

	45 50	2.8	2.5
	158 61	3.2 3.6	2.2
	ر. د ر ز ز ز ا	4.0	2.0
			1.8
1.25	₩I.	4	1.6

1.1

È

ŀ

h

MICROCOPY RESOLUTION TEST CHART NATIONAL BUREAU OF STANDARDS - 1963 - A

ARO 19511.3-MS

1.1.1.1.1.1.1



TEMPERATURE COMPENSATION IN THE '2:17' TYPE MAGNETS

FINAL REPORT

K. S. V. L. Narasimhan, F. E. Camp, Bao-Min Ma, C. J. Willman

MARCH 1986



86

U. S. ARMY RESEARCH OFFICE

Contract - DAAG29-83-C-0007

CRUCIBLE MATERIALS CORPORATION CRUCIBLE RESEARCH CENTER PITTSBURGH, PA.

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

THE VIEW, OPINIONS, AND/OR FINDINGS CONTAINED IN THIS REPORT ARE THOSE OF THE AUTHOR(S) AND SHOULD NOT BE CONSTRUED AS AN OFFICIAL DEPARTMENT OF THE ARMY POSITION, POLICY, OR DECISION, UNLESS SO DESIGNATED BY OTHER DOCUMENTATION.

REPORT DOCUMENTATIO	IN PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
APA 19511.3-MS	NT/A	
	N/A	
	• • • - •	Final Report
Temperature Compensation in the	'2:17' Type	$\frac{1}{120} \frac{1}{1983} = \frac{1}{100} \frac{1}{1985}$
Magnets		6. PERFORMING ORG. REPORT NUMBER
AUTHOR(.)	······································	B. CONTRACT OR GRANT NUMBER(#)
K. S. V. L. Narasimhan, F. E. Ca C. J. Willman	mp, Bao-Min Ma,	DAAG29-83-C-0007
PERFORMING ORGANIZATION NAME AND ADDR Crucible Materials Corporation	ESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Crucible Research Center P. O. Box 88, Pittsburgh, Pa. 1	.5230	
CONTROLLING OFFICE NAME AND ADDRES		12. REPORT DATE
		March 1986
Post Office Pow 19911		13. NUMBER OF PAGES
Research Triangle Dork NG 277	00	17
MONITORING AGENCY NAME & ADDRESS(II dill	Frent from Controlling Office)	15. SECURITY CLASS. (of this report)
		Unclassified
		15. DECLASSIFICATION/DOWNGRADING SCHEDULE
Approved for public release; d	istribution unlimit	m Report)
Approved for public release; d DISTRIBUTION STATEMENT (of the ebetract enterna NA	istribution unlimit red in Block 20, 11 different from	m Report)
Approved for public release; d DISTRIBUTION STATEMENT (of the ebetract enterno NA SUPPLEMENTARY NOTES The view, opinions, and/or fin those of the author(s) and sho Department of the Army position designated by other documentat KEY WORDS (Continue on reverse elde II necessar)	istribution unlimit red in Block 20, 11 different fro dings contained in uld not be construct n, policy, or decis ion.	ted. m Report) this report are ed as an official sion, unless so
Approved for public release; d DISTRIBUTION STATEMENT (of the abstract onto NA SUPPLEMENTARY NOTES The view, opinions, and/or fin those of the author(s) and sho Department of the Army positio designated by other documentat KEY WORDS (Continue on reverse elde if necessary Magnets, Travelling Wave Tubes, Nd-Co, NdFeB.	istribution unlimit red in Block 20, 11 different from dings contained in uld not be construe n, policy, or decis ion. Temperature Compen	ted. m Report) this report are ed as an official sion, unless so usation, Sm-Co, Pr-Co,
Approved for public release; d DISTRIBUTION STATEMENT (of the ebstrect enterna NA SUPPLEMENTARY NOTES The view, opinions, and/or fin those of the author(s) and sho Department of the Army position designated by other documentat KEY WORDS (Continue on reverse elde II necessary) Magnets, Travelling Wave Tubes, Nd-Co, NdFeB.	istribution unlimit red in Block 20, 11 different from dings contained in uld not be construe n, policy, or decis ion. and identify by block number) Temperature Compen	ted. m Report) this report are ed as an official sion, unless so sation, Sm-Co, Pr-Co,
Approved for public release; d DISTRIBUTION STATEMENT (of the obstract enternation NA SUPPLEMENTARY NOTES The view, opinions, and/or fin those of the author(s) and sho Department of the Army position designated by other documentat KEY WORDS (Continue on reverse side if necessary) Magnets, Travelling Wave Tubes, Nd-Co, NdFeB. ABSTRACT (Continue on reverse side if necessary) Development of temperature compo and NdFeB type of alloys. A numproduce energy product in excess Computer programs were developed then processed successfully into materials can produce temperature not exceeding 22 MGOe. Further pensated magnets with an energy	istribution unlimit red in Block 20, 11 different from dings contained in uld not be construct n, policy, or decis ion remperature Compen met identify by block number) Temperature Compen ensated magnets was mber of alloys have s of 40 MGOe in the d for identifying k o temperature compe re compensated magn work is necessary product execution	this report are ed as an official sion, unless so undertaken in both '2:17' been identified that can uncompensated material. ey compositions that were nsated magnets. Current ets with an energy product to develop temperature com- 30 MCOc

.

Proposal Number 19511-MS Funding Document DAAG29-83-C-0007

Temperature Compensation in the '2:17' Type Magnets

Pr and Nd Substituted '2:17' Magnets for Elevated Temperature Application

The program was conducted in three phases. Phase I dealt with identifying composition ranges between  $RCo_5-R_2Co_{17}$  that can produce maximum induction. Anisotropy field and saturation magnetization were measured on a series of Sm, Pr, and Nd alloys. The results indicate that Pr, Nd or a combination of both can be effectively utilized for increasing the saturation induction and yet maintain reasonable values of anisotropy field. Energy products greater than 40 MGOe are possible.

