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Magnetic Properties of Alloys Containing Mischmetal, Cobalt, Copper, Iron, and Magnesium

By J. W. Walkiewicz, J. S. Winston, and M. M. Wong

UNITED STATES DEPARTMENT OF THE INTERIOR

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MAGNETIC PROPERTIES OF ALLOYS CONTAINING MISCHMETAL, COBALT, COPPER, IRON, AND MAGNESIUM

by

J. W. Walkiewicz,[1] J. S. Winston,[2] and M. M. Wong[3]

ABSTRACT

The Bureau of Mines investigated alloys containing mischmetal (MM), cobalt, copper, magnesium, and iron for use in permanent magnets in place of the scarce samarium-cobalt alloys. The magnetic properties of MM-Co, MM-Co-Cu, MM-Co-Cu-Mg, and MM-Co-Cu-Fe-Mg alloys were evaluated. Magnets were fabricated by powder metallurgy consisting of arc-melting the metals, crushing and grinding the resultant alloys, alining and compacting the powder, and sintering the compacts.

Magnetic values of ${}_{M}H_c$ = 4.7 kOe, ${}_{B}H_c$ = 4.07 kOe, B_r = 6.81 kG, and $(BH)_{max}$ = 10.0 MGOe were obtained with a MM-Co alloy containing 36±0.5 wt-pct MM. By substituting copper and magnesium for part of the cobalt, the values for ${}_{M}H_c$ and ${}_{B}H_c$ were increased to 29.0 kOe and 5.89 kOe, respectively. This intrinsic coercivity value exceeded that of Sm-Co alloy obtained in our laboratory. The addition of iron to MM-Co-Cu-Mg alloys resulted in an increase of B_r to 6.90 kG and $(BH)_{max}$ to 10.3 MGOe. Copper and magnesium contents of these alloys were optimized to obtain maximum values of ${}_{M}H_c$.

INTRODUCTION

Samarium-cobalt alloys became the mainstay of the rare-earth-cobalt magnet industry because high-coercivity powder could be readily prepared by simple grinding. The high cost and scarcity of samarium, however, limited Sm-Co magnets to sophisticated applications where cost was secondary to performance. Magnet suppliers are eager to develop rare-earth-cobalt (RE-Co) alloys in which mischmetal (MM), the least expensive, most abundant, and naturally occurring mixture of rare-earth metals, is substituted for some or all of the samarium.

As the application for mischmetal-samarium-cobalt (MM-Sm-Co) magnets increased, the availability of samarium metal became a serious concern for

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magnet manufacturers and potential consumers. Recently, the auto industry has shown considerable interest in RE-Co alloys for use in motors and gages. According to David Fry (2)[4] of General Motors Research Laboratory, the application of Sm-Co magnets in automobiles would require over 20 times the current yearly production of samarium metal. High-volume demands can be met only through the use of the more abundant mischmetal.

The availability of cobalt metal is also a serious concern for magnet producers. Nearly all cobalt metal is imported. This excessive dependence on foreign sources can be lessened through substitution of other metals for cobalt. Replacement of copper and iron for cobalt in MM-Co alloys would not only decrease the demand for cobalt but also improve the magnetic properties.

The need to decrease the demand for samarium has prompted research on MM-Sm-Co and MM-Co magnets. Magnetic properties of compacted, but not sintered, $MMCo_5$ powders were measured by Strnat (16-17) and by McCaig (8-9). They reported intrinsic coercivities of 2.5 to 4.6 kOe and energy products of 2.3 to 3.1 MGOe. The results of sintered MM-Sm-Co magnets were first reported by Benz and Martin (1, 7). Maximum values of intrinsic coercive force of 20 kOe and energy product of 20 MGOe were obtained with MM-Sm-Co alloys containing more samarium than mischmetal. Das (3) reported an energy product of 20 MGOe for a MM-Sm-Co alloy containing equal amounts of samarium and mischmetal. Properties of MM-Sm-Co magnets with lesser amounts of samarium were determined by Ratnam and Wells (15). They reported intrinsic coercivities in the range of 10 to 14 kOe and energy products of 10 to 16 MGOe for MM-Sm-Co magnets with 6 to 9 wt-pct Sm in the final composition and 15 to 25 pct Sm in the total rare-earth content. Nagel (10-12) obtained a maximum intrinsic coercive force of 24 kOe and an energy product of 18 MGOe with an alloy composition of $MM_{0.6}Sm_{0.4}Co_5$.

A detailed study of MM-Co alloys containing no samarium addition was first reported by Johnson and Fellows (4-5). They obtained a maximum intrinsic coercive force, $_{M}H_c$, of 6.4 kOe and a maximum energy product, $(BH)_{max}$, of 8.8 MGOe with a MM-Co alloy containing 40.2 wt-pct MM (near stoichiometric MM_2Co_7). Nagel (12) reported values for maximum intrinsic coercive force and energy product, $_{M}H_c$ = 9.0 kOe and $(BH)_{max}$ = 14.5 MGOe, for the $MMCo_5$ alloy. The coercivity value was increased by a factor of 2.5 by postsintering heat treatment and subsequent controlled cooling of the alloy to room temperature. Narita Yamamoto (13) also reported a maximum coercive force, $_{M}H_c$ = 9.0 kOe, for a MM-Co alloy containing 39.8 wt-pct MM.

The use of copper to enhance the coercivity of RE-Co magnets was reported by Nesbitt and Wernick (14). They prepared RE-Co-Cu magnets with a substantial intrinsic coercive force by casting and subsequent heat treatment. Properties of MM-Co magnets containing copper prepared by powder metallurgy were reported by Kawaguchi and Yamamoto (6). They obtained typical intrinsic coercivities of 4.5 kOe (maximum coercivity, $_{M}H_c$ = 6.3 kOe) and energy products of 4.2 MGOe with an alloy composition of 34.2 wt-pct MM, 50.2 Co, and 15.6 Cu (approximately $MM_4Co_{15}Cu_4$).

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[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

To decrease the demands for samarium and cobalt and to improve the coercivity of the magnets, the Bureau of Mines investigated MM-Co magnets with partial substitution of copper, magnesium, and iron for cobalt. This paper presents the results of the studies of MM-Co and MM-(Co,Cu,Fe,Mg) magnets prepared by powder metallurgy. The effects of copper, magnesium, and iron on the magnetic properties of selected alloys will be discussed.

EXPERIMENTAL PROCEDURES AND EQUIPMENT

Alloy Preparation

The mischmetal used was a commercial product with most of the samarium removed that had a rare-earth composition range of 52.1-57.8 wt-pct Ce 23.4-33.4 La, 10.8-17.9 Nd, and 3.4-6.6 Pr. Analysis was made by standard chemical methods with an accuracy of ±5 pct. Based on a typical rare-earth composition of 55 wt-pct Ce, 25 La, 15 Nd, and 5 Pr, the atomic weight of the mischmetal was approximately 140.5. Using this value, the mischmetal content was 32.3 wt-pct for $MMCo_5$, 40.5 wt-pct for MM_2Co_7, and 21.9 wt-pct for MM_2Co_{17}. Since MM_2Co_{17} has a low anisotropy, its formation would result in a drastic reduction of coercivity. To minimize the formation of MM_2Co_{17}, a based compound slightly richer in mischmetal than dictated by the stoichiometry of $MMCo_5$ was prepared. For convenience, this alloy containing 33.5 wt-pct MM will be denoted $MMCo_5$. Because $MMCo_5$ requires a relatively high sintering temperature at which a loss of magnetic properties would result, a low-melting sintering aid alloy was used. Test compositions were prepared by blending $MMCo_5$ with MM_2Co_7 in desired ratios. The sintering aid MM_2Co_7 was a stoichiometric compound containing 40.7 wt-pct MM.

