 Mg, and balance Co. The minus 35-mesh blends were ground for 90 min and sintered at 1,000° C.

As shown in figure 5, peak values of intrinsic and normal coercivity were obtained with alloys containing 36.5 pct M30, and peak remanence values were obtained with 37 pct M30. Maximum energy products were 11.8 and 11.7 MGOe obtained with alloys containing 37 pct M30-5 pct Cu and 36.5 pct M30-6 Cu, respectively. The best composition was 36.5 pct M30, 6 Cu, 0.24 Mg, and balance Co; this was the same alloy composition with which the best magnetic properties were obtained with mischmetal M50.

Effect of Copper Content

The effect of copper content on the magnetic properties of alloys containing 36.5 and 37 pct M30 was investigated. The M30-Co-Cu-Mg charges were ground for 90 min and sintered at 1,000° C.

As shown in figure 6, the best results were obtained with a 6 pct Cu content for both 36.5 and 37 pct M30 contents. Except for the remanence, which remained almost constant over the range of 4 to 7 pct Cu, the magnetic properties had well-defined peak values.

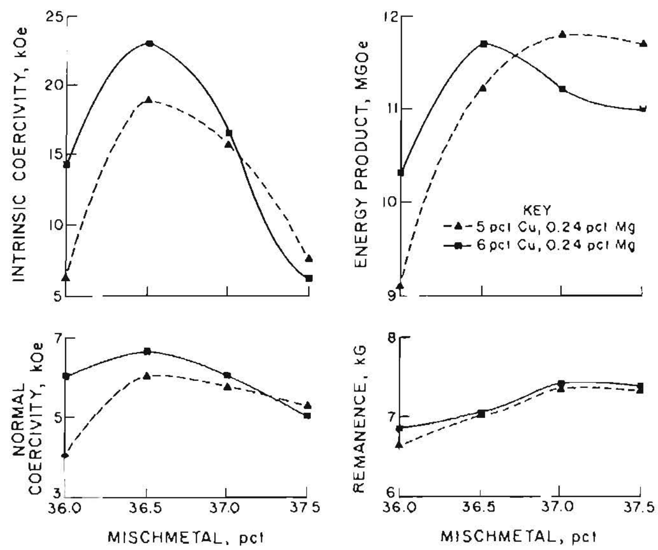

FIGURE 5. - Effect of mischmetal content on the magnetic properties of M30-Co-Cu-Mg alloys.

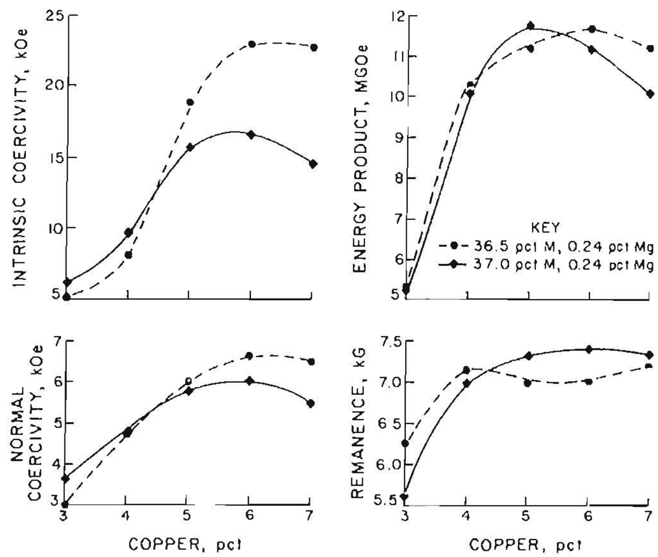

FIGURE 6. - Effect of copper content on the magnetic properties of M30-Co-Cu-Mg alloys.

MAGNETIC PROPERTIES OF M20-Co-Cu-Mg

Effect of Mischmetal Content

Tests were conducted to determine the effect of mischmetal on the magnetic properties of M20-Co-Cu-Mg alloys. The mischmetal content was varied between 36 and 37.5 pct. The alloys contained 5 and 6 pct Cu, 0.24 Mg, and balance Co. The minus 35-mesh blends were shatterbox-ground for 90 min and sintered at 1,010° C.