Phase II addressed the issue of temperature compensation in the '2:17' type of magnets to permit the utilization of these magnets in travelling wave tubes operating at 200-250°C. A computer assisted composition selection procedure was adopted that allowed pinpointing compositions that will yield best temperature compensation. Magnets fabricated from the identified compositions produced temperature coefficient that satisfied the program goals (+0.0008% per °C over a temperature range of -50 to room temperature and -0.007% per °C over room temperature to 250°C).

Phase III dealt with developing temperature compensation in the NdFeB type of alloys. Nearly 3000 compositions were generated through the computer. Combinations of light rare earth with heavy, heavy rare earth-with heavy and two heavy rare earth with light rare earth were examined. Two compositions were chosen and processed into magnets.

Listed below are their composition, magnetic properties, and temperature coefficients.

Magnet #1: (Nd<sub>0.24</sub>Ho<sub>0.70</sub>Er<sub>0.06</sub>)<sub>15</sub>Fe<sub>79</sub>B<sub>6</sub>, ATC-112 + 24% Alloy #6

B <sub>r</sub> = 7,900 Gauss H <sub>c</sub> = 7,700 Oe H <sub>ci</sub> = 14,400 Oe	Temperature Range	Temperature Coefficient α (% per °C)	
$BH_{max} = 15.2 MGOe$ H <sub>k</sub> = 13,000 Oe	-50 to +150	-0.0345 (-0.013 predicted)	/
Density = 7.8 gm/cc	-50 to +25 +25 to +100	+0.0081 -0.0399	

M

Magnet #2: (Nd<sub>0.24</sub><sup>Ho</sup>0.64<sup>Dy</sup>0.13)15<sup>Fe</sup>79<sup>B</sup>6, ATC-110 + 18% Alloy #4

$B_r = 7,700 \text{ Gauss}$ $H_c = 7,700 \text{ Oe}$ $H_{c1} = 20,600 \text{ Oe}$	Temperature Range ( <sup>O</sup> C)	Temperature Coefficient a(% per °C)	· · · · · · · · ·
$BH_{max}^{T} = 14.8 MGOe$ $H_{k} = 18,300 Oe$ Density = 7.98 gm/cc	-50 to +150 -50 to +75 -25 to +75	-0.0299 (-0.012 predicted) -0.0033 -0.0066	Code
	-50 to 0	+0.0152	JIOF

## IEEE TRANSACTIONS ON MAGNETICS, VOL. MAG-21, NO. 5, SEPTEMBER 1985

#### TEMPERATURE COMPENSATION IN THE '2:17' TYPE MACNETS

F. E. Camp, K. S. V. L. Narasimhan, and J. C. Hurt

#### ABSTRACT

Compensation for the temperature dependence of magnetic flux has been investigated in the '2:17' type permanent magnet alloys. A computer assisted composition selection procedure was adapted and one of the identified compositions, Sml.18Dy.81Cd.01Co9.76Fe4.19 Cu.83Zr.34, was processed into magnets. The measured temperature coefficients correlated satisfactorily with the prediction. Dysprosium was found to be a better substituent for Sm than either Gd or Er in providing temperature coefficient of linearity.

#### INTRODUCTION

Temperature compensated magnets have found application in devices such as gyros, accelerometers, and to a certain extent, in travelling wave tubes. Samarium cobalt magnets have been successfully temperature compensated by alloying with heavy rare earths<sup>1-4</sup>. For a fully compensated SmCo<sub>5</sub> magnet, the maximum energy product attainable is 7.0 MGOe<sup>5</sup>. Further miniaturization of devices is possible only if the BH<sub>max</sub> is increased further to possibly 16-20 MGOe. We have investigated rare earth-cobalt '2:17' type of alloys to improve the BH<sub>max</sub> of a fully compensated magnet.

Temperature compensation in '2:17' type alloys has been investigated by various authors6,7. However, a generalized approach for identifying the alloys that can provide the needed temperature coefficient has not been made. Such an approach is necessarv to permit alloy development suited to the need of a particular device since the flux in the gap is dependent not only on the characteristics of the magnet but also on the temperature variation of the device gap. This publication presents an analytical approach to composition selection and the results on an alloy from this selection.

#### EXPERIMENTAL

The molar composition of the base alloy was  $Sm_2Co_{9.76}Fe_{4.15}Cu_{.83}2r_{.34}(Sm_2TM_{15})$ . This and four heavy rare earth analogs. SmDyTM\_{15}, SmErTM\_{15}, SmGdTM\_{15}, and SmHoTM\_{15} were each induction melted under argon gas and cast into split copper molds. The ingots were crushed to 75µm powder and thermomagnetic measurements made over the temperature range of -60°C to 220°C. The Faraday technique was used with an applied field of 5 kilo-oersteds.

The composition that was predicted to have the smallest temperature coefficients was Sm<sub>1.18</sub>Dy.g1Gd.01 TM<sub>15</sub>. It was induction melted by the above procedure and pulverized to -60 mesh powder. Jet milling with irgon gas produced an average particle size of  $\sim$ 5 microns. The base alloy, Sm<sub>2</sub>TM<sub>15</sub>, was also jet milled to  $\sim$ 5 microns. Magnets (lem diameter x 7cm long) were pressed, sintered between 1150-1200°C for I hour, solutionized for 5 hours between 1120-1160°C, then quenched. They were then further heat treated at 500-850°C and slowly cooled to 400°C then naturally cooled to room temperature.