Mischmetal-cobalt and MM-(Co,Cu,Fe,Mg) alloys were melted in a nonconsumable arc furnace. The purity of the metals was 99.9 wt-pct. Charges of 60 to 100 grams were melted, turned over, and remelted 5 times to achieve uniformity. After melting, the alloy was removed from the inert-gas furnace, crushed into small pieces, mixed, weighed into charges of 70 to 75 grams, and melted two additional times to insure homogeneity. Because it vaporizes at a much lower temperature than the other metals, magnesium was not included in the initial metal charge but was added to the alloy product after the fifth melting. This procedure kept the magnesium vapor loss at a minimum.

The base compounds and sintering aid compounds are listed in table 1. Quantitative analysis for mischmetal and cobalt was determined by wet-chemical methods and X-ray fluorescence. Copper, iron, and magnesium contents were determined by atomic absorption. Oxygen content, which varied between 0.02 and 0.14 wt-pct, was determined by neutron activation.

TABLE 1. - Composition of alloys prepared by arc-melting,[1] [2] weight-percent

Mischmetal	Copper	Iron	Magnesium
33.5	0.0	0.0	0.0
40.7	0	0	0
40.7	0	0	.34
33.5	14.0	0	0
33.5	14.0	0	.49
33.5	14.0	0	.62
33.5	14.0	7.0	0
44.0	0	28.0	0

[1]These alloys were used in the experiments.
[2]Remainder was cobalt.

Metallographic examination of the as-cast materials indicated the two-phase structure of RE-Co alloys shown in figure 1. Since the arc-melted alloys were rapidly cooled, the microstructures are in a nonequilibrium condition. Figure 1 also shows the microstructures of alloys containing small amounts of magnesium. Electron microprobe examination of the specimen confirmed that the two phases in the photomicrographs were $MMCo_5$ and MM_2Co_7. No concentrations of magnesium were detected by the microprobe, thus indicating a uniform distribution of magnesium.

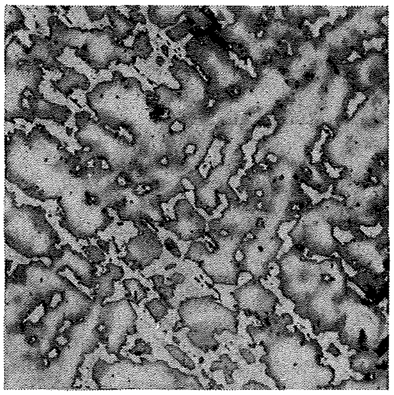
Figure 1*A* shows a MM-Co alloy containing 33.5 wt-pct MM. The darker phase is $MMCo_5$, and the lighter background phase is MM_2Co_7. In figure 1*B*, the only visual effect of the magnesium addition was the formation of a more finely divided $MMCo_5$ phase. Figure 1*C* shows the distribution of $MMCo_5$ (light phase) and MM_2Co_7 (dark phase) of a MM-Co alloy containing 40.7 wt-pct MM and 59.3 wt-pct Co. The addition of magnesium to the sintering aid compound (fig. 1*D*) increased the acicular appearance of the microstructure.

Figure 1*E* shows the dendritic structure of a MM-Co-Cu alloy containing 33.5 wt-pct MM, 14 wt-pct Cu, the remainder Co. Magnesium addition to the copper-containing alloy resulted in no obvious change in microstructure (fig. 1*F*). Two distinct phases were observed with the scanning electron microscope and X-ray microprobe, and the approximate compositions were $MMCo_4Cu$ and $MM_2Co_{5.5}Cu_{1.5}$.

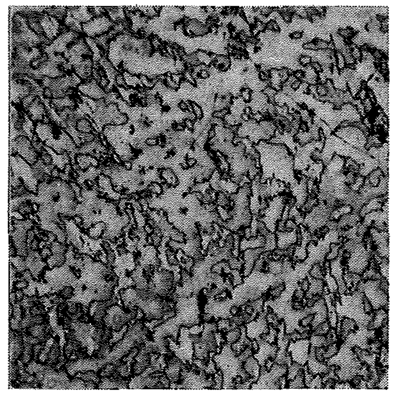
Powder Preparation

The as-melted alloys were crushed and passed through a 35-mesh sieve. Alloy compositions were obtained by blending the as-melted materials in the desired proportions. Fifty-gram lots of the blended charges were ground in toluene with a Spex shatterbox.[5] The temperature of grinding was controlled at approximately minus 60° C by surrounding the shatterbox container with Dry Ice. Grinding periods varied from 60 to 180 minutes. Products with average

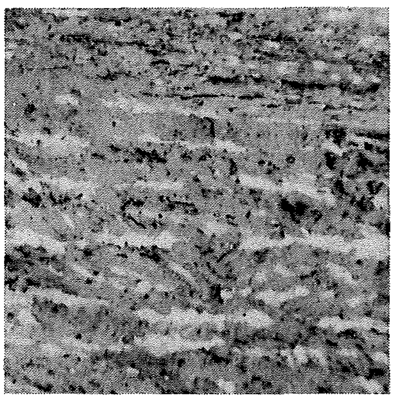
[5]Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.



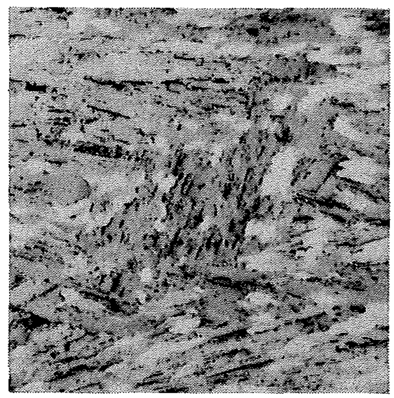
A, 33.5 MM



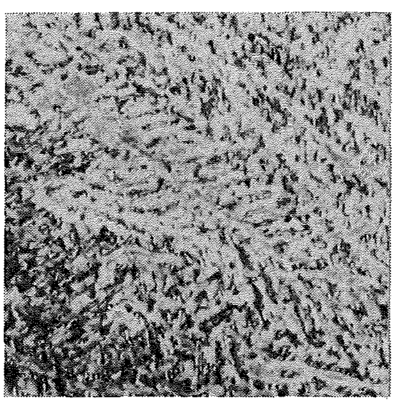
B, 33.5 MM, 0.24 Mg



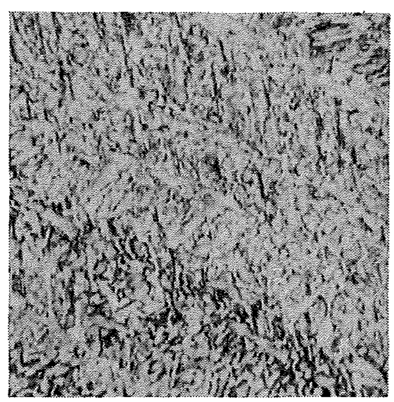
C, 40.7 MM



D, 40.7 MM, 0.34 Mg



E, 33.5 MM, 14 Cu



F, 33.5 MM, 14 Cu, 0.49 Mg

FIGURE 1. - Effect of magnesium addition on microstructure of as-melted MM-Co and MM-Co-Cu alloys. Compositions are in weight-percent. (X 200)

Fisher Sub-Sieve Sizer measurements ranging between 3.6 and 2.5 µm were obtained. The powders were vacuum dried and stored under helium to minimize oxidation.

