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13. ABSTRACT *(Maximum 200 words)*

Our efforts in permanent magnets have been focused on the search for new phases and alloys with high magnetization, large anisotropy, and high Curie temperature that can be used for permanent magnet development and on the magnetic hardening behavior of R-Fe-B magnets. The systems studied include Fe-Mo, Co-Zr-B and as-cast Nd(Pr)-rich alloys with coercivities exceeding 6 kOe obtained in the latter two samples. Small additions of Al and Cu have been found to increase the coercivity of melt-spun R-Fe-B magnets substantially (by as much as 8 kOe). The microstructure of the substituted samples is more homogenous with the secondary Nd-Al(Cu)-rich phases uniformly distributed throughout the sample. In addition, disturbed lattice regions were observed at most of the grain boundaries. In Cu-substituted melt-spun samples several faults have been observed inside the 2:14:1 grains. This is the first time that defects were observed in a 2:14:1 matrix and they have been attributed to the small solubility of Cu on Fe. As-cast Nd(Pr)-$Fe_{1-x}Mn_x$-B samples have been found to have large coercivities at cryogenic temperatures. The large coercivities observed are due to domain wall pinning at atomic-size defects caused by the random Mn site occupation (leading to sites with fluctuations in exchange and anisotropy) because of the extremely thin domain walls.

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MAGNETIC HARDENING STUDIES AND NOVEL TECHNIQUES FOR PREPARATION OF HIGH PERFORMANCE MAGNETS

FINAL REPORT

George C. Hadjipanayis

April 28, 1992

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1. Program Objectives

Our efforts in permanent magnet research are focused in the following three areas:

i. Search for new alloys and compounds with high magnetization, large anisotropy and Curie temperature which can be used for permanent magnet development.

ii. Investigation of magnetic hardening in novel permanent magnets by correlating the magnetic properties with the microstructure.

iii. Use of novel processing techniques to obtain fine grain microstructures that would yield high coercivity.

2. Summary of Research Findings

In this contract, we focused our efforts in the areas of new phases—new alloys and in the magnetic hardening behavior of R-Fe-B magnets. Our studies have been very successful and led to numerous publications and presentations at international meetings. Below we describe some of our findings.

2.1 New Phases-Alloys

2.1.1 New Phases in As-Cast Binary Nd(Pr)-Fe Alloys

Our recent studies on Nd-rich, Nd-Fe alloys with eutectic composition aimed at depicting the phase which is liquid at sintering temperatures have shown the existence of new anisotropic phases which originally were believed to be oxygen stabilized. A relatively high coercivity ($\sim$ 6 kOe) was found in as-cast Nd-Fe binary alloys and was attributed to a metastable phase with a Curie temperature $T_c = 250°C$ which is magnetically hard. This phase has been observed as finely dispersed elongated and spherical particles ($\approx 5\ \mu m$) embedded in a nonmagnetic Nd-rich matrix. Another phase was also observed in as-cast binary Nd Fe alloys with $T_c \simeq 230°C$ which is believed to be magnetically soft. Recently, Moreau et al. (1990) determined the structure of the latter phase and found it to be hexagonal with composition Nd_5Fe_{17}. The magnetically hard metastable phase was also observed in as-cast samples and it was found to transform to $Nd_2Fe_{14}B$ after a heat treatment at around 500–600°C. It may be that this metastable phase is formed with oxygen.

2.1.2 In-Situ Crystallization Studies of R-Fe-B Ribbons

The amorphous to crystalline transformation in R-Fe-B ribbons was studied *in situ* in a transmission electron microscope and with X-ray diffraction. Metastable phases of α-Fe(R) and Fe_3B were found to form during crystallization before the final $R_2Fe_{14}B$ phase is formed. The Fe_3B phase is believed to be important for the formation of the 2:14:1 phase because its "local unit structure" is one of the basic building blocks in the 2:14:1 unit cell.

2.1.3 $R_2Fe_{17}N_x$

Ternary compounds of $R_2Fe_{17}N_x$ (R=Nd, Sm) have been prepared by heat treating fine powders of R_2Fe_{17} alloys in N_2 gas. The Sm- Fe-nitrides were found to retain the Th_2Zn_{17} structure of the original alloys but with increased lattice constants (a and c). The Curie temperature increases strongly with x up to 475°C. In $Sm_2Fe_{17}N_x$, the introduction of interstitial nitrogen atoms also leads to an easy axis anisotropy. However, $Nd_2Fe_{17}N_x$ still has an easy-plane anisotropy. A coercive field of 6 kOe has been obtained in Sm-Fe-N powders.