Camp and Narasimhan are with Colt Industries, Urucible Research Center, Pittsburgh, PA 15230, and Hurt is with the Army Research Office, Research Triangle Park, NC 27709. After hysteresis loops were determined for centerless ground and cut samples, temperature coefficients of magnetization were measured with an oscillating sample magnetometer. The magnetized sample (0.75cm diaLeter x 3cm long) and the pick-up coil were positioned within a cooling/heating environmental chamber. When thermal equilibrium was reached, the sample was driven through the coil at a constant speed. The magnetic flux so generated was measured and integrated over the length with a 6.5 digit voltmeter input to a desk computer.

#### RESULTS AND DISCUSSION

The thermomagnetic data determined by the Faraday technique are shown in Figure 1. The base alloy has a large negative temperature coefficient of magnetization over the entire temperature range, while the curves for the alloys containing Dy, Er, Gd, or Ho show less variation and have positive temperature coefficients in their cooler regions. This phenomenon, which is typical of heavy and light rare earth-transition metal (Fe, Co) alloys of the 1:5 and 2:17 stoichiometry, suggests a method of approaching temperature independence of magnetization with the judicious selection of heavy rare earth combinations and concentrations.

We have generated a number of theoretical magnetization curves from these experimental data. A simplifying assumption was made that, at a given temperature, magnetization is an additive property with the number of rare earth atoms. Implicit in this assumption is that crystal field effects are unchanged by the addition of heavy rare earths.

Incremental interpolations were calculated between the base alloy and each heavy rare earth analog. These interpolations resulted in families of curves or data arrays for each heavy rare earth. A large number of magnetization vs temperature curves were then computer generated from these data arrays. Various concentrations of either two, three, or all four heavy rare earths were considered.



Figure 1. Magnetization vs temperature data measured for the Sm and heavy rare earth substituted for Sm alloys. TM=Co<sub>9.76</sub>Fe<sub>4.19</sub>Cu<sub>1.83</sub>Cr<sub>.34</sub>.

Due to space limitations, we have selected certain families of curves for inclusion here on the basis of two criteria--those showing the greater linearity, and others displaying the effects of all the heavy rare earths considered. Figures 2, 3, 4 and 5 show the hypothetical curves for two heavy rare earth additives. The formulations predicting the lowest temperature coefficients are shown on these figures and are listed in Table I. The coefficients were calculated by the least squares method.



Figure 2. Computer generated curves for the Gd and Ho substituted alloys.



Figure 3. Computer generated curves for the Dy and Gd substituted alloys.



Figure 4. Computer generated curves for the Dy and Er substituted alloys.



Figure 5. Computer generated curves for the Er and Gd substituted alloys.

# Table I. Alloys with Predicted Low Temperature Coefficients of Magnetization

Alloy	Temperature -50 to 25°C	Coefficient, <u>25°C to</u>	250°C <sup>−1</sup>
Sm <sub>1.18</sub> Dy.81 <sup>Gd</sup> .01 <sup>TM</sup> 15	+.00624	003	788
Sm <sub>1.18</sub> Gd.81 <sup>Ho</sup> .01 <sup>TM</sup> 15	+.00713	003	793
Sm <sub>1.42</sub> Er.09 <sup>Gd</sup> .49 <sup>TM</sup> 15	+.00298	016	54
Sm1.18 <sup>Gd</sup> .81 <sup>Dy</sup> .01 <sup>TM</sup> 15	+.00705	009	901
Sm <sub>1.18</sub> Ho.81 <sup>Gd</sup> .01 <sup>TM</sup> 15	+.012	012	21

Figures 6 and 7 show typical curves for three heavy rare earth components, and Figure 8 contains some curves for all four heavy rare earths. There is less linearity exhibited in these multi-component predictions than was evident in the two component results.

The alloy predicted to have the lowest temperature coefficient, Sm1.18Dy.81Gd.09TM15, was prepared and fabricated into a magnet. The following magnetic properties were measured:  $B_{T}=8,900$ Gauss,  $H_{c1}$ =7,750 Oersted,  $H_{c}$ =6,300 Oersted, and BHmax=16.5 MGOe. The results of temperature coefficient measurements are shown in Figure 9 along with the predicted curve for this alloy. Although the experimental curve lies below the predicted curve (absolute magnetization values smaller by 5%), there is good agreement between the shapes of the curves and their respective slopes. The low temp-erature coefficients are +.0008%°C<sup>-1</sup>(experimental) versus +.00624% oc-1 (predicted). The other set of coefficients is -.00774%°C<sup>-1</sup>(experimental) and -.00788Z°C-1(predicted). This is indicative of the validity of this procedure to predict the general shape of magnetization versus temperature curves for various alloys incorporating heavy rare earths for cemperature compensation.

Previous work has shown the temperature compensation benefits of  $Gd^8$  and  $Er^7$ , with which we concur. The former has the disadvantage of lowering magnetization values more so than others. We have shown that Dy is also an excellent candidate. It will provide linearity over a broader temperature range than Er does. This is graphically displayed by comparing curves 1 and 5 in Figure 4, where the higher Dy content (Curve 5) shows less variation over the  $-50^{\circ}C$  to  $222^{\circ}C$ temperature range than the corresponding Er curve. It is also displayed by noting the difference in curve shapes between Figures 6 and 7, where Dy and Er, respectively, are dominant in otherwise identical ternary heavy rare earth systems. Dy has an additional economic advantage as being the least expensive of the four heavy rare earths considered.



Figure 6. Computer generated curves for three component rare earth alloys.



Figure 7. Computer generated curves for three component rare earth alloys.



Figure 3. Computer generated curves for four component rare earth alloys.



Figure 9. Experimental and predicted temperature dependence of magnetization data for Sm<sub>1.18</sub> Dy.81Gd.01TM<sub>15</sub> alloy. The numbers on the curves refer to the temperature coefficient of magnetization over the low (-50° to 0°C) and high temperatures (0° to 250°C).

