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Magnetic characterization of oxidized Fe-Nd alloys

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In this work results of oxidation experiments on Fe-Nd alloys are presented. Samples were prepared by melting the metals and Nd oxide, and by melting the metals, stabilizing the alloys through long heat treatments, and oxidizing them in low-oxygen partial pressures. Two mechanisms of oxidation are observed, one with precipitation of a fine Nd_2O_3 dispersion in the alloy matrix, with simultaneous displacement of the phase compositions to Fe-rich values. Eventually, pure Fe striae are formed. The second mechanism corresponds to the direct formation of a mixed oxide and Nd_2O_3.

I. INTRODUCTION

It has been suggested that in the intergranular region of the Fe-Nd-B magnets, composed mainly by a Nd-rich eutectic liquid, magnetically ordered phases are formed and that some of these can be oxygen stabilized.[1,2] It is suggested also that these phases have a role in the mechanism of the high coercivity observed in these hard magnetic materials.[1–3]

Besides this, high-coercivity values are observed in Nd-rich alloys containing great amounts of the binary eutectic liquid.[4–7] These alloys present metastable magnetically ordered phases that show a peculiar time evolution under short heat treatments at 600 °C.[5–7] There is the possibility that these phases can be also oxygen stabilized.

Given the similarity between the binary and ternary eutectic liquids, it seemed important to study the behavior of alloys of the Fe-Nd system under controlled oxidation conditions. This work reports the results obtained in this kind of experiment.

II. EXPERIMENT

For the purposes of this work two different sets of samples were prepared. The first set corresponds to samples prepared by melting, in an arc furnace under high-purity argon, Fe and Nd metals mixed with Nd_2O_3. The stoichiometries of the alloys were in the vicinity of the binary eutectic composition. They were $Fe_{25}Nd_{65}O_{10}$ (on the Fe-rich side of the eutectic), and $Fe_{15}Nd_{75}O_{10}$ and $Fe_5Nd_{85}O_{10}$ (both on the Nd-rich side of the eutectic). Each sample was melted three times, being turned between the meltings in order to obtain better homogeneity. After this they were heat treated at 600 °C under inert atmosphere for short and long periods, and then analyzed.

For the second set of samples we chose to melt two compositions in the Fe-rich part of Fe-Nd system. The first composition was $Fe_{85}Nd_{15}$ and the second was $Fe_{70}Nd_{30}$. After melting in the arc furnace, these samples were encapsulated in silica bulbs under argon and heat treated at 650 °C for 32 days. The purpose of this treatment was to stabilize the phases $Fe_{17}Nd_2$ and $Fe_{17}Nd_5$ in the alloy with composition $Fe_{85}Nd_{15}$, and $Fe_{17}Nd_5$ and Nd in the alloy with composition $Fe_{70}Nd_{30}$. The homogenization of these alloys has been verified by metallography and by thermomagnetic analysis (TMA).

After this heat treatment, the homogenized samples were cut into small pieces and heat treated at 650 °C under several low-pressure oxygen atmospheres. These conditions were obtained in an oxidation chamber made up of a quartz tube evacuated by a vacuum system comprising a mechanical and an oil diffusion pump, the oxidation chamber maintained under an oxygen flux regulated by a precision needle valve. In this way, experiments were carried out at 10^{-3}, 10^{-2}, 10^{-1}, and 1 mbar for 48 h.

The oxidized samples were analyzed by optical metallography, TMA, and electron microprobe measurements.

III. EXPERIMENTAL RESULTS AND DISCUSSION

In the case of the first set of samples, consisting of alloys with compositions in the vicinity of the eutectic composition, the metallographic analysis of the as-cast samples showed the presence of primary precipitates and the eutectic with different morphologies, some of them occurring simultaneously in the same sample. For the sample $Fe_{25}Nd_{65}O_{10}$ the primary precipitates were the $Fe_{17}Nd_2$ and Nd_2O_3 phases, and the eutectic is clearly showing three different morphologies [Fig. 1(a)]. The TMA results for this sample show the presence of a magnetically ordered phase with a Curie temperature T_c of 240 °C, corresponding to the metastable phase designated as P1 in the binary Fe-Nd system.[5,6] The TMA measurements indicate also the presence, in small quantity, of a phase with a Curie temperature of 100 °C.

For the as-cast samples $Fe_{15}Nd_{75}O_{10}$ and $Fe_5Nd_{85}O_{10}$ the primary precipitates are the Nd and Nd_2O_3 phases, and the eutectic presents only one globular morphology. The TMA results indicate the presence of the phase with T_c of 240 °C. There also appears a small signal at 160 °C, indicating the presence of a different phase.

