Microstructure and magnetic properties of binary Nd$_{80}$Fe$_{20}$ with Ga additions

M. Stoica$^{1}$, M. Emmi$^{1,2}$, S. Ram$^2$, A. Wiedenmann$^{3,4}$, O. Perroud$^{3,5}$, J. Eckert$^{1,6}$

$^1$ IFW Dresden, Institute for Complex Materials, P.O. Box 270116, D-01171 Dresden, Germany
$^2$ Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India
$^3$ Hahn Meitner Institute Berlin, Glienicker Strasse 100, D-14109 Berlin, Germany
$^4$ present address: Institut Laue-Langevin (ILL) Grenoble, France
$^5$ present address: Université Paul Cézanne Aix-Marseille III, France
$^6$ also at TU Dresden, Institute of Materials Science, D-01062 Dresden, Germany

E-mail: m.stoica@ifw-dresden.de

Abstract. In this work, structural and magnetic properties of metastable Nd-rich Nd$_{80}$Fe$_{20}$ binary and (Nd-Ga)$_{80}$Fe$_{20}$ ternary alloys are investigated. The specimens were prepared at different cooling rates, varying from 5 to 150 K/s by using copper mold casting and at $10^6$ K/s by melt spinning. Specimens with different dimensions were prepared in order to change the cooling rate. The aim of the present work was to characterize a metastable hard magnetic phase referred to as “A1” in Nd$_{80}$Fe$_{20}$ alloys, which forms as a part of the fine eutectic depending on the cooling rate. In order to stabilize the formation of A1, (Nd$_{100-x}$Ga$_x$)$_{80}$Fe$_{20}$ ($x = 5, 10, 15$) alloys were rapidly cooled at a solidification rate of $\leq 150$ K/s.

1. Introduction
The observation of metastable Nd-Fe binary phases in Nd-Fe-B magnets stimulated a careful re-analysis of Nd-Fe binary alloys in order to understand the phase formation [1]. The role of other additives like B, C, Al, and O for stabilizing metastable Nd-Fe phases has also been intensively studied [2-4]. Despite these extensive studies of the binary Nd-Fe alloy system the overall consistent information available is limited. Different authors have reported different results for the same composition. One of the reasons for this discrepancy is that the phase selection in the binary Nd-Fe system depends sensitively on the cooling rate, the purity of the elements, and the starting composition. In most of the studies arc melting and copper mold casting were used as sample preparation techniques, which impose different cooling rates depending on the sample geometry and apparatus in use. Therefore, in spite of the same starting composition different studies show different results due to a variation of the cooling conditions.

It is known that a metastable hard magnetic phase forms for compositions close to the Nd-Fe eutectic [5]. Therefore, it is essential to understand the correlation between cooling rate and microstructure for quantification of the magnetic properties of Nd-Fe alloys. For this purpose, Nd$_{80}$Fe$_{20}$ alloys prepared at different cooling rates in the range of 25-150 K/s were systematically analyzed. These alloys contain Nd and the most disputable metastable hard magnetic A1 “phase”, which justifies the selection of this

* To whom any correspondence should be addressed.
particular composition. Further, the addition of Ga was investigated. Ga has a positive heat of mixing with Nd and Fe [6] and helps to refine the big Nd grains. By adding Ga, the formation of the hard magnetic A1 phase may be promoted and the overall magnetic properties may become better.

The purpose of this work was to study the influence of the cooling rate and small compositional variation on the structure of metastable Nd-Ga-Fe alloys. Additionally, the magnetic properties and the changes induced by variation of cooling rate and composition will be discussed in the light of the structural modification.

