Recent Progress in 2:17-Type Permanent Magnets

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Efforts to develop and refine, by experiment, a model for the metallurgical behavior of $Sm_2(Co,Fe,Cu,Zr)_{17}$ alloys are reviewed. A summary of how the results of these studies have been utilized to improve, by 10 to 20%, the energy products of the 2:17-type magnets over a wide range of temperatures, up to 300 °C, is presented. The potential for further improvement of energy products and extension of the operating temperature range is assessed.

1 Introduction

THREE families of rare earth-transition metal permanent magnets are currently in commercial production. The intermetallic phases upon which they are based are $SmCo_5$, $Sm_2(Co,Fe)_{17}$, and $Nd_2Fe_{14}B$. Key intrinsic magnetic properties for single crystals of these are given in Table 1, and typical hard magnetic properties of commercially produced permanent magnets corresponding to these phases are given in Table 2. The relatively low magnetization of $SmCo_5$ is reflected by correspondingly low energy products in both uncompensated and temperature-compensated versions. They have a maximum use temperature of 250 to 300 °C. $SmCo_5$-base magnets have been commercially available since the mid-1970s; it is a mature technology and significant improvements are not anticipated. Likewise, the high magnetization of $Nd_2Fe_{14}B$ is reflected in correspondingly large energy products, between room temperature and 100 °C, of permanent magnets based on this phase. Announced in late 1983,[5,6] and in commercial production since 1984 to 1985, Nd-Fe-B-type permanent magnets have found acceptance in a wide variety of applications, most notably in the computer industry. The low Curie temperature of $Nd_2Fe_{14}B$ and

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large, negative temperature coefficients of B_r and $_MH_c$ severely limit the usefulness of Nd-Fe-B magnets for elevated temperature applications. Intense efforts to increase the operating range of Nd-Fe-B base magnets have met limited success. A maximum use temperature of 150 °C has been achieved, but at a significant sacrifice in energy product.

The combination of high magnetization and high Curie temperatures of $Sm_2(Co,Fe)_{17}$ make 2:17-type permanent magnets attractive for a number of applications requiring high energy products combined with long-term stability for continuous operation up to 300 °C and also for those requiring low temperature coefficients of magnetization and coercivity over the temperature range from –50 to 300 °C. The potential of the 2:17 family, or "second generation," of permanent magnets was announced in 1972,[7] and techniques for making practical magnets were reported in 1977.[8] The 2:17-type magnets became commercially available in 1981 to 1982. Numerous worldwide investigations to understand the metallurgical behavior and the development of coercivity in 2:17 magnets were reported between 1977 and 1983. (This work is reviewed in Ref 9.) Since the announcement of the potential of permanent magnets based on $Nd_2Fe_{14}B$, efforts to improve the performance of 2:17 magnets have been largely neglected, except at the University of Dayton.

Since 1982, the University of Dayton Research Institute and Magnetics Laboratory, with the financial support of the U.S.

Table 1 Magnetic Properties of Some Rare Earth-Transition Metal Phase Single Crystals

Type	$4\pi M_s$, kGauss	H_A, kOe	Curie temperature (T_C), °C	Ref
$SmCo_5$	11.1	350	720	1
$Sm_2(Co_{0.7}Fe_{0.3})_{17}$	14.5	54	856	2,3
$Nd_2Fe_{14}B$	16.6	67	312	4

Table 2 Magnetic Properties of Commercially Available Rare Earth-Transition Metal Permanent Magnets

Type	B_r, kGauss	$_MH_c$, kOe	$(BH)_{max}$	Temperature coefficient, %/°C at RT $B; H$
$SmCo_5$	8 - 10	15 - >30	16 - 22	– 0.04; – 0.30
$Sm_2(Co,Fe,Cu,Zr)_{17}$	10 - 5	10 - >25	20 - 28	– 0.03; – 0.37
$Nd(Dy)-Fe(Co)-B$	10.5 - 12.5	10 - >20	28 - 40	– 0.11; – 0.80
With HRE temperature compensation				
$Sm_{0.5}Gd_{0.5}Co_5$	6.1	>30	9	– 0.0028; – 0.25
$(Sm_{0.5}Gd_{0.5})_2, TM_{17}$	8.0	>25	15	– 0.0068; – 0.37
$Nd,Dy-Fe,Co-B$	11.7	>20	32	– 0.105; – 0.61

Army Research Office,[10] has investigated the metallurgy and processing of the 2:17 alloys to improve the performance of the magnets. Permanent magnets with higher operational temperatures combined with higher energy densities are required for improved performance of motors, generators, actuators, and traveling wave tubes. Similarly, inertial guidance systems (gyros and accelerometers) require higher and more uniform magnetic fields over wide temperature ranges. Many important new designs for DOD, NASA, and commercial aerospace systems are critically dependent on magnetic field devices and components capable of continuous operation at 300 °C and higher. These include starters and primary power generators that will be placed in the cores of the gas turbines, actuators to replace the hydraulic systems for the aircraft control surfaces, and motors for fuel pumps and environmental and power conditioning systems. Only the 2:17 family of permanent magnets has the potential for meeting these requirements in the foreseeable future.

Processing the multicomponent $Sm(Co,Fe,Cu,Zr)_z$ alloys into permanent magnets involves a complex metallurgical system. Three independent compositional variables (Fe, Cu, and Zr) are strongly interactive with each other and with four heat treating steps required to develop high coercivity (sintering, solutionizing, isothermal aging, and ramp cooling). In addition, oxygen and carbon picked up during the processing of the alloy powders directly influence the Sm and Zr contents, respectively, of the metallic portions of the magnets. At the University of Dayton, we have focused our efforts on developing[11-13]and refining by experiment[9,14-18]a model for the metallurgical behavior of the magnet alloys and on utilizing the results to increase the remanence and energy products of the magnets.[19-23] This article summarizes the results of these studies, presents some previously unpublished high-temperature properties, reassesses the potential for the 2:17 family of magnets, and suggests experiments for achieving this potential.

