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**POWDER METALLURGICAL PROCESSING OF MAGNETOSTRICTIVE
MATERIALS BASED ON RARE EARTH-IRON INTERMETALLIC COMPOUNDS**

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ABSTRACT

Procedures are described for fabrication of high density rare earth-iron magnetostrictive compounds by powder metallurgical techniques. The fabrication involves a sequence of steps which includes preparing the pre-alloyed compounds, pulverizing them into a fine powder, compacting in suitable sizes and shapes, and sintering. Samples prepared by these procedures are carefully characterized by scanning electron microscopy, x-ray diffraction, dilatometry, and magnetic measurements. Process steps are found to exert important influences upon densities, microstructure and magnetic properties attained after densification. Investigations on a number of these process steps, including milling time and medium, sintering, and magnetic powder alignment are described.

In the course of characterization of the solid-state sintered compounds, a previously unknown oxygen-stabilized intermetallic compound with the composition corresponding to the formula $R_{12}Fe_{32}O_2$ (R = any of several rare earth elements) was discovered. To prevent the formation of this compound, the rare earth content of alloys before the sintering should be in excess of the stoichiometric composition.

Samples prepared by solid-state sintering showed poor sinterability. High densities were achieved by a liquid phase sintering approach which also resulted in a large grain size. Both large grain size and high density were found to improve the magnetostrictive properties. The magnetostrains observed in the sintered products are comparable to those of arc cast materials.

The results of dilatometry indicate that the liquid-phase sintering kinetics are in reasonable agreement with the concept of a phase boundary reaction as the rate limiting factor. Magnetic powder orientation prior to the sintering is found to improve the magnetostriction substantially. The magnetostrains observed in the oriented compounds, though containing $\approx 20\%$ porosity, are far superior to those of arc cast and highly dense liquid-phase sintered materials.

I. INTRODUCTION

In the last fifty years, the magnetostriction phenomenon has developed from a laboratory curiosity into a major field with ever increasing technical applications. Today magnetostrictive materials are used for the generation of high intensity mechanical vibration, sound and ultrasound. One of the diverse areas of applications of these materials is "Echo Sounders" to detect and locate submarines and ships, to check for cracks, to accelerate chemical reactions and to generate cavitation effects.¹ Magnetostrictive delay lines with their high performances have resulted in their increasing use in magnetic information storage systems in digital computers, aircraft navigation and radar systems.²⁻³ These materials have also recently gained a growing importance in the field of reactor safety, where acoustic monitoring can make major contributions to an early detection of failures in reactors and high temperature systems⁴.

The phenomenon of magnetostriction in rare earth-iron intermetallic compounds has brought about new energy conversion materials available for the above technological applications. Among these compounds, the R-Fe₂ (Laves phase) has recently received considerable attention by many investigators⁵. A brief historical review of the emergence of these compounds will follow this introduction. Outstanding among the properties of these Laves-phase compounds are their high room temperature magnetostrictions⁶ ($\lambda_s > 10^{-3}$ ppm), larger by nearly two orders of magnitude than that of previously known materials. Noteworthy is also their large "ΔE effect"⁷, which is defined as $\frac{E_s - E_0}{E_0}$ (where E_s and E_0 are

respectively the Young Moduli at magnetically saturated and magnetically unsaturated states. The largest "AE effect" known prior to rare earth compounds was that of soft magnetic materials such as well-annealed Ni with values ranging from 1 up to 10%. For rare earth-iron compounds "AE effect" as high as 160% has been reported⁸. Since changes in the modulus of elasticity are related to changes in sound velocity in the material, the huge "AE effect" in these compounds makes them potentially invaluable materials for variable acoustic delay lines and variable frequency resonators.

However, the realization of the full potential of rare earth-iron compounds in these applications depends on the successful fabrication of these materials in suitable sizes and shapes. Since the Laves phases, like most intermetallic compounds, are extremely brittle, they do not lend themselves to conventional fabrication processes such as machining or casting. This research is, therefore, concerned with studying the capability of powder metallurgy as a method of manufacturing these materials with appropriate magnetic properties. The objective of the investigation has been directed toward studying magnetostrictive properties of the powder metallurgically-prepared products, and characterizing the parameters involved in the processing such that through proper control of these parameters, parts with improved magnetostrictive properties can be made.

Following the introduction, after a brief historical review of the subject in Chapter II, Chapter III presents a description of the experimental methods and procedures employed in this research. Chapter IV describes some details of the powder metallurgical processing of the Laves

phase compounds. Chapter V contains the solid state sintering studies of the Laves phases: First, the possibility of tailoring the magnetic behavior of Laves phases is discussed, then, the effects of changes in the various processing parameters such as milling time and medium, compacting pressure, sintering temperature and duration on the sintered products are described. Also in this chapter, the presence of a previously unknown phase, called the β compound⁹, is reported and means for controlling its formation discussed. Chapter VI is devoted to the crystal structure determination and some magnetic properties of the discovered new phase, β -compound. Liquid-phase sintering studies¹⁰ are described in Chapter VII, while Chapter VIII gives the description of various experimental procedures for static and dynamic magnetostriction measurements along with the data obtained for differently processed materials. Another important advantage of a powder metallurgical approach is introduced in Chapter IX which constitutes the preparation of grain oriented Laves phases. These materials are reported to have greatly enhanced magnetostrictive properties¹¹. Summary and conclusions based on the experimental results along with further avenues of exploration are presented in Chapter X.

II. BACKGROUND AND HISTORICAL REVIEW

The magnetostrictive phenomenon in magnetic metals has been known to man as far back as 1842, when J. P. Joule observed it in a piece of iron for the first time. It was not until 1929 that the possibility of using these materials as mechanical oscillators was considered by Pierce, who showed that the resonance of metal rods could be used for the frequency control of vacuum tubes¹². Before the 1960's the choice of magnetostrictive materials, as transducer elements, was limited to nickel and its alloys, piezoelectric crystals such as quartz and polarized ferroelectric ceramics such as barium titanate. At that time, it was being gradually recognized that although the rare earths resemble one another chemically as well as in many of their physical properties, they do have extremely different magnetic properties. They exhibit the largest known magnetic moments, as high as $10 \mu_B$ ¹³, and tremendous magnetic anisotropies, making it possible to alloy them together to obtain a wide range of substances with different magnetic properties. This striking manifestation of variety in magnetic properties was basically attributed to the unfilled 4f electron shells of these materials. Neutron studies as well as other measurements (such as transport properties, magnetic susceptibility, Mössbauer Spectroscopy, yielded valuable information on the magnetic properties of the rare earths.

The potential application of rare earths for development of highly efficient ultrasonic transducers was not raised until Legvold et al.¹⁴ found that single crystals of dysprosium and holmium both showed, at low temperatures, magnetostrictions of some two orders of magnitude

greater than nickel and its alloys. Some explanations regarding the temperature dependence and atomic origin of the high magnetostrictions in these metals are given in the literature.¹⁵⁻¹⁶ A major drawback in the practical applications was the low temperatures required for the operation of transducers using those materials with such low ordering temperatures. In this respect, Gadolinium has the highest Curie point of $17\pm 1^\circ$, but it is almost non-magnetostrictive. An investigation on the possible magnetostriction of various rare earth intermetallic compounds was started. Several groups of rare earth and transition metals along with some of their magnetic properties had already been reported¹⁷. Noteworthy among those was the binary system R-T₂ (where R represents any of several rare earth or yttrium atoms and T represents Fe, Co, or Ni). Subsequent measurements showed that R-Fe₂ in this system had spectacular room temperature magnetostrictions¹⁸⁻¹⁹, the highest among rare earth-transition metal as well as among the other rare earth-iron intermetallic compounds.

Magnetism Background

R-Fe₂ compounds form in the cubic Laves or C₁₅ phase belonging to space group $Fd\bar{3}m-O_h^7$ with 8R in a): (000; 0 1/2 1/2; $\bar{1}$) + 000, 1/4 1/4 1/4 and 16 Fe in d): (000; 0 1/2 1/2; $\bar{1}$) + 5/8 5/8 5/8; 5/8 7/8 7/8; $\bar{1}$ (Fig. 1). The point symmetry of the rare-earth atoms is cubic with their positions the same as positions of carbon atoms in diamond structures. The iron atoms have corner sharing tetrahedral sites with the point symmetry of each iron atom $\bar{3}m$ and the threefold axis lying along one of the [111] directions. The large magnetostrictions and magnetic anisotropies observed in this

system basically derives from the large magnetoelastic energy of the R ions with their spins parallel to one another and antiparallel to the Fe spins due to an indirect exchange. The strong R-Fe exchange in these compounds gives rise to the ferromagnetic alignment of rare earth iron moments at much higher temperatures than observed for pure rare earth elements. This and the strong Fe-Fe exchange give these compounds high Curie points well above room temperature (Table 1).