Alinement and Compaction

The powder was alined and compacted in air in a magnetic field of 8 kG. The alinement apparatus consisted of a 1,200-turn coil wound with No. 10 AWG magnetic wire and an iron core 1 inch in diameter and 6 inches 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 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) applied. The die was removed from the coil, and the powder was further 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 theoretical. The density of the green compacts was determined by direct measurements of the mass and volume.

Sintering Procedure

The compacts were enclosed in stainless steel sheaths welded shut at one end and fitted with a removable plug at the open end. Extra compacts were placed at each end to serve as getters for gaseous contaminants. The sheaths were evacuated and backfilled with helium. This arrangement provided a more 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 hours at temperatures between 970° and 1,010° C to obtain the best magnetic properties. The relatively long sintering time was necessary because of the low density of the green compacts.

The sintered magnets were cooled to ambient temperature by either of two methods. The method with the faster cooling rate, referred to as air-quench (AQ), consisted of removing the samples from the heat zone of the furnace and cooling to room temperature. The furnace-cool (FC) method had a slower cooling rate. The samples remained in the heat zone until the temperature was approximately 400° C and then were air-quenched to room temperature. The density of the sintered magnet was determined by immersion in isopropyl alcohol.

Magnetic Property Measurements

The magnetic properties were measured with an O. S. Walker hysteresisgraph that was designed to plot B versus H hysteresis loops. The magnetic induction (B) was obtained by integrating the voltage change in the search coil closely fitted around two sample magnets. 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 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

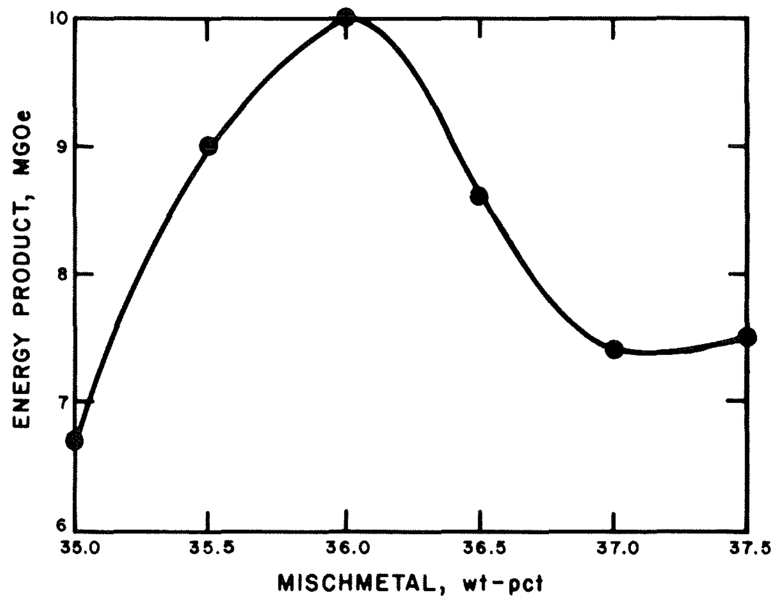


FIGURE 2. - Effect of mischmetal content on energy product of MM-Co alloys.

obtained from Karl J. Strnat at 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

Effects of Composition on Magnetic Properties and Density of MM-Co Alloys

Studies were made to determine the best MM-Co composition and to show the effect of composition on each of the following magnetic properties: Intrinsic coercive force, $_MH_c$; normal coercive force, $_BH_c$; remanence, B_r; and energy product $(BH)_{max}$. The mischmetal content of the magnet was varied between 35.0 and 37.5 wt-pct in increments of 0.5 wt-pct. Each composition was prepared by blending a $MMCo_5$ base compound with a MM_2Co_7 sintering aid compound. The minus 35-mesh alloys were shatterbox-ground for 135 minutes, sintered for 2 hours, and air-quenched. The results are shown in figure 2 and summarized in table 2, which is a tabulation of the highest value of energy product obtained at each composition. The other magnetic properties listed are those of the same sample; they are typical, but not necessarily the highest values. An energy product of 10 MGOe and remanence of 6.81 kG were the largest values obtained for any MM-Co alloy. The best MM-Co composition was 36±0.5 wt-pct MM and 64±0.5 wt-pct Co.

TABLE 2. - Effect of mischmetal content on the magnetic properties of MM-Co alloys

MM, wt-pct	Sinter temp., ° C	Density, g/cm^3	$_MH_c$, kOe	$_BH_c$ kOe	B_r, kG	$(BH)_{max}$, MGOe
35.0	980	7.4	3.0	2.80	5.80	6.7
35.5	990	7.8	3.7	3.39	6.47	9.0
36.0	990	8.0	3.5	3.34	6.81	10.0
36.5	990	8.0	2.8	2.64	6.62	8.6
37.0	990	8.1	2.7	2.25	6.55	7.4
37.5	990	8.1	2.3	2.24	6.42	7.5

As shown in table 3, there was a marked dependence of sintered density on the mischmetal content on the alloy. The average density and the variation were determined for MM-Co alloys containing 34.5 to 38.5 wt-pct MM. All samples were prepared from powders ground for 135 minutes, sintered at 980° C for 2 hours, and then air-quenched.

TABLE 3. - Influence of mischmetal content on the density of MM-Co alloys[1]

MM, wt-pct	Average density,[2] g/cm^3
34.5	6.8±0.3
35.0	7.4± .3
35.5	7.7± .3
36.0	7.9± .2
36.5	8.0± .1
37.0	8.1± .1
37.5	8.0± .1
38.5	8.0± .1

[1]Sintered at 980° C for 2 hours.
[2]± indicates range of maximum variation.

Based on the rare-earth content of the mischmetal used, the theoretical densities were approximately 8.3 g/cm^3 for $MMCo_5$ and 8.2 g/cm^3 for MM_2Co_7.

The average density of the sintered MM-Co alloy containing 36±0.5 wt-pct MM was approximately 95 pct of theoretical. In order to obtain physically stable magnets, a closed-pore structure with a density greater than 85 pct of theoretical was required. This was determined from examination of the microstructure of the sintered samples. Of the alloy samples tested, only the 34.5-wt-pct-MM alloys did not show a closed-pore structure.

Effect of Grinding on Magnetic Properties of MM-Co Alloys

Of all the steps involved in the fabrication of MM-Co magnets, comminution of the bulk alloy to a fine powder was the most critical because reproducibility was difficult to control. All charges were shatterbox ground in toluene at minus 60° C. Grinding at this low temperature improved magnetic properties and minimized oxidation of the ground product (18).

The oxygen content of the as-melted alloys was typically 0.08 wt-pct, but ranged from 0.02 to 0.14 wt-pct. For alloys ground for 135 minutes, the oxygen content ranged between 0.4 and 0.9 wt-pct with a typical value of 0.6 wt-pct. The difference in oxygen content between the sintered magnet and the original powder was negligible.

To evaluate the effects of comminution time on magnetic properties, MM-Co alloys containing 36±0.5 wt-pct MM (36.5, 36.0, and 35.5 wt-pct MM) were ground for periods ranging from 60 to 180 minutes. The green compacts were sintered at 980° C for 2 hours. Sintering at higher temperatures improved values of remanence and energy product slightly, but greatly decreased the coercivity values. As shown in table 4, the best grinding time was 135 minutes and gave a product with an average particle size of 2.7±1 µm for all compositions tested.

