AIP | Journal of Applied Physics

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Citation: Journal of Applied Physics **86**, 2334 (1999); doi: 10.1063/1.371060

View online: http://dx.doi.org/10.1063/1.371060

View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/86/4?ver=pdfcov

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Evidence for the stable existence of the Fe_2Nd phase in the Fe–Nd system

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(Received 2 November 1998; accepted for publication 10 May 1999)

We did directional solidification experiments on $Fe_{20}Nd_{80}$ alloys at several low cooling rates in order to observe the solidification sequence, displayed along the length of the sample. We also took measurements of the transition temperatures around the eutectic temperature using a Calvet type calorimeter. Our results show that the formation of the eutectic $L \leftrightarrow (Nd)+Fe_{17}Nd_2$ occurs first, and is followed by the eutectic $L \leftrightarrow (Nd)+Fe_2Nd$. The calorimetric measurements give the temperature of the first eutectic to be 688 °C, the temperature of the peritectic formation of the phase Fe_2Nd to be 682 °C and the temperature of its eutectoid decomposition as 659 °C. Thermomagnetic measurements give the Curie temperature of the Fe_2Nd phase as 250 °C. A new phase diagram for this system is proposed. [S0021-8979(99)05516-4]

I. INTRODUCTION

The phase relations for the Fe–Nd system have been of great interest since the discovery of the $Fe_{14}Nd_2B$ compound and the powder metallurgical process for permanent magnet fabrication from it,[1] since the eutectic binary liquid plays an important role in the sintering and in overall magnetic performance of the magnet.[2] The first experimental studies of the system pointed out the existence of the Fe_2Nd phase, and two thermal events around the Nd-rich eutectic were reported in differential thermal analysis (DTA) measurements.[3] Later, it was verified that the phase was not stable in the system, and instead, the phase $Fe_{17}Nd_5$ was confirmed.[4–6] The Fe_2Nd phase was obtained in high-pressure experiments.[7] For the as-cast samples, the eutectic always showed a very fine microstructure, with at least two morphologies: one of them termed ''feathered'' and the other globular.[2–10] Measurements of hysteresis cycles showed that as-cast alloys containing substantial amounts of the eutectic presented high coercive fields, and the phase responsible for the magnetic properties presented Curie temperature around 240 °C, and was metastable under 600 °C heat treatments.[2,9,11] Due to the very fine morphology, it was not possible to determine the stoichiometry of this ordered phase (termed P_1).[2,10,11] Recently, Obrucheva *et al.*[12] analyzed Nd-rich as-cast alloys with x-ray microdiffraction and electron microprobe and strongly suggested that the P_1 phase have stoichiometry Fe_2Nd.

It was then supposed that a metastable ordered phase formed during the solidification of the eutectic liquid. This implied that a metastable eutectic reaction $L \leftrightarrow (Nd)+P_1$ occurred together with a second metastable eutectic $L \leftrightarrow (Nd)+Fe_{17}Nd_2$ (the truly stable eutectic should be $L \leftrightarrow (Nd)+Fe_{17}Nd_5$, usually not observable due to nucleation kinetic reasons).[9,10] The first eutectic would give the origin to the feathered morphology and the second the globular one. It was clear that the study of the phase relations in this region of the phase diagram would require experimental techniques able to cope with phenomena occurring in a small temperature interval and able to produce morphologies coarser than the ones obtained in the usual melting procedures. Experiments on directional solidification[13] reveal three types of grain structure for ternary system Fe–Nd–B; fine and coarse grains and columnar grains are observed. Columnar grains are found in the central portion of the samples, where directional solidification takes place. The increase of these grains leads to a higher B_r and BH_{max} in this cast ingot. The objectives of this work is to report results obtained in alloys with composition around the eutectic studied using directional solidification (DS) and very slow Calvet-type calorimetric measurements and to propose one new equilibrium phase diagram for the binary system Fe–Nd.

II. EXPERIMENTAL PROCEDURES

Samples were obtained by arc melting appropriate proportions of 99.99% pure iron and 99.9% pure neodymium. For the DS experiments, samples were housed in CaF_2 crucibles. Directional solidification was done for the composition $Fe_{20}Nd_{80}$ (at%) in a rf furnace in argon at 2 atm pressure. Cooling rates, measured as the speed of the vertical movement of the crucible, were 1, 10, and 20 mm/h. As the DS technique makes the microstructure of the sample change along its length according to the sequence expected from the phase diagram, we divided our samples in three parts: the inferior (the first one to solidify), medium and superior (the last to be solidified). This division is valid for all the characterization techniques used.