#### CONCLUSIONS

The proposed method of predicting the behavior of heavy rare earth additions to alloy systems may be used in place of the "trial and error" procedures. Dy additions result in improved temperature compensation over a broad temperature range. Gd is effective over the same range, but significantly lowers the magnetization. Erbium will give results similar to Dy, but over a smaller temperature range. Dy has the added advantage of being the least expensive.

#### Acknowledgments

We thank E. J. Dulis for his interest in this work and M. Quinn for his help in the earlier part of the program.

This work was supported by a grant from Army Research Office Contract No. DAA629-83-C-007.

#### REFERENCES

- 1. M. G. Benz, R. P. Laforce and D. L. Martin, AIP Conf. Proc., No. 18, 1173 (1974).
- F. G. Jones and M. Tokunaga, IEEE Trans. Magn., Vol. MAG-12, 968 (1976).
- K. S. V. L. Narasimhan, M. G. H. Wells and D. V. Ratnam, J. App. Physics, 49, 2072, (1978).
- K. S. V. L. Narasimhan, J. App. Physics, Vol. 52, No. 3, 2512 (1980).
- K. S. V. L. Narasimhan, Fifth International Workshop on Rare Earth-Cobalt Permanent Magnets and Applications, Roanoke, Va., June 1981, University of Dayton, 629 (1981).
- F. Rothwarf, H. A. Leupold, A. Tauber, J. T. Breslin, R. L. Bergner and J. J. Winter, The Rare Earths in Modern Science and Technology, Vol. 2, edited by G. J. McCarthy, J. J. Rhyne and H. B. Siber (Plenum, New York 1980).
- H. F. Mildrum, J. B. Krupar and A. E. Ray, J. Less-Common Met. 93, 261 (1983).
- R. L. Bergner, H. A. Leupold, J. T. Breslin, F. Rothwarf and A. Tauber, J. App. Physics, 50, 2349, (1979).

The material contained in this paper is intended for general information only and should not be used in relation to any specific application without independent study and determination of its applicability and suitability for the intended application. Anyone making use of this material or relying thereon, assumes all risk and liability therefrom.

### IEEE TRANSACTIONS ON MAGNETICS, VOL. MAC-21, NO. 5, SEPTEMBER 1985

Pr AND Nd SUBSTITUTED '2:17' MAGNETS FOR ELEVATED TEPERATURE APPLICATION

C. J. Willman and K. S. V. L. Narasimhan

#### ABSTRACT

Results of Pr. Nd and (PrNd) substitution in the '1:17' type permanent magnet alloys are presented. Microstructural studies, crystal structure, anisotropy field (H<sub>A</sub>), Curie temperature (T<sub>C</sub>), and saturation magnetization (M<sub>S</sub>) were used as tools for the evaluation of these alloys. Pr. Nd and (PrNd) increases M<sub>S</sub> without significantly affecting the T<sub>C</sub>. H<sub>A</sub> decreases when Sm is replaced by Pr. Nd or (PrNd). Several of the alloys investigated show promise to be permanent magnets.

#### INTRODUCTION

'2:17' type of permanent magnets have been in production for the last several years. The general stoichiometry is about  $RM_{7,4-7,7}$  where M is a combin-ation of Fe. Co. Cu.  $Zr^{4,-}$ . The maximum energy product attainable is 33 MGOe<sup>2</sup>. Further increase in the BHmax is possible if the saturation magnetization (Mg) is increased by increasing the number of moment carrying atoms, i.e., Fe and Co. Samarium has a very small magnetic moment to contribute. Shimoda at al3 and Ray et al4 have increased the M value from 7.4 to 3.35 by increasing the iron content and successfully made magnets. The Mg value reported was 11,500 - 11,300 Gauss. The maximum energy product attainable is ]3-35 MOOe assuming the anisotropy field is high and  $3H_{max}$  can be approximated to  $3r^{2/4}$ . The increase in iron content alone is not able to increase the saturation magnetization past 12,000 Gauss. It is possible to increase the induction by decreasing the copper content since copper acts as a diluent for the magnetic moment. However, copper is vital for the generation of coercive force and hence cannot be reduced significantly. We, therefore, added Pr and Nd to increase the saturation induction and the results of these investigations are presented in this paper.

#### EXPERIMENTAL PROCEDURE

The alloys were prepared by induction melting the elements and casting the alloy into a copper mold.

- <u>X-ray Data</u>: X-ray diffraction data was obtained using a Norelco X-ray Generator (+0kV, 12mA) in conjunction with a 11+.7 Debve Scherrer camera. CrKs radiation was used on -100 mesh alloy powher. The resulting powder patterns were indexed. An iterative least squares technique was used to halculate the lattice parameters of each alloy.
- 1. Curie Temperature Evaluation: Homogenized allow was crushed to -100 mesh and TMA (thermomagnetic analysis) was used to determine  $T_{\rm C}$  and other magnetic phases. A field of 1 kOe was used for this study.
- 3. Saturation Magnetization: Homogenized allow was crushed and ground to ~400 mesh in argon. Ali~ quots of 50-80 mg were measured into the VSM vibrating sample magnetometer) holder. The VSM was calibrated with a Ni standard using JNI = 54.40 emu/g at 295K. Honda plots were extrapolated to obtain J saturation.

Willman and Narasimhan are with Colt Industries, Crucible Research Center, Pittsburgh, PA 15230. Anisotropy Field: Alloy was crushed to -325 mesh. The powder was then dispersed in paraffin wax and aligned in a 25 kOe field and allowed to harden in the presence of a field. The field required to saturate in the direction parallel and perpendicular to the easy direction were evaluated. HA was determined as the field required to saturate the material in the perpendicular direction.