2 Metallurgical Behavior of 2:17-Type Permanent Magnet Alloys

2.1 Background

Ray[11-13] proposed a model for the metallurgical behavior of $Sm(Co,Fe,Cu,Zr)_z$ alloys during their preparation to form high-density, magnetically oriented, sintered bodies and subsequent heat treatment to develop high coercivity. The model has been used to provide a basis for experiments not only to develop improved permanent magnet properties and permit more accurate assessments of the potential of 2:17-type magnets, but also to test and refine the model itself. A detailed description and account of the basis for the original model was given earlier,[9] prior to the experiments to refine it, which are described below. Only the principal features will be described here, without detailing the evidence upon which the model is based.

It is generally agreed that high coercivity in $Sm(Co,Fe,Cu,Zr)_z$ magnets is related to the development of a fine-scale, cellular microstructure consisting of three coherent phases. The model proposes that the cellular microstructure develops from an essentially stoichiometric, single-phase precursor that is retained in metastable solid solution on rapid cooling

to room temperature from the solutionizing temperature. The crystal structure of the precursor is rhombohedral, space group $R\bar{3}m$, Th_2Zn_{17}-type, hereafter denoted as 2:17R. A key feature of the model is that Zr, as Zr-vacancy pairs, occupy some of the 6c, or dumbbell, sites in the 2:17R precursor at the solutionizing temperatures. This effectively stabilizes the 2:17R precursor, at Fe contents greater than 5 to 10 wt.%, as it is cooled below the magnetic ordering temperatures, by significantly reducing the preference of Fe for the dumbbell sites. At room temperature, the precursor is supersaturated not only by the Zr-vacancy pairs, which represent disorder in the 2:17R structure, but also by Cu. Reheating to the isothermal aging temperature provides the thermal energy to initiate Zr-rich and Cu-rich coherent precipitates. The Cu-rich precipitate, or cell boundary phase, is known to have the $SmCo_5$ crystal structure. The structure of the Zr-rich precipitate, referred to as the platelet or Z-phase, has been the subject of considerable controversy. Our original model, based in part on the Sm-Co binary phase diagram, suggested that the platelet phase very probably had the hexagonal, space group $P6_3/mmc$, $ThNi_{9.5}$-type crystal structure. We proposed that either the precipitation of the boundary and platelet phases occurs simultaneously, or that the platelet phase precipitation must precede that of the boundary phase.

Many features of our proposed model for the metallurgical behavior of the 2:17 magnet alloys were not in agreement with earlier studies.[9] We have conducted several experiments to test the validity of our model, which are described below. All of these studies have utilized a single set of alloys corresponding to the nominal composition $Sm(Co_{0.90-v}Fe_vCu_{0.08}Zr_{0.02})_{8.35}$. Details of the preparation and heat treatment of these alloys and their metallurgical and magnetic properties were given earlier.[24]Although containing somewhat less Fe and more Cu, these alloys conform in all essential respects with the metallic portions of our best magnet compositions.

2.2 High-Resolution TEM Studies of the Microstructure Development

High-resolution transmission electron microscopy (HREM) studies conducted at the University of Pittsburgh[14] showed the alloy with $v = 0.23$, solutionized at 1160 °C for 24 hr, then rapidly cooled to room temperature, to be single phase, highly twinned, and have the 2:17R crystal structure. No evidence was observed to indicate that a phase transformation from the "2:17H" structure had taken place on cooling from the solutionizing temperature, as suggested by Rabenberg et al.[25] On the contrary, the heavy twinning on planes normal to the c-axis is taken as strong evidence that the precursor phase has the 2:17R structure at the solutionizing temperature. The "2:17H" structure cannot develop twins on these planes. HREM microstructures also showed the platelet phase precipitation to precede the precipitation of the boundary phase. Isothermal aging of the single-phase precursor for short periods at 840 °C show a twinned 2:17R matrix phase containing a thin, coherent, well-developed platelet phase and only a few areas of partially developed boundary phase. The platelet phase precipitate was observed to be only 0.8 nm thick along its c-axis and thus cannot have the $SmCo_3$-type crystal structure, with $a = 0.5$ nm and $c = 2.4$ nm as proposed by Rabenberg et al.

Table 3 Comparison of Compositions of AEM Determined Phases [15] in the Cellular Microstructure(a)

	Sm	Co	Composition, at.% Fe	Cu	Zr
Nominal	10.7	59.8	20.5	7.1	1.8
Analyzed, ICP	10.5	60.0	20.6	7.1	1.8
Matrix phase					
AEM	10.5	61.7	22.4	4.8	0.4
SEM-EDS	10.4	61.6	22.2	4.8	1.0
Boundary phase					
AEM	17	33.6	4.8	43	1.2
SEM-EDS	16.4	45.3	9.5	27.5	1.4
Platelet phase					
AEM	5-8	60	13.5	5	14 - 17
SEM-EDS	8.4	59.1	13.8	5.1	13.6

Note: The nominal and inductively coupled plasma (ICP) analysis compositions of the bulk alloy are given in the first two rows (from Ref 18). (a) After solutionizing at 1160 °C for 24 hr, quenched, then aged at 800 °C for 72 hr with SEM-EDS analysis[16] of the same alloy as-cast and heated at 800 °C for 40 hr.

Table 4 SEM-EDS Analysis of an Alloy Corresponding to the Platelet Phase Composition

	Sm	Zr	Composition, at.% Co	Fe	Cu
Alloy	5.6	10.9	58.7	12.8	3.9
Light	6.1	18.3	58.6	12.9	4.1
Dark	0.8	24.4	59.1	12.9	2.8

Note: From Table 3. The alloy was heated at 1100 °C for 25 hr, then at 800 °C for 40 hr. The dark areas are located at the centers of the light matrix phase grains. They comprise 10 to 15% of the microstructure and appear to have a dendritic origin (from Ref 18).

2.3 Analytical Electron Microscopy Studies of the Cellular Microstructure

Analytical electron microscopy (AEM) studies were conducted at the University of Pittsburgh on the solutionized (24 hr at 1160 °C) and rapidly quenched single-phase precursor and on the cellular microstructure developed on subsequent isothermally aging (72 hr at 800 °C).[15] The quantitative results of this study are given in the following section, along with the results of scanning electron microscopy (SEM)/energy dispersive X-ray spectroscopy (EDS). The AEM study showed the platelet phase to comprise approximately 8% and the boundary phase 6% of the fully developed cellular microstructure. All diffraction maxima of the platelet could be indexed on the basis of a hexagonal unit cell, with $a = 0.5$ nm and $c = 0.8$ nm. The platelet phase was found to be much more Zr-rich and Sm-depleted, and the boundary phase was more Cu-rich than previously reported.