Our calorimetric experiments were done in a Calvet-type calorimeter, model HT1000D, from Setaram, run in the scan-

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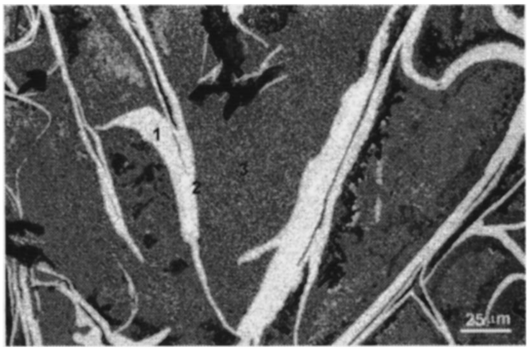

FIG. 1. Microstructure of 20 mm/h $Fe_{20}Nd_{80}$ DS sample (upper part): (1) Fe_2Nd phase; (2) $Fe_{17}Nd_2$ phase; (3) primary Nd.

ning mode. The scanning rate used for most of our experiments was 0.05 °C/min in the temperature range of interest.

All samples directionally solidified and run in the calorimeter were characterized by metallography. We also used thermomagnetic analysis (TMA), consisting of the measurement of the ac susceptibility as a function of the temperature. TMA runs were done up to 400 °C at rates of 40 °C/min. Some of the samples were analyzed in an electron microprobe in order to determine the chemical composition of the phases of interest.

III. RESULTS AND DISCUSSION

All the DS samples showed similar microstructures, differing only in the coarseness as the cooling speed decreased. We observed the precipitation of the globular eutectic described by the reaction $L \leftrightarrow Fe_{17}Nd_2 + (Nd)$ followed by the feathered eutectic, now in sizes big enough to identify the phases unambiguously. We observed also the phase comprising the feathered eutectic in a peritectic morphology with the $Fe_{17}Nd_2$ and (Nd) phases (Fig. 1). Using the slowest speed DS samples that provided the biggest grains of this phase, we did electron probe microanalysis and determined its composition to be Fe_2Nd with high confidence. These results point

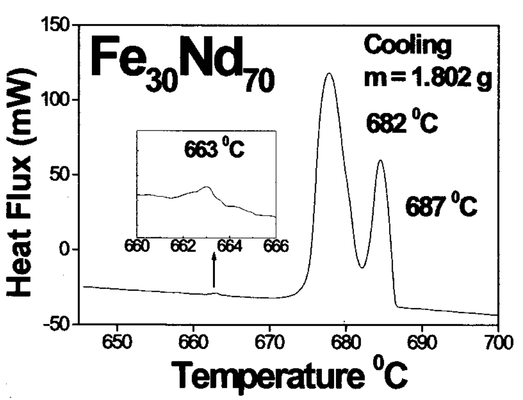

FIG. 2. Calvet measurement of the $Fe_{30}Nd_{70}$ sample at 0.05 °C/min. The small signal at 659 °C is the eutectoid decomposition of the Fe_2Nd phase (inset curve), the 682 °C signal corresponds to the peritectic formation reaction of the Fe_2Nd phase, and the signal at 688 °C is the eutectic reaction $L \leftrightarrow Fe_{17}Nd_2 + (Nd)$.

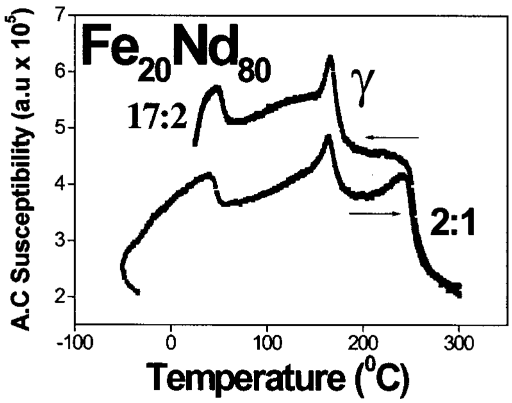

FIG. 3. TMA pattern of the sample containing the phase Fe_2Nd ($T_c = 250$ °C). A second transition (denominated by γ) at 166 °C could not be addressed to a known phase in the microstructure.

to the interpretation that even with very low cooling rates achieved in the DS experiments, we have first the precipitation of the eutectic comprising the $Fe_{17}Nd_2$ phase, followed by the precipitation of the eutectic comprising the Fe_2Nd phase that seems to be stable and that forms peritectically from the $Fe_{17}Nd_2$ and (Nd) phases (Fig. 1).