A STATE AND SHALL AND A SALES AND SALES AND SALES

#### DISCUSSION

The X-ray diffraction patterns of the alloys studied could be indexed to a  $\text{Th}_2\text{Ni}_2$ - (hexagonal) type structure. This structure is characteristic of high-temperature, disordered  $\text{Sm}_2\text{Co}_17^5$ . The ascast alloys were 2-phase. With increased Fe substitution for Co and with rare earth substitutions for Sm, more complex microstructures were observed. Homogenization of the as-cast structure was

possible between 1165-1185°C for most alloys (see Figures 1 through 3). Those alloys having complex microstructures were more difficult to homogenize.





Figure 2a 125X \*RE=Nd, x=0.1, v=0.2 Prior to Heat Treatment



Figure 2b 125X \*RE=Nd, x=0.1, v=0.2 After Heat Treatment



Figure 3a 125X \*RE=Nd, x=0.3, v=0.4 Prior to Heat Treatment



Figure 3b 125X \*RE=Nd, x=0.3, v=0.4 After Heat Treatment

Most secondary phases were able to be solutionized with the exception of a white phase. This phase was intermined to be an Fe-Co rich phase. The presen e of this phase was particularly prominent in those allovs (as-cast condition) having the largest substitutions of Fe for Co (v=0.3, 0.-).

Figures - and 5 illustrate the magnetization VS temperature blots obtained for these allovs. As expected, Fe substitution for Co was found to increase the Curie temperature. Pr. Nd, 50%Pr-50%Nd substitution for Sm tid not affect the Curie temperature significantly.

The saturation magnetization of these alloys increases with increasing Fe, Pr, Nd, or Pr/Nd substitutions. Some of the alloy samples were exception-ally difficult to saturate and consequently  $M_S$  was more difficult to measure.



Figure 4. Temperature dependence of magnetization at an applied field of 1 kOe.

Table I illustrates the magnetization observed at an applied field of 18 kG, and the value of the magnetization extrapolated to infinite field. Calculation of the theoretical  $3H_{max}$  ( $B_s^{-1/4}$ ) is also included in Table I.

The substitution of Pr. Nd, Pr/Nd for Sm in most cases decreased the anisotropy field,  $H_A$ . Fe substitution for Co usually decreased the anisotropy field. The effect of these substitutions is illustrated in Figures 6 and 7. Nd and Pr in the '2:17' alloys prefer a basal plane<sup>6</sup> and substitution of these elements reduces the overall preference of the rare earth sublattice to the magnetically easy C-direction, hence a decreased anisotropy field. The preference of iron sublattice in the '2:17' alloy is in the basal phase and the effect of iron substitution is also to decrease the inisotropy field.



Figure 5. Temperature dependence of magnetization at an applied field of 1 kOe.

Table I. Base Alloy:  $Sm_{1-x}^{(RE)}x^{(Co}.90-v^{Fe}v^{Cu}.08^{Zr}.02)^{3.35}$ 

<u>Allov</u>	5.3kg <sup>31</sup>	de v Extradolatea	35 <sup>1</sup> - Theo. SH- <sub>33</sub> MCCe
San), San),", San), San),", San)' (San),",		_]. 733 733 734	13.90
24, (m),(,,7m),() 24, (m),(,7m),() 24, (m),(,7m),()	12,056	-1,133 -1,3	22.22 16.90 40.31
?또, (m),),/m(),)	11,341	12.39	-1.29
?또, (m),),/m(),)	12,1-1	12.376	28.29
?또, (m),),/m(),_	12,-08	12.775	-7.29
?v, (m), ;, (m), ;	12.911	12,005	-23
?v, (m), ;, (m), ;	12.123	12,025	
?v, (m), ;, (m), ;	12.179	12,044	
Nd, (=),1,7=).1	11,346	12,113	16.11
Nd, (=),1,7=).1	12,715	12,319	-1.18
Nd, (=),1,7=).2	11,563	11,353	13.12
3d, cm).3, cm).2	11,984	12,139	16.34
3d, cm).3, cm).3	12,308	12,942	-1.37
3d, cm).3, cm).4	12, <b></b> 7	12,653	-5.30
3d, (₩),3,7=0,2	12,738	12,984	-2.13
3d, (₩),3,7=0,3	13,107	13,231	-3.76
3d, (₩),5,7=0,.	13,312	13,773	-3.31
2: Nd, (=), 1, (=), 2 2: Nd, (=), 1, (=), 2 2: Nd, (=), 1, (=), 2 2: Nd, (=), 1, (=), 2	11,340 12,448 12,984	11,912 12,602 13,130	15.47 19.70 41.16
Pr: Nd. (=0.3, 7=0.2	12,305	12,1-3	)6.90
Pr: Nd. (=0.3, 7=0.3	12,398	12,370	-11
Pr: Nd. (=0.3, 7=0.3	12,385	12,390	-1.5-
2r Na.(=0.5,7=0.2 2r Na.(=0.5,7=0.3 2r Na.(=0.5,7=0.3	12,-08 12,266	12,011	)))) 44.)]d 43.)?)

"Measurement performed on non-homogenized sample.

2

best available copy.

The results indicate that Pr. Nd. or a compination of both iam be effectively utilized for increasing the saturation induction and vet maintain reasonable values of anisotropy field. These allows could be used for the fabrication of magnets. In an allow containing (=0.3, a combination of Pr and Nd is more effective in maintaining the inisotropy field than either Nd or Pr alone. This affects that changes the stabilization energy.