2.4 Physical and Magnetic Properties of the Platelet Phase

A single-phase alloy corresponding to the platelet phase composition in the cellular microstructure was prepared and its magnetic properties measured.[16] Professor I.R. Harris of the University of Birmingham (England) noted that the composition of the platelet phase in our AEM experiments was very close to that of a phase they observed in the grain boundary of a cast alloy of similar composition.[26] We performed EDS analy-

sis on our cast $Sm(Co_{0.67}Fe_{0.23}Cu_{0.08}Zr_{0.02})_{8.35}$ alloy after annealing at 800 °C for 40 hr. A comparison of the results obtained by AEM on the solutionized and isothermally aged cellular microstructure and on the same alloy in the as-cast and annealed condition is given in Table 3. The similarity of the compositions of the platelet phase in the cellular microstructure and the phase in the grain boundary of the as-cast alloy suggested that the Zr-rich platelet phase might be a stable phase in the quinary alloy system.
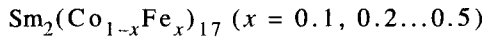
Several alloys close to the platelet phase composition were prepared by arc melting the elemental constituents. The alloys were first solutionized for 25 hr at 1100 °C and then annealed for 40 hr at 800 °C. A heavily twinned, nearly single-phase alloy was observed for the composition 7.4 at.% Sm, 59.2 at.% Co, 12.6 at.% Fe, 4.2 at.% Cu, and 16.6 at.% Zr by optical and secondary electron microscopy. The compositional mode backscattered electron image showed the single-phase grains to contain dark areas, about 10% of the total area, within a lighter matrix. The absence of phase boundaries separating the light and dark regions indicates that both have the same crystal structure. The compositions of these areas are given in Table 4. Although differing significantly between the light and dark areas, the Sm and Zr contents add up to 25% in both, indicating a 1:3-type structure with Sm and Zr occupying the same positions. All the principal X-ray diffraction peaks can be indexed on the basis of a hexagonal unit cell, with $a = 0.492$ nm and $c = 0.799$ nm, in close agreement with the earlier electron diffraction re-

sults for the platelet phase precipitate. Thus far, we have not found a satisfactory atomic arrangement to match the compositions, unit cell dimensions, and diffraction intensities.
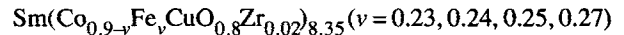
Thermal magnetic analysis of the alloy described in the preceding paragraph showed two peaks, corresponding to Curie temperatures, T_C, of about 180 and 210 °C. The saturation magnetization of the alloy was determined to be 3450 Gauss, based on a specific magnetization, $\sigma = 33.5$ emu/g, measured on loose powders less than 37 μm, and a pycnometric density of 8.2 g/cm^3. The results of attempts to estimate the anisotropy field of the platelet phase alloy were inconclusive. The low Curie temperatures and low room-temperature saturation magnetization indicate the platelet phase has a much more negative effect on the remanent induction of 2:17 magnets than would be predicted on the basis of simple dilution of $4\pi M_s$ of Sm$_2$(Co,Fe)$_{17}$ by Zr-substitution.

2.5 Fe-Site Populations in Sm$_2$(Co,Fe)$_{17}$ and Sm(Co,Fe,Cu,Zr)$_{8.35}$ Alloys

Mössbauer experiments on the Fe-site populations in:

$$\text{Sm}_2(\text{Co}_{1-x}\text{Fe}_x)_{17} \quad (x = 0.1, 0.2...0.5)$$

and

$$\text{Sm}(\text{Co}_{0.9-\nu}\text{Fe}_\nu\text{CuO}_{0.8}\text{Zr}_{0.02})_{8.35}(\nu = 0.23, 0.24, 0.25, 0.27)$$

were conducted at the Institute of Physics, University of Sao Paulo.[17] A description of the preparation of the ternary alloys was given earlier.[3] The quinary alloys are the same as those used for the HREM and AEM experiments. The strong preference of Fe to occupy the dumbbell sites in R$_2$(Co,Fe)$_{17}$ phases is well established (see Ref 9), but direct quantitative evidence of the degree of this preference, obtained by neutron diffraction experiments,[27] were only available for Nd$_2$(Co,Fe)$_{17}$. The Fe-site preference can be represented by:

$$\text{R}_2(\text{Co}_{1-x}\text{Fe}_x)_{17} = \text{R}_2(\text{Co}_{1-y}\text{Fe}_y)_{15}(\text{Co}_{1-z}\text{Fe}_z)_2$$
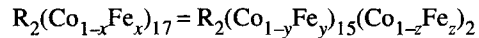
where the Fe-site preference for the dumbbell sites ($6c$) over the three planar sites ($9d$, $12f$, and $12h$), for a given value of x, is the ratio z/y. For $x = 0.3$ and R = Nd, Herbst et al. found $z/y = 3.0$. The present results for R = Sm and $x = 0.3$ is $z/y = 4.4$, significantly higher than for R = Nd.

For the quinary magnet compositions, assuming no Cu atoms occupy $6c$ sites, we can write:

$$2\,\text{Sm}(\text{Co}_{0.90-\nu}\text{Fe}_\nu\text{Cu}_{0.08}\text{Zr}_{0.02})_{8.35} =$$
$$\text{Sm}_2[(\text{Co}_{1-y}\text{Fe}_y)\text{Cu}_{0.09}]_{15}[(\text{Co}_{1-z}\text{Fe}_z)_{0.66}(\text{Zr}_{0.17}\text{vac}_{0.17})]_2$$

2:17 R (disordered dumbbell sites)
10.7 Sm, 59.8 Co, 20.6 Fe,
7.1 Cu, 1.8 Zr

10.7 Sm

1st Stage

10.9 Sm

Matrix Phase (~ 92%)
Sm-rich 2:17R,
10.9 Sm, 59.9 Co
Sm-rich 21.2 Fe, 7.3 Cu, 0.8 Zr

8.4 Sm

Platelet Phase (~ 8%)
Hex. a=0.5 nm, c=0.8 nm
8.4 Sm, 59.1 Co,
13.8 Fe, 5.1 Cu, 13.6 Zr