Figure 7 shows the magnetic properties as a function of the total rare-earth content. The best mischmetal content was 37 pct for M20. In comparison the best rare-earth content was 36.5 pct for both M50 and M30. Except for the intrinsic coercivity, peak magnetic values did not vary significantly due to the difference in copper content. The greatest value of intrinsic coercivity was obtained with 6 pct Cu, and best values of normal coercivity, remanence, and energy product were approximately the same at 5 and 6 pct Cu.

Effect of Copper Content

The effect of copper on the magnetic properties of an alloy containing 37 pct M20, 0.24 Mg, and balance Co was

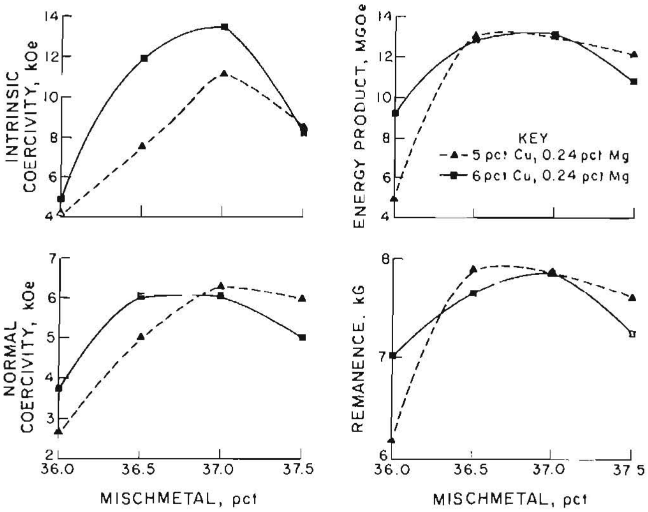

FIGURE 7. - Effect of mischmetal content on the magnetic properties of M20-Co-Cu-Mg alloys.

determined for the range of 3 to 7 pct Cu. Each blended charge was ground for 90 min and sintered at 1,010° C.

As shown in figure 8, peak magnetic properties were obtained with copper contents of 5 and 6 pct as previously discussed. The effect of copper on the magnetic properties of alloys containing M20 was similar to its effect with alloys containing M30. Maximum values were obtained over the range of 5 to 6 pct Cu. In comparison, the magnetic properties of alloys containing M50 varied as a function of copper concentration, with all peak values precisely defined at the single copper content of 6 pct.

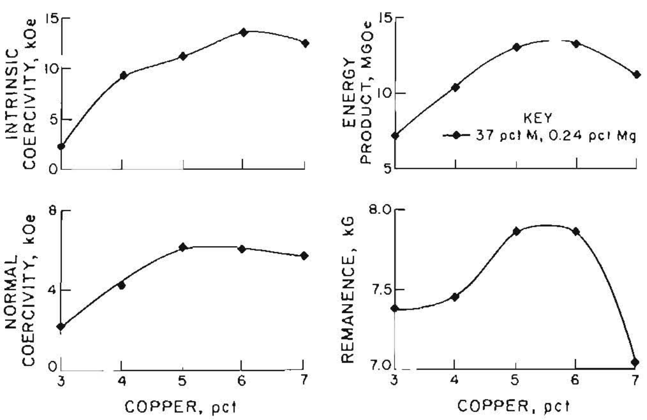

FIGURE 8. - Effect of copper content on the magnetic properties of M20-Co-Cu-Mg alloys.

Effect of Magnesium Content

A study was made to determine the effect of magnesium on the magnetic properties of an alloy containing 37 pct M20, 6 Cu, and balance Co. Each charge was ground for 90 min and sintered at 1,010° C.

Figure 9 shows the results. A well-defined peak of intrinsic coercivity was obtained at 0.24 pct Mg, and a fairly well-defined peak of normal coercivity was obtained at 0.16 pct Mg. No well-defined peaks were observed for remanence and energy product. Remanence value was approximately constant for the entire range of 0.04 to 0.36 pct Mg. The energy product values were maximum in the range of 0.12 to 0.24 pct Mg. In comparison to M50, the magnetic properties of alloys containing M20 showed less dependence on magnesium content.

