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HARD MAGNETIC Fe-BASED / 2:14:1 SYSTEM

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This paper presents our results related to the dependence of the magnetic hysteresis parameters on the microstructure of the two phase $\alpha Fe/Nd_2Fe_{14}B$ alloys obtained by rapid quenching from the melt technique as thin (thickness lower than 30μm) ribbons. We have studied the influence on the magnetic properties of the annealing procedures performed on the as-cast specimens: isothermal annealing and magnetic field annealing, which due to their peculiarities, induce a specific microstructure. In conjunction with this, we have also studied the influence of the additions such as Cu, Nb, and Ga at the NdFeB base composition, respectively Co substitution for Fe and Dy substitution for Nd with the aim to improve the hard magnetic properties. Macroscopic investigations are completed by specific studies as irreversible susceptibility χ_{irrev} which gives qualitative information on the intergrain interactions.

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1. Introduction

Magnetic properties of NdFeB alloys are determined by structure and component phases. Permanent magnet behavior of the two-phase Fe-based/$Nd_2Fe_{14}B$ systems results from the magnetic hardening of the Fe-based soft magnetic phase by the $Nd_2Fe_{14}B$ hard magnetic phase through exchange interactions when the structure is refined to the nanometer scale. If the grains are single domain particles of the same order of magnitude as the double domain wall width of the 2:14:1 phase and are uniformly distributed, then they will be coupled through exchange interactions, ensuring in this way hard magnetic properties of high performance to the entire ensemble [1].

In this work we present some results concerning the effect of some alloying elements and different types of treatment performed on the as-cast precursor alloys, on the magnetic properties: isothermal treatment and magnetic-field annealing. In our investigation we focus on $Nd_8Fe_{86-x}B_6M_x$ system with multiple substitution of Cu, Nb, Ga, Co for Fe and Dy for Nd.

2. Experiment

NdFeB alloys at which we added Cu, Nb, Ga, Co and Dy were cast by arc melting the pure constituents. The ingots were subjected to consecutive melting in order to achieve a high degree of homogeneity. $Nd_8Fe_{82}CuNb_3B_6$ (A), $Nd_8Fe_{77}Co_5CuNb_3B_6$ (B) $Nd_8Fe_{80}Co_5GaB_6$ (C) and $Nd_7DyFe_{86}B_6$ (D) rapidly quenched ribbons, with amorphous (A, B and C) and nanocrystalline (D) structure, were produced under an argon atmosphere by melt-spinning technique at a wheel circumferential speed of 27m/s By using the same processing parameters, ribbons produced from each compositions were typically between 22 and 28μm thick. Differential Thermal Analyses (DTA) scans and thermomagnetic curves were performed in order to follow the crystallization process of the as-cast amorphous samples and to magnetically characterize the formed phases during the crystallization steps respectively. The amorphous samples were subsequently heat treated at 750^0C for different periods of time of 1,3 and 5 min. Supplementary, another part of the same sort of ribbons was subjected to an external applied magnetic field of 0.8T during the same types of annealing. D-type samples were treated separately since they revealed a nanocrystalline structure in as-cast state. The hysteresis MH loops together with recoil curves corresponding to each treatment were measured with a vibrating sample magnetometer (VSM) in a maximum applied field of 1.6T.

3. Results and discussion

In order to decide on the proper annealing temperatures for which a stable two-phase structure is obtained, DTA and thermomagnetic investigations have been performed. It was observed that the complete crystallization leading to the final stable two-phase Fe-based/$Nd_2Fe_{14}B$ crystalline structure takes place through two or three stages corresponding to the formation of some metastable phases [2]. We performed these measurements on the initially amorphous samples. The identified ferromagnetic phases [3] along with their Curie temperature are noted in table 1.

Table 1. The Curie temperature of the amorphous and identified metastable phases in $Nd_8Fe_{82}CuNb_3B_6$ and $Nd_8Fe_{77}Co_5CuNb_3B_6$ initially amorphous ribbons.