This interpretation of the sequence of microstructures observed in the DS experiments is confirmed by calorimetric measurements performed in the alloys with compositions $Fe_{30}Nd_{70}$ (hypoeutectic) and $Fe_{20}Nd_{80}$ (hypereutectic). The Calvet signal showed three thermal events for the 30–70 sample, at (on average of several runs) 659, 682 and 687 °C (Fig. 2). For the hypereutectic alloy the Calvet signal shows only one event at (on average) 688 °C. Tentatively, we advance the following interpretation of these data: the small signal at 659 °C is the eutectoid decomposition of the Fe_2Nd phase, the 682 °C signal corresponds to the peritectic formation reaction of the Fe_2Nd phase and the signal at 688 °C is the eutectic reaction $L \leftrightarrow Fe_{17}Nd_2 + (Nd)$. In this context it is missing the explanation of the appearance of the eutectic involving the phase Fe_2Nd that reveals it to be metastable. It is interesting to note that in the DS samples the first part to cool displays the globular eutectic, while the medium and superior parts show essentially the feathered eutectic, as if there is a sequence of two eutectics.

Samples containing almost only the Fe_2Nd phase, chosen by metallographic examination, show a Curie temperature of

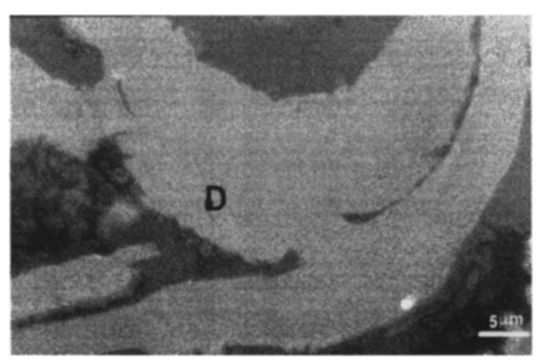

FIG. 4. Microstructure of the 1 mm/h $Fe_{20}Nd_{80}$ DS sample, showing magnetic domains in the Fe_2Nd phase (D).

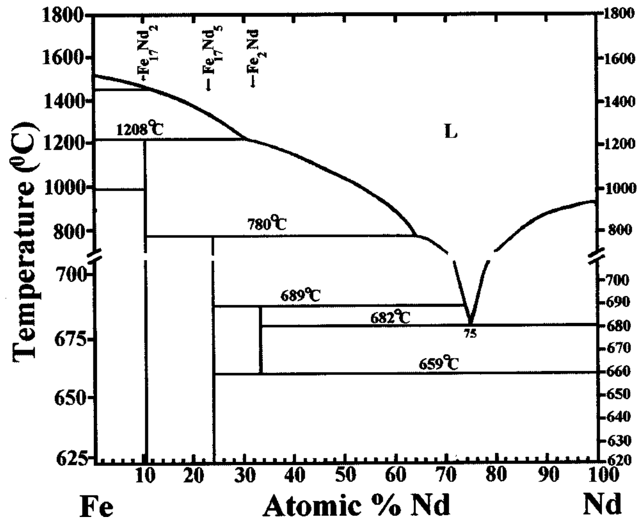

FIG. 5. New binary phase diagram proposed for Fe-Nd system.

250 °C in the TMA measurements (Fig. 3), which are in good agreement with the results reported by Landgraf *et al.*[5] for one phase denoted as A1, which contains 34,5% Nd. A second transition at 166 °C could not be addressed to a known phase in the microstructure. The third transition at 52 °C corresponds to the T_c of the phase $Fe_{17}Nd_2$. Metallographic examination showed that the Fe_2Nd phase strongly modifies incident polarized light, indicating that it is not cubic. We also observed the presence of domains (Fig. 4), indicating that the magnetization is axially ordered.

The union of this data enables us to construct a new proposal of the equilibrium phase diagram for this system[14] (Fig. 5). The region in the neighborhood of the eutectic reaction is amplified by a factor of 10 times with relation to the upper part of the diagram. In Fig. 5 we can observe three isothermal lines which correspond to the peritectic reactions in the system. One new and important feature of this phase relation is included in this diagram, the isothermal line which corresponds to the eutectoid decomposition reaction (at 659 °C).

IV. CONCLUSIONS

Using the directional solidification technique in alloys with composition around the eutectic, we were able to obtain the two eutectic morphologies normally observed in as-cast samples in a coarser form and whose microstructure changes along the length of the samples. The obtained sizes were big enough to allow a very precise determination of the stoichiometry of the phase participating in the second eutectic as being Fe_2Nd. This experiment also showed very clearly the peritectic formation of this phase. The Calvet-type scanning calorimeter allowed us to obtain thermal events that can be ascribed, tentatively, to the eutectic temperature (688 °C), the peritectic temperature of the phase (682 °C) and to its eutectoid decomposition (659 °C), TMA measurements give the Curie temperature of the phase as 250 °C and metallographic examination under polarized light shows the phase to be magnetically ordered, with domains indicative of axial anisotropy. Our data lead us to propose a new phase diagram for this system, however x-ray microanalyses of this new phase are necessary for a possible identification of its structure.

ACKNOWLEDGMENTS

The authors gratefully thank Dr. A. C. Ribeiro of the IFGW-Unicamp for electron microprobe analysis and CnPQ Brazilian agency for financial support.

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