2. Experimental

The present work deals with rapidly solidified Nd-Ga-Fe alloys. High purity elements (Nd (99.9 wt.%), Fe (99.99 wt.%), and Ga (99.9 wt.%)) were used as starting materials. The prealloyed ingots were prepared from small lumps of each chemical constituent. The elements were melted in an arc-melting furnace under an argon (99.999 wt.%) pressure of 6 x 10^4 Pa. The pre-alloyed ingots were used as precursor materials for further sample preparation. In order to obtain a variety of stable and metastable phases, nonequilibrium cooling from the melt was considered essential. Techniques like melt spinning and centrifugal copper mold casting were utilized to employ a wide range of cooling rates. High cooling rates of typically 10^6 K/s are achieved in melt spinning experiments [7]. The gradient in the cooling rate along the thickness of the ribbons was not considered in the present study. The high cooling rates employed in melt spinning limit the sample size to thin metal films or sheets of about 50 mm thickness. These specimens are difficult to be used for a large number of experiments, which require bulk samples. Bulk nanocrystalline alloys are usually prepared by copper mold casting. There, the cooling rate primarily depends on the geometry of the mold. Cooling rates were measured both directly and indirectly [8]. Direct measurements involve temperature measurements using thermoelectric or pyrometric methods. However, uncertainties are implicit in the calculation of cooling rates because of the poor accuracy of the temperature measurement and its local fluctuations. Indirect measurements of the cooling rate are usually performed by determining its value from various microstructural features such as the dendrite arm spacing [9,10]. In these methods, the microstructure-cooling rate correlations at low cooling rate are assumed to remain valid at higher cooling rates. Despite the accuracy criteria, these methods are widely used in measuring the local average cooling rate [8-10]. However, the cooling rate is not homogeneous and varies along the length and the diameter of the specimen. According to our expertise and in order to keep things as simple as possible, only cylindrical rod-shaped samples were produced, with various diameters and the same length of 5 cm. Further, we consider that the rods with 3 mm diameter were cooled at 150 K/s, the 5 mm diameter rods at 100 K/s and the 7 mm diameter rods at 50 K/s. The cooling rate of 25 K/s corresponds to the master alloy left to solidify in contact with the water cooled bottom copper plate of the arc melter. For characterization, the specimens were cut from the bottom 5 mm region to exclude the effect of a gradient in the cooling rate along the length of the specimens. The phases were identified by X-ray diffraction (XRD) using Mo Kα (λ = 0.07093 nm). Metallographic investigations were carried out using a JEOL 6400 scanning electron microscope (SEM) equipped with an energy-dispersive spectrometer (EDX). The magnetic properties were measured by using a vibrating sample magnetometer (VSM) with a maximum applied field of 2 T.

3. Results and discussion

a) Binary Nd_{80}Fe_{20} rapidly quenched alloys

For studying the effect of the cooling rate, Nd_{80}Fe_{20} alloys were prepared at different cooling rates of ~ 150, 100, 50, and 25 K/s and analyzed by x-ray diffraction (XRD) (results published elsewhere [11]). The samples cooled at ≥ 50 K/s show diffraction peaks of dhcp Nd and fcc Nd-rich phases. On the other hand, the samples cooled at ~ 25 K/s exhibit distinct Nd_{2}Fe_{17} peaks in addition to the peaks of dhcp Nd and fcc Nd-rich phases. No sample shows peaks of the hexagonal Nd_{5}Fe_{17} phase in the as-cast state. These results define the range of cooling rates for the formation of the Nd_{2}Fe_{17} phase in
hypereutectic Nd$_{80}$Fe$_{20}$ alloys. The XRD patterns for the Nd$_{80}$Fe$_{20}$ mold-cast alloys prepared at different cooling rates can be summarized as follows:

1. dhcp Nd, rhombohedral Nd$_2$Fe$_{17}$, and fcc Nd-rich peaks if the cooling rate is $\leq$ 25 K/s.
2. dhcp Nd and fcc Nd-rich peaks with no indications for the formation of Nd-Fe intermetallic phases for cooling rates $\geq$ 50 K/s.

Figure 1 shows a scanning electron microscopy (SEM) back-scattered micrograph of the cross-section of a Nd$_{80}$Fe$_{20}$ sample cooled at ~ 150 K/s (mold-cast rod with 3 mm diameter). Two notable features observed from the micrograph are the gray equiaxed Nd grains and the eutectic ($E$). The eutectic lamellae are irregular and discontinuous along the cross-section of the specimen. The size of the eutectic lamellae and, hence, the interlamellar spacing varies from one region to the other. This inhomogeneous microstructure suggests a non-uniform heat flow and different local cooling rates.