TABLE 4. - Effect of grinding time on the magnetic properties of MM-Co alloys

Grinding time, minutes	Particle size, μm	Sintered density g/cm^3	$_MH_c$, kOe	$_BH_c$, kOe	B_r, kG	$(BH)_{max}$, MGOe
36.5 WT-PCT MM[1]						
60.............	3.5	7.5	1.5	1.41	5.25	4.0
75.............	3.6	7.5	1.5	1.39	5.20	3.7
90.............	2.8	7.7	2.3	2.19	5.43	5.8
105.............	2.9	7.7	2.3	2.14	5.30	5.4
120.............	2.6	7.9	2.2	2.10	5.78	6.5
135.............	2.6	7.9	2.7	2.40	5.69	6.5
150.............	2.5	7.9	2.6	2.46	5.62	6.5
165.............	2.5	7.9	2.3	2.28	5.62	6.4
180.............	2.5	7.8	2.5	2.46	5.54	6.3
36.0 WT-PCT MM[1]						
105.............	3.0	8.0	1.7	1.59	6.31	5.8
120.............	2.8	8.0	1.9	1.87	6.52	6.8
135.............	2.7	8.1	2.1	2.02	6.46	7.2
150.............	2.6	8.1	1.9	1.84	6.52	6.7
35.5 WT-PCT MM[2]						
120.............	2.8	7.7	3.2	2.98	6.77	8.8
135.............	2.7	7.9	3.5	3.41	6.78	10.0
150.............	2.6	7.9	3.1	2.93	6.65	9.5

[1]Sintered at 980° C for 2 hours and then furnace-cooled.
[2]Sintered at 980° C for 2 hours and then air-quenched.

Effect of Sintering on Magnetic Properties of MM-Co Alloys

Although magnetic properties were very sensitive to the sintering temperature, reproducible results were easily obtained because there was no problem in controlling the temperature to within ±2° C. The complete sintering cycle for MM-Co and MM-(Co,Cu,Fe,Mg) alloys is illustrated in figure 3.

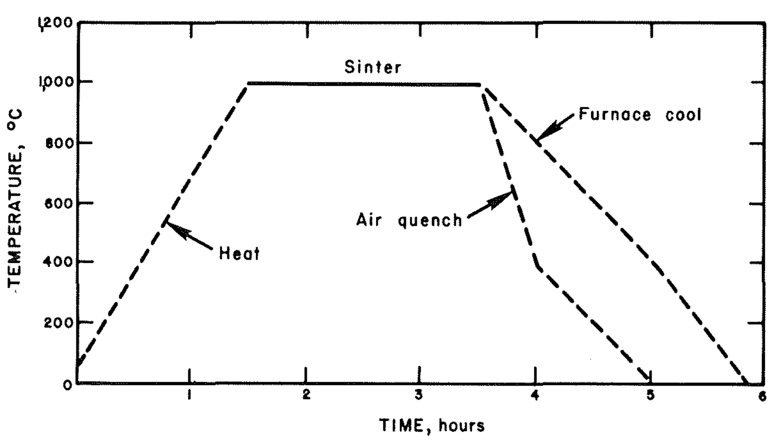


FIGURE 3. - Thermal cycle for sintering MM-Co and MM-(Co,Cu,Fe,Mg) alloys.

Tests were performed to determine the effect of sintering temperature on the magnetic properties of MM-Co alloys. The mischmetal content of the alloys was varied between 35.0 and 37.5 wt-pct in increments of 0.5 wt-pct. Each charge was shatterbox ground for 135 minutes, sintered between 970 ° and 1,010° C for 2 hours, and then air-quenched.

Table 5 shows that no sintering temperature gave the best values for all magnetic properties. For all the alloys tested, the highest intrinsic normal coercivities occurred at a sintering temperature of 980° C. Maximum values of remanence and energy product were obtained at sintering temperatures between 980° and 1,010° C, depending on the alloy composition. Poorly sintered samples with low densities and magnetic values were obtained at a temperature of 970° C. This was especially true for alloys containing 35.0 and 35.5 wt-pct MM. For all the MM-Co compositions evaluated, 36.0 wt-pct MM gave the best magnetic properties when the sintering temperature range was maintained between 980° and 1,000° C.

TABLE 5. - Effect of sintering temperature on the magnetic properties of MM-Co Alloys[1]

MM, wt-pct	Sinter temp., ° C	Density, g/cm^3	$_MH_c$, kOe	$_BH_c$, kOe	B_r, kG	$(BH)_{max}$, MGOe
35.0......	970	7.0	1.7	1.59	5.44	4.4
	980	7.5	3.0	2.80	5.84	6.7
	990	7.6	2.8	2.60	5.92	6.4
	1,000	7.7	2.6	2.49	6.05	5.8
35.5......	970	7.2	3.5	3.35	5.61	6.7
	980	7.7	3.6	3.39	6.11	7.4
	990	7.9	3.0	2.84	6.24	7.6
	1,000	7.9	2.8	2.69	6.24	7.1
36.0......	970	7.9	2.7	2.49	6.11	7.4
	980	8.0	4.1	3.75	6.13	8.5
	990	8.1	3.5	3.27	6.60	9.2
	1,000	8.2	3.3	3.09	6.67	9.6
	1,010	8.2	1.7	1.56	6.72	5.4
36.5......	980	8.1	3.6	3.35	6.15	8.0
	990	8.2	3.2	2.99	6.24	8.1
	1,000	8.2	2.9	2.71	6.24	7.8
	1,010	8.2	1.9	1.84	6.49	6.3
37.0......	980	8.1	3.4	3.10	5.66	6.7
	990	8.2	3.0	2.80	5.93	7.0
	1,000	8.2	2.7	2.59	5.97	6.6
	1,010	8.2	1.8	1.77	6.16	5.8
37.5......	980	8.0	3.1	2.68	5.38	5.6
	990	8.1	2.7	2.47	5.46	5.6
	1,000	8.2	2.6	2.32	5.35	5.2

[1]All alloys were ground for 135 minutes, sintered for 2 hours, and air-quenched.

Tests were also performed to determine the effect of cooling on the magnetic properties of the sintered alloys. MM-Co alloys containing 34.5 to 37.5 wt-pct MM were ground for 135 minutes, sintered at 980° C for 2 hours, and cooled to room temperature. In one method (air-quenching), the sintered alloys were cooled quickly by moving the samples from the heat zone to an air-cooled section of the furnace tube. In the other method (furnace-cooling), the magnets remained in the heat zone until the temperature dropped to approximately 400° C and were then moved to the air-cooled zone of the furnace and cooled to ambient temperature. The time-temperature relationship is illustrated in figure 3.

As shown in table 6 and figure 4, sintered magnets that were air-quenched yielded the best magnetic properties. The data showed that the coercive forces, both normal and intrinsic, were significantly improved by the faster cooling rate. The highest magnetic values were obtained in the composition range of 36±0.5 wt-pct MM. The data obtained supported the previous determinations that 36 wt-pct MM was the best MM-Co composition. The results in table 6 also show that the effect of cooling rate on the density of the sintered magnets was negligible.