Effect of Grinding

A study of alloys containing M20 was made to ~~determine the effect~~ of grinding on the magnetic properties of alloys containing 37 pct M20, 6 Cu, 0.24 Mg, and balance Co. Thirty-gram charges were shatterbox-ground in toluene at minus 60° C for 30 to 135 min. The green compacts were sintered at 1,010° C.

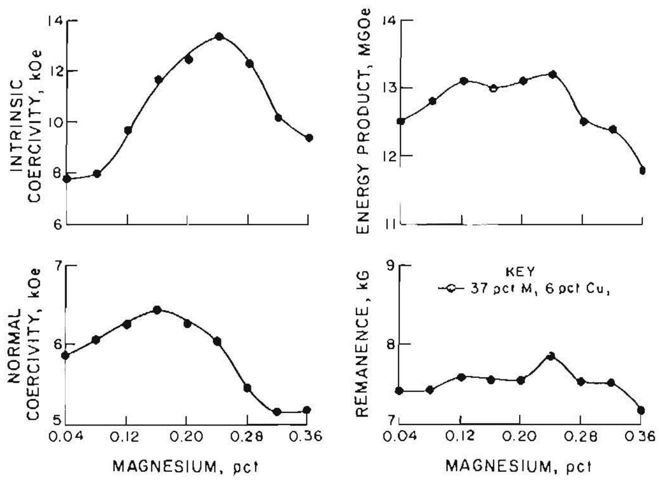

FIGURE 9. - Effect of magnesium content on the magnetic properties of M20-Co-Cu-Mg alloys.

As shown in figure 10, all maximum magnetic properties were obtained with the sample that was ground for 90 min. The average Fisher Sub-Sieve particle size was 3.1, 2.4, and 2.3 µm for comminution times of 30, 90, and 135 min, respectively. Because of the similarity in rare-earth content, studies with M10 and M30 were conducted with a 90-min grinding duration rather than a 60-min duration, which was best for alloys containing M50.

MAGNETIC PROPERTIES OF M10-Co-Cu-Mg

Effect of Mischmetal Content

The effect of the rare-earth content on the magnetic properties of alloys containing synthetic mischmetal M10 was determined. The mixture contained the least amount of lanthanum of all the synthetic mischmetals. The rare-earth content was varied between 36 and 37.5 pct M10. The alloys contained 5 and 6 pct Cu, 0.24 Mg, and balance Co. The minus 35-mesh blends were shatterbox-ground for 90 min and sintered at 1,020° C.

Figure 11 shows the effect of mischmetal content on the magnetic properties. Copper content had a substantial effect. Definite peaks were observed at 6 pct Cu, whereas the values were relatively constant at 5 pct Cu. Intrinsic and normal coercivity values of magnets containing

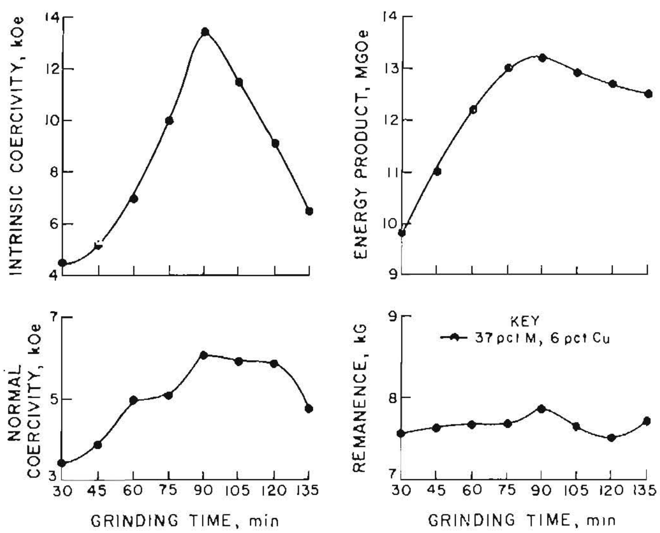

FIGURE 10. - Dependence of magnetic properties on the comminution time of M20-Co-Cu-Mg alloys.

