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Microstructure and Composition in Rapidly-Quenched NdFeB-Based Hard Magner Alloys

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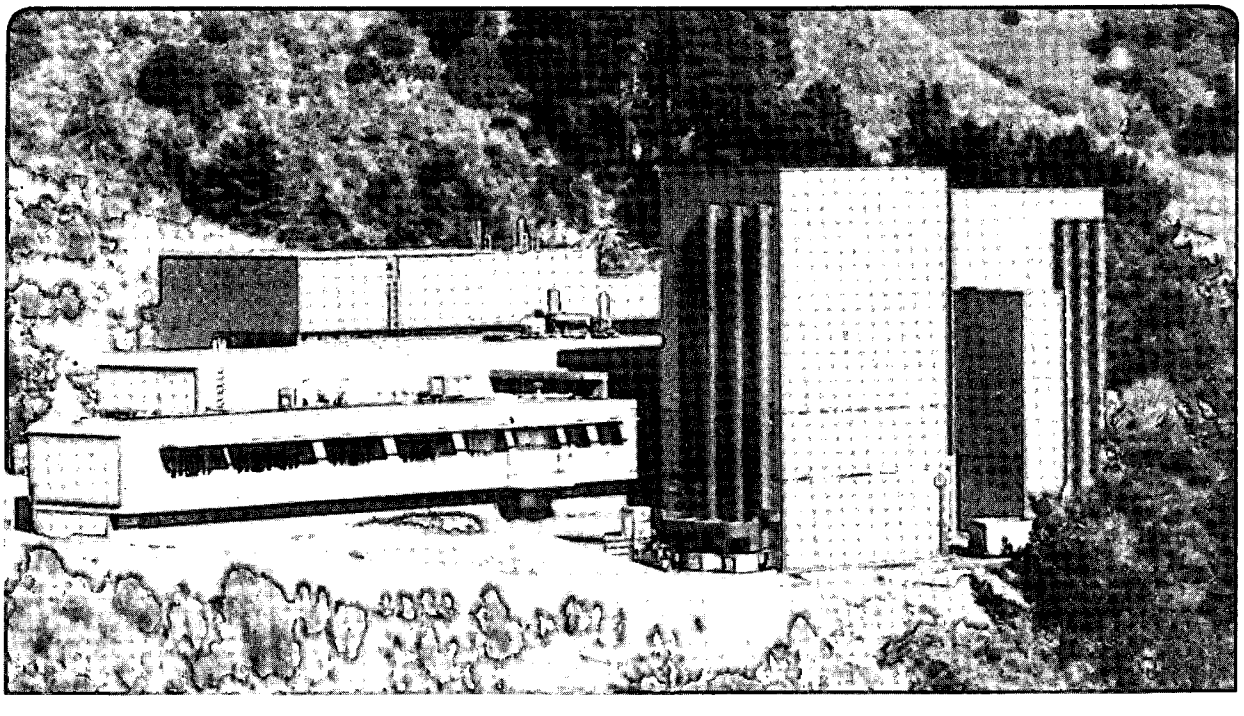

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MICROSTRUCTURE AND COMPOSITION IN RAPIDLY-QUENCHED NdFeB-BASED HARD MAGNET ALLOYS

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ABSTRACT

A detailed study of the microstructure and composition in hot-pressed (MQ-2) and die-upset (MQ-3) magnet alloys based on the $Nd_2Fe_{14}B$ composition, utilizing high resolution and analytical transmission electron microscopy (TEM), is reported. The initial magnetic properties of the two samples show different behaviors, which are attributed to the difference in the anisotropy of the grain structure and the grain boundaries. The hot-pressed sample shows faceted grains of the 2-14-1 phase, while die-upset sample shows plate-like grains, together with larger equiaxed grains that contain a speckling of precipitates in the grain interior. The grain structure and composition remain rather similar in the two samples. The grain boundary phase averages approximately one nanometer to more than ten nanometers in width. The thicker grain boundaries are Nd-rich, while the thinner grain boundaries in the hot-pressed sample exhibit an Fe-rich composition near that of the $NdFe_3$ phase. Nd-rich phases are found at the grain boundary junctions of both samples, with the Nd:Fe ratio near 7:3 in the die-upset sample, and up to 3:2 in the hot-pressed sample. The significance of the microstructure and the grain boundary phases on the magnetic behavior in the two samples is discussed.

