Transmission electron microscope characterization of cast and hot-worked $R$-Fe-B:Cu($R$=Nd,Pr) permanent magnets

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The hard magnetic properties of hot-worked $R$-Fe-B permanent magnets are improved by the addition of a minor amount of Cu (up to 2 at. %). Transmission electron microscope investigations show that the reason for the increase of the coercivity is the fact that Cu is mainly dissolved in the intergranular region separating the hard magnetic 2:14:1 grains. The results obtained are similar in Nd-Fe-B:Cu and Pr-Fe-B:Cu magnets. The intergranular region has been observed to consist of a eutectic consisting of two phases: the Nd- or Pr-rich phase and the orthorhombic NdCu- or PrCu-phase. This corresponds to the eutectic decomposition of the liquid intergranular phase during cooling. It is suggested that the decrease of the melting temperature of the intergranular phase leads to a better wetting behavior and separation of the hard magnetic grains, and therefore to an enhancement of the coercivity.

I. INTRODUCTION

Rare-earth iron-boron-based permanent magnets exhibit the highest energy density products obtained so far. Two major limitations have hindered these materials from widespread use. One is the decrease of the coercivity at elevated temperatures, and the other is the relatively high cost for mass production of anisotropic magnets by the conventional powder metallurgical sintering process or by the rapid quench/hot-press/die-upset method. Another cost for mass production of anisotropic magnets is the separation of the hard magnetic grains. The purpose of our investigations is to characterize the multiphase microstructure of hot-worked $R$-Fe-B:Cu($R$=Nd,Pr) permanent magnets and to compare the results with sintered or melt-spun magnets.

II. EXPERIMENT

A set of a hot-pressed Nd$_{17}$Fe$_{76}$B$_5$Cu$_2$ magnets, which was supplied by the C.N.R.S. Grenoble, Laboratoire Louis Neél, and a set of cast and annealed Pr$_{17}$Fe$_{77.5}$B$_4$Cu$_{1.5}$ magnets, which were supplied by the Philips Research Laboratories, Eindhoven, were investigated by analytical transmission electron microscope (AEM). The Pr-containing magnet was annealed for 1 day at 975°C. The magnets were examined in a JEOL 200 CX scanning transmission electron microscope fitted with a high takeoff angle energy-dispersive Si-detector and a low takeoff angle Ge-detector for light-element x-ray analysis.

III. RESULTS

Our previous AEM investigations of sintered Nd$_2$Fe$_{14}$B-based magnets revealed a multiphase microstructure consisting of at least three types of phases: the hard magnetic Nd$_2$Fe$_{14}$B phase, the Nd$_{1+e}$FeB$_4$ phase, and the low-melting, intergranular Nd-rich phase. In addition new intergranular phases, such as NbFe$_2$, NbFeB$_2$, Al$_2$Fe$_1$Nd$_6$, and NdGa, were detected in $R$-Fe-B:Cu magnets. The 2:14:1 phase is always found to be free of crystal defects and containing a minor amount of dissolved Cu (up to 1 at. % Cu). Besides the 2:14:1 phase the R-rich phases with the fcc crystal structure are also shown in Fig. 1. It should be mentioned that in neither the Nd-rich phase nor in the Pr-rich phase is a significant Cu-content found in the corresponding x-ray spectra.

In contrast to previous transmission electron microscopy (TEM) investigations of R-Fe-B-based magnets, we found in the Cu-containing magnets grains with a grain size up to several μm and a composition similar to the 2:14:1 grains, but showing a high defect density within the grain interior (Fig. 2). The reason for the occurrence of this phase is not yet known. The identification of the planar defects is currently undertaken.

