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High-resolution electron microscopy studies of nanophases in Nd–Fe–B alloys

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High-resolution transmission electron microscopy observations on rapidly solidified Nd–Fe–B alloys are presented. The results show the existence of nanophases of different compositions to the nominal $Nd_2Fe_{14}B$ as-prepared alloy, which was detected prior to the fast-quenching process. In particular, iron-enriched nanophases are commonly found among the wide variety of nanophases in the final alloy. The possible mechanisms, as well as their relevance to the understanding of the properties of these magnetic materials, are also discussed.

1. Introduction

Magnetic materials have always represented a very exciting field of research and development not only because of the scientific puzzles yet to be answered but also because of the huge market that magnetic materials and their derivatives represent in today's technologically oriented world [1–6]. More specifically, perhaps the most significant parameter, technologically speaking, for these materials to have, is the ability to store energy in a volume unit of material. Accordingly, the older magnet technology, which is still in use for many applications, based in ferrite (iron, barium and strontium oxides) was able to provide up to 3.6 MGOe [6]. Comparatively the Nd–Fe–B materials first developed in the early 80s yield up to 64 MGOe [4–7]. Not surprisingly then, much effort has been dedicated in the past ten years to study and develop novel preparation techniques, structure of stable phases as well as microstructures of a number of variants of the original Nd–Fe–B alloy.

Roughly speaking, two methods have been used so far to prepare permanent Nd–Fe–B magnets: the standard powder metal/sinter technique [7] and the use of rapidly solidified materials [1]. The defense of either technique has occupied a number of researchers over the last few years; nevertheless, agreement exists in that the much finer grain structure of the latter method offers some interesting advantages, and it also represents an issue that has become more fashionable with the presence of the so-called "nanophase technologies" [8].

Specifically, in the area of microstructural characterization of Nd–Fe–B alloys, most of the studies available [9, 10] deal meanly with standard metallographic or texture analysis of the grain structure of the specimens, and the corresponding changes as a function of temperature, sintering conditions, and so on. The scarcity of the studies of micro or even nanophases present in these alloys is a fault, especially when one recalls that some very important magnetic properties strongly depend on grain-boundary structure, because of effects such as microseggregation, as has been investigated by some groups [11–13]. In the present work, we report our results on high-resolution transmission electron microscopy (HRTEM) observations of nanophases in rapidly-quenched Nd–Fe–B alloys, and also discuss the possible relevance of these findings to the understanding of the microstructure–properties relationships in these materials.

2. Experimental procedure

2.1. Preparation of Nd–Fe–B alloys

Commercial metals (Nd, 96%, Molycorp; Fe, 99%, Baker and $FeB_{1.2}$, 97.16%, Elkem Metals) were

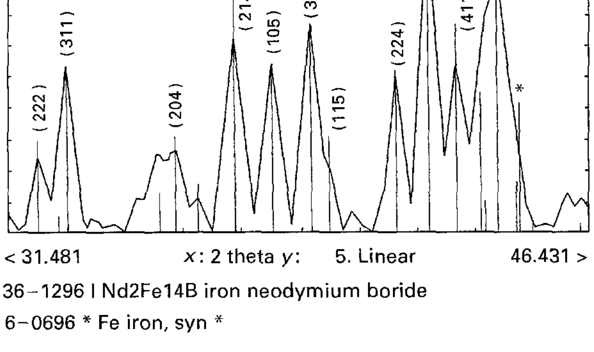

Figure 1 X-ray powder diffractogram of the Nd–Fe–B alloy before rapid quenching.

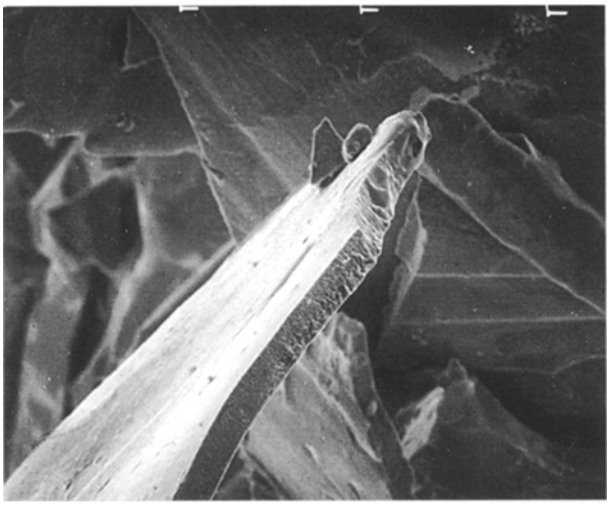

Figure 2 Scanning electron microscopy image of a typical $Nd_2Fe_{14}B$ ribbon.