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INTRODUCTION

High quality hard magnet alloys based on the $Nd_2Fe_{14}B$ composition are generally manufactured by rapid solidification processing (melt-spinning) followed by thermo-mechanical treatments[1] or by powder metallurgy with

post-sintering treatments.[2] Magnets produced by either technique possess structure-sensitive properties such as energy product and coercivity that are lower than the theoretical limits. One of the reasons for the difference is the presence of second phases and grain boundaries that can act as pinning or nucleation sites. Sintered magnets achieve their coercivity via the nucleation of reverse domains. However, there are still disagreements on the mechanisms for demagnetization in melt-quenched and die-upset alloys. Models that have been proposed to explain the behavior of die-upset magnetic alloys include strong pinning model,[3-4] nucleation model,[5] and microcrystalline model.[6] A review of these models is given by Herbst.[7] Observation of the domain structures of a thin die-upset magnet sample in an electron microscope using the Lorentz technique indicates that magnetization proceeds by domain wall motion restricted by pinning at grain boundaries,[8] while investigations on interaction mechanisms by analysis of the time-dependent magnetizing curves after thermal demagnetization agrees with the nucleation-controlled mechanism.[9]

Preliminary microstructural studies of die-upset NdFeB samples with the nominal composition $Nd_{13.75}Fe_{80.25}B_6$ show the presence of an Fe-rich phase at the grain boundaries.[10-11] It was proposed that this phase provides possible exchange coupling between grains and potential reversed domain nucleation sites. In this paper, we present microstructure and phase analyses of hot-pressed (MQ-2) and die-upset (MQ-3) magnet alloys studied by high resolution and analytical transmission electron microscopy (TEM). The relationship between the observed microstructure and magnetic properties, and in particular, the effects of the secondary and grain boundary phases on the reversal mechanisms in these materials are discussed.

EXPERIMENTAL TECHNIQUES

The magnet alloys were obtained from the General Motors Research and Development Center. The processing techniques and steps have been described elsewhere.[12-14] Over-quenched melt-spun ribbons were consolidated at 750°C to form the hot-pressed sample; and further deformed at 800°C to produce the oriented die-upset magnet. The dependence of remanence and coercivity upon maximum magnetizing field were investigated up to applied fields of 20 kG in thermally-demagnetized samples with a Quantum Design SQUID magnetometer.[10] Samples for TEM studies were prepared from slices of the bulk. They were ultrasonically cut into 3 mm discs, mechanically thinned and dimpled, and then ion-milled at liquid nitrogen temperature until transparent to the electron beam. High resolution and anlytical TEM was performed in a top-entry and side-entry JEOL 200CX, respectively, operating at 200 kV. The electron beam size used for microanalysis ranged from 10 to 12 nm in diameter.

RESULTS

Comparison of the magnetic data of the two samples measured at 77°C (350°K) is shown in Figures 1a) and b). In general, while both samples display a linear increase in properties with applied field, the die-upset sample acquires its saturation magnetization M_s at lower maximum field than does the hot-pressed sample (Figure 1a). The initial susceptibility of the hot-pressed sample is substantially lower that of the die-upset sample, indicating that it is much more difficult to magnetize the former. The hot-pressed sample reaches a much higher coercivity value, but the remanence is poor.