The Mössbauer spectroscopy of $R-Fe_2$ compounds shows three different types of spectra²¹, although these compounds have identical crystal structures. This has been accounted for by assigning different directions of easy magnetization (with each axis having a different distribution of iron ions about it) to the respective compounds.

III. CHARACTERIZATION TECHNIQUES

A. Optical Microscopy

The metallographic preparation of the samples consisted of standard cold mounting and polishing with emery papers down to 8 μm grade. Then the samples were polished with 1 μm grade diamond paste on woolen cloths. Further polishing was done on rotary polishing wheels using 0.05 μm Al_2O_3 water suspension. The final surface finish was obtained by etching with 1% Nital and vibratory polishing with a Linde γ -alumina water suspension for durations up to 2 minutes. This was usually repeated three times. All the optical photographs were taken with a Zeiss Universal Photomicroscope Ultraphot II.

B. Magnetic Domains Observation

For observation of magnetic domains, the preparation of the metallic surface is of most importance. In order to obtain a true picture of the magnetic domains, the surface should be completely free from any strain-induced anisotropy due to the polishing. Rare earth-iron Laves phase compounds, like other intermetallic compounds, are hard and brittle. Therefore, it is conceivable that after several short periods of etching and vibratory polishing, the material will have almost a strain-free surface. However, for viewing domains of most samples, the preparation included a final electropolishing in a solution of phosphoric acid saturated with chromic trioxide. The Kerr effect did not give clear pictures of magnetic domains in the sintered materials around compositions where the magnetic anisotropy was minimal. However, a magnetic powder pattern technique was successfully applied to reveal the domain patterns.

The colloidal suspension of magnetite was prepared by Elmore's method²² with the modification suggested by Baker et al.²³ The colloidal suspension was subjected to a polarizing field of 20 KOe in order to increase the sensitivity of the technique. With a small pipette, a few drops of this colloid were applied on the surface of the sample. The samples were placed on end and excess colloid was carefully blotted. The patterns formed on the surface were subsequently used for metallography.

C. Scanning Electron Microscopy

Partially sintered and fully densified samples were also examined by a scanning electron microscope (SEM), operated at 20 KV. Polished samples, prepared the same way as for the optical microscopy, were coated partially with a conductive thin film of carbon. For preliminary viewing and area selections the real time mode (TV-scan) and for final image adjustments and photographic recording the high resolution mode (a slow raster scan) were used. In conjunction with the SEM, an energy dispersive spectrometer (EDAX International Inc.), linked to a minicomputer, was used for quantitative point analysis of the phases observed.

D. X-Ray Analysis

For identification of phases present in the samples, x-ray diffraction patterns were obtained using a Picker diffractometer with an x-ray monochromator. Cu K α radiation was employed throughout the analysis. The samples were scanned over 110°(2 θ) at 2°/Min. Slower speeds (down to 0.25°/Min) were used in scanning selected peaks whenever necessary.

The degree of preferred orientation in the samples was also checked by x-ray diffraction spectra and x-ray pole figures. Samples measuring approximately 2 cm^2 by 0.3 cm thick were polished through a 1 μ diamond wheel and, after etching, were used to obtain x-ray diffraction patterns and pole figures. Plane orientations were determined by the Schulz method²⁴. Intensities of (440) reflections were recorded as ω (the angle of reflecting plane with the sample, and ϕ (the azimuth angle from the longitudinal directions of the sample) were changed.

E. Dilatometry

The linear shrinkage measurements during the liquid-phase sintering were carried out by means of dilatometry. Cold pressed samples of approximately 6 mm diameter and 10 mm length were placed in the chamber of the dilatometer which had a vacuum of better than 5×10^{-6} mm Hg during the operation. It required less than 20 seconds for the furnace to reach a set point temperature. The temperature was controlled within $\pm 5^\circ\text{C}$ by the feedback from the output of a delicate thermocouple welded to the sample and by a program controller.

F. Permeability measurements

The permeability of sintered cylindrical samples was measured by a fluxmetric method²⁵. A water-cooled Helmholtz coil system was used to apply uniform magnetic fields, up to 1 K Oe , to the sample. By surrounding a short close-fitting pick-up coil at the center of the sample, the magnetic induction (B) in the sample was determined. Assuming that the sample behaves like a line-dipole, corrections were made for the demagnetizing field and the cross sectional area difference

between the sample and the pick-up coil²⁶. Figure 2 shows the test equipment used for the permeability measurements.

G. Density Measurements

The true densities of the sintered samples were determined from gravimetric weighings and a fluid-displacement technique. Samples were initially weighed in air, then placed in a chamber which was evacuated and subsequently flooded with distilled water. The saturated weights of the carefully-blotted samples were immediately determined. The samples were, once more, reweighed while suspended in distilled water. Density was calculated from dry, saturated and suspended weights, using appropriate temperature corrections. The factor found to cause some erroneous results, was the formation of bubbles on the surface of water and adhering to the sample holder. The bubble formation was reduced by adding a drop of Kodak 200 photoflow to the water.

IV. INTRODUCTION TO THE POWDER METALLURGICAL PROCESSING TECHNIQUES

The general procedure for making parts from rare earth-iron intermetallics by the powder metallurgy techniques is as follows:

A. Compound Preparation

The compounds preparation consisted of arc melting elemental iron and rare earth (Table 2), on a water cooled copper hearth. Prior to the arc melting, the chamber was pumped several times to below 10^{-3} Torr, each time introducing a partial pressure of purified argon to purge any residual air in the chamber. The arc melting was conducted under a Zr gettered argon atmosphere and repeated several times, each time flipping the sample button in order to ensure good metallurgical homogeneity. The samples were later wrapped in thin tantalum foils and sealed into evacuated quartz capsules for homogenizing anneals up to 1100°C .

B. Crushing

Arc melted buttons of R-Fe_2 had to be crushed to a size range suitable for subsequent ball milling. Due to the brittleness of R-Fe_2 compounds, the crushing was easily done by a mortar and pestle. In this respect, crushing of some iron deficient alloys (Chapter VII) was somewhat difficult because of their higher ductility. The crushing was generally done under either an argon cover gas or acetone to prevent sparking. The particle size after crushing was such that it would pass easily through a 20 mesh (840 micron spacing) sieve.

C. Ball Milling

The 20-mesh powder produced by crushing had to be further reduced in size for subsequent processing. This was achieved by putting the coarse powder in an 80 cm³ hardened steel container with 10 steel balls of ≈ 1 cm diameter as the grinding media. The container was filled with toluene to cover the powder and the balls. After closing the container tightly, it was placed in a planetary ball milling machine operating at constant speed of 450 rpm.

D. Drying

The method for drying consisted of decanting the liquid after ball milling and rinsing the powder with acetone several times. Additional acetone was removed as much as possible with an absorbent paper. Then, the drying was accomplished by vacuum evaporation of acetone in a glovebox. With large batches of the powder, a heater was used to avoid the slow drying rates caused by freezing of the acetone.

E. Compaction

Rubber tubing, 0.6 cm I.D. and 3.8 cm long, was manually filled with powder. The packing degree of the particles was improved by some vibration compaction. The tubing was sealed by rubber plugs and placed inside a perforated steel tube for isostatic compaction. The choice of compacting pressure was based on: the effect of green density on handling, sintered density, equipment available and the economics of the process. Isostatic pressures in the range of 50-70 kg/mm² were found to be satisfactory. In this range, no systematic effect of pressure on densities of liquid phase sintered specimens

was observed. This finding is in agreement with the work of Price et al.²⁷, who showed that there is no influence of green density on the density of liquid phase sintered compacts.

F. Sintering

The sintering of specimens was performed in a Brew furnace with a dynamic vacuum of better than 4×10^{-6} mm Hg. The cold pressed samples were wrapped in Ta foils, contained in an alumina crucible, and positioned at the center of the hot zone. The temperature was measured by a platinum-platinum 10% rhodium thermocouple, encapsulated in a small piece of alumina and placed close to the samples.

The detailed studies and variations of some of these processes will be described in the following chapters.