ことのないではない シングリング

		: 1	· ] 4
• :	39	:-	5ē
;	32	:5	1
: :	:6	15	35
:: -	÷9	:9	.:5
	÷ 9	4.7	
			. + : +
· -		-	DC
· —			
	52 34	58	÷0 37
	52 34 32	:a 33 22	+0 37 31
2 2 3 2 3 2 3	32 34 32 (Nd) <sub>X</sub> (Co <sub>30 - V</sub> F	58 33 22	34 ÷0 37 31
2 2 3 2 3 2 3 2 3 2 3 2 4 2 4	52 34 32 7 Na) <sub>V</sub> (Co <sub>30 - V</sub> F 7 1 0 2	58 33 22 9,,200 <u>8 2,00 2,9,18</u> 7, 1 2 3	30 37 31 / + 0,4

4 + 3	39	\$7	58
<ul> <li>.</li> </ul>	34	57	35
(122	50	53	24
e + 2 5 -	39	29	24

Figure 5. Anisotropy field matrix for alloys studied.



Figure 1. Typical magnetization vs  $H_A$  in easy and har: Hirections for one set of alloys.

#### CONCLUSION

The effect of Pr. Nd or a combination of Pr and Nd is to increase the saturation magnetization without adversely effecting the anisotropy field. A few of the compositions show promise for utilization as permanent magnets. The potential energy product of several of the alloys exceed 40 MGOe.

#### Acknowledgments

We want to thank Dr. J. C. Hurt and Mr. E. J. Dulis for their interest in this work.

This work was supported by a grant from Army Research Office Contract No. DAA629-33-C-007.

#### REFERENCES

- T. Ojima, S. Tomizawa, T. Yoneyama and T. Hori, IEEE Trans. Mag., MAG-13, p. 1317 (1977).
- R. K. Misnra, J. Thomas, T. Yoneyama, A. Fukuno and T. Ojima, J. Applied Physics, 52, p. 2517 (1981).
- T. Shimoda, I. Okonogi, K. Kasai and K. Teraisni, IEEE Trans. Mag., MAG-16, p. 991 (1980).
- 4. A. E. Ray, H. F. Mildrum and J. B. Krupar, IEEE Trans. Magnetics, MAG-19, p. 2044 (1983).
- 5. (a) Y. Khan, Acta Cryst. 1329, p. 2503 (1973).
  (b) W. Ostertag and K. Strnat, Acta Cryst. 21, p. 560 (1966).
- 6. W. E. Wallace and K. S. V. L. Narasimhan, "Science and Technology of Rare Earths," p. 193-413, Academic Press, 1980; edited by E. C. Subbarao and W. E. Wallace.
- 7. K. S. 7. L. Narasimhan, W. E. Wallace, R. D. Hutchens and J. E. Greedan, AIP Conf. Proc. 18, p. 1212 (1973).

The material contained in this paper is intended for general information only and should not be used in relation to any specific application without independent study and determination of its applicability and suitability for the intended application. Anyone making use of this material or relying thereon, assumes all risk and liability therefrom. NdFeB MAGNETS WITH ZERO TEMPERATURE COEFFICIENT OF INDUCTION

> Bao-Min Ma, K. S. V. L. Narasimhan\*, and J. C. Hurt\*\*

\*Crucible Materials Corporation Crucible Research Center P. O. Box 88, Pittsburgh, Pa. 15230

\*\*U. S. Army Research Office
 P. O. Box 12211
Research Triangle Park, N. C. 27709

#### ABSTRACT

Temperature compensation for the induction of NdFeB type magnets has been investigated. A computer assisted alloy selection method was adopted to identify composition of zero temperature coefficient of induction over -50 to 200°C. Selected alloys were processed into magnet by the conventional powder metallurgy method. The experimental temperature coefficient on the sintered magnet correlated with the prediction satisfactory. Holmium is an essential ingredient required for temperature compensation of NdFeB magnets. A magnet,  $(Nd_{0.23}Ho_{0.64}Dy_{0.13})_{15}Fe_{79}B_6$  with  $B_r$  of 7,700 Gauss,  $H_c$  of 7,700 Oe,  $H_{ci}$  of 20,600 Oe,  $BH_{max}$  of 14.8 MGOe and temperature coefficient of -0.029% per <sup>o</sup>C over -50 to +150 was obtained.

#### INTRODUCTION

Neodymoum-iron-boron magnets have high energy product [1-3]. However, the temperature dependence of magnetic induction is about -0.08% to -0.12% per °C over -50 to  $150^{\circ}$ C. We have investigated heavy rare earth alloying to improve the temperature dependence. A computer assisted composition selection procedure developed for SmCo<sub>5</sub> and the 2:17 [4-7] alloys has been extended to NdFeB alloys.

In excess of 3000 alloy compositions were generated from the magnetization data of  $Nd_2Fe_{14}B$  and  $HRE_2Fe_{14}B$  alloys. The magnetization of  $(NdHRE)_2Fe_{14}B$ was computed by adding the Nd and HRE moment linearly. The details are presented in this publication.

#### EXPERIMENTAL

A data base of the temperature dependence magnetization and anisotropy field of  $Nd_2Fe_{14}B$  as well as  $HRE_2Fe_{14}B_8$  (where HRE = Ho, Dy, Er, Tm and Tb) were constructed over -50°C to +250°C at 25°C intervals.

The substitution of heavy rare earth was assumed to replace the Nd sites. The magnetization of the combination of NdHRE<sub>2</sub>Fe<sub>14</sub>B was calculated by adding the Nd and heavy rare earth moment linearly. The temperature coefficient  $\alpha$  is defined as:

# $\alpha$ (% per <sup>o</sup>C) = 100% \* [M(T<sub>2</sub>)-M(T<sub>1</sub>)]/[M(T<sub>1</sub>)\*(T<sub>2</sub>-T<sub>1</sub>)]

and calculated by a least square linear fitting. A Hewlett-Packard 85 computer with memory space of 32K was utilized to conduct these calculations.