The microstructure of the hot-pressed sample is shown in Figure 2. It exhibits mostly faceted 2-14-1 nanometer-sized grains with low-contrast grain boundary regions typically on the order of 2 - 3 nm (Figure 2a). Shown in the inset is a typical energy dispersive x-ray (EDX) spectrum from the main 2-14-1 phase. Since boron could not be detected with this technique, the ratio of Nd to Fe in this phase is 1:7. EDXS analysis of the thin grain boundary regions indicates an iron-rich phase with Nd:Fe ratio between 1:4 and 1:5, as has been reported in previous studies on related die-upset magnets.[10-11] The microstructure also contains pockets of noticeably different contrast with sizes up to ten nanometers at the junctions between many grains, suggestive of a different phase material. Figure 2b) shows a high-resolution image of such a grain junction; it has a nanocrystalline structure, a signature of possible recrystallization of this unidentified phase, and a Nd:Fe atomic ratio ranging from 2:3 to 3:2.

The microstructure of the die-upset sample is shown in Figure 3. It consists of plate-like grains, approximately 600 nm in length by 150 nm in width, together with larger equiaxed grains that contain a speckling of precipitates in the grain interior (Figure 3a). Another phase, similar to that found in the hot-pressed sample, is also observed at the grain junctions in both the plate-like and equiaxed regions of this sample. It too possesses a nanocrystalline structure and a Nd-rich composition, with a Nd:Fe ratio up to 3:1, close to that that determined by Mishra.[8,15] Figure 3b) shows a higher magnification of a plate-like region with many of the second phase pockets. Strong strain contrast is visible around these pockets, which may indicate an incoherent interface between the main 2-14-1 grains and the second-phase grains. The boundaries along the length of the plate-grains are usually free of a grain boundary phase, although it has also been observed that the second phase at the grain junctions in some cases extends into the grain boundaries, but decreases in thickness and eventually diminishes. The exact composition of the materials found in the thin grain boundary region (in the order of 1-2 nm) is in question due to the spreading of the electron beam through both the main-phase grains and the grain boundary phase. EDX spectra show either composition of the main 2-14-1 phase, or of a phase that is rich in Nd compared to the grains.

DISCUSSION

Although the microstructures of the two samples are quite different - the hot-pressed sample has an isotropic structure while the die-upset sample has an anisotropic plate-like grain structure - the grain boundary structure and composition remain rather similar. Information obtained during the course of the study can be divided into two categories: that obtained from meso-scale (10 nm range) features and that obtained from fine-scale (1-3 nm range) features. In general, materials in the thicker grain boundary regions is found to be Nd-rich, while that found in the thinner grain boundary regions is found to be Fe-rich in the hot-pressed microstructure and remains indeterminate in the die-upset microstructure.

The presence of second phases, in the grains and at the grain boundaries and grain boundary junctions, is thought to be responsible for the reversal mechanisms in these magnetic alloys. Exact determination of their microstructure and composition thus is important in improving the magnetic properties. However, the role that the second phases play is difficult to determine because different studies of similar materials have reported different structures and phase constitution. Clearly the microstructures and phase constituents are very dependent upon composition. Mishra and his colleagues reported finding of a BCC structure with a lattice parameter close to that of β-Nd,[16] and Nd-rich phases,[8,15-17] including Nd oxides,[15] in a Nd-rich B-deficient rapidly quenched alloy, while in Nd-rich B-rich alloys, Chu et al. reported finding of $Nd_5Fe_2B_6$ grains and amorphous Nd-rich grain boundaries in rapidly quenched samples, and hexagonal structured Nd-rich intragranular precipitates in the hot-pressed samples.[17]

In the case of the two related magnets studied here, differences in the magnetic behavior can be explained by microstructural differences, because both the thicker and the thinner intergranular regions were found to have roughly the same composition and structure in both magnets. The grain boundary junctions were observed in both samples, although those in the die-upset sample seem to have a higher Nd:Fe ratio than those in the hot-pressed sample. The higher coercivity in the hot-pressed sample most likely stems from the difficulty in magnetizing randomly-oriented grains. There is no evidence from room-temperature magnetic data for pinning-controlled coercivity; the linear approach to both coercivity and remanence are characteristic of nucleation-controlled reversal.[18] The poor remanence in the hot-pressed sample is due to the approximately random orientation of the grains, and alignment of the grains upon die-upsetting is responsible for the increase in the remanence.