According to eutectic growth theory, the interlamellar spacing is constant for a given growth rate [12]. However, if the growth rate increases, one would expect the interlamellar spacing to decrease by the formation of new lamellae. The energy dispersive x-ray (EDX) analysis identifies the primary grains as Nd crystallites. The volume fraction of primary Nd crystallites is estimated to be about 57 vol.%. This is much higher than the expected value of about 12 vol.% from the Nd-Fe phase diagram [1]. This discrepancy is due to the fact that some of the eutectic Nd has submerged with the primary Nd crystallites. The size of the eutectic lamellae is smaller than 1 µm and, therefore, their composition could not be determined with high enough accuracy. A line-scan along the eutectic region shows that the Fe content is higher in the bright region than in the gray one. This type of eutectic structure observed in the Nd-Fe alloys is referred to as Nd + Al [1].

As was shown previously [11,13], the hard magnetic properties are strictly related to Al regions. Therefore, a higher volume fraction of Al will make the samples magnetically harder. The samples cooled at rates between 75 and 150 K/s show similar features with a large coercivity of 0.44-0.48 T and a remanence of 7.4-9.7 Am$^2$/kg [11,13]. On the other hand, the alloys cooled at rates below 75 K/s show a two-phase magnetic behavior with a step in the demagnetization curves near to zero field. This is due to the presence of the soft magnetic Nd$_2$Fe$_{17}$ phase along with the hard magnetic Al regions.

It has been also shown that the structure of the samples changes with the variation of the cooling rate [11,13]. In order to extend the Al zones, i.e. to enhance the hard magnetic properties, it is not enough to play only with the cooling rate. The other possibility which can be considered is to use addition of an element which may refine the structure. In this way the big Nd grains may become smaller, the Al zone extends and as a consequence the overall hard magnetic properties may be improved. Such an element is Ga: it has a positive heat of mixing with both Nd and Fe [6] and, therefore, a very limited solubility.

b) Ternary (Nd$_{100-x}$Ga$_x$)$_{80}$Fe$_{20}$ ($x = 5, 10, 15$) rapidly quenched alloys

Figures 2 (a)-(d) show the XRD patterns for (Nd$_{100-x}$Ga$_x$)$_{80}$Fe$_{20}$ ($x = 5, 10, 15$) melt spun and mold-cast alloys prepared under identical conditions (i.e., ribbons, similar rod diameter and casting conditions).
The alloys display diffraction peaks corresponding to \(\alpha\)-Nd, \(\text{Nd}_2\text{Fe}_{17}\), \(\text{Fe}_5\text{Nd}\) and \(\text{Nd}_5\text{Fe}_{17}\) phase. There are two observations to be noted from these XRD patterns. First, according to the Nd-Fe binary phase diagram [1], an eutectic of Nd + \(\text{Nd}_5\text{Fe}_{17}\) is expected to form along with primary crystallites of Nd. However, the observed XRD patterns give no indications for the formation of \(\text{Nd}_5\text{Fe}_{17}\) (except in case of melt spun ribbon samples, Fig. 2 (a)). This implies that either the formation of \(\text{Nd}_5\text{Fe}_{17}\) is suppressed due to non-equilibrium cooling conditions or the fraction of the \(\text{Nd}_5\text{Fe}_{17}\) phase is below the detection limit of XRD. According to the Nd-Fe phase diagram, the expected amount of \(\text{Nd}_5\text{Fe}_{17}\) is about 26 vol.% for the Nd$_{80}$Fe$_{20}$ alloy, which is well above the detection limit of XRD. It has been reported [13] that the \(\text{Nd}_5\text{Fe}_{17}\) phase is usually not formed in as-cast Nd-Fe alloys due to its slow formation kinetics by the peritectic reaction between the Nd-rich liquid and the \(\text{Nd}_2\text{Fe}_{17}\) phase. Therefore, the first indication from the XRD patterns is that the eutectic in mold-cast Nd-Fe-Ga alloys is not Nd + \(\text{Nd}_5\text{Fe}_{17}\).