2nd Stage

16.7 Sm
Boundary Phase (~6%)
Hex. (1:5) a=0.5 nm, c=0.4 nm
16.7 Sm, 33.6 Co,
4.8 Fe, 43.0 Cu, 1-2 Zr

10.5 Sm
Matrix Phase (~86%)
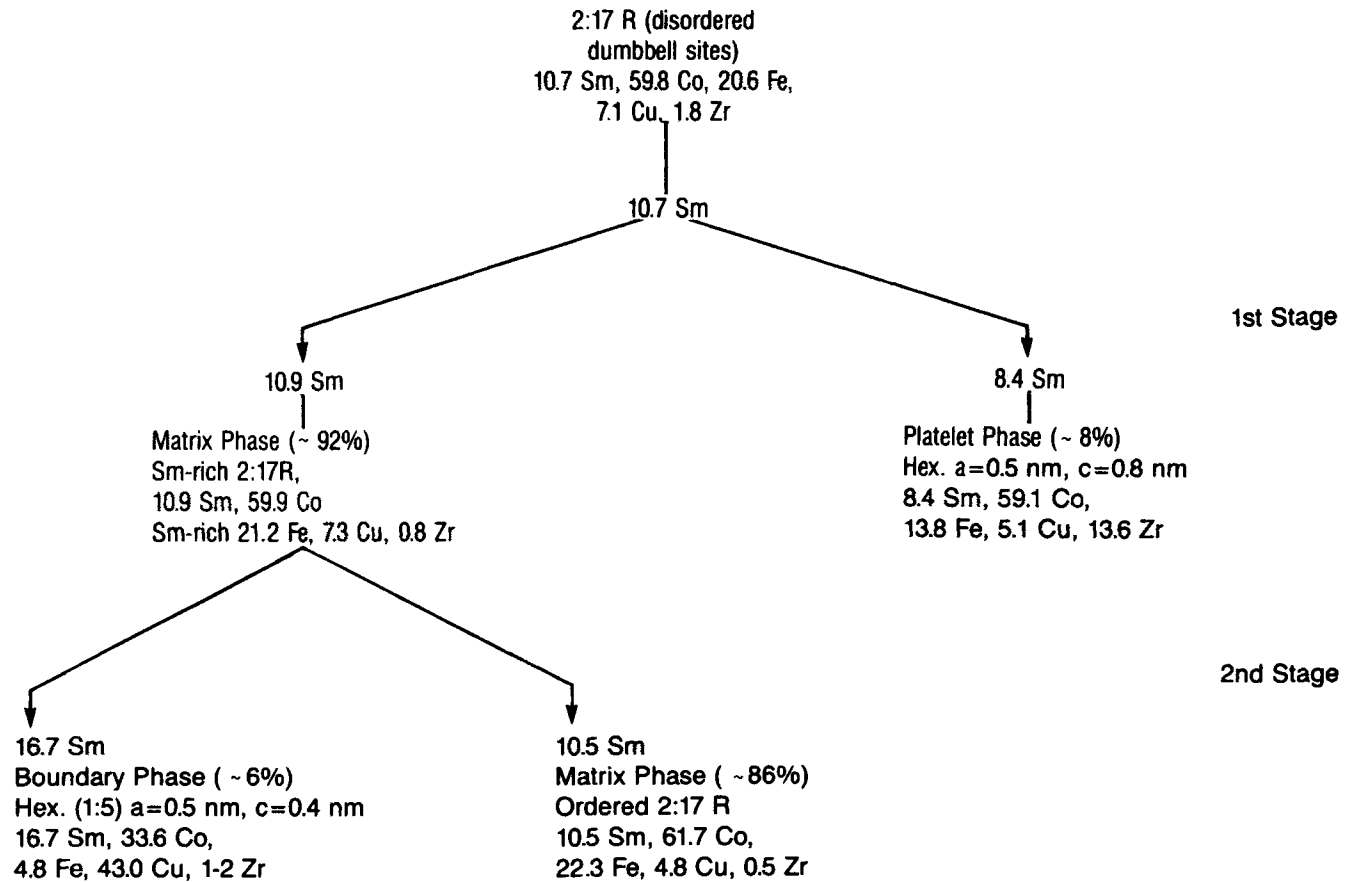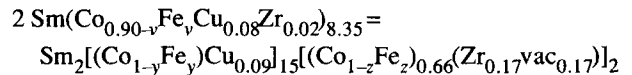Ordered 2:17 R
10.5 Sm, 61.7 Co,
22.3 Fe, 4.8 Cu, 0.5 Zr

Fig. 1 Experimental determined isothermal aging reactions at 800 °C for a solutionized (1170 °C, 24 hr) and quenched 2:17 magnet alloy.[18]

For $v = 0.23$ to 0.27, the average value observed for the $6c$ site preference of Fe was $z/y = 2.7 \pm 0.05$. Thus, the Mössbauer spectroscopy results show that, in addition to occupying part of the available $6c$ sites, the Zr also reduces the preference of Fe for the remaining dumbbell sites.

2.6 Revised Model for the Metallurgical Behavior of 2:17-Type Magnet Alloys

Neutron diffraction experiments at the University of Missouri, Columbia,[28] to locate the Zr atoms in the 2:17R precursor structure at room temperature and at the Argonne National Laboratory[29] to determine the crystal structure of precursor phase at the solutionizing temperature have been unsuccessful due to the large absorption effects of the Sm component. However, all of our indirect evidence indicates that the precursor crystal structure is stoichiometric 2:17R at the solutionizing temperature and that this structure is retained on rapid cooling to room temperature. We continue to believe that Zr, as Zr-vacancy pairs, occupy dumbbell sites ($6c$ in $R\overline{3}m$) at $00 \pm z$, with $z \approx 0.1$, thereby reducing the number of Fe-Fe pairs that would otherwise occupy the sites. This assumption is not only a plausible explanation for the observed changes in the lattice constants,[9,12] but is also now strongly supported by Mössbauer experiments.[17]