These samples were subjected to 600 °C heat treatments for 0.5, 1.0, 2.0, and 24 h. The general behavior was that the P1 phase transformed to the $F_{17}Nd_5$, with a drastic change in the morphology. This is illustrated by Fig. 1(b), which shows the $Fe_{25}Nd_{65}O_{10}$ sample treated at 600 °C during 0.5 h. This behavior is similar to that one observed for the binary alloys under the same conditions.[5,6] It is apparent that the presence of the Nd_2O_3 precipitates do not introduce any modification in the behavior of the metallic part of the sample, behavior similar to that observed in the

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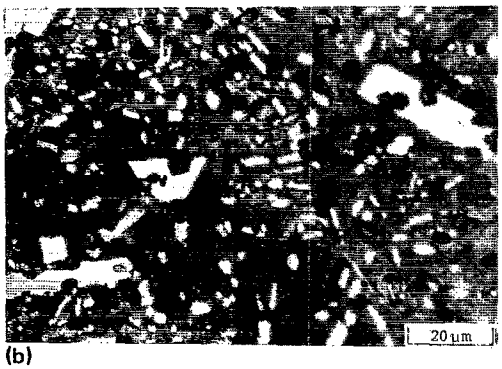
(a)



(b)

FIG. 1. Micrographies of the $Fe_{25}Nd_{65}O_{10}$ sample (a) in the as-cast state and (b) heat treated at 600 °C for 0.5 h.

binary samples. It is noted, however, that the TMA signals at 100 °C for the alloy $Fe_{25}Nd_{65}O_{10}$ and 160 °C for the alloy $Fe_5Nd_{85}O_{10}$ are still present after up to 2 h of the heat treatment, though the microstructures change markedly after these treatments. These two signals do not show up for the 24-h treatment (or longer treatments), for example, in $Fe_{25}Nd_{65}O_{10}$ annealed for 21 days at 600 °C. It was not possible to identify these phases metallographically or by electron microprobe.

The samples of the second set of alloys showed a typical diffusion pattern, as observed in diffusion couples.[8] One observes a layer of oxidized material from the surface to the interior of the material. It is surprising that even for thick layers there is not significant lattice expansion during oxidation, once the oxidized layer is well connected to the main body of the samples. This can be observed also comparing the sizes of the oxidized and nonoxidized parts of the same grain of one of the phases present in any of the samples. This is illustrated in Fig. 2, which shows the $Fe_{85}Nd_{15}$ sample after 48 h oxidation at 10^{-1} mbar. Another interesting feature is that the diffusion front is well uniform, since both phases in the samples are presenting continuous frontiers through them, indicating that the diffusion velocity is approximately the same for the phases.

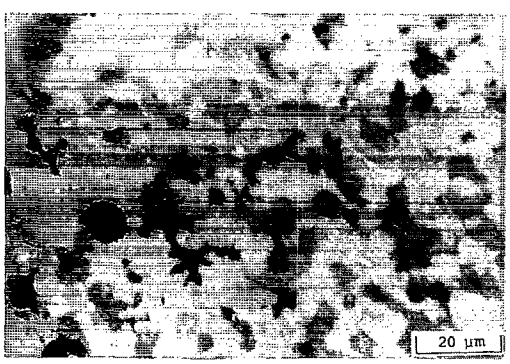


FIG. 2. Micrography of the $Fe_{85}Nd_{15}$ heat treated at 650 °C for 31 days, followed by oxidation treatment at 650 °C for 48 h at 10^{-1} mbar.

As a general feature, the samples present a typical oxidation pattern from the surface to the core. In the outer regions the oxidation is more severe, as revealed by the darker gray color of this region. As we move to the core, the gray tones become lighter, until we encounter the unaffected core, with the typical white-yellow color of the Fe-rich phases. The Nd phase gives a typical dark gray color oxide. A closer examination of the oxidation pattern of the Fe-rich phases indicates that the dark color is associated with a greater amount of a very fine dispersion of oxide particles in the phase. Under low magnification this set of fine precipitates looks like a continuous color. The oxygen concentration lowers as we move to the core, and the amount of precipitate diminishes, giving the lighter tones observed. In the outer regions one can observe the appearance of white striae. Electron microprobe revealed them to be pure Fe. This behavior is similar to the one reported previously for heavily oxidized Pr alloys.[9]

Besides this oxidation pattern, another one is observed to occur simultaneously, and can be seen in Fig. 2. This is the transformation of the $Fe_{17}Nd_5$ phase into a mixed oxide (gray color in Fig. 2) and pure Nd_2O_3 (dark gray color in Fig. 2). Electron microprobe measurements indicate the stoichiometry of this mixed oxide as $Fe_{21}Nd_{27}O_{52}$. This phase can be assumed to be the phase $FeNdO_3$, stable in the Fe-Nd-O ternary system.[10] This hypothesis is supported by the oxidation mechanism, since together with the mixed oxide one encounters fine precipitates of the oxide Nd_2O_3. The electron microprobe indicates the presence of these precipitates giving a higher Nd indication than the one expected by the stoichiometry of the phase.

IV. CONCLUSIONS

From the above observations we can conclude the following.

For the alloys with the metals and Nd_2O_3 oxide melted together, the evolution of the metallic part of the alloy during short heat treatments at 600 °C is similar to what is observed for the corresponding binary alloys.

For the alloys first stabilized and then oxidized, two different mechanisms of oxidation are observed: decomposition of the phases into Nd_2O_3 fine precipitates and Fe-richer phases, until finally pure Fe coalesces in the form of striae. The second mechanism corresponds to the formation of the mixed oxide $FeNdO_3$ and Nd_2O_3 and occurs simultaneously with the first type.

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