TABLE 6. - Effect of cooling rate on the magnetic properties of sintered MM-Co alloys

MM, wt-pct	Cooling method	Density, g/cm^3	$_MH_c$, kOe	$_BH_c$, kOe	B_r, kG	$(BH)_{max}$, MGOe
34.5..	Furnace cooling..	6.8	2.2	2.07	5.35	3.9
	Air quenching....	6.8	2.6	2.40	5.31	4.3
35.0..	Furnace cooling..	7.3	3.1	2.92	5.79	6.0
	Air quenching....	7.4	3.3	3.11	5.80	6.3
35.5..	Furnace cooling..	7.8	2.8	2.68	6.29	8.3
	Air quenching....	7.9	3.5	3.26	6.47	9.0
36.0..	Furnace cooling..	8.0	3.1	2.87	6.11	7.8
	Air quenching....	8.0	4.1	3.75	6.28	8.5
36.5..	Furnace cooling..	8.1	2.8	2.59	5.87	6.9
	Air quenching....	8.1	3.6	3.35	6.15	8.0
37.0..	Furnace cooling..	8.1	2.8	2.58	5.59	6.1
	Air quenching....	8.1	3.4	3.10	5.66	6.7
37.5..	Furnace cooling..	8.0	2.6	2.34	5.23	5.1
	Air quenching....	8.0	3.1	2.68	5.38	5.6

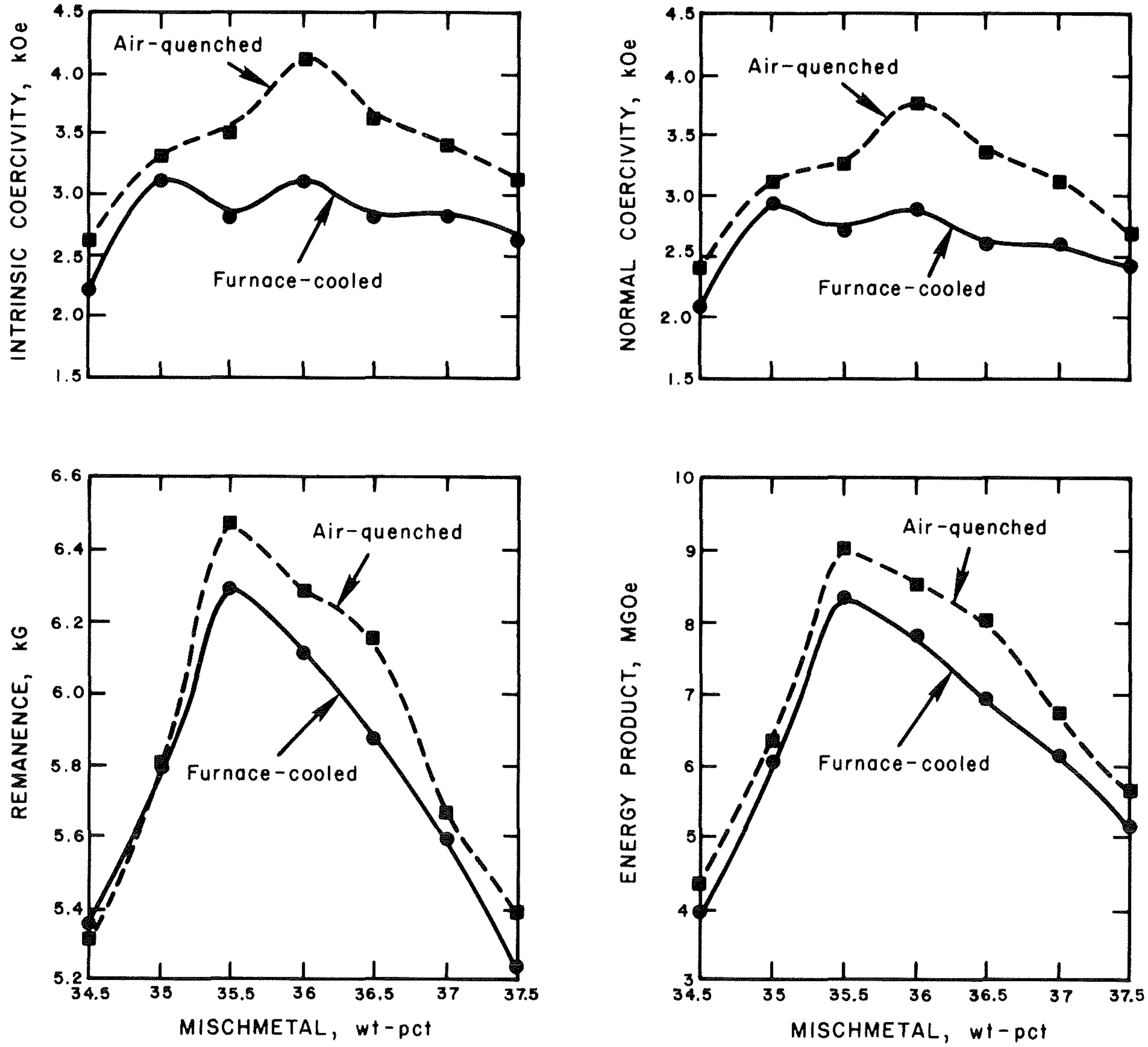


FIGURE 4. - Influence of cooling method on magnetic properties of sintered MM-Co alloys.

Effect of Copper Content on Magnetic Properties of MM-Co-Cu Alloys

On the basis of the preceding data, MM-Co alloys containing 35.5 and 36.0 wt-pct MM were selected to determine the effect of substitution of copper, magnesium, and iron for part of the cobalt on the magnetic properties. Magnesium was evaluated because preliminary tests showed that high coercivities were obtained only with MM-Co-Cu alloys that contained more than a trace of magnesium impurity in the mischmetal.

Copper substitution was accomplished by blending $MMCo_5$ and MM_2Co_7 with an alloy approximating the composition of $MMCo_4Cu$. Each charge was shatterbox ground for 135 minutes, sintered at 980° C for 2 hours, and then air-quenched.

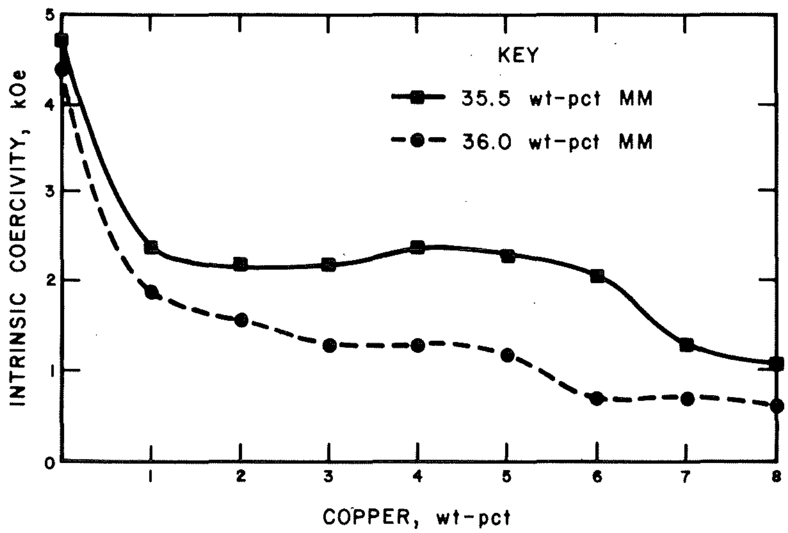


FIGURE 5. - Effect of copper content on the intrinsic coercive force of MM-Co-Cu alloys.

As shown in figure 5, the intrinsic coercivity was appreciably decreased as the amount of copper in the alloy was increased. There was a range of copper concentration in which the intrinsic coercive force leveled off before further decreasing. The normal coercive force, remanence, and energy product behaved similarly as shown in table 7. The values, $_{M}H_{c}$ = 4.7 kOe and $_{B}H_{c}$ = 4.07 kOe, obtained with the alloy containing 35.5 wt-pct MM (no copper), were the largest values of intrinsic and normal coercivities obtained.