The high-temperature solubility of Zr in the 2:17R crystal structure appears to be due to the atomic size and electronic structure of the Zr atom (Hf behaves similarly[30]) and to the entropy of mixing. At lower temperatures, the disorder represented by the Zr-vacancy pairs becomes destabilizing. At the isothermal aging temperatures, the strong tendency of the 2:17R crystal structure to order is initiated by the precipitation of the Zr-rich platelet phase. This results in a matrix phase slightly Sm-rich of 2:17 stoichiometry. The reestablishment of 2:17 stoichiometry and the fact that the matrix phase is super-
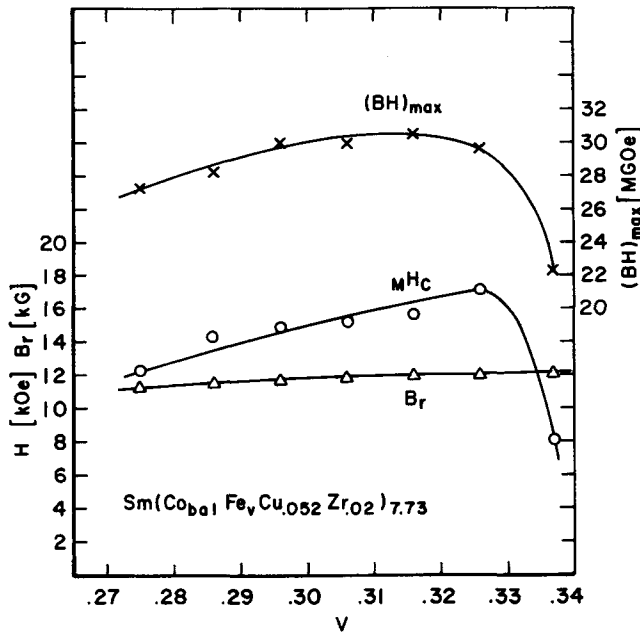
saturated by Cu appear to be the driving forces for the subsequent precipitation of the Cu-rich 1:5 boundary phase. A revised model for the development of the cellular microstructure, incorporating much of the experimental evidence described above, is given in Fig. 1.

3 Experiments to Improve the Performance of the Magnets

3.1 Magnets with Higher Fe Content

Substituting Fe for Co significantly increases the saturation magnetization of Sm_2Co_{17},[1] and this is a obvious approach to improving the magnetic properties of 2:17 magnets. However, attempts to raise B_r and $(BH)_{max}$ above 30 MGOe by increasing Fe content above approximately 15 wt.% resulted in unacceptable losses in coercivity.[8] Sun et al.[31] reported that Zr content must be increased linearly with increasing Fe content to maintain high coercivity. If this were true, then attempting to raise B_r by increasing Fe would be essentially negated by the increased Zr content. Our model, however, strongly supported by Mössbauer experiments,[17] indicates that Zr-vacancy pairs not only occupy dumbbell sites that would otherwise be occupied by Fe-Fe pairs, but also significantly reduce the preference of Fe-Fe pairs to occupy the dumbbell sites. Our experience is
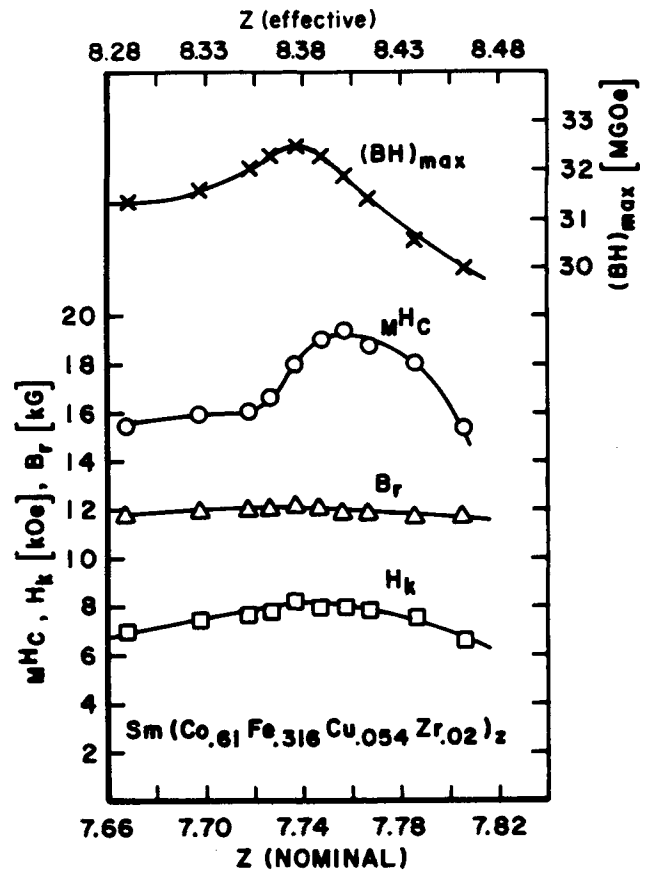

Fig. 2 Variation of magnetic properties versus Fe content, v, in $Sm(Co_{bal}Fe_vCu_{0.52}Zr_{0.02})_{7.73}$.[19]

Fig. 3 Permanent magnet properties of $Sm(Co_{0.61}Fe_{0.316}Cu_{0.054}Zr_{0.02})_z$ as a function of z (nominal), bottom scale, and z (effective), top scale. The latter are corrected for the oxygen content of the magnets.[20]

Table 5 Temperature Coefficients of Magnetic Properties of $Sm_{0.54}Gd_{0.46}(Co_{0.63}Fe_{0.29}Cu_{0.06}Zr_{0.02})_{7.69}$