V. SOLID-STATE SINTERING STUDIES

A. Compound Selection

Although $R\text{-Fe}_2$ compounds show very large magnetostrains at room temperature, the realization of these magnetostrains in a transducer will be considerably difficult because of large magnetocrystalline anisotropy of these materials⁶ which necessitates application of large magnetic fields. For most magnetostrictive transducers the figure of merit is λ^2/E ⁶ (where λ is the magnetostriction and E is the anisotropy energy). Thus, materials with high magnetostrictions and low magnetic anisotropies will be most suitable for such applications. Except for some preliminary investigations on DyFe_2 and GdFe_2 , throughout the research emphasis was placed on the pseudobinary compound $\text{Tb}_x\text{Dy}_{1-x}\text{Fe}_2$ with $x \approx 0.3$. The motivation for the choice of this compound was due to the work of A. E. Clark et al.²⁸ This is based on Table 3, showing that the first and second order anisotropy constants (K_1 and K_2) for TbFe_2 and DyFe_2 compounds have opposite signs while their magnetostriction constants are of the same polarity. Consequently, a pseudobinary combination of the two compounds in the form of $\text{Tb}_{.3}\text{Dy}_{.7}\text{Fe}_2$ was found to have minimal magnetic anisotropy along with a high magnetostriction⁶ ($\lambda_s \approx 1100 \times 10^{-6}$).

B. Sintering Procedure

Cold pressed samples of $\text{Tb}_{.3}\text{Dy}_{.7}\text{Fe}_2$ were prepared as described in Chapter IV. Initially, the samples were wrapped in Ta foils and put into quartz tubes. Before sealing, the tubes were connected to a high vacuum system and heated with a torch intermittently in order to degas

the samples. The sealed tubes were subsequently placed in the sintering furnace. At a later stage, however, a dynamic vacuum furnace was utilized to reduce oxidation and to make higher sintering temperatures possible. The temperature of the furnace was increased gradually in order to allow degassing of the samples. Various sintering cycles for durations up to 48 h were tried. The sintered products were examined by optical and scanning electron microscopy as well as x-ray diffraction.

C. Characterization of Sintered Products

Samples prepared using the above described method exhibited very poor sinterability. Densities higher than 87% of theoretical density were not achieved. X-ray diffraction patterns of the samples also showed the presence of an appreciable fraction of a foreign phase. Immediate attention was paid to the identification of this unknown phase which was identified as a new oxygen stabilized intermetallic compound of composition $R_{12}Fe_{32}O_2$ (R = a rare earth element). The determination of the crystal structure and some magnetic properties of this new compound, which hereafter will be referred to as β -compound, will be the subject of the following chapter.

D. Effect of Ball Milling Procedure

The relatively low oxygen content of β -compound results in its large volume fraction. The absorbed surface layer on the milled powder particles can provide the oxygen necessary for the formation of this intermetallic. In an effort to control the formation of β -compound, the effects of liquid medium and the milling time on the particle size and on the amount of oxygen absorbed by the powder were studied.

1. Effect of Liquid Medium

Several liquid media were evaluated in terms of their efficiency in producing low-oxygen content pulverized powder. The comparison of oxygen content of the powders was done by the relative amounts of β -compound observed in the sintered samples. In this respect, hexane and isopropyl alcohol, for a given milling time, showed almost the same amount of β -compound. However, for equal milling times, the average particle size for both liquids was consistently larger (~40%) than that for toluene. The high efficiency of toluene and the relatively low oxidation of the powder were the main criteria for the choice of toluene as the liquid medium in all subsequent ball millings. Mixtures of toluene with mineral oil, which had been reported to have some effect on lowering the oxidation level³⁰, were also tried. They were, however, abandoned due to the residual impurities observed in the sintered compounds.

2. Effect of Milling Time

Milling time studies showed that the 20 mesh materials could be reduced to a powder with an average particle size of 30 microns in about 16 minutes (Figs. 3,4). As the milling time increased, the amount of β -compound in the sintered products was also increased. This was attributed to the higher oxygen absorption by the powder as the particle size was reduced resulting in greater surface activity.

E. Effect of Deviation from the Stoichiometric Composition

Only by adding 3-4 at % rare earth in excess of the stoichiometric composition could the presence of β -compound be completely eliminated.

The excess rare earth reacted with the available oxygen to yield a dispersion of sesquioxides. The oxygen content of these oxides being high, their volume fraction was relatively low. An iron content in excess of the stoichiometric composition led to the precipitation of $R-Fe_3$ phase, in samples which were slowly cooled from the sintering temperature (Fig. 5). The appearance of these precipitates was attributed to a solubility range of the Laves phase, extending toward the iron rich composition at elevated temperatures (Fig. 6).

VI. OXYGEN STABILIZED INTERMETALLIC COMPOUNDS OF RARE EARTH-IRON

A. Introduction

During the course of solid-state sintering studies of R-Fe₂ compounds, a new phase in the sintered samples was observed (figs. 7,8). X-ray diffraction patterns of these samples showed several lines which could neither be attributed to other known R-Fe compounds nor to the oxides or nitrides. Observation of this unknown phase, β phase, imposed the immediate goal of its identification and characterization before any further work on powder metallurgical development could proceed. For this purpose a series of Dy-Fe alloys with compositions of Fe in 60-80 at % range, at 2 at. % increments was prepared. This series of alloys was subjected to various powder preparations and sintering methods described before. Maximum amount of β -phase was observed to form near the composition of 72 at. % Fe. The extraneous lines observed were mainly residual DyFe₂ intermetallic, some Dy₂O₃ sesquioxide, and DyN nitride.

B. Crystal Structure Determination

1. Unit Cell

The x-ray diffraction spectra were utilized to investigate the crystal structure of the β -phase. Approximately half of the observed Q values ($Q = \frac{1}{d^2}$) were used as input to a computer program to find a lattice for the crystal by Ito's method. The program fitted a reduced triclinic cell whose calculated Q values would match, within a limit of error, the observed values. The Niggli matrix of this cell was checked to see if it could be transformed to a cell of higher

symmetry. (In the interest of brevity, the theory and mathematical relations involved in this procedure will not be repeated here and for details, the reader is advised to consult references 31-33). By examining the first 22 Q values (Table 4), the program generated 4748 possible cells which were able to index 90% or more of the observed Qs. The unique cells were used in another run of the program to find the cells matching 100% of all the experimental Qs. These cells are given in Table 5.

Observation of the reduced cell matrices of these cells revealed they did not have symmetries higher than orthorhombic. Therefore, the possibility for some of the Q values to be of higher orders seemed reasonable. A search among the Q values was conducted and any Q value which showed at least two other higher orders was automatically assumed to be a second order. The results of this search are tabulated in Table 6.

The previous 22 Q values along with the four tentative first-order Qs were once more used as input to the computer program. From the 1093 possible reduced cells examined a cell with ($A=B=C=7.67915 \text{ \AA}$; $\cos\alpha = \cos\beta = \cos\gamma = -0.33333$) was found to be of interest. The Niggli matrix of the cell: $\begin{pmatrix} 58.97 & 58.97 & 58.97 \\ -19.66 & -19.66 & -19.66 \end{pmatrix}$ showed it was isometric with an I-centered lattice. The transformation matrix of the cell (101/110/011) gave a body-centered cubic unit cell with $8.8668 \text{ \AA}$ lattice parameter. The diffraction pattern was successfully indexed on the basis of this unit cell, confirming that Qs (No. 2 and 6) were second order.

2. Atom Positions

A literature search revealed that the only known crystal structures compatible with the cubic symmetry, lattice parameter and composition ratios of the two components were those of the binary compound $\text{Ca}_3\text{Ag}_8^{34}$ and the similar ternaries $\text{R}_3\text{Ni}_6\text{Si}_2^{35}$ belonging to the space group $\text{Im}\bar{3}\text{m}$ (Int. Tab. No. 229). The crystal structure of the β -compound was tentatively assumed to belong to the same space group with 4 formula units per unit cell, and a composition ratio corresponding to the formula Dy_3Fe_8 . To verify this assumption, the experimental diffraction intensities were compared to computer generated ones. The computer program used as input the assumed space group, the atom position coordinates, and the lattice constants. It computed the diffraction line positions and intensities. The intensities of the individual reflections were calculated according to $I = P|F|^2|LP|$, with P the multiplicity, $|F|^2$ the structure factor and LP the combined Lorentz-polarization factor, corrected for the x-ray monochromator. Good agreement between the experimental and the computer results was obtained. In the R-Fe binaries no mention has ever been made of the presence of R_3Fe_8 compounds and it was unlikely that they should have been overlooked. It seemed, therefore, reasonable that the β -compound had been stabilized in the sintered powder compacts by a ternary component.

Oxygen stabilized intermetallic compounds have been observed in intra-transition metal systems. Notable examples are the Ti_2Ni type phases, a large number of which are oxygen stabilized derivatives of nonoccurring binary phases. The effect of oxygen is to multiply by a factor of three the number of binary combinations for which the Ti_2Ni

structure is stable³⁶. The $T_3' T_3'' O$ and $T_3' T_3'' C$ phases^{37,38} (T' , T'' = transition metals) are further examples of metalloid stabilized compounds which have no binary counterparts. Chemical analysis of the β -compound revealed the presence of 0.94 W.%O, 0.05 w%C and 0.09 W%N. Based on crystal structure considerations, as well as the results of the chemical analysis, the actual formula of the β -compound should be $Dy_{12}Fe_{32}O_2$. The complete diffraction pattern of this compound is given in Table 7. The occurrence of the β -compound in R-Fe systems other than Dy-Fe was observed for R=Gd, Tb, Ho, Er and Y. The measured lattice parameters of these compounds are given in Table 8.