The presence of excess iron in the grain boundary phase has several important consequences with regards to inter-grain interactions. One result is that it is possible that the grains are exchange-coupled as well as

magnetostatically coupled. The presence of a ferrous, possibly ferromagnetic, intergranular phase also allows for the existence of lower-anisotropy sites for reverse magnetization nucleation, consistent with experimental data, while at the same time it may reduce the probability of domain wall pinning at the intergranular phase.

CONCLUSIONS

High resolution and analytical transmission electron microscopy was used to study the microstructure and composition in hot-pressed (MQ-2) and die-upset (MQ-3) $Nd_2Fe_{14}B$-based magnet alloys. The hot-pressed sample with the nominal composition $Nd_{13.75}Fe_{80.25}B_6$ shows faceted grains of the 2-14-1 phase, while die-upset NdFeB samples having the same bulk composition show plate-like grains, together with larger equiaxed grains that contain a speckling of precipitates in the grain interior. The thinner grain boundaries exhibit an Fe-rich composition near that of the $NdFe_3$ phase, while the thicker intergranular phases are Nd-rich. Nanocrystallites with Nd:Fe ratio near 7:3 are also found at the grain junctions in the equiaxed grain regions of the die-upset samples. The initial magnetic properties of the two samples show different behaviors, which is attributed to the difference in the anisotropy of the grain structure. The high coercivity and low remnance of the hot-pressed sample result from the random orientation of the grains. The Fe-rich phase at the grain boundaries in both samples could provide exchange-coupling between the grains and sites for possible reverse magnetization nucleation.

REFERENCES

1. J.J. Croat, J.F. Herbst, R.W. Lee, and F.E. Pinkerton, J. Appl. Phys.55, 6, 2083 (1984).
2. M. Sagawa, S. Fujimura, N. Togawa, H. Yamamoto, and Y. Matsura, J.Appl. Phys. 55, 6, 2078 (1984).
3. Gaunt, Philos. Mag. B 48, 261 (1983).
4. F.D. Pinkerton and C.D. Fuerst, J. Appl. Phys. 69, 5817 (1991).
5. M. Gronnefeld and H. Kronmuller, J. Magn. Magn. Mat. 88, L267 (1990).
6. J.D. Livingston, in *Soft and Hard Magnetic Materials with Applications*, Ed. J.A. Salsgiver, K.S.V.L. Narasimhan, P.K. Rastogi, H.R.Sheppard, and C.M. Maucione, ASM, Metals Park, Ohio, 71 (1986).
7. J.F. Herbst, Rev. Mod. Phys. 63, 819 (1991).
8. R.K. Mishra and R.W. Lee, Appl. Phys. Lett. 48, 733 (1986).
9. L. Folks, R. Street, and R.C. Woodward, J. Appl. Phys. 75, 6271 (1994).
10. L. Henderson Lewis, Y. Zhu, and D.O. Welch, J. Appl. Phys. 76, 10, 6235 (1994).

11. Y. Zhu, J. Tafto, L. Henderson Lewis, and D.O. Welch, Phil. Mag. Lett. 71, 297 (1995).
12. R.W. Lee, Appl. Phys. Lett. 46, 790 (1985).
13. C.D. Fuerst and E.G. Brewer, J. Appl. Phys. 73, 5751 (1993).
14. C. D. Fuerst, E.G. Brewer, R.K. Mishra, Y. Zhu, and D.O. Welch, J. Appl. Phys. 75, 4208 (1994).
15. R.K. Mishra, Appl. Phys. Lett. 62, 3, 967 (1987).
16. R.K. Mishra, J. Magn. Magn. Mat. 54-57, 450 (1986).
17. T.-Y. Chu, L. Rabenberg, and R.K. Mishra, J. Appl. Phys. 69, 8, 6046 (1991).
18. G. C. Hadjipanayis and A. Kim, J. Appl. Phys. 63, 3310 (1988).