T, °C	$4\pi M_s$	B_r	$_BH_c$	$_MH_c$	$(BH)_{max}$
−50	0.0076	...	...	...	...
−25	0.0065	...	...	...	...
0	0.0051	...	...	...	...
25	0.0033	0.0038	−0.016	−0.36	−0.021
50	0.0011	0.0003	−0.039	−0.40	−0.023
100	−0.0039	−0.0069	−0.058	−0.49	−0.031
150	−0.0099	−0.0140	−0.108	−0.59	−0.058
200	−0.0165	−0.0210	−0.290	−0.73	−0.106
250	−0.0236	−0.0290	−0.890	−0.88	−0.180
300	−0.0309				
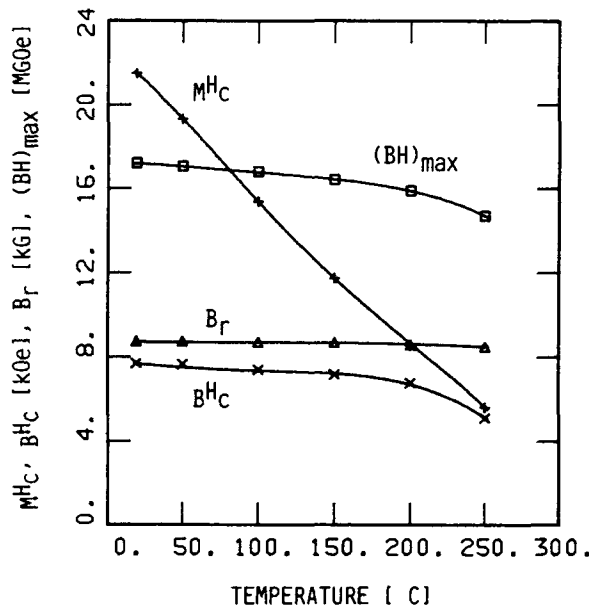
Fig. 4 Variations of permanent magnet properties versus temperature for $Sm_{0.54}Gd_{0.46}(Co_{0.63}Fe_{0.29}Cu_{0.06}Zr_{0.02})_{7.69}$.[21]

that Zr content need not exceed the amount sufficient to occupy approximately one-sixth of the dumbbell sites, or one-third as Zr-vacancy pairs, in the single-phase 2:17 precursor.

Most of the early development work on 2:17-type magnets was performed on compositions with Fe levels of 15 to 20 wt.%.[8] Our experiments have been to determine magnetic properties at Fe contents of 20 to 25 wt.%.[19,20]Figure 2 shows the variation of the magnetic properties versus Fe content in $Sm(Co_{bal}Fe_vCu_{0.056}Zr_{0.02})_{7.73}$. With increasing Fe content, the remanence gradually increases. The intrinsic coercivity also increases with Fe content up to $v = 0.32$, then drops sharply with any additional increase. The highest energy products attained to date are $(BH)_{max}$=32 to 34 MGOe for a batch of magnets of nominal composition of $Sm(Co_{0.616}Fe_{0.312}Cu_{0.052}Zr_{0.02})_{7.73}$.

Variations of the magnetic properties for $Sm(Co_{0.61}Fe_{0.316}Cu0.054Zr0.02)_z$ as a function of the TM/Sm ratio, z, are given in Fig. 3. The Sm content is very sensitive to oxygen pickup during the comminution of the alloys to fine powders. Oxygen, most of which is picked up during the final milling step, forms Sm_2O_3, reduces the effective Sm content of

the alloy by 6.27 times the weight fraction of the oxygen. Thus, two values for this TM/Sm ratio are given, z(nominal) on the lower scale and z (effective) on the top scale. The latter values have been corrected for the oxygen content, which averaged about 0.3 wt.%, and represent the Sm contents of the metallic part of the magnets. It can be observed that the magnetic properties attain maximum values for 8.35 < z (effective) < 8.40. This is in agreement with the model of Ray[11,12] which proposes that the single-phase solid solution precursor to the cellular microstructure has a slightly disordered rhombohedral (Th_2Zn_{17}-type $R\overline{3}m$) crystal structure and is essentially stoichiometric 2:17. The disorder occurs at the dumbbell sites, which are randomly shared by transition metal pairs and Zr-vacancy pairs. Taking the effect of the vacancies into account shifts z (effective) very close to the stoichiometric 8.5 to obtain the optimum composition for the magnetic properties.

3.2 Magnets with Improved Temperature Compensation

Temperature-compensated permanent magnets with high energy products and very low temperature coefficients over a wide range of operating temperature are required to upgrade existing device performances and to meet the operational restraints imposed by proposed designs of new devices. We have employed our experience with high Fe content compositions to improve the magnetic properties of temperature-compensated versions by substituting the heavy rare earth Gd for part of the Sm.[21] Figure 4 summarizes the variation of the magnetic properties of $Sm_{0.54}Gd_{0.46}(Co_{0.63}Fe_{0.29}Cu_{0.06}Zr_{0.02})_{7.69}$withtemperature from 20 to 250 °C. B_r is almost constant over this temperature range and $(BH)_{max}$ remains above 16 MGOe to 200 °C. Even though the intrinsic coercivity drops sharply with increasing temperature, the normal induction coercivity, $_BH_c$, decreases only slightly up to 200 °C. Table 5 lists the temperature coefficients of magnetic properties for this magnet composition. The energy product at room temperature is $(BH)_{max}$= 19 MGOe.

Preparing large numbers of magnets with varying compositions and then measuring the temperature coefficients of their magnetic properties over wide temperature ranges is laborious and time-consuming. This is especially true when more than one heavy rare earth is employed. We have developed algorithms to predict saturation magnetization and its temperature coefficients on the basis of experimental data obtained for Sm_2TM_{17} and Gd_2TM_{17} magnet alloys. Figure 5 shows the temperature dependence of magnetization at 15 kOe for $Sm_{1-x}Gd_x(Co_{0.63}Fe_{0.29}Cu_{0.06}Zr_{0.02})_{7.69}$. In this figure, the solid lines

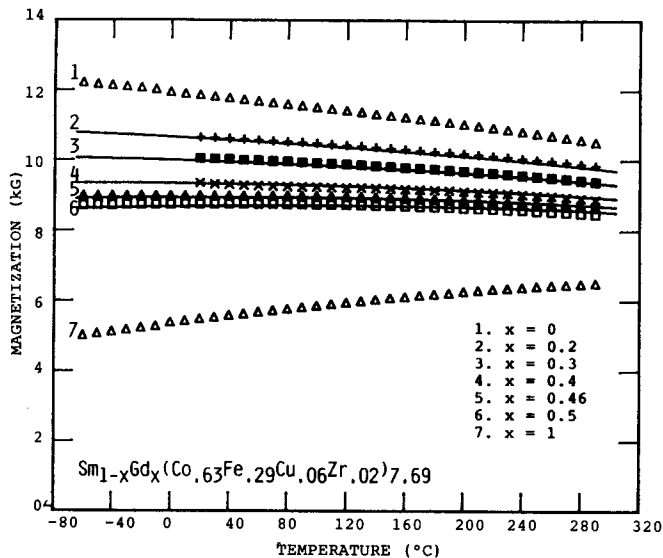**Fig. 5** Dependence of magnetization at 15 kOe as a function of temperature for $Sm_{1-x}Gd_x(Co_{0.63}Fe_{0.29}Cu_{0.06}Zr_{0.02})_{7.69}$.[21]

represent calculated results, whereas various symbols (squares, triangles, etc.) represent those data obtained by measurement.