C. Atomic Distribution in the β -Compound

The distribution of atoms is given in figure 9. The atomic position parameters for sites e and h were determined by trial and error to give the best fit between the experimental and the computer diffraction patterns. Since the x-ray diffraction method is rather insensitive to the presence of oxygen atoms, their positions are only tentative. The spatial arrangement of the atoms in the β -compound structure can be viewed as a network of Fe_{II} atoms located on pairs of parallel $\{110\}$ planes. The two planes of each pair are interconnected at regular intervals by the Fe_I atoms (Figs. 10,11). This network leaves empty spaces around the $(0,0,0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ positions, which are filled by regular R octahedra with an oxygen atom at their center.

D. Stability of the β -Compound

It is not clear at present whether the β -compounds are thermodynamically stable, or only metastable, with respect to their decomposition

into a rare-earth oxide (presumably R_2O_3) and a binary R-Fe intermetallic. If the latter were the case, it would account for the β -compound not having been observed in previous investigations. In the course of ternary R-Fe-O system studies, oxygen is usually introduced in the form of rare-earth sesquioxides. It is not implausible that the high stability of these oxides would prevent their partial reduction to form a β -compound. In the present case, the method of preparation was different, in that high specific area R-Fe compound powder was exposed to a low oxygen pressure at elevated temperatures.

E. Magnetic Properties of the β -Compound

The discovery of a new compound has always been exciting. This was especially the case for the β -compound. Other oxygen-containing rare earth-iron compounds, specifically the orthoferrites $RFeO_3$ and the garnets $R_3Fe_5O_{12}$, are of utmost interest for practical applications such as bubble domain technology, high power microwave and magneto-optic devices. The usefulness of these compounds, gave a reasonable promise that the β -compound would be a rewarding subject for study especially when it was an unexpected encounter in the sintering of R- Fe_2 compounds. Preliminary measurements of temperature dependence of magnetization of Dy-based β -compound by a vibrating sample magnetometer showed a magnetic ordering temperature of $265 \pm 5^\circ K$ (Fig. 12). The residual magnetization after the abrupt decrease at $260^\circ K$ is probably due to the presence of the minority $DyFe_2$ phase. Since the β -compound is paramagnetic at room temperature, it does not contribute to the magnetostriction. In the interest of pursuing the main objective of this thesis, any further research on the compound was left to other interested investigators.

VII. LIQUID PHASE SINTERING OF $R-Fe_2$ COMPOUNDS

A. Introduction

Existence of foreign phases and porosity will have an adverse effect on both mechanical and magnetic properties of sintered $R-Fe_2$ compounds. The foreign phases (other than the sesquioxides) were eliminated by using an excess of rare earth metals during the course of solid-state sintering. However, the process was not conducive to highly dense materials. The presence of pores reduces the permeability of the sintered products (Fig. 13) by increasing the demagnetizing field and by decreasing the magnetization per unit volume. The porosity was drastically reduced by employing a liquid-phase sintering approach. A detailed presentation of the liquid-phase sintering is given by V. N. Ereminko et al.³⁹

B. Liquid Phase Sintering of $R-Fe_2$ Compounds

The binary Laves compounds $TbFe_2$ and $DyFe_2$ are formed peritectically as a result of a reaction between iron rich phases and a rare earth rich, low melting liquid (Fig. 6). Even though the ternary Dy-Tb-Fe phase diagram is not available, it is reasonable to assume that the pseudo-binary $Tb_{.3}Dy_{.7}Fe_2$ compound is formed in a similar way. In order to provide a liquid component in the course of the sintering, the compound preparation and procedures described in Chapter V were followed except that the starting material consisted of two different alloys containing 55 and 66.7 at.% Fe respectively. These initial compositions were chosen in such a manner that by taking 25% of the iron poor alloy, the

final homogenized composition of the product corresponded to 63.7 at.% Fe, necessary for the elimination of the oxygen stabilized phase. The iron deficient component of the mixture constituted the liquid phase at the sintering temperature. Higher than a 25% liquid fraction led to loss of shape of the compact during sintering. The composition of the iron poor phase, its relative fraction, the sintering temperature and the rate of heating are critical parameters of the process. The cold pressed mixture of the two powders was heated gradually to 800°C, and then, at the highest possible rate (50 deg/min) to the sintering temperature of $1135 \pm 5^\circ\text{C}$. At lower heating rates in this upper temperature range, the increased mobility of the atoms leads to rapid homogenization, thereby reducing the liquid phase fraction to values at which it is not effective.

C. Initial Sintering Kinetics of R-Fe₂ Compounds

In the sintering procedure described, the iron deficient alloy becomes liquid and therefore, the liquid phase sintering kinetics are expected to prevail during the initial stages. Liquid-phase sintering can be divided into three stages for the purpose of analysis: First, rearrangement of solid particles upon formation of the liquid phase; second, solution and precipitation of the solid phase in the liquid; and third, a solid-phase sintering which is generally slower than the second stage. Kingery⁴⁰ has presented a thermodynamic analysis of the densification rate during the first two stages. The equations derived are based on the assumptions of spherical particles, complete wetting of the solid by the liquid, solution of the solid in the liquid phase,

and constant grain size. The relations can be used for the sintering of Laves phases to identify the rate-controlling mass-transport process. If the diffusion is rate controlling, the isothermal dependence of linear shrinkage on time is expressed as:

$$\Delta L/L_0 = (6k_2\delta D C_0 \gamma_{LV} V_0/k_1 RT)r^{-4/3} t^{1/3}$$

where:

- $\Delta L/L_0$ = fractional shrinkage
- k_2 = a dimensionless constant
- δ = boundary thickness between contacting particles
- D = Diffusion coefficient in the liquid phase
- C_0 = Concentration of Laves phase in the liquid under a flat surface
- γ_{LV} = liquid-vapor surface energy
- V_0 = molar volume of Laves phase
- k_1 = the ratio of pore to particle radius (r)
- t = time

If the phase boundary reaction is the rate controlling step, the sintering kinetics are represented by:

$$\Delta L/L_0 = (2k_3k_2 \gamma_{LV} C_0 V_0/k_1 RT)r^{-1} t^{1/2}$$

where k_3 is a rate constant for the phase boundary reaction. The above equations suggest that data of linear shrinkage versus time should give an indication of the sintering mechanism involved.

D. Results of Dilatometry

A typical isothermal shrinkage is plotted by the $\log (\Delta L/L_0) - \log t$ in Fig. 14. The value of L_0 was taken as the initial length of cold "green" compact corrected for thermal expansion at the sintering temperature. The slope of the line representing the solution-precipitation stage is much lower than predicted by the rate-controlling mechanisms described above. A. L. Prill et al.⁴¹ have found that large amounts of shrinkage during the rearrangement stage will result in an apparent low time exponent of the linear shrinkage and erroneous identification of the rate-controlling process. The data taken were reanalyzed, taking into account the length and time at the end of the rearrangement stage. Figure 15 shows the replot of the data with corrected shrinkage and time.

E. Discussion

As the data in Fig. 14 indicate, a good amount of densification is rapidly reached by the rearrangement process, possibly because of a large amount of liquid present at the sintering temperature. The solution precipitation stage which starts at the first break of the curve contributes mostly to changing the grain sizes and shapes. Therefore, this method of liquid-phase sintering not only gives densities as high as 97% of the theoretical density, but also leads to a large grain size (Fig. 16). Grain boundaries are effective barriers to domain wall motion. Globus et al.⁴² have given a relation between the grain size and the permeability in the form of:

$$i-1 = \frac{8\pi M_s}{H} \frac{\Delta V}{V} \propto r$$

where:

- M_s = saturation magnetization
- r = radius of the sphere of crystallite grain
- $\frac{\Delta V}{V}$ = volume change of the domain per unit volume
- μ = permeability

Their results show products with a large grain size will be preferred because of their higher permeabilities.

The slopes of lines through the replotted data (Fig. 15) are close to 0.5 (a least square fit through the data points corresponding to 1135°C sintering temperature gave a slope of .48 with a correlation coefficient above .99). A time exponent of 0.5 for the linear shrinkage isotherms shows the mechanism of sintering is rate limited by a phase boundary reaction process rather than diffusion in the liquid phase. Figure 17 shows the magnetic domains in a liquid-phase sintered sample, revealed by the Bitter technique.