Two criteria were set for the composition selection: (1) the selected composition must have a saturation magnetization greater than 7,500 Gauss at  $25^{\circ}$ C, and (2) the temperature coefficient of the induction must be less than -0.01% per °C over -50 to +200°C. The replacement of Nd with each individual heavy rare earth were scanned from 0 to 100% at 2% increments. Both the temperature dependence magnetization curve and temperature coefficient  $\alpha$  were examined simultaneously. Neodymium mixed with two or three heavy rare earths were also examined at 2% increments respectively.

Selected alloy compositions were prepared by vacuum induction melting and cast into a copper mold. Ingots were processed into magnets by the traditional powder metallurgy method utilizing a process similar to that used for SmCo<sub>5</sub>.

The temperature coefficient of induction,  $\alpha$ , of the sintered magnets with length to diameter ratio (L/D) of 1.0-1.2 were measured by the open circuit technique (OCT) [3] from -50 to +150°C at 25°C intervals. The demagnetization curves of the sintered magnets were also measured by closed circuit technique (CCT) for the same temperature range.

The Curie temperature of the cast alloy or sintered magnet were measured by thermomagnetic analysis (TMA) under an applied field of 4 kOe. Samples were crushed to -400 mesh powder then sealed under inert atmosphere into a Vycor capsule for measurement.

#### RESULTS AND DISCUSSION

Two of the  $R_2Fe_{14}B$  alloys,  $Dy_2Fe_{14}B$  and  $Tb_2Fe_{14}B$ , have temperature coefficient  $\alpha$  less than -0.01 per <sup>o</sup>C as shown in Table I.

Table	I.	The Saturation Magnetization M <sub>S</sub> at
		25°C and Temperature Coefficient
		of Heavy Rare Earth HRE2Fe1/B Allovs

$R_2Fe_{14}B$	M s	Temperature Coefficient
R=	(Gauss)	<u>% per °C(-50 to +200)</u>
Ho	7,060	+0.016
ТЪ	5,970	-0.007
Dy	6,160	+0.007
Gđ	7,450	-0.053
Er	7,890	-0.042
Tm	9,810	-0.078

Owing to the higher magnetic moment of  $Nd_2Fe_{14}B$ , the combination of Nd with one of the heavy rare earth results in an increased magnetization. The slope of the overall curves can also be adjusted by varying the relative amount of Nd-HRE combination. Illustrated in Figure 1 are the temperature dependence magnetization curves of  $(Nd_{1-x}Ho_x)2Fe_{14}B$ , where x = 0 to 1.0 in steps of 0.2.



Figure 1. Computer simulated temperature dependence magnetization curves of  $(Nd_{1-x}Ho_x)$  $2Fe_{14}B$ , where x = 0, .2, .4, .6, .8, and 1.0.

The combination of Nd with other single heavy rare earth were also examined for the entire composition range at 2% increments. Similarly, a combination of Nd with either two or three heavy rare earths were examined. Listed in Table II are the representative compositions of low temperature coefficient alloys with their saturation magnetization at  $25^{\circ}$ C. Table II. The Saturation Magnetization at 25°C and the Temperature Coefficient of R<sub>2</sub>Fe<sub>14</sub>B Type Magnet Generated by Computer Aid Alloy Composition Selection Method

* (	of Ra	re E	arth	in	R2 Fe	1 4 B	Ms ( 25 )	Temper Coeffi (% pe	ature cient r °C)
Nd	<u>Ho</u>	Dy	Gd	Er	<u>Ta</u>	ТЬ	(Gause)	<u>-50 to 150</u>	<u>-50 to 200</u>
9	91						7800	+0.021	-0.006
8	85		7				7700	+0.018	-0.008
5	85				10		7710	+0.021	-0.008
10	55	35					7400	+0.015	-0.009
8	85			7			7720	+0.021	-0.007
6	85				9		7760	+0.020	-0.010
10	86					4	7770	+0.017	-0.008
10	72	16	2				7650	+0.015	-0.010
14	40	40	6				7710	-0.000	-0.021
8		38		52		2	7660	+0.001	-0.035
8	84			6	2	-	7770	+0.019	-0.009

Figures 2 and 3 show the computer simulated curves for various heavy rare earth containing  $Nd_2Fe_{14}B$ alloys. From these curves, selected alloy compositions were processed into magnets. The properties of these low temperature coefficient magnets are listed in Table III.



Figure 2. Computer simulated temperature dependence magnetization curves of (NdHoEr)<sub>2</sub>Fe<sub>1</sub>4B, (NdHoGd)<sub>2</sub>Fe<sub>1</sub>4B, and (NdHoDyGd)<sub>2</sub>Fe<sub>1</sub>4B on the corresponding sintered magnets with slightly higher Nd content.



Ċ

Figure 3. Computer simulated temperature dependence magnetization curves of (NdHoDy)<sub>2</sub>Fe<sub>14</sub>B, (NdHoDyGd)<sub>2</sub>Fe<sub>14</sub>B and (NdHoEr)<sub>2</sub>Fe<sub>14</sub>B of the corresponding low temperature coefficient sintered magnets.

# Table III.Magnetic Properties of Temperature<br/>Compensated R2Fe14B Type Magnet

	1 05	RIN	RzFi	1]4B		В,	H <sub>e</sub> .	H <sub>c1</sub>	BH	Н,	DENSITY
No	Ho	Dy	En .	Tn	Gø	(GAUSS)	(OE)	(0E)	(MGOE)	(OE)	(ew/cc)
65	35	-	•	-	-	9,800	9,400	16,450	22.8	14,400	7.35
60	36	•	•	4	-	8, 900	7,700	11,950	16.8	6,400	7.06
61	36	-	3	•	-	8,900	8,800	14,900	20.3	10,500	7.24
32	63	-	5	-	-	7,900	7,700	14,400	15.2	13,000	7.80
65	32	•	•	-	3	8,900	7,750	10,850	17.6	8,700	7.11
61	31	7	-	-	1	9, 350	9,000	20,470	20.3	19,850	7,44
29	64	12	-	-	-	7,700	7,700	20,600	14.8	18,300	7.98