3.3 Magnets with Light Rare Earth Substitutions

Another approach to increasing the saturation magnetization of $Sm_2(Co,Fe,Cu,Zr)_{17}$ permanent magnets is by the partial substitution of light rare earths for Sm, because Pr, Nd, and Ce all have higher atomic magnetic moments than Sm. Akioka *et al.*[32,33] have recently made resin-bonded magnets of nominal composition $Sm_{0.5}Nd_{0.4}Ce_{0.1}(Co_{0.672}Cu_{0.08}Fe_{0.22}Zr_{0.028})_{8.35}$ and $Sm_{0.5}Pr_{0.5}(Co_{0.672}Cu_{0.08}Fe_{0.22}Zr_{0.028})_{8.35}$. The magnetic properties of these magnets are $B_r = 8.1$ kGauss, $_MH_c = 10.6$ to 11.2 kOe, and $(BH)_{max} = 14.5$ MGOe. These values are comparable to the properties of resin-bonded magnets containing only Sm as the rare earth component. However, Koo[34] reported that partial substitution of Pr or Nd for Sm in sintered $Sm_{1-x}R_x(Co_{0.62}Fe_{0.28}Cu_{0.08}Zr_{0.02})_{7.4}$ magnets resulted in severe deterioration of $_MH_c$ and $(BH)_{max}$ and also reduced B_r.

Our experiments show that partial substitution of light rare earths for Sm in $Sm_2(Co,Fe,Cu,Zr)_{17}$ magnets not only increases B_r and $(BH)_{max}$, but also improves the loop squareness of the demagnetization curve.[22,23] Figure 6 shows variations of magnetic properties versus light rare earth content, x, in $Sm_{1-x}LRE_x(Co_{0.643}Fe_{0.276}CuV_{0.061}Zr_{0.02})_{7.63}$, with LRE = $Pr_{0.5}Nd_{0.5}$. With increasing LRE, the intrinsic coercivity, $_MH_c$, decreases monotonically, whereas the induction coercivity, $_BH_c$, remains essentially the same up to $x = 0.4$. The remanence, B_r, increases with continuously increasing LRE content. B_r for $x = 0.5$ is 12 kGauss, or about 670 Gauss higher than that for $x = 0$. The maximum energy product, $(BH)_{max}$, is increased by LRE substitution up to $x = 0.3$. The best result we have obtained so far is $B_r = 12.5$ kGauss for $x = 0.5$. Our experiments also show that LRE substitution does not strongly affect the Curie temperature and the temperature coefficients of $4\pi M_s$ of 2:17 magnets.
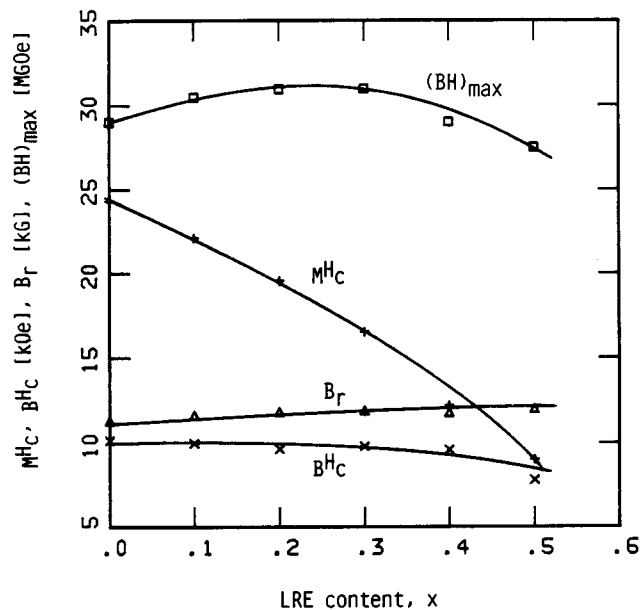

Fig. 6 Variations of magnetic properties versus LRE content, x, in $Sm_{1-x}(Co_{0.643}Fe_{0.276}Cu_{0.061}Zr_{0.02})_{7.63}$, with LRE = $Pr_{0.5}Nd_{0.5}$.[23]

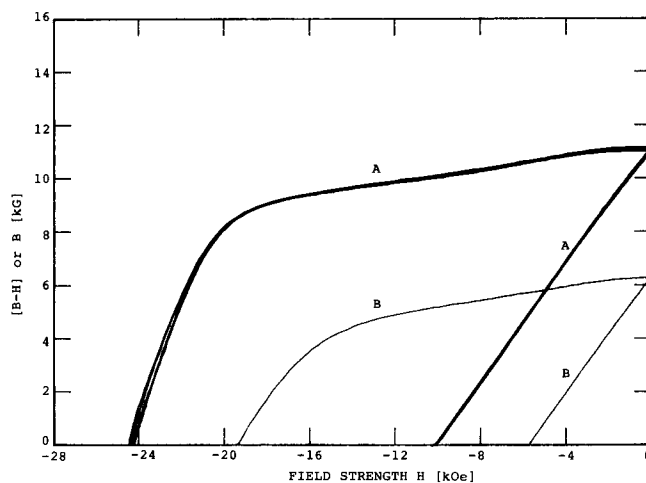**Fig. 7** Demagnetization curves for magnets of nominal composition $Sm(Co_{0.633}Fe_{0.276}Cu_{0.071}Zr_{0.02})_{7.73}$ after 5 min exposure to various elevated temperatures. (A) Curves for exposures at 50, 100, 200, 300, 400, and 500 °C. (B) Curve for 600 °C exposure.