employed to prepare the alloys. In the procedure, a mixture of iron and $FeB_{1.2}$ powders was first prepared and then small pellets of neodymium were added and mixed in a ball mill. The powders were

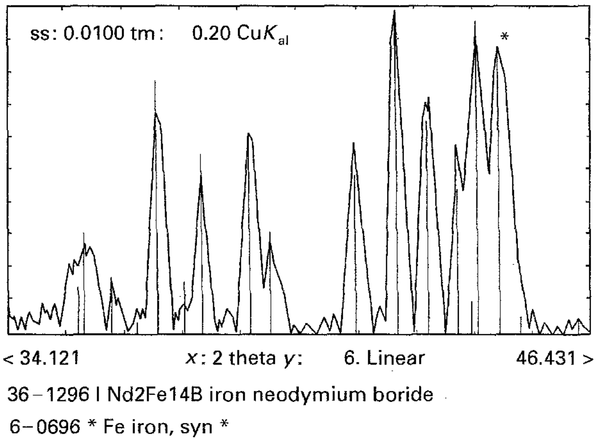

Figure 3 X-ray powder diffractogram of the rapidly quenched ribbons.

pressed into a cylindrical shape at a pressure between 4 and 5 ton cm^{-2}. A 10 kW induction furnace, operating at 7 kV and under vacuum, to prevent any oxidation (because the neodymium is extremely susceptible to form oxides), was employed to form the alloy in