F. Liquid-Phase Sintering of Powder Rolled Laminates

The liquid-phase sintering approach was extended to the preparation of powder rolled thin plates. Potential application of these thin plates and laminates in magnetostrictive devices will be in reducing the eddy current losses at high frequencies¹. The method consisted of preparing the appropriate powder and rolling it into thin porous strips.

The experiment was carried out in a special device (Fig. 18b) with horizontally arranged rolls, rotating at a speed of approximately 10 rpm. The roll surfaces were initially run-in by rolling some extra powder, fed to the system at constant angle by means of a gate. The rolled strips were placed in a Ta holder (Fig. 18a) to prevent their disintegration, and the assembly was subjected to the same sintering cycles as for the rod-shape compacts. X-ray diffraction of the sintered laminates showed the presence of oxide and nitride of rare earth. Most likely, the powder exposure to the air during the rolling, and the high porosity of the rolled strip had been the source of the extraneous phases. The foreign phases were eliminated by performing the rolling experiment under an argon cover gas.

VIII. MAGNETOSTRICTION MEASUREMENTS

For temperature dependence and magnetostriction determination, a multi-chambered cryostat with a superconducting magnet and associated measuring systems were used.

A. Cryostat

The cryostat used, consists of six chambers (Fig. 19). The innermost chamber is the SAMPLE chamber which goes straightly to the core of a superconducting magnet. Surrounding the SAMPLE chamber is the POT chamber with a transfer valve to transfer some liquid helium from the liquid He chamber (BATH) to the POT whenever very low temperatures are needed. POT and BATH chambers are isolated from each other by an evacuated chamber (ISO). DEWAR is the vacuum chamber surrounding the liquid He(BATH) and liquid N_2 chambers.

The associated vacuum system is shown in Figs. 20 and 21. By this system five chambers can be evacuated with a mechanical pump. In addition, POT, ISO and DEWAR can also be evacuated with a diffusion pump. The He(g) and N_2 (g) lines are also provided for the chambers. N_2 (g) can be used with DEWAR and ISO chambers only. The system is equipped with an automatic liquid N_2 fill relay to keep the liquid level in the chamber constant.

B. Superconducting Magnet

The superconducting magnet is located at the bottom of the BATH chamber. It is wound with Nb 44% Ti filaments in a Cu matrix. It has a capability of delivering a maximum of 50 (KOe) in 50 seconds

and a minimum sweep rate of 50 (KOe) in 5×10^4 seconds through a 60 A power supply. The field is controlled by the current of power supply, which has also a corresponding analog output to record the generated field automatically (Fig. 22). In order to protect the magnet from operating without sufficient He, it is interlocked with a four-stage He level detector system, with each detector approximately 10 cm apart.

C. Method of Magnetostriction Measurements

For measurements of the magnetostriction of the samples prepared, the bridge strain gauge technique was used because of the compactness of the technique as well as its high accuracy when used with a temperature and magnetic field compensation circuitry. In order to compensate for the temperature and magnetoresistance effects, for each of the active strain gages on the sample a corresponding "Dummy" gauge of the same type and lot number was mounted on a piece of arc melted and homogenized YFe_2 . The choice of YFe_2 was due to the fact that it is an isostructural non-magnetostrictive ($\lambda_s < 2 \times 10^{-6}$) compound with the thermal coefficient of expansion in range with that of R- Fe_2 compounds. The strain gauges used were Micro-Measurements Wk-06-062AU-120 which were bonded to the samples by the (M500) bonding agent, one longitudinally and one transversely. Each active and its corresponding (Dummy) gage made two arms of a bridge, resulting in a total of two independent bridges. Each bridge circuitry was then completed by a Daytronic Model 9170 strain gauge conditioner, which was also used for initial balancing and calibration of the system (Fig. 23). The samples with the active and dummy strain gauges were mounted on a copper plate of

a probe, made for holding them at the core of the superconducting magnet (Fig. 24). The probe consisted of a stainless steel tube with a copper mounting block. A screw-on copper cup was provided to maintain a thermal equipotential. Several copper disks were soldered to the stainless steel tube to facilitate the alignment of the probe in the sample chamber of the cryostat.

D. Control of Temperature

The temperature was controlled by a cryogenic temperature controller and a 10 Ω -resistance shielded heating coil around the copper housing. The voltage developed by a calibrated gallium arsenide diode temperature sensor, mounted next to the sample, was used to automatically control the temperature fluctuations. Initial temperature adjustments, however, were done manually to avoid possible burning of the heating coil. Several iron-constantan thermocouples, mounted at different places near the sample, showed no temperature gradient along the sample.

E. Operating Procedure

Before the operation, ISO and DEWAR were filled with N₂ gas and evacuated. This was done several times to ensure that only N₂ gas remained inside these chambers. The chambers were subsequently diffusion pumped to pressures better than (1 μ Hg) and sealed off. (As the BATH was filled with He, the residual N₂ gas in ISO and DEWAR would liquify to give an excellent vacuum). The sample probe was carefully inserted in the SAMPLE Chamber. SAMPLE, BATH and POT chambers were several times flushed with He(g) and evacuated to ensure that only He gas remained inside. The chambers were filled with

approximately 2500 μ of He. The whole system, with the automatic liquid N_2 fill unit on, was left overnight to precool. This was necessary to save on the amount of liquid He consumed. Next day, liquid He was transferred first at a slow rate to cool the magnet. The magnet resistance ($\approx 1300 \Omega$ at room temperature) was used to monitor the magnet temperature. As the magnet resistance dropped to zero, the transfer rate was increased to fill the BATH. The liquid He level was determined by the four lights connected to the four level detectors. Each time that the liquid was past a detector (a green light on) the transfer line was raised about 10 cm in order that liquid He could be transferred to the top of He level. After filling the BATH, the desired temperature was maintained in the SAMPLE chamber by the heater and automatic temperature controller. The magnet could then be turned on to obtain the desired field.

F. Magnetostriction of the Sintered Compacts

Using the above experimental set-up, the magnetic field dependence of the longitudinal and transverse magnetostrictions of a solid-state sintered $Tb_{0.3}Dy_{0.7}Fe_2$ sample was measured (Fig. 25). The temperature dependence of the magnetostrictive coefficient $|\lambda_{11} - \lambda_1|$, shown in Fig. 26, was determined by carrying out two sets of measurements, one in the presence of an applied magnetic field of 25 KOe, and the other without the field. This procedure had to be followed in order to correct for the difference in the thermal expansion coefficient of the test sample and the adjacent reference sample. Noteworthy is the aspect of curve λ_{11} in Fig. 25, suggesting that even at the highest applied field, the magnetostriction is far from saturation. The density

of the sample was only 82% of theoretical density. The liquid phase sintering approach was able to reduce the residual porosity and thereby increase the magnetoelastic force and energy density of the sintered compounds.

The static magnetostrictive behavior of liquid-phase sintered compacts was measured using essentially the same strain gauge technique as described above but with a new set-up to be used later for the dynamic magnetostriction measurement. The results obtained (Fig. 27), indicate that both with regard to the magnetostrains attained, and the rate of approach to saturation, the sintered products are comparable to those reported on cast samples²⁸. The magnetic field dependence of magnetostriction coefficients for a liquid-phase sintered laminate of DyFe_2 is shown in Fig. 28.

G. Dynamic Magnetostriction Measurements

A new experimental set-up was utilized to study the magnetostriction of sintered compacts under the combined influence of a bias and an alternating field. The bias field was supplied by a short solenoid magnet, powered by a 180 kw power supply. It was established that the magnetic field of this magnet over the length of the sample was adequately uniform. The sample probe (Fig. 29) was accurately placed at the center of a solenoidal winding and then, the assembly was secured at the bore of the short solenoid magnet. The circuitry shown in Fig. 30 was able to energize the solenoidal winding to provide alternating fields up to ± 500 Oe at various frequencies. The calibration of the field was done in terms of alternating currents passing through the

solenoidal winding. The strain gage bridges were balanced by means of a Q plug-in unit and a dual beam oscilloscope. The alternating strains were recorded on a light-sensitive paper by an oscillograph. To minimize any possible temperature rise in the sample, the alternating field was applied only for a short period of time (up to 20 seconds). The frequency of the dynamic field was chosen at 160 Hz ($\omega \approx 1000$) because it was low enough to reduce the eddy current losses and far from the harmonics of 60 Hz.

H. Results of Dynamic Measurements

At a constant frequency, the magnitude of the dynamic strain attained was roughly proportional to the magnitude of the applied alternating field until the dynamic field had a value approximately equal to the bias field. As the alternating field exceeded this value, some frequency distortion of the dynamic strain began to occur. The considerable strains observed (Fig. 31), are indicative of the advantage of these materials in applications where a high power broad-band low frequency source is desirable.