Sample	T_C (^oC) amorphous phase	T_C (^oC) –identified metastable phase	T_C (^oC) stable phases
$Nd_8Fe_{82}CuNb_3B_6$	126	208 [$Nd_3Fe_{62}B_{14}$] after heating 1h/600^{o}C	320 [$Nd_2Fe_{14}B$] after heating at 750^{o}C 770 [αFe] after heating at 600^{o}C
$Nd_8Fe_{77}Co_5CuNb_3B_6$	190	230 [$Nd_3(Fe,Co)_{62}B_{14}$] after heating up to 600^{o}C	370 [$Nd_2(Fe,Co)_{14}B$] after heating at 700^{o}C 820 [α(Fe,Co)] after heating at 600^{o}C

From DTA and thermomagnetic results there was inferred that the proper annealing temperatures necessary to obtain the intended Fe-based/$Nd_2Fe_{14}B$ two-phase system from the amorphous phase, should be at least 700^{O}C. The values of the magnetic hysteresis parameters for A, B, C samples are given in table 2.

The thermomagnetic treatments at temperatures lower than the Curie temperature of the involved ferromagnetic phases are frequently used for soft magnetic materials to increase the permeability by inducing an anisotropy along the direction of the applied field. In our case, the annealing temperature of 700^{o}C has been chosen between the Curie temperatures of the component stable phases. The effect of the magnetic-field m-f annealing and stress relief treatment on the investigated samples is revealed in table 2 through the values of coercivity and remanence.

Table 2. Coercivity H_c(kOe) and remanence M_r(emu/g) of the investigated alloys.

Composition	annealing 5min/700^{o}C	m-f annealing 5 min/700^{o}C/0.8T	stress-relief 40min/250^{o}C
$Nd_8Fe_{82}CuNb_3B_6$ (A)	H_c=3.5 M_r=74.9	H_c=3.3 M_r=67.8	H_c=2.7 M_r=59.8
$Nd_8Fe_{77}Co_5CuNb_3B_6$ (B)	H_c=2.3 M_r=87	H_c=2.5 M_r=71.6	H_c=4.7 M_r=87.5
$Nd_8Fe_{80}Co_5GaB_6$ (C)	H_c=2.5 M_r=52	H_c=2.8 M_r=56.4	H_c=3.9 M_r=61.6

One can observe that for the Co free sample, the m-f annealing slightly reduces the coercivity which further decreases after stress-relief treatment, whereas for the Co containing samples, the coercivity increases by annealing in an external applied magnetic field and by subsequently performing a stress relief treatment. After magnetic and stress relief treatments, the remanence decreases for sample A and increases for sample C. For sample B, the magnetic field applied during annealing leads to a decrease of the remanence, but the stress relief treatment enhances it to the same value as that obtained by conventional annealing. The behavior of the Co containing samples subjected to the magnetic field could be explained by a directional ordering process of the ferromagnetic Fe-Co atomic pairs in α(Fe,Co), in which the lattice parameter is changed inducing local strains. These internal stresses result in an increased coercivity. By maintaining the ribbons to a temperature lower than the Curie temperature of the hard phase ($T_{C(Nd2(Fe,Co)14B)}=360^{o}C$), the internal stresses existing within the samples that probably suppress the moments alignment in external applied magnetic field are relieved resulting in an increase of the exchange coupling effect between the grains ($\delta M>0$ and increases) and hence and improvement of coercivity and remanence.

The increase of the remanence accompanied by the increase of the coercivity is closely related to the grains' refinement and distribution [4]. For a mean grain size approaching the exchange length l_{ex} of the α (Fe, Co) phase, almost all magnetic moments of the soft phase are aligned to the direction of the H=1.6T applied field. This leads to an enhanced remanence as compared to the case when the diameter of the soft magnetic grains exceeds l_{ex}. The simultaneous increase of the coercivity is a consequence of the reduced size of the grains and their homogeneous distribution. In the two-phase $\alpha Fe/Nd_2Fe_{14}B$ based magnets, the coercivity is determined by the nucleation of reversed domains within the soft magnetic phase that initiates an in-avalanche demagnetization process. But with decreasing the grain size, the nucleation of reversed domains is suppressed by exchange interaction between hard and soft magnetic phases (so called exchange hardening) leading to an increased coercivity. The difference between the behavior of the samples (B) and (C) as concerns the tendency in evolution of the remanence and coercivity is definitely related to the difference in grains size. For a detailed explanation of the behavior of the $\alpha Fe/Nd_2Fe_{14}B$ samples with or without Co addition, further investigations (including Mössbauer studies) are necessary.

