MAGNETIC PROPERTIES OF MISCHMETAL-(Co,Cu,Fe,Mg) ALLOYS

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ABSTRACT

To relieve the dependence for critical and strategic minerals through conservation and substitution the Bureau of Mines, U. S. Department of the Interior, 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 selected MM-Co-Cu-Mg and MM-Co-Cu-Fe-Mg alloys were evaluated. Magnets were fabricated by powder metallurgy that consisted of arc-melting the metals, crushing and grinding the resultant alloy, aligning and compacting the powder, and sintering the green compacts.

Magnetic values of $_MH_c$ = 4.7 kOe, $_BH_c$ = 4,070 Oe, B_r = 6,810 G, and $(BH)_{max}$ = 10.0 MGOe were obtained with an MM-Co alloy containing 36.0 $\pm$.5 wt-pct mischmetal. By substituting part of the cobalt with copper and magnesium, the value for $_MH_c$ was increased to 29.0 kOe and that for $_BH_c$ to 5,890 Oe. The intrinsic coercivity value exceeded that of Sm-Co alloy, $_MH_c$ = 27.4 kOe, which was obtained in our laboratory. The addition of iron to MM-Co-Cu-Mg alloys resulted in an increase of B_r to 6,900 G and $(BH)_{max}$ to 10.3 MGOe. Copper and magnesium contents of these alloys were optimized to obtain maximum value of $_MH_c$.

INTRODUCTION

Samarium-cobalt became the mainstay of the rare earth/cobalt magnet industry mainly because high-coercivity powder could be readily prepared by simple grinding. Mischmetal, a naturally occurring, cerium-rich mixture of the rare earths, is considerably more abundant than samarium. Many attempts were made to fabricate MM-Co magnets using powder metallurgy techniques that were successful in producing high-performance Sm-Co magnets. The detailed study of MM-Co alloys with no samarium addition was reported by Johnson and Fellows[1,2]. They obtained a maximum intrinsic coercive force, $_MH_c$, of 6.4 kOe and a maximum energy product, $(BH)_{max}$, of 8.8 MGOe with an MM-Co alloy containing 40.2 wt-pct mischmetal (near stoichiometric MM_2Co_7). Nagel, Klein, and Menth[3] reported a maximum $_MH_c$ = 9.0 kOe and $(BH)_{max}$ = 14.5 MGOe using $MMCo_5$. The coercivity was enhanced by a postsintering heat treatment and subsequent controlled cooling of the alloy to room temperature. This method increased coercivity values by a factor of 2.5. Narita and Yamamoto[4] also reported a maximum $_MH_c$ = 9.0 kOe for an MM-Co alloy containing 39.8 wt-pct mischmetal.

The use of copper to enhance the coercivity of rare earth/cobalt magnets was reported by Nesbitt and Wernick[5]. They prepared R-Co-Cu magnets with a substantial intrinsic coercive force by casting and subsequent heat treatment. The results 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 $_MH_c$ = 6.3 kOe) and energy products of 4.2 MGOe with an alloy composition, in wt-pct, of 34.2 MM/50.2 Co/15.6 Cu (approximately $MM_4Co_{15}Cu_4$).

To reduce the requirements for samarium and cobalt, both scarce materials, the Federal Bureau of Mines investigated MM-Co magnets with partial substitution of cobalt by copper, magnesium, and iron. This paper presents the results of laboratory 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

Mischmetal-cobalt and MM-(Co,Cu,Fe,Mg) alloys were prepared by nonconsumable-arc-melting 99.9-wt-pct pure metals. The mischmetal was samarium-free and had a rare-earth composition range of, in wt-pct: 52.1-57.8 Ce, 23.4-33.4 La, 10.8-17.9 Nd, and 3.4-6.6 Pr. Charges of 60 to 100 grams were melted, inverted, 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 ensure homogeneity. Since magnesium vaporized at a much lower temperature than the other component metals, magnesium was not included with the initial metal charge but rather was added to the alloy product after the fifth melting. This procedure kept the magnesium vapor loss to a minimum.