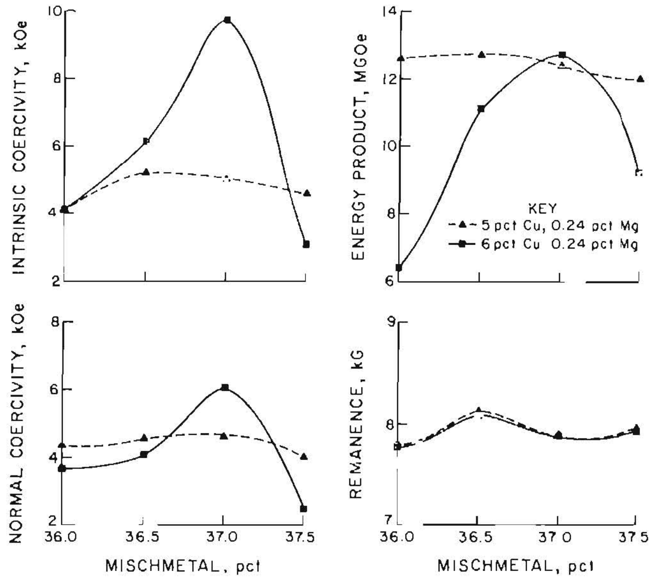

FIGURE 11. - Effect of mischmetal content on the magnetic properties of M10-Co-Cu-Mg alloys.

M10 were considerably less in comparison to those of magnets containing M20, especially for alloys containing 5 pct Cu. Peak energy product values of samples containing M10 and M20 were comparable. Only the remanence of magnets containing M10 showed improvement over that of samples with M20 and was greater than 8.0 kG. The mischmetal content of 37 pct gave the best results for intrinsic coercivity, normal coercivity, and energy product.

Effect of Copper Content

The effect of copper on the magnetic properties was determined for alloys containing 36.5 and 37 pct M10, 0.24 Mg, and balance Co. The copper was varied between 4 and 7 pct. Each alloy was ground for 90 min and sintered at 1,020° C.

As shown in figure 12, decreased values of intrinsic and normal coercivity were obtained for both 36.5 and 37 pct rare-earth contents in comparison to the results obtained with the other synthetic mischmetals that were evaluated. The effect of copper on the remanence and energy product was similar to its effect on alloys containing M50, M30, and M20. All peak magnetic values were obtained at 6 pct Cu for samples containing 37 pct

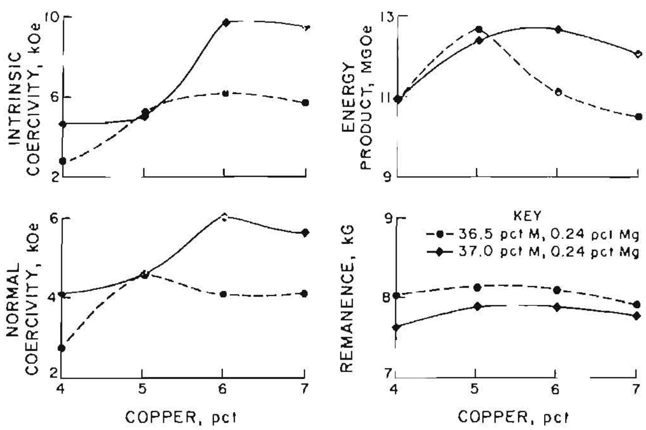

FIGURE 12. - Effect of copper content on the magnetic properties of M10-Co-Cu-Mg alloys.

M10. Peak values of normal coercivity, energy product, and remanence were obtained at 5 pct Cu for samples containing 36.5 pct M10.

MAGNETIC PROPERTIES OF M-Co-Cu-Mg: EFFECT OF LANTHANUM CONTENT

The effects of mischmetal, copper, and magnesium on the magnetic properties have been discussed. The effect of lanthanum on the magnetic properties obtained with the best M-Co-Cu-Mg compositions is shown in figures 13 and 14 and in table 2. The data are a summary of the maximum observed values of the magnetic properties of samples containing 36.5 and 37 pct M, 5 and 6 Cu, 0.24 Mg, and balance Co. The grinding and sintering conditions were as previously described.