2.1.4 $Sm_2Fe_{17}C_x$

A systematic investigation of the magnetic and structural properties of as-cast $Sm_2Fe_{17}C_x$ compounds with $0 \leq x \leq 1.5$ has been made with X-ray diffraction, thermomagnetic analysis and SQUID magnetometry. Crystal structure studies have shown that the ternary carbides form a rhombohedral Th_2Zn_{17} type structure. The lattice constants at room temperature increase with x indicating that carbon substitutes interstitially like nitrogen. The Curie temperature increases strongly with x from $T_c = 130°C$ for $x = 0$ to 247°C for $x = 1$. The introduction of interstitial carbon atoms into the 2:17 structure leads to a dramatic change of the magnetic anisotropy of $Sm_2Fe_{17}C_x$ compounds. The value of K_1 increases with increasing x and a transition from an "easy plane" to an "easy axis" anisotropy takes place.

2.1.5 Fe-Mo Alloys

The as-spun $Fe_{80}Mo_{20}$ ribbons were found to be magnetically soft with a coercivity smaller than 180 Oe. After a heat-treatment at temperatures in the range of 600–670°C, the coercivity was found to increase to 600 Oe and the magnetization decreased. It is suggested that Mo clustering takes place with heat-treatment and this may explain the decreased magnetization and increased coercivity of the samples. Mo-rich clusters can act as domain wall pinning centers and therefore can lead to an increased coercivity.

2.1.6 Co-Zr-Alloys

Very large coercivities ($H_c \sim$ 6–7 kOe) have been obtained in melt-spun Co-Zr(Hf)-B-Si alloys after a heat-treatment at around 600°C. The high coercivities have been attributed to a heavily faulted $Co_{11}Zr_2$. The saturation magnetization of these alloys is low (M$\sim$60–80 emu/g) when compared with the values for Nd-Fe-B magnets; but the Co-Zr-B based alloys have a higher Curie temperature (450°C), better temperature characteristics, they are ductile and they do not seem to corrode as easily as Nd-Fe-B. The high ductility of these magnets could lead to a less expensive manufacturing process as compared to sintering.

2.2 Magnetic Hardening Studies

2.2.1 Nd-Fe-B Sintered Magnets

We have investigated the effect of Al and post-sintering heat treatment on the hard magnetic properties of Nd-Fe-B based magnets.

i. Effect of Al Substitutions The effect of Al on the coercivity of Nd-Dy-Fe(Al)B magnets has been investigated with magnetic measurements, differential scanning calorimetry, and microstructure studies. The Al containing samples were found to have a much higher coercivity, a relatively steeper initial magnetization curve, a different $H_c(H_{cf})$ curve, and a larger temperature coefficient of coercivity than the samples without Al. Morphology studies made with a scanning electron microscope did not show any significant differences between the two samples. The only evident difference, found in x-ray and electron diffraction data, was in the c/a ratio of the $Nd_2Fe_{14}B$ tetragonal phase which was higher for the sample with Al. Another difference was observed in the magnetization reversal mechanism. In the Al-containing samples the magnetization is reversed by changing the magnetization of entire grains, while for the samples without Al the magnetization is reversed by dividing into domains inside the grains.

ii. Microstructure of Cu-Substituted R-Fe-B Magnets The coercivity of melt-spun Pr-Fe-B ribbons was found to increase with the addition of Cu. The change in size and shape of grains with Cu substitution were investigated by transmission electron microscopy (TEM) and the grain boundary structure was further examined with high resolution electron microscopy (HREM). For small substitutions only "disturbed lattice" regions were observed at most of the grain boundaries. Secondary phases rich in the added elements were observed mostly at tripled grain boundaries and sometimes at grain boundaries in samples with larger amounts of substitution. To our surprise, several faults have been observed in the 2:14:1 grains which were free of defects in non-Cu containing samples. The origin of these faults and the nature of disturbed lattice regions are not yet well understood. The grain size in the substituted samples does not decrease much with further substitution. However, the shape of grains changed from polyhexagons to facets. The enhancement in coercivity was attributed to the grain size reduction and the modification of microstructure at the grain boundary regions.

iii. Effect of Heat Treatment Studies of the differently heat-treated magnets performed with scanning electron microscopy on fractured and polished samples, revealed a morphology consisting of the majority 2:14:1 phase grains ($\sim$ 8–15 μm) and smaller grains of minority B-rich and Nd-rich phases. The biggest difference in morphology between the different kind of samples was in the shape of $Nd_2Fe_{14}B$ grains. The shape of the grains after sintering was irregular with a lot of sharp edges, corners, and concave surfaces. The post-sintering and subsequent annealing processes changed the grain shapes to more regular polyhedra having flat surfaces and less sharp edges and corners. In our opinion, the irregular shapes, sharp edges or corners might be the places of higher demagnetizing fields and therefore easier nucleation or unpinning of domain walls.