The final alloy product was crushed until it passed through a 35-mesh sieve. Samples of this material were analyzed for individual rare earths and cobalt by standard chemical separation method, copper, iron, and magnesium by atomic absorption, and oxygen by neutron activation. Using a Spex shatterbox, 50-gram lots of the minus 35-mesh material were blended and ground for 135 minutes in toluene at -60° C. This resulted in powders with an average particle size in the range of 2.5 to 2.8 μm measured by a Fisher Sub-Sieve Sizer. After vacuum drying, the powders were aligned in air in a magnetic field of 8 kG and compacted at 310 MPa (45,000 psi). The green compacts obtained were 1.1 cm in diameter by 0.5 cm long with a density of approximately 60 pct theoretical. The compacts were enclosed in stainless steel sheaths, sintered in helium in a tube furnace for 2 hours at 980° C, and then air-quenched while in the tube furnace. These grinding and sintering conditions were used throughout this study except as noted. The magnetic properties of the sample were measured with an O. S. Walker hysteresisgraph.

RESULTS AND DISCUSSION

In our previous studies with MM-Co alloys, optimum magnetic properties of $_MH_c$ = 4.7 kOe, $_BH_c$ = 4,070 Oe, B_r = 6,810 G, and $(BH)_{max}$ = 10.0 MGOe were obtained with an alloy containing 36.0$\pm$.5 wt-pct mischmetal. On the basis of these findings, MM-Co alloys containing 35.5 and 36.0 wt-pct mischmetal were selected for this investigation to determine the effects of copper, magnesium, and iron substitution on the magnetic properties. Magnesium was chosen as one of the alloying additions because in our preliminary tests high coercivities were obtained only with MM-Co-Cu alloys that contained more than a trace of magnesium as an impurity.

Copper substitutions for cobalt were made by blending near-stoichiometric $MMCo_5$ (33.5 wt-pct MM) and MM_2Co_7 (40.7 wt-pct MM) with a copper-containing alloy approximating $MMCo_4Cu$ (33.5 wt-pct MM/14.0 wt-pct Cu). (The remaining percentage of the alloy mentioned here and subsequently, is cobalt).

As shown in figure 1, the intrinsic coercivity was greatly reduced as the amount of copper was increased. There was a range of copper content for which the intrinsic coercive force leveled off before decreasing again. The normal coercive force, $_BH_c$ and energy product behaved somewhat similarly. In general, the remanence, B_r, decreased linearly as the copper content was increased in the alloys, but the decrease was not as drastic as it was for the coercivities and energy product.

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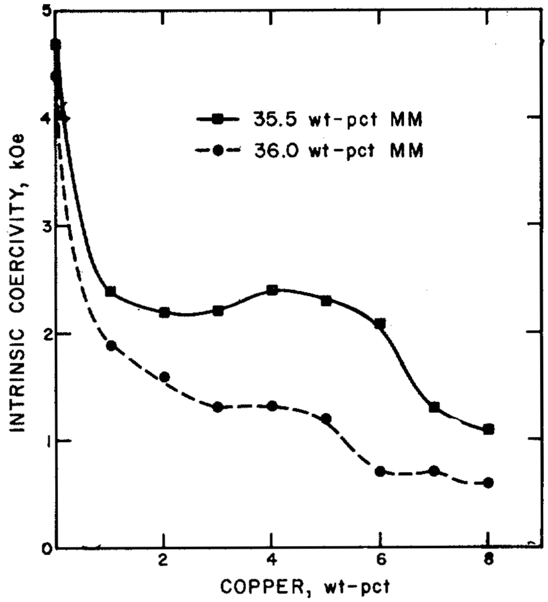

Fig. 1 - Effect of copper on the intrinsic coercive force of MM-Co-Cu alloys.

Samples containing copper and magnesium were prepared by blending the compounds previously described, together with various combinations of the following alloys: $MM_2(Co,Mg)_7$-40.7 MM/0.34 Mg, $MM(Co,Cu,Mg)_5$-33.5 MM/14.0 Cu/0.49 Mg, and $MM(Co,Cu,Mg)_5$-33.5 MM/14.0 Cu/0.62 Mg, all expressed in wt-pct.

Remarkable results were obtained by adding 0.1 to 0.3 wt-pct magnesium to the MM-Co-Cu alloys, as illustrated in figure 2. The effect of copper-magnesium addition was a drastic increase of the intrinsic coercivity to values previously attainable only with Sm-Co alloys. A maximum $_MH_c$ = 29.0 kOe was obtained with MM-Co-Cu-Mg alloy containing, in wt-pct, 35.5 MM/6.0 Cu/0.30 Mg. This value exceeded the maximum $_MH_c$ = 27.4 kOe previously obtained with Sm-Co alloys in our laboratory. As can be seen by the nearly identical curves in figure 2, the effect of the difference in mischmetal content on the intrinsic coercive force was negligible.