Two magnets with the nominal composition of  $(Nd0.24Ho0.70Er0.06)_{15}Fe_{79}B6$ , magnet A, and  $(Nd0.23Ho0.64Dy0.13)_{15}Fe_{79}B6$ , magnet B, were selected for (1) the closed circuit temperature dependence demagnetization curve measurement and (2) the open circuit temperature dependence of induction measurements. Figures 4 and 5 are the temperature dependence demagnetization curves of these two magnets. The temperature dependence magnetic properties of these two magnets are summarized in Figure 6a and 6b respectively. In figures 7 and 8, the temperature dependence magnetization curves of magnet A and B are normalized to their values of -50°C. Shapes of the

Shapes of the computer generated curves and the experimental curves favorably compare. The temperature coefficients are tabulated in Table IV. The other two magnets with higher Nd contents are also listed for comparison.



Figure 4. The temperature dependence demagnetization curves of (Nd<sub>0.23</sub>Ho<sub>0.70</sub>Dy<sub>0.13</sub>)<sub>15</sub>Fe<sub>79</sub>B<sub>6</sub>.



Figure 5. The temperature dependence demagnetization curves of (Nd0.24Ho0.70Er0.06)15Fe79B6.



CANTERNAL CONTRACTOR

おたいなかななな くらいたいがいい

Figure 6a. The temperature dependence magnetic properties of Magnet A.



Figure 6b. The temperature dependence magnetic properties of Magnet B.



- Figure 7. The experimental and computer simulated temperature dependence magnetization of Magnet A normalized to their values of -50°C.
- Figure 8. The experimental and computer simulated temperature dependence magnetization of Magnet B normalized to their values of -50°C.
- Table IV. The Comparison of the Temperature Coefficient a of the Experimental Results with Computer Simulated Results

Magnet	X of R in RisFereBa					Temperature Coefficient a	
	Nd	llo	Dz	Ez	Gd	x per °C (-50 <u>experimental</u>	to +150) <u>simulation</u>
A	24	70		6		-0.034	-0.013
В	23	64	13			-0.029	-0.012
С	61	31	7		1	-0.070	-0.061
D	65	35				-0.074	-0.063

We have extended the computer technique for the computation of anisotropy field utilizing anisotropy field variation with temperature of  $Nd_2Fe_{14}B$  and (HRE) $_2Fe_{14}B$  alloys. The room temperature anisotropy field compare within 5 kOe of the computed fields.

#### CONCLUSION

Computer simulation technique employed produced alloy compositions that compare favorably with experimental observation on sintered magnets. Number of alloys with varying levels of temperature compensation are available from the rare earth-iron-boron alloys.

#### ACKNOWLEDGEMENT

We thank Mr. E. J. Dulis for his interest in this work and the technical assistance of Mr. T. W. Sloan is appreciated.

#### REFERENCES

- K. S. V. L. Narasimhan, J. Appl. Phys. 57, 4081, (1985).
- M. Sagawa, S. Fujimura, N. Togawa, H. Yamamoto and Y. Matsuura, J. Appl. Phys. 55, 2083, (1984).
- 3. R. W. Lee, E. G. Brewer and N. A. Schaffel, IEEE Trans. Magn., MAG-21, 1958, (1985).
- 4. M. G. Benz, R. P. Lorfce and D. L. Martin, AIP Conf. Proc., No. 18, 1173, (1974).
- 5. K. S. V. L. Narasimhan, Proc. Fifth International Workshop on Rare Earth Cobalt Permanent Magnets and Their Applications, Roanoke, Va., June 1981, University of Dayton, p. 629 (1981).
- H. A. Leupold, E. Potenziani, A. Tauber, and H. F. Mildrum, J. Appl. Phys. 55, 2097, (1984).
- 7. F. E. Camp and K. S. V. L. Narasimhan, IEEE Trans. Magn., MAG-21, 1970, (1985).
- K. Sagawa, S. Fujimura, H. Yamamoto, Y. Matsuura, S. Hirosawa, and K. Hiraga, Proc. 8th International Workshop on Rare Earth Magnets and Applications, Ed. by K. J. Strnat, University of Dayton, p. 587 (1985).

#### FIGURES

- 1. Computer simulated temperature dependence magnetization curves of  $(Nd_{1-x}Ho_x)_2Fe_{14}B$ , where x = 0, .2, .4, .6, .8, and 1.0.
- 2. Computer simulated temperature dependence magnetization curves of (NdHoEr)<sub>2</sub>Fe<sub>14</sub>B, (NdHoGd)<sub>2</sub>Fe<sub>14</sub>B, and (NdHoDyGd)<sub>2</sub>Fe<sub>14</sub>B on the corresponding sintered magnets with slightly higher Nd content.

- 3. Computer simulated temperature dependence magnetization curves of (NdHoDy)<sub>2</sub>Fe<sub>14</sub>B, (NdHoDyGd)<sub>2</sub>Fe<sub>14</sub>B and (NdHoEr)<sub>2</sub>Fe<sub>14</sub>B of the corresponding low temperature coefficient sintered magnets.
- 4. The temperature dependence demagnetization curves of (Nd0.23Ho0.70Dy0.13)15Fe79B6.
- 5. The temperature dependence demagnetization curves of (Nd0.24Ho0.70Er0.06)15Fe79B6.
- 6a. The temperature dependence magnetic properties of Magnet A.
- 6b. The temperature dependence magnetic properties of Magnet B.
- 7. The experimental and computer simulated temperature dependence magnetization of Magnet A normalized to their values of  $-50^{\circ}$ C.
- 8. The experimental and computer simulated temperature dependence magnetization of Magnet B normalized to their values of  $-50^{\circ}$ C.