Transmission electron microscope studies showed a rather perfect crystal structure of the main phase for all samples. Interactions between domain walls in the main phase and the spherulites of Nd-rich phase were observed. However, we do not think that this interaction was strong enough to explain the high coercivity. We think that the changes of coercivity which occur after heat-treatment are related to macroscopic changes of the grain morphology rather than microscopic changes at around grain boundaries.

iv. Effect of Carbon, Oxygen and Nitrogen on the Microstructure The effect of carbon, oxygen and nitrogen on the microstructure of Nd-Fe- B magnets has been examined in three sintered magnets containing different amounts of the above elements. Carbon was introduced during the melting process while oxygen and nitrogen were introduced during powder processing. All samples had a coercivity greater than 10 kOe. Scanning electron microscopy data showed that the low oxygen and nitrogen magnet had mainly the α-Nd phase as a primary Nd-rich phase at the grain boundaries. When oxygen was high, the α-Nd phase disappeared and instead the gray Nd-oxide appeared as a primary Nd-rich phase. When both oxygen and nitrogen contents were high, a Nd-oxide appeared as a primary Nd-rich phase instead of α-Nd or light grey Nd-oxide. The phase change at grain boundaries may be responsible for the corrosion rate of Nd-Fe-B magnets. TEM data revealed that the Nd-oxides inside the samples were mainly fcc Nd_2O_3. The important effect of carbon when combined with an appropriate oxygen content was to help segregate inclusions in triple conjunctions and to clean and stabilize the grain boundaries.

2.2.2 High Coercivity in As-Cast Nd-Fe-B Based Alloys

High coercivities were obtained in as-cast $R_{17}Dy_xFe_{77}B_yM_{1.5}$ alloys with R=Pr, Nd, M=Al, Cu, Fe, Ag, and x = 0, 1.5, y=3, 5 after a homogenization heat treatment in the temperature range of 900–1100°C. In some samples it was found that further annealing at a lower temperature (600–750°C) leads to a substantial increase in coercivity. Our studies showed that high coercivities can also be obtained in as-cast Nd-Fe-B(M) samples and in samples with other substitutions M besides Cu. In the Nd-Fe-B(M) samples, the highest coercivities ($\sim$ 6 kOe) have been obtained in Ag-substituted samples.

In as-cast Pr-Fe B(M), the highest coercivities have been obtained with Cu and Al substitutions. Addition of small amounts of Dy led to an increase in coercivity in Nd-Fe-B(M) but to a decrease in H_c in Pr-Fe-B(M). Microstructural studies showed the presence of three phases consistent with the thermomagnetic data. The majority phase was $R_2Fe_{14}B$ while the minority phase was rare-earth and Cu-rich. The other phase was R_2Fe_{17}. The R-Cu-rich phase was observed at the grain boundaries of the $R_2Fe_{14}B$ phase. The addition of impurities appeared to promote the formation of this phase which was uniformly distributed at grain boundaries after a homogenization heat treatment.

2.2.3 High Coercivity in As-Cast Mn-Substituted R-Fe-B Alloys

The structural and magnetic properties of $Pr_{13}Fe_{82-x}Mn_xB_5$ alloys have been studied in a wide temperature range. X-ray diffraction data showed the presence of 2:14:1 phase in all the samples. A maximum coercivity of 30 kOe at 10 K was observed in a sample containing 22% Mn, which dropped rapidly to a value of 8 kOe at 40 K and was negligible at temperatures above 120 K. The coercivity of the Mn-free sample was less than 1 kOe at 10 K. The Curie temperature of the alloys dropped drastically with Mn substitution from 580 to 120 K for the x=3 sample. Initial magnetization data showed a domain wall pinning-like behavior. It is suggested that this domain wall pinning occurs at atomic size defects because of the extremely thin size of domain walls in these alloys.

2.2.4 High Coercivity in Melt-Spun R-Fe-C

In previous studies, we have shown that carbon can be substituted for much of the boron in R-Fe-B alloys and the 2:14:1 phase can still be formed. At that time it was reported that 75% of boron can be substituted with carbon in alloys containing neodymium and praseodymium. The anisotropy field and saturation magnetization were found to decrease substantially with carbon addition. In Dy-Fe-C the 2:14:1 phase was found to be formed with carbon and a high coercivity was observed in as-cast samples. Recently, we have prepared melt-spun R-Fe-C alloys and we studied their magnetic properties. The highest coercivities (10–15 kOe) were obtained in melt-spun $Nd_{14}Fe_{80}C_6$ and $Pr_{14}Fe_{80}C_6$ samples which were heat treated at 750°C for 2–15 minutes. The Curie temperature of the $(Nd, Pr)_2Fe_{14}C$ phase was approximately 290°C. The high coercivities are attributed to a fine grain microstructure (grain size, 800 Å) which is formed during crystallization. The same behavior has been observed in melt-spun Nd(Pr)-Fe-B alloys.

The $(Nd, Pr)_2Fe_{14}C$ phase is believed to be present in as-cast alloys too. However, the phase is formed at low temperatures (below 900°C) and therefore very long annealing times are needed to obtain a single-phase sample.

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