3.4 Effect of Short–Time Exposures to High Temperatures

Some applications require permanent magnet elements to sustain high-temperature exposures for short time periods. Figure 7 shows demagnetization curves for our $Sm_2(Co,Fe,Cu,Zr)_{17}$ permanent magnets exposed at various temperature from 50 to 600 °C for 5 min. Short-time exposures up to 500 °C have little effect on the magnetic properties. Irreversible losses of magnetic properties were observed at 600 °C.

Table 6 Potential for 2:17-Type Permanent Magnets

Base	$4\pi M_s$(a), kGauss	B_r(b), kGauss	$(BH)_{max}$(c), MGOe	$(BH)_{max}$(d), MGOe	$(BH)_{max}$ at 300 °C(e), MGOe
$Sm_2(Co_{0.80}Fe_{0.20})_{17}$	14.00	11.7	32.6	17.6	23.6
$Sm_2(Co_{0.75}Fe_{0.25})_{17}$	14.25	11.9	33.8	18.3	24.5
$Sm_2(Co_{0.70}Fe_{0.30})_{17}$	14.50	12.1	35.0	18.9	25.3
$Sm_2(Co_{0.65}Fe_{0.35})_{17}$	14.75	12.3	36.2	19.6	26.2
$SmPr_{0.5}Nd_{0.5}(Co_{0.72}Fe_{0.28})_{17}$	...	12.5	37.5	20.2	27.2

(a) $4\pi M_s$ for single crystals of base compositions. (b) B_r (magnet) = 83.3% $4\pi M_s$ (single crystal) dilution by precipitates, Cu and Zr, Sm_2O_3, ZrC, porosity, alignment. (c) $(BH)_{max}$ (uncompensated) = 96% $B^2_r/4$. (d) $(BH)_{max}$ (HRE temperature compensated) = 54% $(BH)_{max}$ (uncompensated). (e) Average temperature coefficients of $(BH)_{max}$ = $- 0.0985\%/°C$.
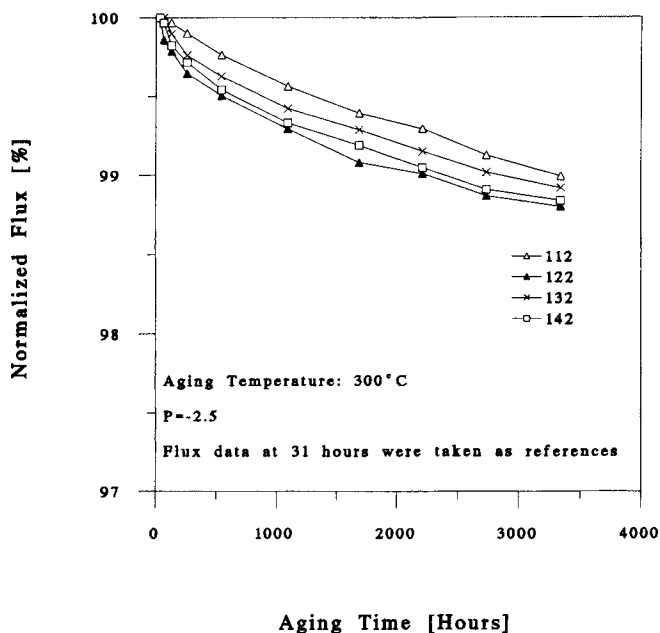

Aging Time [Hours]

Fig. 8 Aging curves for $Sm(Co_{bal}Fe_{0.276}Cu_xZr_{0.02})_{7.73}$ magnets at 300 °C. The flux of each magnet was normalized to its flux after 31 hr. The four curves are for magnets with varying Cu contents, $x = 0.04, 0.05, 0.06$, and 0.07.

3.5 High Temperature Aging of 2:17-type Magnets

Long-term stability at elevated temperatures is important for many applications. We observed a 1 to 3% irreversible loss on aging our 2:17 magnets for 300 °C for 30 hr, most occurring within the first 2 hr. Figure 8 shows the flux changes of 2:17 magnets with different intrinsic coercivities. The flux data at 31 hr were taken as references points. After 3240 hr at 300 °C, the irreversible losses for all magnets are about 1% or approximately 2.5% per year.

4 Conclusions

Better understanding of the metallurgical behavior of $Sm_2(Co,Fe,Cu,Zr)_{17}$ alloys has led to significant improvements of the magnetic properties of 2:17-type permanent magnets. The improved metallurgical model combined with the experience gained in developing processing techniques for the magnets permits a realistic assessment of the potential of this family

of magnets. The potential is summarized in Table 6. The saturation magnetizations, $4\pi M_s$, of single crystals of $Sm_2(Co_{1-x}Fe_x)_{17}$, with $0.20 \le x \le 0.35$ (from Ref 1), form the basis of this assessment. The remanent inductions, B_r, of the magnet alloys are reduced, by dilution, by the Zr-rich (platelet phase) and Cu-rich (boundary phase) precipitates and by the unavoidable pickup of oxygen, as Sm_2O_3, and carbon, as ZrC, during processing of the alloy powders. Further reduction of B_r occurs due to imperfect alignment of the powder particles and by a degree of porosity in the magnet body. The maximum energy product, $(BH)_{max}$, for a given remanent induction, is $B^2_r/4$, reduced by several factors related to the intrinsic coercivity developed during heat treatment, and exhibited by a less than square second quadrant hysteresis loop shape. The energy product reduction for fully temperature-compensated magnets are those we observed for Gd-substituted, high-Fe compositions in these studies. Likewise, the energy products available for continuous operation at 300 °C are based on the experimentally determined temperature dependence of the energy products of magnets produced in this study.

Approximately 20% improvement over the energy products of the best commercially produced 2:17-type permanent magnets has been achieved, and we believe at least 10% and perhaps 15% of this increase can be attained in commercial production. We believe it is probable that the operating temperature of the 2:17-type permanent magnets can be extended to 350 °C and possibly to 400 °C by adjustments to the Fe/Cu ratio and heat treatment protocols.

Further improvement is possible, but largely dependent on developing a better model for the metallurgical behavior of the magnet alloys during slow cooling from the isothermal aging temperatures. Optimizing the heat treatments for the high-Fe compositions should improve the loop squareness and may permit high coercivities to be developed at even higher Fe contents. Combining the light rare earth substitutions with the higher Fe levels and optimized heat treatments could lead to energy products higher than those given in Table 6.

Acknowledgments

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