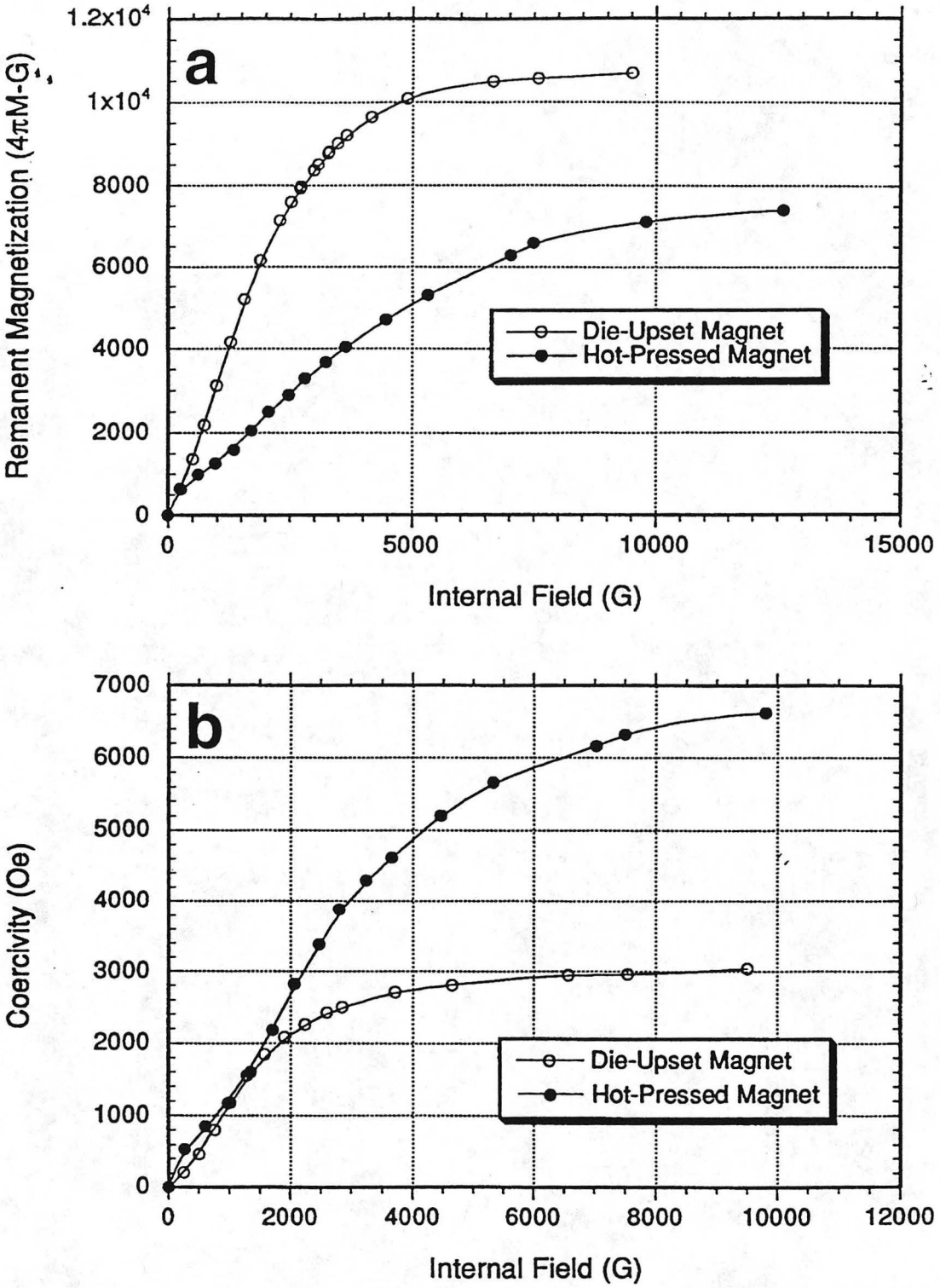

Figure 1. Development of a) remanent magnetization B_R, and b) coercivity H_{ci}, with internal field at T = 77°C (350°K)