As shown in figures 13 and 14, peak values of intrinsic coercivity were obtained at a mischmetal content of 36.5 pct and at a lanthanum content of 30 pct (M30) and decreased rapidly as the lanthanum was decreased to 10 pct (M10). The normal coercivity was approximately the same at 50 and 30 pct La and decreased when the La content was decreased, especially for samples containing 36.5 pct M. Since the rare-earth component, La, when alloyed with Co, Cu, and Mg, is the primary source of the coercivity of M-Co-Cu-Mg alloys, the dependency of coercivity on the La content was expected.

TABLE 2. - Effect of composition on the magnetic properties of M-Co-Cu-Mg alloys

Composition,[1] pct	Rare-earth mixture[2]	Density, g/cm^3	$_MH_c$, kOe	$_BH_c$, kOe	B_r, kG	$(BH)_{max}$, MGOe
36.5 M,5 Cu..	M50	8.01	15.4	6.06	7.07	10.6
	M30	8.00	18.9	6.01	7.01	11.2
	M20	8.01	7.5	5.00	7.89	13.1
	M10	8.00	5.2	4.54	8.12	12.7
36.5 M,6 Cu..	M50	8.05	21.4	6.62	7.12	11.6
	M30	8.05	22.9	6.63	7.04	11.7
	M20	8.09	11.9	6.04	7.65	12.9
	M10	8.04	6.1	4.06	8.09	11.1
37.0 M,5 Cu..	M50	8.11	12.3	6.06	6.47	9.8
	M30	8.08	15.7	5.77	7.34	11.8
	M20	8.09	11.1	6.26	7.86	13.0
	M10	8.08	5.0	4.57	7.87	12.4
37.0 M,6 Cu..	M50	8.16	19.3	6.46	6.86	11.0
	M30	8.14	16.5	6.03	7.42	11.2
	M20	8.08	13.4	6.04	7.86	13.2
	M10	8.11	9.7	6.03	7.87	12.7

[1]Alloys contain 0.24 pct Mg and balance Co.

[2]Rare-earth mixtures, in pct: M50 contains 50 La, 30 Pr, 20 Nd; M30 contains 30 La, 50 Pr, 20 Nd; M20 contains 20 La, 60 Pr, 20 Nd; M10 contains 10 La, 70 Pr, 20 Nd.

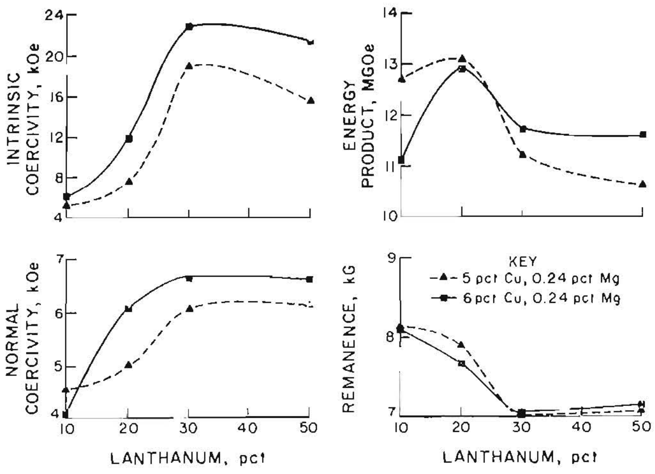

FIGURE 13. - Effect of lanthanum and copper on the magnetic properties of a 36.5-pct-M alloy.

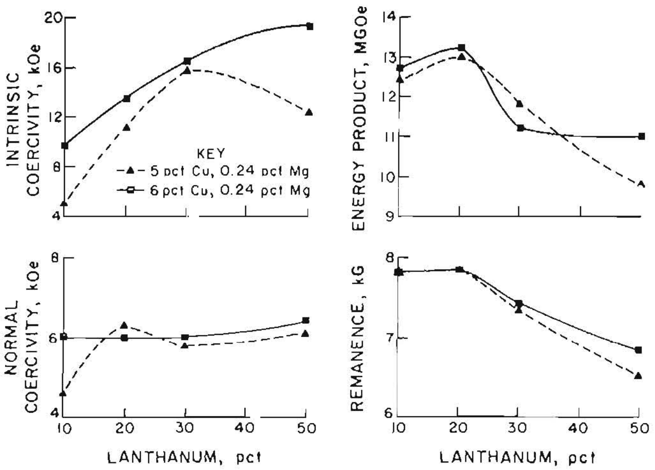

FIGURE 14. - Effect of lanthanum and copper on the magnetic properties of a 37-pct-M alloy.