TABLE 7. - Dependence of the magnetic properties on the copper content of MM-Co-Cu alloys

Copper, wt-pct	$_{M}H_{c}$, kOe	$_{B}H_{c}$, kOe	B_r, kG	$(BH)_{max}$, MGOe
35.5 WT-PCT MM				
0	4.7	4.07	6.49	9.4
1	2.4	2.25	5.75	5.1
2	2.2	2.09	5.71	5.1
3	2.2	2.04	6.18	6.6
4	2.4	2.27	6.18	6.2
5	2.3	2.10	5.36	4.6
6	2.1	1.99	5.38	4.1
7	1.3	1.29	5.72	4.2
8	1.1	1.00	5.79	3.4
36.0 WT-PCT MM				
0	4.4	3.81	6.19	8.0
1	1.9	1.85	6.57	6.7
2	1.6	1.50	6.32	5.1
3	1.3	1.21	6.32	4.6
4	1.3	1.23	5.84	4.0
5	1.2	1.18	5.22	4.0
6	.7	.69	5.88	2.1
7	.7	.60	5.61	1.9
8	.6	.59	5.53	1.8

Effect of Copper and Magnesium Contents on Magnetic Properties of MM-Co-Cu-Mg Alloys

Remarkable results were obtained by adding 0.1 to 0.3 wt-pct Mg to the MM-Co-Cu alloys, as illustrated in figure 6. The effect of copper concentration in an alloy containing magnesium on the magnetic properties is shown in table 8.

TABLE 8. - Effect of copper concentration on the magnetic properties of MM-Co-Cu-Mg alloys

Composition, wt-pct		$_MH_c$, kOe	$_BH_c$, kOe	B_r, kG	$(BH)_{max}$, MGOe
Copper	Magnesium				
35.5 WT-PCT MM					
0	0.09	3.7	3.34	5.44	5.5
1	.20	2.2	2.06	5.84	5.4
2	.10	3.7	3.40	6.16	8.0
3	.20	1.7	1.67	5.69	4.9
4	.09	16.8	5.15	6.13	7.9
5	.18	28.6	5.50	5.80	8.0
6	.30	29.0	5.37	5.67	7.6
7	.20	22.6	5.12	5.61	7.2
8	.20	21.1	5.24	5.71	7.5
36.0 WT-PCT MM					
0	0.12	4.1	3.75	6.36	8.6
1	.20	2.4	2.25	6.32	7.5
2	.20	3.0	2.67	6.24	7.2
3	.20	2.8	2.53	5.95	6.3
4	.18	19.1	5.37	5.72	7.7
5	.18	27.6	5.50	5.79	8.0
6	.15	28.8	5.21	5.54	7.2
7	.20	24.5	5.42	5.79	7.8
8	.20	23.2	5.19	5.56	7.2

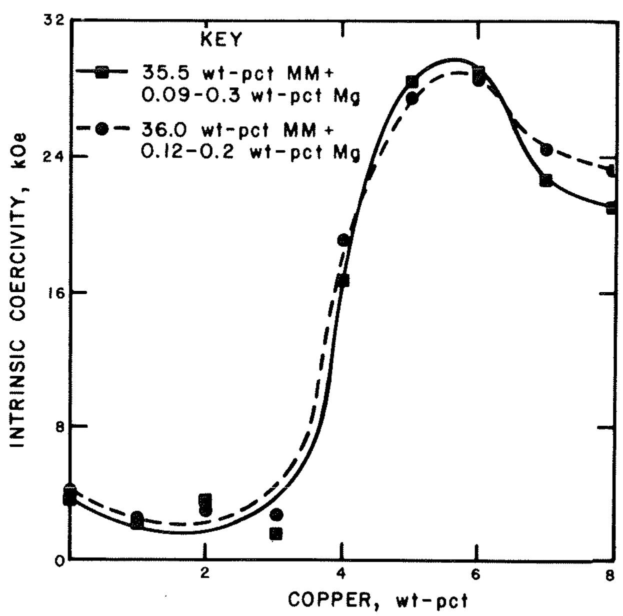


FIGURE 6. - Effect of copper concentration on the intrinsic coercive force of MM-Co-Cu-Mg alloys.

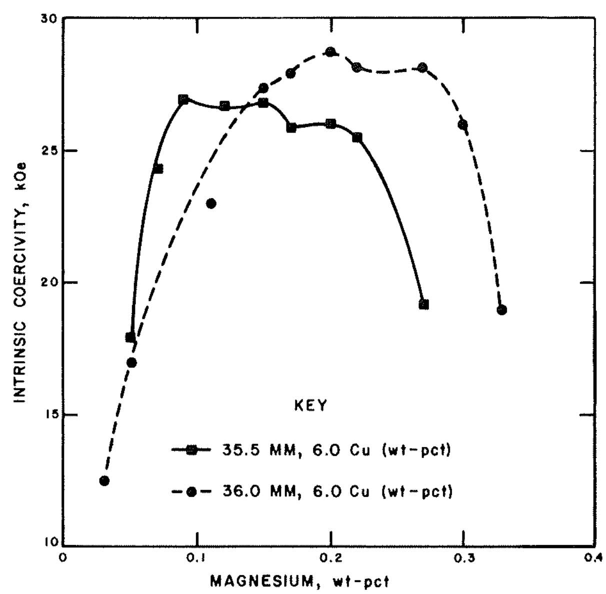


FIGURE 7. - Effect of magnesium content on the intrinsic coercive force of MM-Co-Cu-Mg alloys.

The result of copper-magnesium addition was a dramatic increase in the intrinsic coercivity to values previously attainable only with Sm-Co alloys. A maximum $_MH_c$ = 29.0 kOe was obtained with an alloy containing 35.5 wt-pct MM, 6.0 Cu, 0.30 Mg, and the remainder cobalt. This value exceeded the maximum $_MH_c$ = 27.4 kOe previously obtained with Sm-Co alloys in the laboratory. The nearly identical curves in figure 6 show that the difference in mischmetal content had very little effect on the intrinsic coercive force.

Based on the above results, a more precisely controlled experiment varying the magnesium content was conducted using the best copper content of 6 wt-pct. Green compacts were prepared from powders ground 135 minutes, sintered at 980° C for 2 hours, and then air-quenched. Figure 7 shows a well-defined range of magnesium concentration for which peak values of intrinsic coercive force were obtained. With a composition of 35.5 wt-pct MM and 6.0 wt-pct Cu, peak coercivities were obtained over the range of 0.09 to 0.22 wt-pct Mg. The 36.0 wt-pct MM-6.0 wt-pct Cu alloy yielded peak values over the range of 0.15 to 0.30 wt-pct Mg. With an addition as small as 0.03 wt-pct Mg to the 36.0 wt-pct MM-6.0 wt-pct Cu alloy, a relatively high value of $_MH_c$ = 12.5 kOe was obtained. The effect of magnesium content on the magnetic properties of the MM-Co-Cu-Mg alloys is reported in table 9.