IX. EFFECTS OF MAGNETIC POWDER ALIGNMENT ON MAGNETOSTRICTION OF R-Fe₂ COMPOUNDS

A. Introduction

The powder metallurgical approach can be further improved by magnetically aligning the powder particles prior to the sintering. Spin orientation diagrams indicate that the pseudobinary compound (Tb_xDy_{1-x}Fe₂) with x close to 0.3, at room temperature, has its axis of easy magnetization along the major cubic symmetry [111] direction²⁹. A powder metallurgical approach can utilize the direction of easy magnetization by alignment of the powder compound in a magnetic field.

B. Alignment Procedure

The powder preparation of the compound consisted of the same steps as described in Chapter IV. Rubber tubing, 0.6 cm, ID and 3.8 cm long, was manually filled with powder. Magnetic alignment of the powder particles was one of the most critical processing steps. The objective during the compacting stage was to maintain a good degree of alignment in the compound by mechanically interlocking the powder particles. To achieve this, the powder was aligned in DC fields up to 20 KOe, then the volume was reduced by evacuating the rubber tube to lock the particles in position. The tube was subsequently hydrostatically compressed at 70 kg/cm². Although in the first set of experiments x-ray examination showed only a small degree of alignment, nevertheless, a definite improvement in magnetostriction was observed⁴³. A substantially higher degree of alignment was achieved when an alternating field of approximately 1000 Oe peak-to-peak at frequencies up to 500 Hz was superimposed on the DC field.

A field of this type produced sufficient particle vibration to facilitate orientation of the base powder. While in the magnetic field, the powder was compacted by hand-applied end compression with a plunger before it was isostatically compressed. The cold pressed samples were subsequently wrapped in Ta foils and sintered in a dynamic vacuum of 3×10^{-6} mm Hg in the 950-1050°C temperature range for durations up to 12 h.

C. Results of Magnetic Alignment and Discussion

Fig. 32 shows the x-ray diffraction patterns of random and magnetically oriented $\text{Tb}_{3.5}\text{Dy}_{0.5}\text{Fe}_2$ compound. In the surface perpendicular to the magnetic field, the diffraction intensity from (220) planes has decreased while the intensity of (222) reflection has increased, to a substantial degree, with respect to the intensities of reflections from these planes in an almost randomly oriented powdered compound. Low field magnetostriction measurements at room temperature show that with regard to both magnetostrains and rate of approach to saturation, the aligned materials, though containing considerable porosity (Fig. 33), is much superior to highly dense (95% theoretical density) liquid-phase sintered compound which is not aligned (Fig. 34). This superiority is possibly due to the effect of the preferred grain orientation on reducing the microstresses at grain boundaries associated with highly magnetostrictive materials. Figure 35 shows that the static permeabilities of the magnetically aligned samples have significantly increased. The shift of permeability maxima to the left (lower fields) indicates that the material has become magnetically softer. Also, it is noteworthy that in rare earth-iron Laves phase compounds $\lambda_{111} \gg \lambda_{100}$ due to a

structural distortion associated with the [111] easy direction of magnetization⁴⁴. (λ_{100} and λ_{111} are single crystal magnetostriction constants of cubic crystals in directions $\langle 100 \rangle$ and $\langle 111 \rangle$ respectively.) Since for a polycrystalline material with random grain orientation, the saturation magnetostriction can be expressed as $\lambda_s = (2\lambda_{100} + 3\lambda_{111})/5$,⁴⁵ magnetic alignment of these compounds, orienting the crystallites along the [111] easy axis, will enhance their saturation magnetostriction drastically. This is illustrated in Fig. 36 where the saturation magnetostriction for the aligned $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_2$ shows a 20% increase over the highly dense liquid phase sintered material.

D. Effect of Alignment on Dynamic Magnetostriction

Dynamic magnetostrictions of magnetically aligned sintered compacts in several fields with different frequencies are shown in Figures 37-40. The results indicate that the aligned products have properties much superior to those of the liquid-phase sintered materials. The higher static and dynamic strains achieved by the alignment can help reduce the magnetic fields required for operation of the transducer device, making the design of a more compact and economical system possible.

E. Effect of Magnetic Anisotropy on the Alignment

It was found that the alignment improves as the value of x in $\text{Tb}_x\text{Dy}_{1-x}\text{Fe}_2$ is increased, as is shown in Fig. 41, where the relative intensity of reflections (222) and (220) planes are plotted against values of (x) . This is attributed to the fact that $\text{Tb}_x\text{Dy}_{1-x}\text{Fe}_2$ has a minimal anisotropy near $x = 0.3$. An increase in (x) will increase the anisotropy making an improvement in the alignment degree possible. This

is evident in x-ray diffraction patterns taken from aligned sintered TbFe_2 materials (Fig. 42). In the plane perpendicular to the direction of the field, the (220) reflection is almost non-existent whereas the reflection from (222) planes has the strongest intensity. Figure 43 shows a (440) pole figure for an aligned TbFe_2 sintered rod with contours of constant intensity around the (440) pole, at the center. Although a decrease in (x) toward a Dy richer compound also will increase the magnetic anisotropy, it was not considered as beneficial, since DyFe_2 has its easy direction of magnetization along the [100] instead of along the [111] direction, thus not contributing much to the magnetostriction.

X. CONCLUSIONS

This study has fulfilled its principal mission in establishing the powder metallurgical approach as the most appropriate technique of manufacturing the highly magnetostrictive rare earth-iron intermetallics. As a result of this study several important processing parameters are characterized. The solid-state sintering studies point to the importance of $R\text{-Fe}_2$ oxidation during the powder preparation and sintering stages. A new oxygen-stabilized intermetallic compound ($R_{12}\text{Fe}_{32}\text{O}_2$) in sintered rare earth-iron powder samples was discovered and its magnetic properties determined. The study also indicates a method of suppressing the formation of this foreign phase in sintered products by adding 3-4 at. % rare earth in excess of the stoichiometric composition. Densities of the products, and thereby their permeabilities, can be greatly improved by employing a liquid-phase sintering approach. The magnetostrictive properties of these sintered products are comparable to those reported on cast samples. Besides the increased density, this method of production gives rise to a large grain size which is also beneficial to the permeability. This is a parameter which has an impact on the performance of the transducer. A low permeability material can result in low efficiency of the transducer because of the incurred resistive losses. In addition, low permeabilities impose certain limitations on the design of the device so that proper continuation of the magnetic path can be maintained.

Another important advantage of the powder approach is its amenability to the magnetic powder orientation. The result of this orientation is a substantially higher permeability of the product. The improved

permeability may allow for a permanent magnet to replace the circuitry of the transducer responsible for supplying the bias field. Further work on the powder technique to fabricate layered thin walled cylinders from the magnetically aligned powder would be a most welcome development. With this common shape in transducer design, an evaluation of the material in terms of the coupling coefficient and the generated power can be made. Also, the powder approach can be extended to making the powder rolled thin laminates whenever reduced eddy current losses are desirable. It is conceivable that the magnetic alignment step can readily be incorporated in the fabrication of laminates to enhance their magnetic properties. Using thin layers of a non-conducting adhesive, these laminates may be bonded together to fabricate various technologically-attractive configurations. Noteworthy is also some preliminary work during the last phase of this research, showing that the magnetic powder alignment is retained during the liquid-phase sintering. Development of this method will combine the beneficial effects of alignment and density, resulting in materials with further improved magnetic properties.

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TABLE 1

EASY DIRECTIONS AND CURIE TEMPERATURES FOR SOME R-Fe₂ COMPOUNDS.*

Compound	Theoretical easy Direction	Experimental easy Direction	The Curie Temperature °K
Tb Fe ₂	$\langle 111 \rangle$	$\langle 111 \rangle$	711
Dy Fe ₂	$\langle 001 \rangle$	$\langle 001 \rangle$	635
Ho Fe ₂	$\langle 001 \rangle$	$\langle 001 \rangle$	612
Er Fe ₂	$\langle 111 \rangle$	$\langle 111 \rangle$	590
Lu Fe ₂	$\langle 111 \rangle$	$\langle 101 \rangle$	610
Tm Fe ₂	$\langle 111 \rangle$	$\langle 111 \rangle$	610

* Values from References 5,20

TABLE 2
REPORT OF ANALYSIS OF
TYPICAL ELEMENTAL IRON AND RARE EARTH USED.