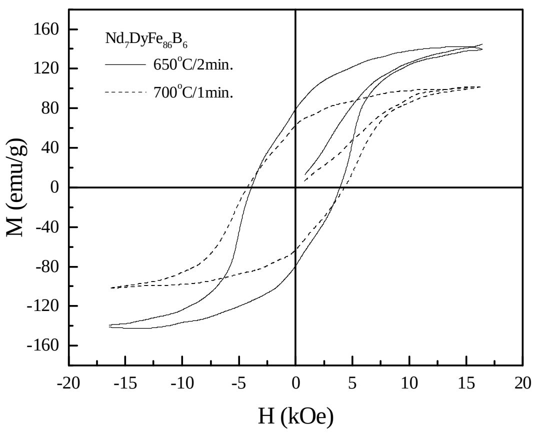

Fig. 3. Hysteresis loops of $Nd_7DyFe_{86}B_6$ ribbons annealed 2 min. at 650°C and 1 min at 700°C.

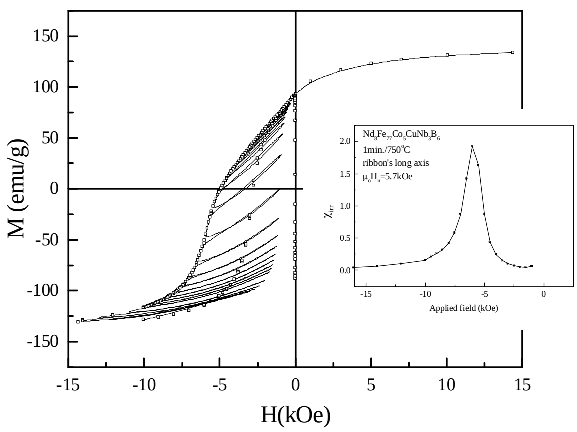

Fig. 4. Hysteresis loop and recoil curves in negative applied field for $Nd_8Fe_{77}Co_5CuNb_3B_6$ ribbon treated 1 min at 750°C. Inset: the calculated irreversible susceptibility.

Dy substitution for Nd has as main effect, the increase of coercivity due to the increase of the magnetocrystalline anisotropy [5]. The $Nd_7DyFe_{86}B_6$ ribbons had a nanocrystalline structure obtained directly from the melt spinning process, with the average diameter of the grains estimated (through Warren-Averbach analyses [6]) at about 13nm. Fig.3 presents the hysteresis loops of the samples annealed 2 min. at 650°C and 1 min at 700°C. Despite a theoretically proper value of the mean grain size in as-cast state, the best magnetic properties were achieved by annealing at 650^{o}C for 2 min, probably due to an inhomogeneous structure.

All samples A, B, C, D reveal an exchange-spring behavior with a high value of the remanent coercivity (for which, by suppressing the field, the sample is demagnetized) of about 7kOe. In fig.4, the recoil loops are drawn only for the $Nd_8Fe_{77}Co_5CuNb_3B_6$ ribbons to avoid the superposing. The mean nucleation field H_n of the reverse domains corresponding to the hard phase can be deduced from the maximum of the dc irreversible susceptibility χ_{irr}=dM$_r$(H)/dH defined as the first derivative of the remanent magnetization as a function of the applied field on the demagnetization run. The value obtained for the Co containing sample, H_n=5.7kOe is closer to the corresponding coercive field H_c=5kOe than in the case of the $Nd_8Fe_{82}CuNb_3B_6$ ribbons annealed in the same conditions (H_n=6 kOe; H_c =4.7 kOe). This fact, together with the well defined sharp peak of the χ_{irr}(H), suggests a good exchange coupling of the component hard and soft magnetic grains especially for the former composition.

4. Conclusions

We presented our results regarding the magnetic properties of $\alpha Fe/Nd_2Fe_{14}B$ alloys at which we added several alloying elements: Cu, Nb, Ga, Co as substitute for Fe and Dy for Nd. The investigated samples were $Nd_8Fe_{82}CuNb_3B_6$, $Nd_8Fe_{77}Co_5CuNb_3B_6$, $Nd_8Fe_{80}Co_5GaB_6$ and $Nd_7DyFe_{86}B_6$ thin ribbons.

Magnetic field annealing slightly increases the coercivity of the Co-containing samples as compared to isothermal annealing and a subsequent stress-relief treatment results in an enhancement of both coercivity and remanence as a consequence of improving the exchange coupling between the grains. We associated these results with a directional ordering process of the ferromagnetic Fe-Co atomic pairs in α(Fe,Co), in which the lattice parameter is changed.

All investigated samples reveal an exchange-spring behavior with a high value of the remanent coercivity.

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