TABLE 9. - Influence of magnesium on the magnetic properties of MM-Co-Cu-Mg alloys

Magnesium, wt-pct	$_MH_c$, kOe	$_BH_c$, kOe	B_r, kG	$(BH)_{max}$, MGOe
35.5 WT-PCT MM, 6 WT-PCT Cu				
0.05...........	17.9	5.24	5.71	7.5
.07...........	24.3	5.30	5.69	7.5
.09...........	26.8	5.50	5.84	7.8
.12...........	26.6	5.25	5.69	7.5
.15...........	26.7	5.32	5.75	7.7
.17...........	25.8	5.55	5.87	8.1
.20...........	26.0	5.42	5.79	7.8
.22...........	25.5	5.86	6.16	9.0
.27...........	19.2	5.89	6.23	9.2
36.0 WT-PCT MM, 6 WT-PCT Cu				
0.03...........	12.5	5.35	6.02	8.1
.05...........	16.9	5.21	5.69	7.4
.11...........	22.9	5.42	5.75	7.8
.15...........	27.3	5.49	5.77	7.9
.17...........	27.9	5.15	5.51	7.1
.20...........	28.7	5.42	5.71	7.7
.22...........	28.2	5.40	5.71	7.7
.27...........	28.1	5.17	5.53	7.1
.30...........	25.9	5.56	5.84	8.1
.33...........	18.9	5.67	6.03	8.6

Effect of Magnesium Addition on the Magnetic Properties of MM-Co Alloys

Thus far, the data have shown that the substitution of copper for part of the cobalt in the MM-Co alloys has resulted in a drastic decrease of magnetic properties, especially the coercivity values. On the other hand, copper substitution for part of the cobalt in the presence of a small amount of magnesium resulted in a tremendous increase of normal and intrinsic coercive forces, particularly the latter.

A study was made to determine the effect of magnesium addition to alloys containing only mischmetal and cobalt. The range of magnesium concentration in the samples was limited by the low magnesium concentration in the master alloy--40.7 wt-pct MM, 0.34 Mg, and the remainder Co. The magnetic properties along with composition, sintering temperature, and density of the samples are given in table 10. Although the magnesium concentration in the magnet was low, the data in table 10 conclusively show that the improvements in magnetic properties were obtained only when both magnesium and copper are present. Magnesium addition to the MM-Co alloy resulted in a negligible change in magnetic properties (fig. 8). For ease of comparison, the magnetic properties of MM-Co alloys listed in table 2 are also included in figure 8. The improvement of normal and intrinsic coercive forces of MM-Co-Cu-Mg alloys was a synergistic effect of copper and magnesium. Copper and magnesium added individually to the MM-Co alloys did not increase the coercivity, but when added simultaneously they increased the coercive force tremendously.

TABLE 10. - Magnetic properties of MM-Co-Mg alloys

Composition, wt-pct		Sinter temp., °C	Density, g/cm^3	$_MH_c$, kOe	$_BH_c$, kOe	B_r, kG	$(BH)_{max}$, MGOe
MM	Mg						
34.5	0.06	980	6.9	2.7	2.44	5.40	4.3
35.0	.09	990	7.4	3.3	3.11	5.80	6.3
35.5	.11	980	7.9	3.5	3.41	6.78	10.0
36.0	.12	990	7.9	3.6	3.32	6.42	9.0
36.5	.15	980	8.0	3.4	3.24	6.11	8.3
37.0	.17	980	8.0	2.7	2.59	5.88	7.2
37.5	.19	980	8.0	2.3	2.18	5.61	6.2

The mechanism through which these alloys achieved the high coercivities is not fully understood. The mechanism was not precipitation-hardening that is applicable to alloys of the types (Sm,Ce) $(Co,Cu,Fe)_{5-7}$ for the following reasons:

1. The intrinsic coercivities exhibited by MM-Co-Cu-Mg alloys are readily obtained with no postsintering heat treatment whereas a postsintering heat treatment is a necessary and complicated step needed to obtain high coercivities for precipitation-hardened magnets.

2. Only 4 to 8 wt-pct Cu is required for the MM-Co-Cu-Mg alloys whereas 10 to 30 wt-pct Cu is required for precipitation-hardened magnets.

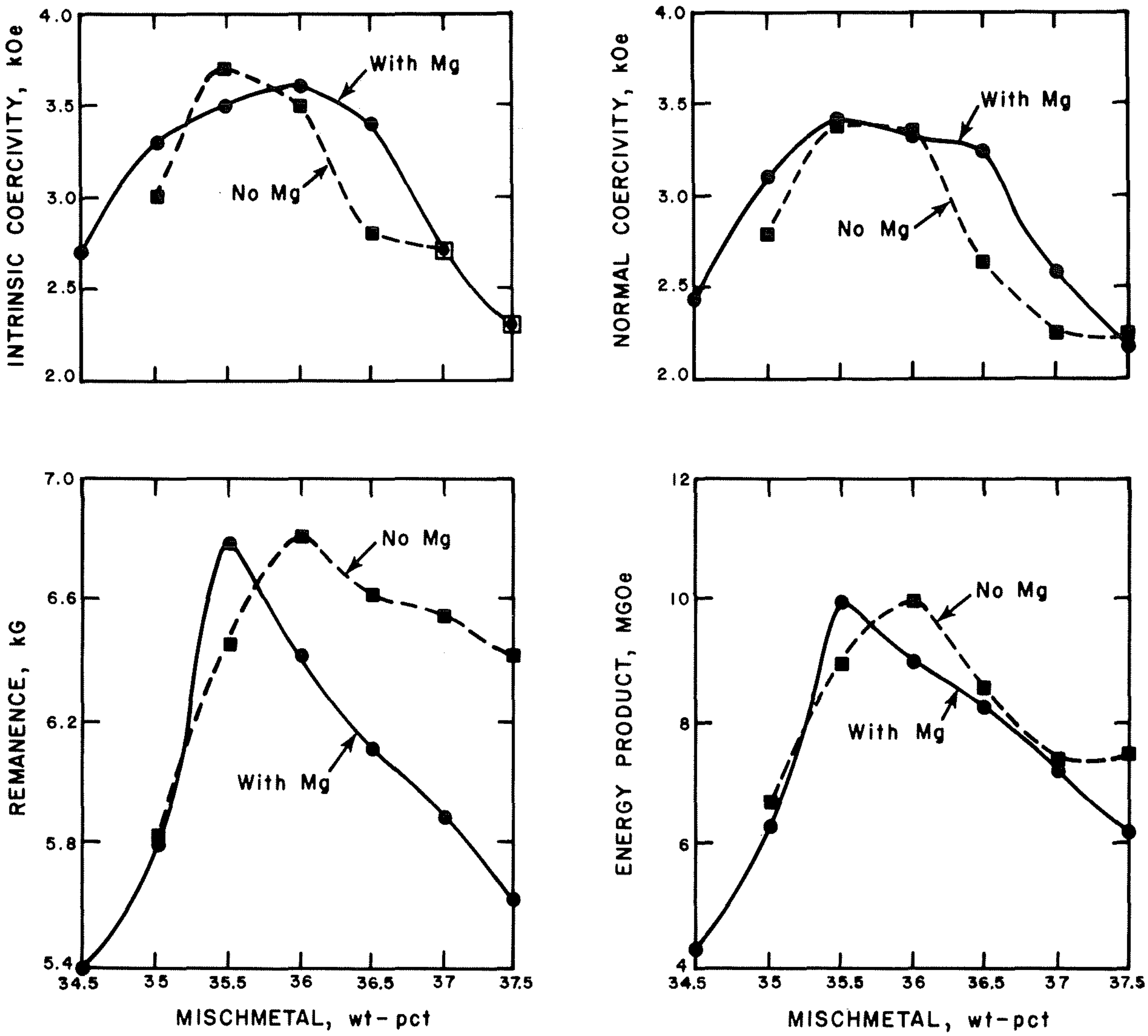


FIGURE 8. - A comparison of magnetic properties of MM-Co-Mg and MM-Co alloys.