In contrast to decreasing coercivities at low lanthanum levels, the remanence increased when the amount of lanthanum was decreased from 50 pct to 10 pct. Since the theoretical value of magnetization is much greater for Pr-Co than for La-Co, remanence was expected to increase when the amount of lanthanum was decreased (tantamount to the praseodymium being increased). Energy product values also increased as the amount of praseodymium was increased. Peak values of approximately 13 MGOe were obtained with magnets containing 20 pct La. The best overall synthetic mischmetal was M20 in the composition range of 36.5 and 37 pct M20, 5 and 6 Cu, 0.24 Mg, and balance Co.

The results of this investigation are very encouraging in two respects. First, the maximum magnetic values obtained with M-Co-Cu-Mg [$(BH)_{max}$ = 13.2 MGOe, B_r = 8.12 kG, $_BH_c$ = 6.63 kOe, and $_MH_c$ = 22.9 kOe] were superior to the best values obtained with MM-Co-Cu-Mg [$(BH)_{max}$ = 9.2 MGOe, B_r = 6.23 kG, $_BH_c$ = 5.89 kOe, and $_MH_c$ = 29.0 kOe] in previous Bureau Research (14). The remanence and energy product were particularly improved. Second, magnets containing synthetic mischmetal showed no obvious signs of oxidation. Magnets containing natural mischmetal (23 to 27 pct La) have also shown no sign of oxidation. This is noted because magnets in which the rare-earth content was entirely lanthanum, La-Co-Cu-Mg, physically deteriorated when exposed for several months to air at room temperature (16). No deterioration was observed for M-Co-Cu-Mg alloys even with a maximum lanthanum content of 50 pct in the synthetic mischmetal. Since the best rare-earth mixture, M20, contained only 20 pct La, the resistance to oxidation would be expected to be superior to that of magnets containing natural mischmetal. The improved magnetic properties and resistance to oxidation indicate that synthetic mischmetal (M-Co-Cu-Mg) with magnetic properties approaching those of Sm-Co may have commercial significance.

MAGNETIC PROPERTIES OF M-Co-Cu-Fe-Mg: EFFECT OF IRON CONTENT

The substitution of iron for cobalt (7) has been reported to increase the saturation magnetization of rare-earth-cobalt magnets. In previous Bureau studies with natural mischmetal (14), as much as 6 pct Fe was added to an alloy containing 36 pct MM, 5 Cu, 0.05 Mg, and balance Co. The best values obtained with the alloy were $(BH)_{max}$ = 10.3 MGOe, B_r = 6.90 kG, $_BH_c$ = 4.43 kOe, and $_MH_c$ = 5.6 kOe. Remanence and energy products were significantly improved with a tolerable loss of intrinsic and normal coercivity. An important benefit was a 17-pct decrease in cobalt requirement through the collective substitution of 6 pct Fe and 5 pct Cu for cobalt.

Studies were conducted to determine the effects of iron on the magnetic properties of M-Co-Cu-Mg alloys containing 37 pct M, 5 and 6 Cu, 0.24 Mg, and balance Co. Synthetic mischmetals, M50 and M20, were evaluated. Iron substitution was made through a sintering aid compound $M_2(Co,Fe)_7$ with a composition of 40.7 pct M, 21 Fe, and balance Co. Alloys containing M50 were ground for 75 min and sintered at 975° C. Alloys containing M20 were ground for 90 min and sintered at 1,010° C.