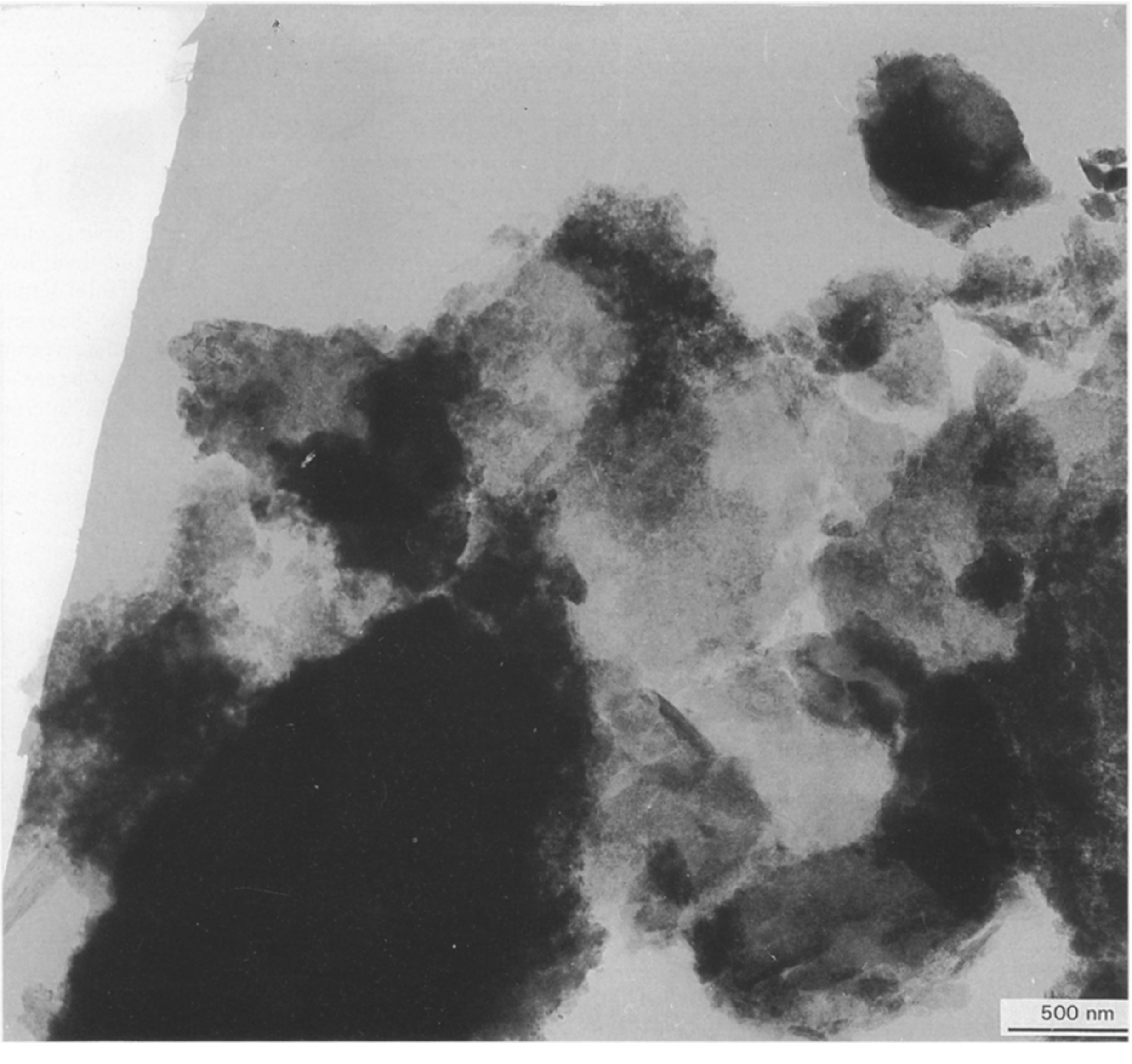

Figure 4 Transmission electron micrograph of the rapidly quenched Nd–Fe–B alloy.