IRON		
Type of Analysis*	Chemical Properties	Specifications %
4	Fe	Major
5	Carbon	<0.005
1	Hydrogen Loss	<0.05
3	Manganese	<0.002
4	Nickel	<0.002
4	Phosphorus	<0.004
5	Sulfur	<0.005
2	Hydrogen	---

TERBIUM		
Type of Analysis	Chemical Properties	Specifications %
3	Terbium	Major
3	Gadolinum	<0.01
3	Yttrium	<0.01
3	Europium	<0.005
3	Dysprosium	<0.01
3	Silicon	<0.01
3	Iron	<0.01
3	Tantalum	---
3	Magnesium	<0.01
3	Calcium	<0.01

- * (1) MPIF Standard 2-48
 (2) Vacuum Fusion
 (3) Spectrographic
 (4) ASTM Analytical Methods
 (5) Combustion

TABLE 3

POLARITIES AND VALUES OF MAGNETOSTRICTION AND
MAGNETIC ANISOTROPY CONSTANTS OF TbFe_2 AND DyFe_2 AT ROOM TEMPERATURE.

	TbFe_2	DyFe_2
$10^6 \lambda_s^\dagger$	+1753	+433
$10^{-4} K_1^\dagger \text{ ergs/cm}^3$	-7600	+2100
K_2^*	+	-

† Values from Reference 6

* Because of large anisotropy, accurate determination of K_2 directly will be difficult. See Reference 29 for estimated values.

TABLE 4

THE FIRST 22 d-SPACINGS OBSERVED FOR THE β -COMPOUND.

No.	d	Q	No.	d	Q
1	3.62219	0.0762	12	1.52014	0.4068
2	3.13680	0.1016	13	1.47735	0.4582
3	2.80400	0.1272	14	1.43751	0.4839
4	2.56077	0.1525	15	1.33690	0.5595
5	2.37024	0.1780	16	1.27999	0.6104
6	2.2174	0.2034	17	1.25412	0.6358
7	2.09069	0.2288	18	1.20678	0.6867
8	1.98341	0.2542	19	1.16443	0.7375
9	1.73837	0.3309	20	1.12624	0.7884
10	1.61767	0.3821	21	1.108	0.8146
11	1.56796	0.4068	22	1.09158	0.8392

TABLE 5

THE REFINED CELLS INDEXING ALL THE OBSERVED Q VALUES.

CELL PARAMETERS							
CELL NO.	A	B	C	Cos α	Cos β	Cos γ	Reduced Cell Matrix
1	4.18013	4.90146	6.60913	.13485	.31624	.42642	$\begin{pmatrix} 17.47 & 24.02 & 43.68 \\ 4.37 & 8.74 & 8.74 \end{pmatrix}$
2	3.85157	4.13055	4.87210	-.36859	-.07906	-.27977	$\begin{pmatrix} 14.83 & 17.06 & 23.74 \\ -7.42 & -1.48 & -4.45 \end{pmatrix}$
3	3.58608	3.78546	4.02056	-.04830	-.40766	-.24359	$\begin{pmatrix} 12.86 & 14.33 & 16.16 \\ - .74 & -5.88 & -3.31 \end{pmatrix}$
4	3.29164	3.69048	3.81444	-.13193	-.27120	-.10200	$\begin{pmatrix} 10.83 & 13.62 & 14.55 \\ -1.86 & -3.41 & -1.24 \end{pmatrix}$
5	3.30463	4.18022	4.90152	.42642	.13485	.31624	$\begin{pmatrix} 10.92 & 17.47 & 24.02 \\ 8.74 & 2.18 & 4.37 \end{pmatrix}$
6	3.18718	3.70059	4.60477	.20742	.18051	.03752	$\begin{pmatrix} 10.16 & 13.69 & 21.20 \\ 3.53 & 2.65 & .44 \end{pmatrix}$
7	3.13495	4.43357	6.27030	0.00000	0.00000	0.00000	$\begin{pmatrix} 9.83 & 19.66 & 39.32 \\ 0.00 & 0.00 & 0.00 \end{pmatrix}$

TABLE 6

AGREEMENT BETWEEN CALCULATED AND OBSERVED VALUES, WHEN

ALL Q VALUES WERE ASSUMED TO BE SECOND ORDER.

Q NO. →	1		2		4		6	
ORDER ↓	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
1	0.0190	----	0.0254	----	0.0381	----	0.0508	----
2	0.0762	0.0762	0.1016	0.1016	0.1525	0.1525	0.2034	0.2034
3	0.1714	----	0.2286	0.2288	0.3431	----	0.4576	0.4582
4	0.3048	----	0.4064	0.4068	0.61	0.6104	0.8136	0.8146
5	0.4762	----	0.635	0.6358	0.9531	----	1.2712	----
6	0.6858	0.6867	0.9144	0.9159	1.3725	1.3737		
7	0.9334	----	1.2446	1.2464				
8	1.2192	1.2210						
9	1.5430	----						

TABLE 7
CALCULATED AND OBSERVED POWDER DIFFRACTION LINE POSITIONS AND
INTENSITIES OF $Dy_{12}Fe_{32}O_{72}$

h	k	l	F^2	d_c	d_o	I_c	I_o
1	1	0	26.1	6.2713		1	
2	0	0	86.9	4.4350		2	
2	1	1	160.8	3.6207	3.6222	21	11
2	2	0	142.6	3.1356	3.1368	6	5
3	1	0	314.9	2.8046	2.8040	48	32
2	2	2	638.9	2.5602	2.5608	54	47
3	2	1	231.1	2.3703	2.3702	36	38
4	0	0	738.8	2.2172	2.2174	40	34
3	3	0	881.5	2.0904	2.0907	100	100
4	1	1	192.3				
4	2	0	81.0	1.9837	1.9834	2	1
4	3	1	115.3				
5	1	0	92.5	1.7394	1.7384	6	5
5	2	1	253.0	1.6193	1.6177	19	14
4	4	0	491.4	1.5678	1.5680	17	19
5	3	0	136.6	1.5210	1.5201	17	18
4	5	3	334.9				
6	0	0	531.0	1.4782	1.4773	10	12
4	4	2	69.5				
6	1	1	223.2	1.4387	1.4375	26	28
5	3	2	295.0	1.3371	1.3369	33	38
6	2	2	578.3	1.2801	1.2800	9	13
4	4	4	555.4				
5	5	0	176.4				
7	1	0	216.6	1.2543	1.2541	5	3
5	4	3	0.4				
6	4	0	111.8	1.2299		1	
7	2	1	58.7				
5	5	2	320.3	1.2069	1.2068	25	23
6	3	3	420.1				
6	4	2	67.6	1.1852		1	
7	3	0	398.4	1.1646	1.1644	13	12
6	5	1	285.6	1.1264	1.1262	12	13
7	3	2	20.0	1.1086	1.1080	3	3
8	0	0	410.2				
7	4	1	300.0				
8	1	1	30.5	1.0917	1.0916	13	16
5	5	4	55.8				
8	2	0	140.1				
6	4	4	5.5	1.0755		1	
6	5	3	99.4	1.0600	1.0597	1	1
8	2	2	94.9	1.0452	1.0449	6	6
6	6	0	390.7				
8	3	1	4.2				
7	5	0	104.2	1.0310	1.0305	10	9
7	4	3	259.4				
6	6	2	338.8	1.0173	1.0171	8	11
8	4	0	276.5	0.9916	0.9912	5	6
9	1	0	20.3	0.9794	0.9791	2	3
8	3	3	159.2				
9	2	1	345.9				
7	6	1	9.3	0.9564	0.9560	25	24
6	5	5	337.7				
8	5	1	58.0				
9	3	0	321.6	0.9349	0.9345	12	14
7	5	4	183.4				
9	3	2	179.2	0.9148	0.9146	8	7
7	6	3	148.1	0.9052	0.9050	9	12
8	4	4	340.7				
8	5	3	82.8	0.8959	0.8957	7	5
9	4	1	112.6				
7	7	0	326.9				
10	0	0	226.2	0.8869		1	
8	6	0	6.3				
7	7	2	187.9	0.8782	0.8779	3	4
10	1	1	51.1				
8	6	2	41.5	0.8697	0.8696	3	3
10	2	0	71.2				
9	4	3	39.0	0.8614		1	
9	5	0	98.1				
10	3	1	30.5				
9	5	2	389.3	0.8456	0.8455	29	31
7	6	5	84.2				
8	7	1	160.3				
7	7	4	379.7	0.8307	0.8305	21	25
8	5	5	129.2				
9	6	1	188.6	0.8165		11	14
10	3	3	171.6	0.8096	0.8096	5	4
10	4	2	137.6				
9	5	4	175.3				
8	7	3	136.3	0.8030	0.8029	16	15
11	1	0	150.1				

TABLE 8
LATTICE PARAMETERS OF $R_{12}Fe_{32}O_{72}$ COMPOUNDS

R	a(Å)
Gd	8.919 ± 0.002
Tb	8.885 ± 0.002
Dy	8.8692 ± 0.0005
Ho	8.8435 ± 0.001
Er	8.815 ± 0.002
Y	8.8832 ± 0.0005