Effect of Copper Concentration on Densities of Sintered MM-Co-Cu-Mg Alloys

The influence of copper concentration on the density of sintered MM-Co-Cu-Mg alloys containing 35.5 and 36.0 wt-pct MM and 0 to 0.33 wt-pct Mg is shown in table 11. The magnesium content did not affect the sintered magnet density; therefore, the density values shown in table 11 are representative for all samples with magnesium content up to 0.33 wt-pct. Addition of 5 and 6 wt-pct Cu to the MM-Co alloys resulted in near-theoretical values of density and significantly narrowed the range of variation. Although the addition of copper decreased the saturation magnetization of the sample, a substantial portion of the loss was compensated for by the increased density. The best copper content range of 5 to 7 wt-pct for obtaining the maximum density corresponds to the best range for obtaining the maximum intrinsic coercivity.

TABLE 11. - Influence of copper content on the density of sintered MM-Co-Cu and MM-Co-Cu-Mg alloys[1 2]

Cu, wt-pct	Average density, g/cm^3	
	35.5 wt-pct MM	36.0 wt-pct MM
0....................	7.7±0.3	7.9±0.2
1....................	7.7± .3	7.9± .2
2....................	7.8± .2	7.9± .2
3....................	7.9± .2	8.0± .2
4....................	8.1± .2	8.1± .1
5....................	8.2± .1	8.2± .1
6....................	8.2± .1	8.2± .1
7....................	8.1± .1	8.1± .1
8....................	ND	8.1± .1

ND Not determined.
[1]Sintered at 980° C for 2 hours and air-quenched.
[2]Samples with 0 to 0.33 wt-pct Mg.

Effect of Cooling on Magnetic Properties of Sintered MM-Co-Cu-Mg Alloys

The effect of different methods of cooling the MM-Co-Cu-Mg alloy from the sintering temperature to room temperature was investigated. With the MM-Co alloys (table 6), air-quenched samples possessed higher values for all magnetic properties than those of the furnace-cooled samples. Table 12 shows that only the intrinsic coercivity was beneficially affected by air-quenching of the MM-Co-Cu-Mg alloy.

TABLE 12. - Effect of cooling method on the magnetic properties of a MM-Co-Cu-Mg alloy[1]

Cooling method	Sinter temp., ° C	Density, g/cm^3	${}_MH_c$, kOe	${}_BH_c$, kOe	B_r, kG	$(BH)_{max}$, MGOe
Furnace cooling	980	8.2	7.7	5.51	6.08	8.8
Air quenching..	980	8.2	16.3	5.71	6.15	8.8
Furnace cooling	985	8.2	12.3	5.84	6.19	9.0
Air quenching..	985	8.2	21.0	5.86	6.19	9.1
Furnace cooling	990	8.2	13.9	5.86	6.08	8.9
Air quenching..	990	8.2	23.2	5.87	6.11	9.0

[1]Composition of alloy was 35.5 wt-pct MM, 5.0 Cu, and 0.10 Mg.

Samples containing 35.5 wt-pct MM, 5 Cu, and 0.10 Mg were ground for 135 minutes, sintered at temperatures between 980° and 990° C for 2 hours, and then cooled to ambient temperature. High values for density, normal coercivity, remanence, and energy product were obtained, because of the addition of copper and magnesium, regardless of the cooling methods used. However, the effect of cooling method on the intrinsic coercivity was pronounced. At a sintering temperature of 980° C, the intrinsic coercive force of the air-quenched sample was more than double that of the furnace-cooled sample.

Effect of Iron Content on Magnetic Properties of MM-Co-Cu-Fe-Mg Alloys

The net effect of copper and magnesium addition to MM-Co alloys was a tremendous improvement in both intrinsic and normal coercivities and a decrease in remanence value. The substitution of iron for cobalt was reported (14) to increase the saturation magnetization of RE-Co magnets. A cursory study was made to determine the effect of iron substitution for part of the cobalt in the MM-Co-Cu-Mg alloys that contained 36.0 wt-pct MM, 5 and 6 wt-pct Cu, and small amounts of magnesium. Iron addition was made through a MM-Co-Fe master alloy, approximately $MMCo_{1.5}Fe_{1.5}$. Each sample was sintered between 980° and 1,000° C for 2 hours and air-quenched. Results are shown in table 13. Set A presents the magnetic properties of samples with maximum energy product, and set B presents those with maximum intrinsic coercivity. The fabrication parameters were not optimized. These tests indicated the potential benefit of iron addition to the MM-Co-Cu-Mg alloys. Improved values of B_r = 6.90 kG and $(BH)_{max}$ = 10.3 MGOe were obtained. These results were obtained with an alloy containing, in wt-pct, MM, 36.0, Co, 52.9, Cu, 5.0, Fe, 6.0, and Mg, 0.05. This composition represents a 17 pct decrease in cobalt requirement.

TABLE 13. - Magnetic properties of MM-Co-Cu-Fe-Mg alloys[1]

Composition, wt-pct			Sinter	$_MH_c$,	$_BH_c$,	B_r,	$(BH)_{max}$,
Fe	Cu	Mg	temp., ° C	kOe	kOe	kG	MGOe
SET A, MAXIMUM ENERGY PRODUCT							
3	5	0.11	990	6.4	4.70	6.60	9.7
4	5	.09	980	7.3	5.27	6.57	9.8
5	5	.07	990	7.5	5.20	6.60	10.0
6	5	.05	990	5.6	4.43	6.90	10.3
3	6	.12	1,000	10.7	6.04	6.55	10.2
4	6	.10	1,000	9.3	5.57	6.62	10.1
5	6	.08	990	8.1	5.16	6.16	8.5
6	6	.06	1,000	5.0	4.00	6.16	8.2
SET B, MAXIMUM INTRINSIC COERCIVITY							
3	5	0.11	980	11.6	5.84	6.39	9.5
4	5	.09	980	7.3	5.27	6.57	9.8
5	5	.07	990	7.5	5.20	6.60	10.0
6	5	.05	990	5.6	4.43	6.90	10.3
3	6	.12	980	15.5	5.60	5.98	8.4
4	6	.10	980	12.5	5.84	6.46	9.7
5	6	.08	980	8.6	4.93	6.02	8.2
6	6	.06	1,000	5.0	4.00	6.16	8.2

[1] 36.0 wt-pct MM.

SUMMARY AND CONCLUSIONS

At the best MM-Co composition of 36±0.5 wt-pct MM and the remainder Co, the following magnetic properties were obtained: ${}_{M}H_{c}$ = 4.7 kOe, ${}_{B}H_{c}$ = 4.07 kOe, B_r = 6.81 kG, and $(BH)_{max}$ = 10.0 MGOe. Partial substitution of cobalt with copper resulted in decreased values for all magnetic properties. However, a simultaneous addition of copper and magnesium to the MM-Co alloys increased the intrinsic coercive force to a maximum value of 29.0 kOe, which surpassed the intrinsic coercivity of 27.4 kOe for the Sm-Co alloy made in our laboratory. Overall, the best and most consistent magnetic properties were obtained with the alloy containing 36.0 wt-pct MM, 6.0 Cu, 0.2 Mg and the remainder Co. Additions of 5 and 6 wt-pct Cu in the MM-Co-Cu-Mg alloys containing 35.5 and 36.0 wt-pct MM increased the densities of the sintered magnets to more than 98 pct of theoretical. Of the two cooling methods evaluated, the air-quench method produced the highest intrinsic coercivity. The addition of Fe to MM-Co-Cu-Mg alloy resulted in a significant improvement of remanence and energy product values.

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