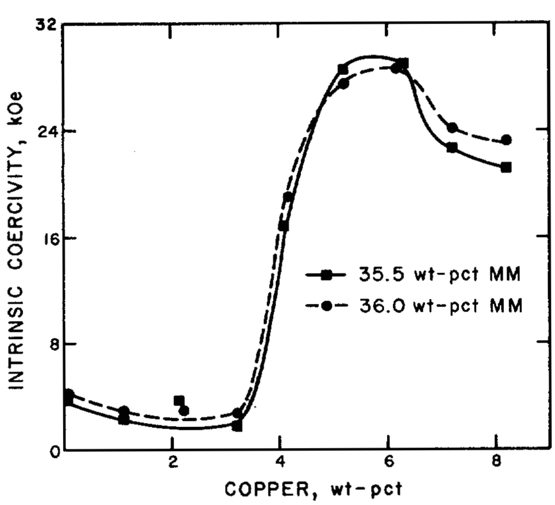

Fig. 2 - Effect of copper on the intrinsic coercive force of MM-Co-Cu-Mg alloys.

A study was conducted to determine the effect of the magnesium addition on two MM-Co-Cu alloys, in wt-pct, 35.5 MM/6.0 Cu, and 36.0 MM/6.0 Cu. Magnesium and copper substitutions were made with various combinations of the blending compounds as described above. As shown in figure 3, there was a fairly well defined range of magnesium concentration for which peak values of intrinsic coercive force were obtained. With a mischmetal content of 35.5 wt-pct, the peak intrinsic coercivities ranged from 26.8 to 25.5 kOe at 0.09 to 0.22 wt-pct magnesium; for the 36.0-wt-pct-mischmetal alloy, peak values ranged from 27.3 to 25.9 kOe at 0.15 to 0.30 wt-pct magnesium. With an addition as low as 0.03 wt-pct magnesium to the 36.0-wt-pct-mischmetal alloy, a relatively high value of $_MH_c$ = 12.5 kOe was obtained.

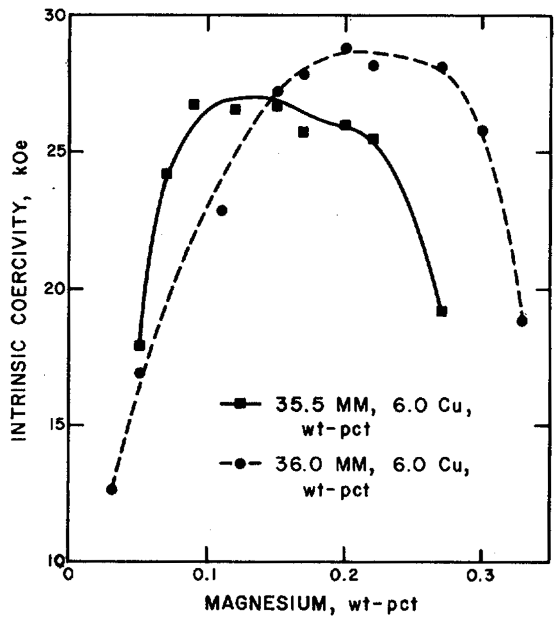

Fig. 3 - Effect of magnesium on the intrinsic coercive force of MM-Co-Cu-Mg alloys.

The influence of copper on the density of MM-Co-Cu and MM-Co-Cu-Mg magnets sintered at 980° C was substantial. No effect of magnesium on the densities of MM-Co-Mg samples was observed. Copper-free MM-Co magnets containing 35.5 and 36.0 wt-pct mischmetal typically possessed densities of 7.7±.3 g/cm^3 and 7.9±.2 g/cm^3, respectively. Density increased as the amount of copper was increased, reaching a maximum value of 8.2±.1 g/cm^3 at copper contents of 5 and 6 pct. This represented greater than 98 pct of theoretical density (8.3 g/cm^3). Although the saturation magnetization of the MM-Co-Cu-Mg alloys decreased as the amount of cobalt replaced by copper increased, a substantial portion of the magnetization was regained with the increased density.

The effect of cooling the sintered alloy samples on the magnetic properties was studied. The sintered magnets were cooled from the sintering temperature to ambient by two methods. The method with a faster cooling rate, referred to as air quench, consisted of moving the samples from the heat zone of the tube furnace immediately after sintering. The other method, referred to as furnace cool, had a slower cooling rate; the samples remained in the heat zone after sintering until the temperature dropped to approximately 400° C and then were moved to an air-cooled zone for cooling to room temperature. Samples were fabricated from an alloy containing, in wt-pct, 35.5 MM/59.5 Co/4.9 Cu/0.10 Mg, and sintered for 2 hours at 980° to 990° C.