FIGURE CAPTIONS

- Fig. 1 Crystal structure of rare earth-transition metal Laves phase compounds.
- Fig. 2 Schematic of the circuitry used for permeability measurements.
- Fig. 3 Milling time dependence of the mean particle size of the ball-milled powder.
- Fig. 4 Typical scanning electron micrographs of the ball-milled powder at various milling times. (a) prior to the ball milling; (b), (c), (d), (e), (f) after 4, 12, 16, 20, 24 minutes respectively. The particles are mostly platelike with some scatter in their sizes.
- Fig. 5 (a) Low density products prepared by solid-state sintering. Black areas are mainly pores. (b) Oxygen stabilized intermetallics (rounded grains) in the Laves phase matrix. Platelike $R-Fe_3$ precipitates are aligned according to the orientation of the parent Laves phase grains. (c) The same sample as in (b), but under polarized light. Some of the $R-Fe_3$ precipitates appear in white. The arrows point to the faint patterns of magnetic domains formed by the Kerr effect.
- Fig. 6 Equilibrium phase diagram of terbium-iron system.
- Fig. 7 (a) An optical micrograph of the foreign phase formed in a sintered compact. (b) The magnetic powder pattern technique shows no pattern on the foreign phase.

- Fig. 8 X-ray point analysis of the Laves and the β phases. Comparison of (a) and (b) in (c) shows the excess of iron in the β -phase.
- Fig. 9 Atomic distribution in the β -compound.
- Fig. 10 Projection of the β -compound structure on the (001) plane.
- Fig. 11 Network of iron atoms in the β -compound projected on the (001) plane.
- Fig. 12 Temperature dependence of the magnetization in nearly single phase Dy-based β -compound.
- Fig. 13 Effect of density on the relative permeability of the sintered compacts of $\text{Tb}_{.3}\text{Dy}_{.7}\text{Fe}_2$ at various fields.
- Fig. 14 Isothermal time dependence of shrinkage of $\text{Tb}_{.3}\text{Dy}_{.7}\text{Fe}_2$.
- Fig. 15 Time and length corrected isotherms of $\text{Tb}_{.3}\text{Dy}_{.7}\text{Fe}_2$.
- Fig. 16 (a) Optical micrograph of a liquid phase sintered sample of $\text{Tb}_{.3}\text{Dy}_{.7}\text{Fe}_2$; 95% of theoretical density. (b) Scanning electron micrograph of liquid phase sintered sample, 97% theoretical density. Pores appear as black and oxides as white areas.
- Fig. 17 (b) Shows the complex colloidal pattern formed on the surface of a liquid phase sintered $\text{Tb}_{.3}\text{Dy}_{.7}\text{Fe}_2$ sample (a). The pattern, after the sample was magnetized in a field of 20 KOe, is shown in (c).
- Fig. 18 (a) A powder rolled thin plate of DyFe_2 along with the tantalum rack used for the support of the plates during the sintering. (b) Powder rolling mill.

- Fig. 19 Schematic drawing of the cryostat.
- Fig. 20 Photograph of the control panel for the superconducting magnet.
- Fig. 21 Schematic drawing of the vacuum system of the cryostat.
- Fig. 22 Photograph of the cryostat and the vacuum system.
- Fig. 23 Schematic diagram of the circuitry for magnetostriction measurements.
- Fig. 24 Probe for magnetostriction measurements: (A) Samples, (B) Heater, (C) Temperature sensor, (D) Copper mount, (E) Dummy specimen, (F) Copper holder, (G) Strain gauges.
- Fig. 25 Magnetic field dependence of the longitudinal (λ_{11}) and transverse (λ_1) magnetostrictive strains in $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_2$.
- Fig. 26 Temperature dependence of the magnetostriction coefficient of $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_2$ at 25 KOe.
- Fig. 27 Room temperature magnetostriction of sintered $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_2$.
- Fig. 28 Room temperature magnetostriction of a powder rolled laminate of DyFe_2 .
- Fig. 29 Sample probe for dynamic magnetostriction measurements.
- Fig. 30 Experimental set-up for dynamic magnetostriction measurements.
- Fig. 31 Room temperature dynamic magnetostriction of $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_2$.
- Fig. 32 X-ray diffraction patterns for an almost randomly oriented powder and a magnetically aligned specimen of $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_2$ compound.
- Fig. 33 (a) Optical micrograph of a magnetically aligned sintered compact. (b) The colloidal agglomeration observed in the same aligned sample.

- Fig. 34 Low field room temperature magnetostriction of an aligned sample and a liquid phase sintered specimen of $\text{Tb}_{.3}\text{Dy}_{.7}\text{Fe}_2$.
- Fig. 35 Effects of alignment and density on the relative permeability of $\text{Tb}_{.3}\text{Dy}_{.7}\text{Fe}_2$.
- Fig. 36 High field room temperature magnetostriction of an aligned sample and a liquid phase sintered specimen of $\text{Tb}_{.3}\text{Dy}_{.7}\text{Fe}_2$.
- Fig. 37-40 Effect of alignment on the dynamic magnetostrictions observed in samples of $\text{Tb}_{.3}\text{Dy}_{.7}\text{Fe}_2$.
- Fig. 41 Changes of x-ray reflection intensity ratios, $(220)/(311)$ and $(?22)/(311)$, vs. the concentrations of Tb and Dy in magnetically aligned specimens of $\text{Tb}_x\text{Dy}_{1-x}\text{Fe}_2$.
- Fig. 42 X-ray diffraction patterns for a magnetically oriented TbFe_2 specimen.
- Fig. 43 The (440) pole figure for a magnetically aligned TbFe_2 rod.

XBL7711-6376

Fig. 1

Fig. 2

XBL 7511-9445 A

Fig. 3

Fig. 4

c XBB770-12700

Fig. 5

XBL755-6353

Fig. 6

a

b

XBB770-12698

Fig. 7

Fig. 8

$R_{12}Fe_{32}O_2$ - Compounds

 $R = Y, Gd, Tb, Dy, Ho, Er$

 Space Group $Im\bar{3}m-O_h^9$ (Int. Tab. No. 229)

Atom Sites

 $12 R$ in $12e\ 4mm$ (x, o, o) $x = 0.28$
 $8 Fe_I$ in $8c\ \bar{3}m$ ($1/4, 1/4, 1/4$)

 $24 Fe_{II}$ in $24h\ mm$ (o, x, x) $x = 0.667$
 $2 O$ in $2a\ m\bar{3}m$ (o, o, o)

 INTERATOMIC DISTANCES IN $R_{12}Fe_{32}O_2$ COMPOUNDS

 IN UNITS OF a , THE LATTICE PARAMETER

$R - 4R$	at 0.396	$Fe_I - 6R$	at 0.355
$- 4R$	at 0.399	$- 6Fe_I$	at 0.276
$- 4Fe_I$	at 0.355		
$- 4Fe_{II}$	at 0.322	$Fe_{II} - 2R$	at 0.322
$- 4Fe_{II}$	at 0.337	$- 2R$	at 0.337
$- 1 O$	at 0.28	$- 2Fe_I$	at 0.276
		$- 4Fe_{II}$	at 0.289
$O - 6R$	at 0.28	$- 4Fe_{II}$	at 0.33

$$a \approx 8.9\text{\AA}$$

Fig. 9

XBL 759-7328

Fig. 10

XBL 781-4443

Fig. 13

Fig. 14

XBL781-4405

Fig. 15

XBL 781-4406

XBB770-12670

Fig. 16

c

XBB770-12797

Fig. 17

a

b

XBB770-12676

Fig. 18

XBL 766-7042

Fig. 19

XBB766-5191

Fig. 20

XBL 766-7043

Fig. 21

XBB766-5192

Fig. 22

XBL 7711-6377

Fig. 23

a

b

XBB 770-12677

Fig. 24

XBL 7511- 9434

Fig. 25

XBL 7511-9433

Fig. 26

XBL 768-7302

Fig. 27

XBL 7712-6638

/Fig. 28

Fig. 29

XBL78I-4408

Fig. 30

XBL 781-4475

Fig. 31

XBL 779-6122A

Fig. 32

a

b

XBB770-12699

Fig. 33

XBL779-6101

Fig. 34

XBL781-4-450

Fig. 35

XBL 779-6100A

Fig. 36

XBL 781-4472

Fig. 37

XBL 781-4474

Fig. 38

XBL 781-4473

Fig. 39

XBL 781-4471

Fig. 40

Fig. 41

XBL 7710-6203

XBL 779-6121A

Fig. 42

XBL 7710-6156 A

Fig. 43