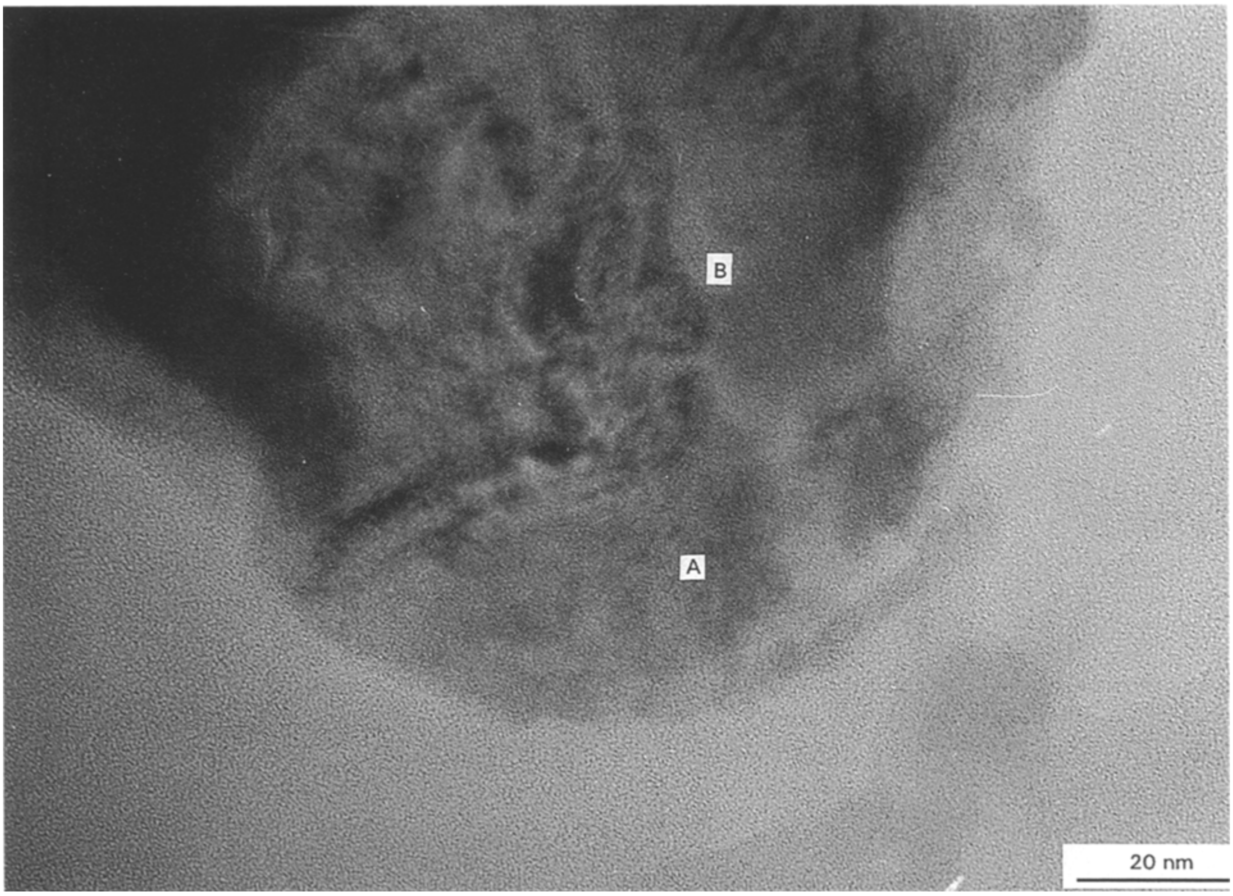

Figure 5 HRTEM micrograph showing lattice spacings corresponding to the $Nd_2Fe_{14}B$ composition.

a quartz crucible, which was designed to have the nominal composition $Nd_2Fe_{14}B$ [5]. A standard device for rapid quenching of alloys was utilized, consisting of a polished copper disc (20.7 cm diameter and 2.5 cm thick) rotating at 1400–1900 r.p.m., which yields a tangential speed of 15–20 m s^{-1}. The alloy was melted *in situ* by the induction furnace under vacuum conditions. The composition of the alloys was checked by X-ray powder diffraction in a Siemens D-5000 diffractometer.

2.2. Sample preparation for high-resolution transmission electron microscopy

The Nd–Fe–B alloys prepared were powdered for X-ray analysis and for HRTEM analysis, by suspending the powders in alcohol and dispersing a drop on to a carbon film deposited on a gold grid. A Jeol-4000EX, 400 keV machine was used in the bright-field mode to obtain lattice images with a resolution below 0.2 nm point-to-point.

3. Results and discussion

Fig. 1 shows a typical X-ray diffractogram of the Nd–Fe–B alloy as prepared, that is, before quenching. As can be observed there, the specimens consist basically of the $Nd_2Fe_{14}B$ composition and it was not possible to detect with this technique evidence of secondary phases or segregation. After rapid quenching, ribbons 1–2 mm wide and 10–20 μm thick were consistently obtained with our experimental apparatus. A typical ribbon is shown in Fig. 2. Scanning electron microscopy showed an alloy with an average grain size of 2–4 μm, which is the expected figure for the experimental conditions used [5]. Some interesting observations can be made, however, from the analysis of the corresponding X-ray diffractograms of the ribbons (Fig. 3). Indeed, a first result is the presence of a peak corresponding to α-Fe, which was not detected whatsoever in the as-prepared alloy. This is due, according to the literature [1] to the segregation of phases. Generally speaking, however, the alloy preserves the $Nd_2Fe_{14}B$ composition, with a broadening of the peaks which coincides qualitatively with the SEM figure for the grain size.

Fig. 4 corresponds to a low-magnification transmission electron micrograph of a typical region of the rapidly quenched alloy. As observed, the detailed microstructure of the material consists of tiny regions, distinctive by their different contrast, below 500 nm in which some fine chunks probably corresponding to segregation, can be seen. A closer look to the bigger regions (Fig. 5) shows spacings that can clearly be identified as corresponding to the tetragonal structure of $Nd_2Fe_{14}B$ [14] and indicated in Fig. 5 as region "A". Also, iron-enriched regions, with the composition $Nd_2Fe_{23}B_3$, identified as region "B" in the figure, are detected together with the nominal $Nd_2Fe_{14}B$