As shown in table I, the effect of the two different cooling methods on the intrinsic coercivity of the alloy was pronounced. Compared with furnace-cooled samples, the intrinsic coercive force of the magnets cooled by the air-quench method was increased by a factor of 2. The data showed little difference in normal coercive force, remanence, and energy product attributable to the two cooling methods.

TABLE I. - Effect of Cooling Method on Magnetic Properties of a MM-Co-Cu-Mg Alloy

Cooling method	Sinter temp, °C	$_MH_c$, kOe	$_BH_c$, Oe	B_r, G	$(BH)_{max}$, MGOe
Furnace cool	980	7.7	5510	6080	8.8
Air quench	980	16.3	5710	6150	8.8
Furnace cool	985	12.3	5840	6190	9.0
Air quench	985	21.0	5860	6190	9.1
Furnace cool	990	13.9	5860	6080	8.9
Air quench	990	23.2	5870	6110	9.0

The net effect of copper and magnesium additions to MM-Co alloys was a drastic improvement of both intrinsic and normal coercivities, but with a reduced value of remanence. The substitution of iron for cobalt was reported[5] to increase the saturation magnetization of R-Co. A cursory study was made to determine the effect of iron additions to MM-Co-Cu-Mg alloys that contained 36.0 wt-pct mischmetal, 5 and 6 wt-pct copper, and small amounts of magnesium. Iron additions were made through the use of an MM-Co-Fe alloy containing, in wt-pct, 44.0 MM/28.0 Co/28.0 Fe. Each sample was sintered at 980° to 1,000° C for 2 hours and air-quenched.

Results of this initial study are shown in table II. Set A presents the magnetic properties of samples with maximum energy product, and Set B presents those of samples with maximum intrinsic coercivity. The various fabrication parameters were not optimized at this point, as can be seen by the range of sintering temperatures at which best properties were attained. These tests indicated the potential of iron addition to MM-Co-Cu-Mg alloys, with improved values of B_r = 6,900 G and $(BH)_{max}$ = 10.3 MGOe, the largest values obtained to date in our laboratory for any alloy of mischmetal and cobalt. These results were obtained with an alloy containing, in wt-pct, 36.0 MM/52.9 Co/5.0 Cu/6.0 Fe/0.05 Mg. The composition represents a 17-pct reduction of cobalt through the substitution of iron and copper.

SUMMARY

Partial substitution of cobalt with copper drastically reduced all magnetic properties. However, the 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 previously obtained in our laboratory. The addition of 5.0 and 6.0 wt-pct copper to MM-Co-Cu-Mg alloys containing 35.5 and 36.0 wt-pct mischmetal increased the average value of density to greater than 98 pct of theoretical. Of the two cooling methods evaluated, the air-quench method produced the greatest values of intrinsic coercivity. The addition of iron to MM-Co-Cu-Mg alloy resulted in significant improvement of remanence and energy product values.

TABLE II. - Effects of Fe on the Magnetic Properties of MM-Co-Cu-Mg Alloys

Fe,Cu,Mg content, wt-pct	Sinter temp, °C	$_MH_c$, kOe	$_BH_c$, Oe	B_r, G	$(BH)_{max}$, MGOe
Set A[1]					
3,5,.11	990	6.4	4700	6600	9.7
4,5,.09	980	7.3	5270	6570	9.8
5,5,.07	990	7.5	5200	6600	10.0
6,5,.05	990	5.6	4430	6900	10.3
3,6,.12	1000	10.7	6040	6550	10.2
4,6,.10	1000	9.3	5570	6620	10.1
5,6,.08	990	8.1	5160	6160	8.5
6,6,.06	1000	5.0	4000	6160	8.2
Set B[2]					
3,5,.11	980	11.6	5840	6390	9.5
4,5,.09	980	7.3	5270	6570	9.8
5,5,.07	990	7.5	5200	6600	10.0
6,5,.05	990	5.6	4430	6900	10.3
3,6,.12	980	15.5	5600	5980	8.4
4,6,.10	980	12.5	5840	6460	9.7
5,6,.08	980	8.6	4930	6020	8.2
6,6,.06	1000	5.0	4000	6160	8.2

[1]Samples possessing maximum energy product.
[2]Samples possessing maximum intrinsic coercivity.

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