Similar to the results obtained in Al- or Ga-doped NdFe-B:Al$_3$Ga) sintered magnets, we also found in the Cu-containing magnets a new intergranular RCu phase. The micrographs of Fig. 3 show clearly that the new Cu-containing phase is separated in the intergranular region from the Pr-rich phase. From x-ray microanalysis, the ratio in at. % of Pr/(Cu + Fe) was determined to be close to 1.0, whereas the total amount of Fe was detected up to 17 at. %. The thickness of the banded structure due to the eutectic decomposition in Fig. 3 is in the order of 100–300 nm, which is larger than the spatial resolution of the x-ray microanalytic technique used. Figure 4 shows the fine-
FIG. 1. Transmission electron micrographs showing the hard magnetic 2:14:1 phases and R-rich phases of the (a) Nd-Fe-B:Cu and (b) Pr-Fe-B:Cu magnets.

grain intergranular NdCu phase in the Nd$_{17}$Fe$_{76}$B$_{5}$Cu$_{2}$ magnet. From electron diffraction the crystal structures of the RCu phases were determined as NdCu: (structure type “FeB,” space group $Pnma$, orthorhombic, $a = 0.73$ nm, $b = 0.45$ nm, $c = 0.56$ nm$^{13}$ and PrCu: (structure type “FeB,” space group $Pnma$, orthorhombic, $a = 0.73$ nm, $b = 0.46$ nm, $c = 0.56$ nm$^{14}$). It should be mentioned that besides the phases mentioned so far, we identified also minor amounts of other phases, such as $\alpha$-Fe and Fe$_3$Pr.

IV. DISCUSSION

The magnetic properties of hot-worked magnets greatly depend on the conditions of deformation at 900–1050 °C and the subsequent annealing process. Recently Shimoda et al.$^{15}$ reported that in hot-rolled Nd-Fe-B:Cu and Pr-Fe-B:Cu magnets a two-step heat treatment is very effective in enhancing magnetic properties. The first treatment carried out at 900–1000 °C enhances $B_r$ and the second one carried out at around 500 °C increases $H_c$ considerably.

As a result of our investigations, we can say that the second heat treatment coincides with the eutectic decomposition temperature $Liq \rightarrow Nd + NdCu$ at 520 °C and $Liq \rightarrow Pr + PrCu$ at 472 °C.$^{16}$ The banded microstructure of Figs. 3(a) and 3(b) clearly indicates the eutectic decomposition in the Pr-containing magnet. From our TEM results it is evident that the formation of the eutectic R-rich

FIG. 2. Grains with a composition close to the 2:14:1 phase, but showing a high defect density within the grain interior: (a) Nd-Fe-B:Cu magnet; (b) Pr-Fe-B:Cu magnet.

FIG. 3. Electron micrographs showing the eutectic separation into the Pr-rich and a PrCu phase within the intergranular region of the Pr-Fe-B:Cu magnet.
and \(RCu\) phases in the intergranular region between the hard magnetic grains enhances the coercivity. The eutectic decomposition within the intergranular region decreases the melting temperature of the intergranular liquid phase during the hot-working and first annealing process and increases the workability of these materials. The intrinsic coercive field of \(R\)-Fe-B-based magnets is primarily controlled by the magnetoocrystalline anisotropy of the hard magnetic 2:14:1 phase. The minor Cu content of this phase does not affect the anisotropy drastically. We suggest that the decrease of the melting temperature of the intergranular phase leads to a better wetting behavior and separation of the hard magnetic grains and therefore to an enhancement of the coercivity, i.e., to a decrease of the coupling exchange field between neighboring grains. Shimoda et al.\(^6\) showed that instead of Cu other additives such as Ag, Au, or Pd are effective in increasing coercivity. All of these phases show an eutectic decomposition in their corresponding binary phase diagrams with Nd and Pr. The eutectic decomposition temperature of Cu is the lowest one, which also explains the highest coercivity increase due to Cu addition.

In summary our TEM study shows that the microstructure of hot-worked Nd-Fe-B-Cu magnets, especially in the intergranular regions, is similar to that of Pr-Fe-B-Cu magnets.

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