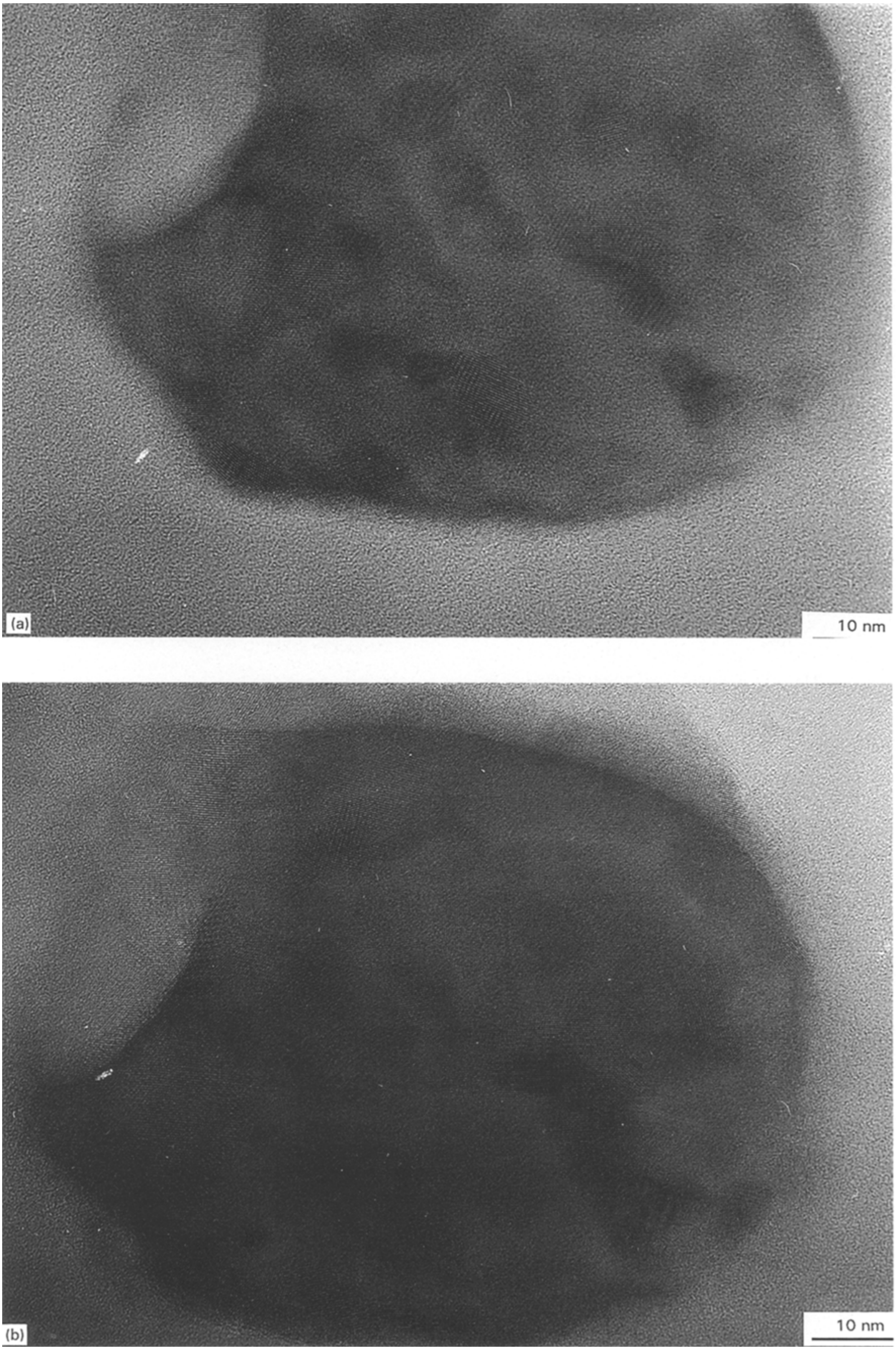

Figure 6 (a and b) HRTEM micrographs corresponding to different phases formed in the rapidly quenched alloy.

composition. In the figure, defects produced by the very rapid cooling are also observed.

Fig. 6a and b, showing another typical area of the specimen, also contains interesting features. First, the presence of nanophases, of the order of 10 nm, is clearly observed, not only because of the contrast itself, but also revealed by the Moiré fringes resulting from the overlapping of two crystals. Some of the phases which can be identified there are $Fe_{20}Nd_3B$, $NdFe_4B_4$, $Nd_{1.1}Fe_4B_4$, Fe_7Nd and BFe_2. The Moiré spacings correspond in the image to the expected overlapping of the above alloys with the "matrix" consisting of $Nd_2Fe_{14}B$. Second, the fact that iron-enriched nanophases (as compared to the nominal composition) are by far more common than other compositions in which neodymium and/or boron were the predominant element. Third, the observation of a sort of preference for the nanophases to contain boron, rather than having only neodymium, which was consistently observed throughout the HRTEM experiments. This result supports the suggestion that the boron atoms play a very important role in the properties of these magnets, because it is thought that their inclusion modifies the Fe–Fe interatomic distance [1, 15], which also could explain why boron is always associated with iron even in the non-stoichiometric nanophases observed here.