As shown in figures 15 and 16, the effect of iron on the magnetic properties was discouraging. Except for remanence, all magnetic properties decreased as the iron concentration was increased. The alloy containing M20 and 5 pct Cu shown in figure 16 was the only alloy that showed any promise. The energy product remained constant over the range of 1 to 3 pct Fe. Although no improvement of remanence and energy product was realized, a decrease in cobalt requirement was obtained with this alloy. The reason for the loss of properties for M-Co-Cu-Fe-Mg in comparison to the effect on MM-Co-Cu-Fe-Mg was not fully understood. The loss may be attributed to the extreme variation of the individual rare-earth components. Compared with natural mischmetal, synthetic mischmetal has a greater praseodymium content and no cerium. A substantial substitution of iron for cobalt is not likely to result in improved magnetic properties with any of the alloys containing synthetic mischmetals.

SUMMARY

A magnet containing synthetic mischmetal, Co, Cu, and Mg was developed that possessed substantially better magnetic properties than its counterpart containing natural mischmetal. Best magnetic properties were obtained with the rare-earth mixture M20, which consisted of 20 pct La, 60 Pr, and 20 Nd. The best M-Co-Cu-Mg composition was in the range 36.5 and 37 pct M, 5 and 6 Cu, 0.24 Mg, and balance Co. Maximum magnetic properties obtained were $(BH)_{max}$ = 13.2 MGOe, B_r = 7.89 kG, $_BH_c$ = 6.26 kOe, and $_MH_c$ = 13.4 kOe as compared to $(BH)_{max}$ = 9.2 MGOe, B_r = 6.23 kG, $_BH_c$ = 5.89 kOe, $_MH_c$ = 29.0 kOe obtained with natural mischmetal. The energy product and remanence values compare favorably with those of the more expensive Sm-Co magnets whose values are $(BH)_{max}$ = 15.1 MGOe and B_r = 7.8 kG.

Iron substitutions for cobalt were made in M-Co-Cu-Fe-Mg alloys containing synthetic mischmetals M50 and M20. There were a drastic loss of coercivity and energy product and a slight improvement of remanence in the range of 1 to 5 pct

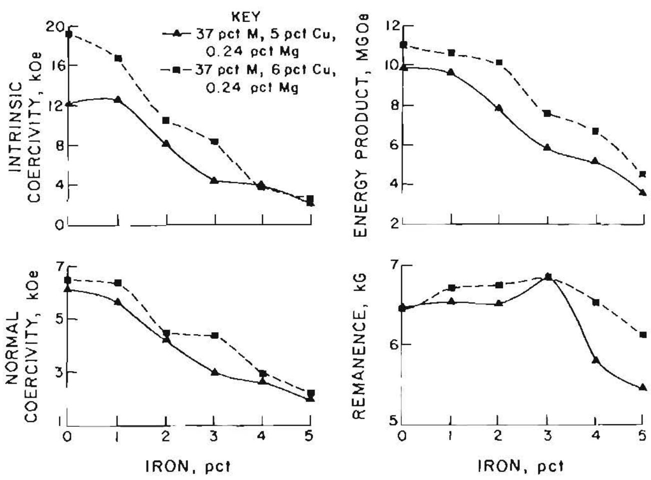

FIGURE 15. - Effect of iron on the magnetic properties of M50-Co-Cu-Fe-Mg alloys.

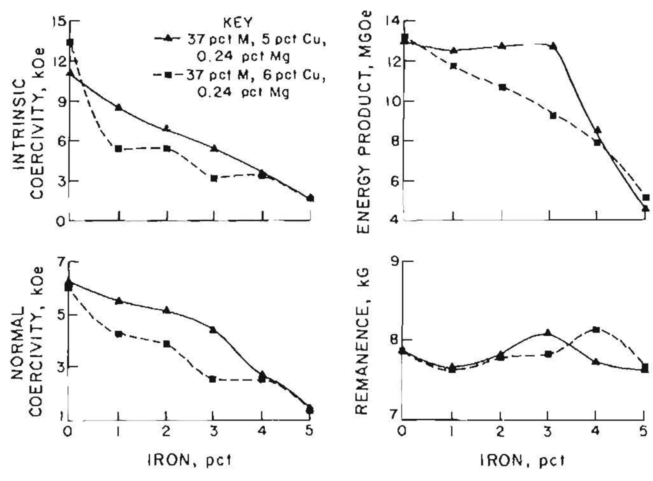

FIGURE 16. - Effect of iron on the magnetic properties of M20-Co-Cu-Fe-Mg alloys.