The second feature of the XRD patterns of as-cast (Nd$_{100-x}$Ga$_x$)$_{80}$Fe$_{20}$ specimens is the absence of diffraction peaks corresponding to any known Nd-Fe-Ga intermetallic phase. This implies that Ga is either dissolved in \(\alpha\)-Nd / Nd-Fe intermetallic phase(s) or present in a separate nanocrystalline or amorphous phase, which cannot be resolved by x-ray diffraction. Further studies [14] have shown without doubt that the Ga atoms are uniformly distributed in the entire volume of the sample. In fact, the structure of the samples and, consequently, the magnetic properties, can be tuned in two ways: by adjusting the cooling rate and by composition variation. In order to explain this behavior better, two extreme cases will be described here: rods with 3 mm diameter (cooled at \(\sim 150 \text{ K/s}\)) and rods with 7 mm diameter (\(\sim 50 \text{ K/s}\)). The samples were checked by SEM with EDX analysis. The results,
corroborated by XRD studies lead to the following: For $x = 5$ (which corresponds to 4 at.% Ga addition to binary Nd$_{80}$Fe$_{20}$), the structure is very refined. Small Nd and Ga grains coexist with A1 hard magnetic zones. Once the Ga content increases, the refinement of the A1 zones is lost and new crystalline soft magnetic phases appear. These crystalline phases were identified as Nd$_5$Fe$_{17}$ and Fe$_2$Nd. The appearance of the Fe$_2$Nd phase is very interesting, because this phase does not appear in the NdFe phase diagram as an equilibrium phase, but some reports mentioned that it may form if some conditions are fulfilled [15]. In our case is clear that the Ga additions and, consequently, the shift of the composition from hypereutectic to hypoeutectic is the reason. At a first glance one cannot say if this phase is completely magnetically ordered; for that, additional neutron diffraction studies should be performed.

Apparently, for samples cast at the same cooling rate (~150 K/s in this case), small Ga additions refine the microstructure. As a consequence, the hard magnetic properties improve. Fig. 3 (a) shows the hysteresis loops recorded for 3 mm diameter samples with different Ga content. The alloy with $x = 5$ shows the highest remanence and coercivity. Its energy product is slightly higher than for similar samples without Ga addition [13]. As the Ga content increases (Fig. 3), the soft magnetic phases start to appear and the hysteresis loops show a characteristic two-phase behavior, with a reduction of coercivity and remanence. This two-phase behaviour appear because of the non-optimal magnetic coupling between hard and soft magnetic phases, i.e. the dimension of the precipitated soft magnetic phases are too big [14].

In the case of 7 mm diameter NdFe samples with different Ga content, the most pronounced refinement of A1 zones is obtained for $x = 10$ (which corresponds to 12 at.% Ga addition). Fig. 3 (b) shows the hysteresis loops for these samples. The sample with the best hard magnetic properties is the one with $x = 10$, as expected from analyzing the SEM micrographs [14]. The sample with $x = 5$ is also hard magnetic, but here the volume fraction of the A1 zones is more limited. When $x$ increases to 15, new soft magnetic phase(s) (especially Fe$_2$Nd) will change the magnetization/demagnetization behaviour and the loop again exhibits the shape characteristic for two-phase magnets.

**4. Conclusions**

The structural and magnetic properties of (Nd$_{100-x}$Ga$_x$)$_{80}$Fe$_{20}$ ($x = 0, 5, 10, 15$) alloys were investigated. According to the Nd-Fe binary phase diagram, the equilibrium eutectic is Nd + Nd$_5$Fe$_{17}$. The phase selection in Nd-Fe alloys depends sensitively on composition and cooling rate. The alloys cooled at 150 K/s reveal the formation of Nd + A1. A1 is a notation used for the Fe-containing regions in the metastable eutectic, which consist of a mixture of nm-sized crystallites and an amorphous phase. The A1 regions are responsible for hard magnetic properties. In order to increase the amount of A1 by
decreasing the size of hexagonal Nd grains, Ga additions were made to the starting binary alloy. Several samples were prepared at the same cooling rate as used for Nd₈₀Fe₂₀. For 4 at.% Ga and a cooling rate of ~ 150 K/s, the structure changes and the hard magnetic properties become better: a coercivity of 4.06 kA/m (which correspond to 0.51 T) and a remanence of 9.76 Am²/kg were measured. For this cooling rate, a further increase in the Ga content induces the appearance of soft magnetic phases and the overall magnetic behavior changes to a two-phase magnet. When the Ga content reaches 12 at.% and the cooling rate is lowered to ~50 K/s, the coercivity slightly increases (to 4.12 kA/m or 0.52 T) and the remanence slightly decreases (to 9.32 Am²/kg), but the energy product remains almost the same. However, in comparison with the starting binary alloy, the addition of a non-magnetic element increases the hard magnetic properties just by changing the structure of the sample. Therefore, the magnetic properties determined only by Nd and Fe can be adjusted by tuning the structure, i.e. by tailoring the composition and the cooling rate.

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