On the other hand, it was observed by HRTEM that neodymium is associated with iron and never with boron in the nanophases. Some polarized neutron studies [16] of $Nd_2Fe_{14}B$ monocrystals showed that the best combination of magnetic moments is closely related to the local environment, atomically speaking, that is, to the local coordination of iron atoms with respect to boron and neodymium. For pure Fe–B alloys, the resulting magnetic moment is very poor, thus the neodymium acts as a sort of coordination and orbital modifier to achieve the observed magnetic properties of Nd–Fe–B alloys.

4. Conclusion

The HRTEM observations presented show that, first, the microstructure of rapidly quenched Nd–Fe–B alloys is far more complicated than which pure X-ray diffractograms could show. Also, the formation of nanophases of the order of 10–50 nm with a variety of compositions, was demonstrated. These results are in agreement with some previous TEM and Auger reports [11] which showed the presence of very fine grains surrounded by an amorphous matrix in these alloys. Despite that, many of the nanophases were identified and, at least qualitatively, could be related to the macroscopic magnetic properties, a number of nanostructures remain to be studied, because the available data on stable and metastable Nd–Fe, Nd–Fe–B and Fe–B alloys is very scarce. The relevance of the detection and study of these nanophases is evident and more work, especially in the direction of comparing rapidly quenched samples with specimens prepared by standard sintering, has to be done. Finally, it would be extremely interesting to perform similar observation on some of the new ternary nitrides ($R_2Fe_{17}N_{3-\delta}$) which seem to open a new chapter in magnetic materials [17, 18].

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References

1. J. J. CROAT, *IEEE Trans. Magn.* **25** (1989) 3550.
2. M. SAGAWA, S. FUJIMURA, M. TOGAWA, H. YAMAMOTO and Y. MATSUURA, *J. Appl. Phys.* **55** (1984) 2083.
3. B. SZPUNAR and J. A. SZPUNAR, *ibid.* **57** (1985) 4130.
4. M. SAGAWA, S. HIROSAWA, H. YAMAMOTO, S. FUJIMURA and Y. MATSUURA, *ibid.* **26** (1987) 785.
5. M. I. ROSALES, MSc Thesis Inorganic Chemistry, UNAM, Mexico City (1990).
6. D. GIVORD, H. LI and J. MOREAU, *Solid State Commun.* **50** (1984) 497.
7. A. HIGUCHI and S. HIROSAWA, *IEEE Trans. Magn.* **25** (1989) 3555.
8. R. P. ADRES, R. S. AVERBACK, W. L. BROWN, L. E. BRUS, W. A. GODDARD III, A. KALDARR, S. G. LOVIE, M. MOSCOVITS, P. S. PEERCY, S. J. RILEY, R. W. SIEGEL, F. SPAPEN and Y. WANG, *J. Mater. Res.* **4** (1989) 704.
9. W. C. CHANG, T. B. WU and S. LIU, *J. Appl. Phys.* **63** (1988) 3531.
10. R. K. MISHRA, E. G. BREWER and R. W. LEE, *ibid.* **63** (1988) 3528.
11. R. K. MISHRA, *J. Mag. Magn. Mater.* **54** (1986) 450.
12. J. F. HERBST, J. J. CROAT, F. E. PINKERTON and W. B. YELON, *Phys. Rev.* **B-29** (1984) 4176.
13. J. F. HERBST and J. J. CROAT, *J. Mag. Magn. Mater.* **100** (1991) 57.
14. JCPDS Tables (1986).
15. J. B. HERBST, J. J. CROAT and F. E. PINKERTON, *Phys. Rev.* **B29** (1984) 4176.
16. D. GIVORD, H. S. LI and F. TASSET, *J. Appl. Phys.* **57** (1985) 4100.
17. J. M. D. COEY and H. SUN, *J. Mag. Magn. Mater.* **87** (1990) L251.
18. G. J. LONG, O. A. PRINGLE, F. GRANDJEAN and K. H. J. BUSCHOW, *J. Appl. Phys.* **72** (1992) 4845.

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