iron. Since iron substitutions were successfully made in magnets containing natural mischmetal, the deleterious effect of iron on magnets fabricated from synthetic mischmetal may have been caused by the difference in the individual rare-earth element contents. Synthetic mischmetal was cerium-free and high in praseodymium compared to natural mischmetal. No more than a few percent iron can be tolerated in magnets containing synthetic mischmetal.

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APPENDIX.--DEFINITIONS OF BASIC MAGNETIC PROPERTIES OF A PERMANENT MAGNET

Magnetic induction, B, is the magnetic field induced in a material by an external magnetic field. It is also referred to as magnetic flux density and is measured in gauss.

Remanence, B_r, is the residual magnetic induction of a material corresponding to a zero external magnetic field in a closed circuit. It is also referred to as the residual flux density and is measured in gauss.

Magnetic field strength, H, is the external magnetizing-demagnetizing field applied to a material. It is measured in oersted.

Normal coercivity, $_BH_c$, is the demagnetizing field required to decrease the magnetic induction of a material to zero. It is a measure of resistance to demagnetization and is measured in oersted. Intrinsic coercivity, $_MH_c$, of a material is the demagnetizing field, numerically equal to the magnetic induction. It is measured in oersted.

Maximum energy product, $(BH)_{max}$, is the greatest amount of energy a material can supply to an external magnetic circuit. It represents the maximum efficiency in which a given amount of magnetic induction will be carried by the smallest amount of material. It is measured in gauss-oersted.

Hysteresis curve is the magnetization-demagnetization curve of a magnetic material. It does not retrace itself as the applied magnetic field, H, is increased and decreased. This lack of retraceability is called hysteresis. As shown in figure A-1, the induction, B, follows the initial magnetization curve as the applied field is increased and returns to a residual value, B_r, as the field is decreased to zero. As the applied field is increased in the opposite direction, the induction becomes zero. The demagnetizing field at this point is called the normal coercive force, $_BH_c$. The product, B × H, shown in the second quadrant, is a figure of merit for permanent magnets. The point of greatest value is known as the maximum energy product, $(BH)_{max}$. As the demagnetizing field is increased beyond the normal coercive force, a condition is achieved in which the internal magnetization of a material is zero. The demagnetizing field at this point is called the intrinsic coercive force, $_MH_c$, and is shown on the hysteresis curve where B = H in the third quadrant. The applied demagnetizing field is increased to maximum, and the material is magnetized in the direction opposite to that of the initial magnetization curve. The process is repeated to return the material to its initial direction of magnetization.

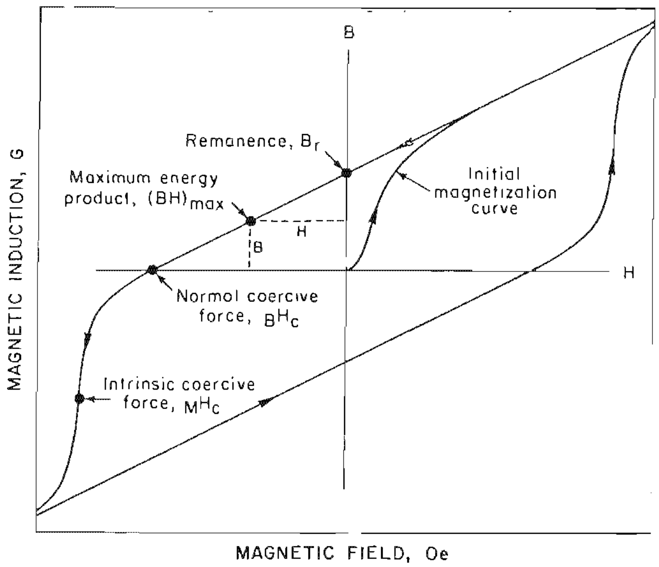

FIGURE A-1. - Hysteresis loop of a permanent magnet material.