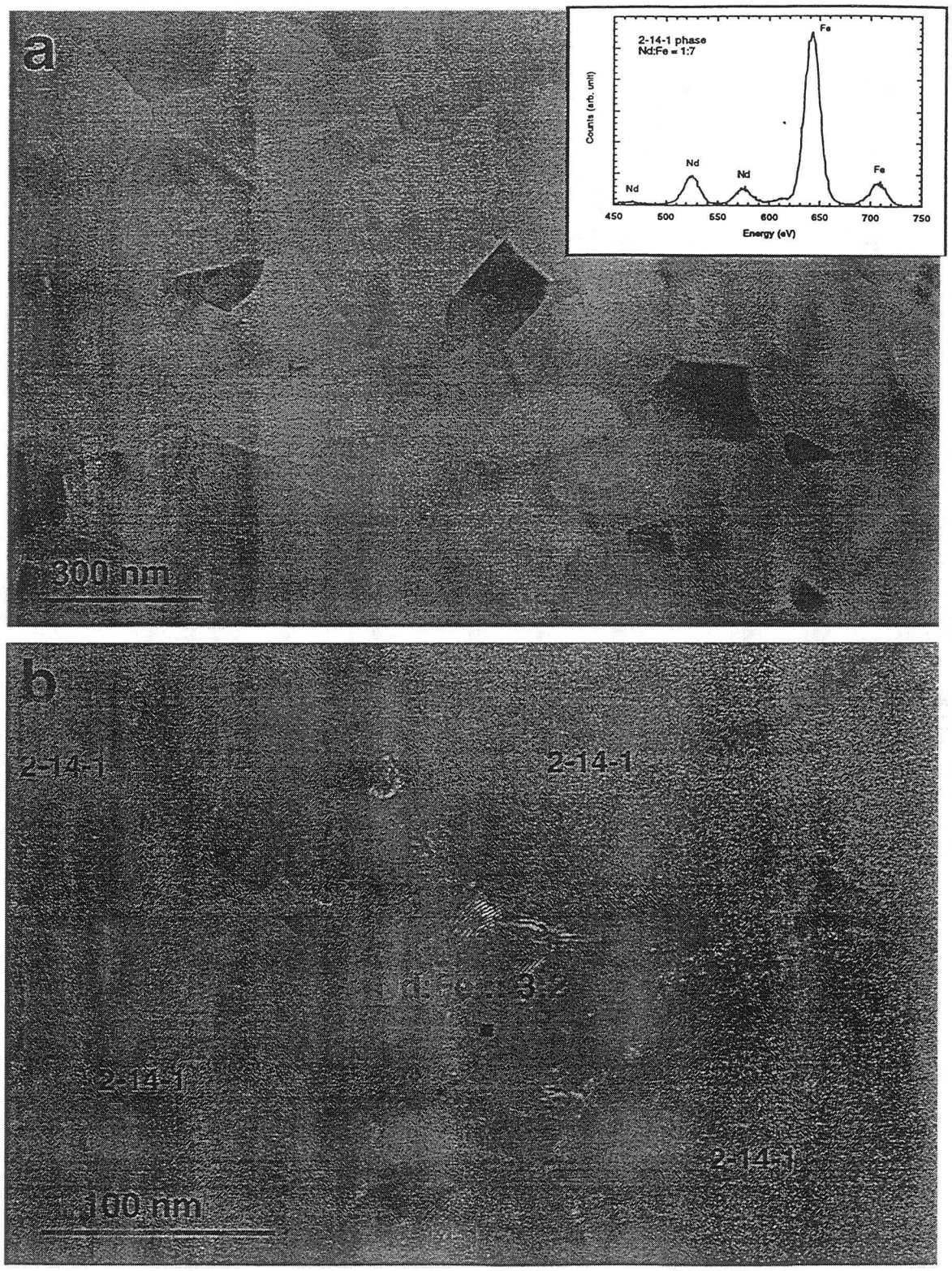

Figure 2. a) Grain structure of the hot-pressed sample, the inset shows the EDX spectrum of the 2-14-1 main phase, and b) high magnification TEM image of a grain boundary junction.

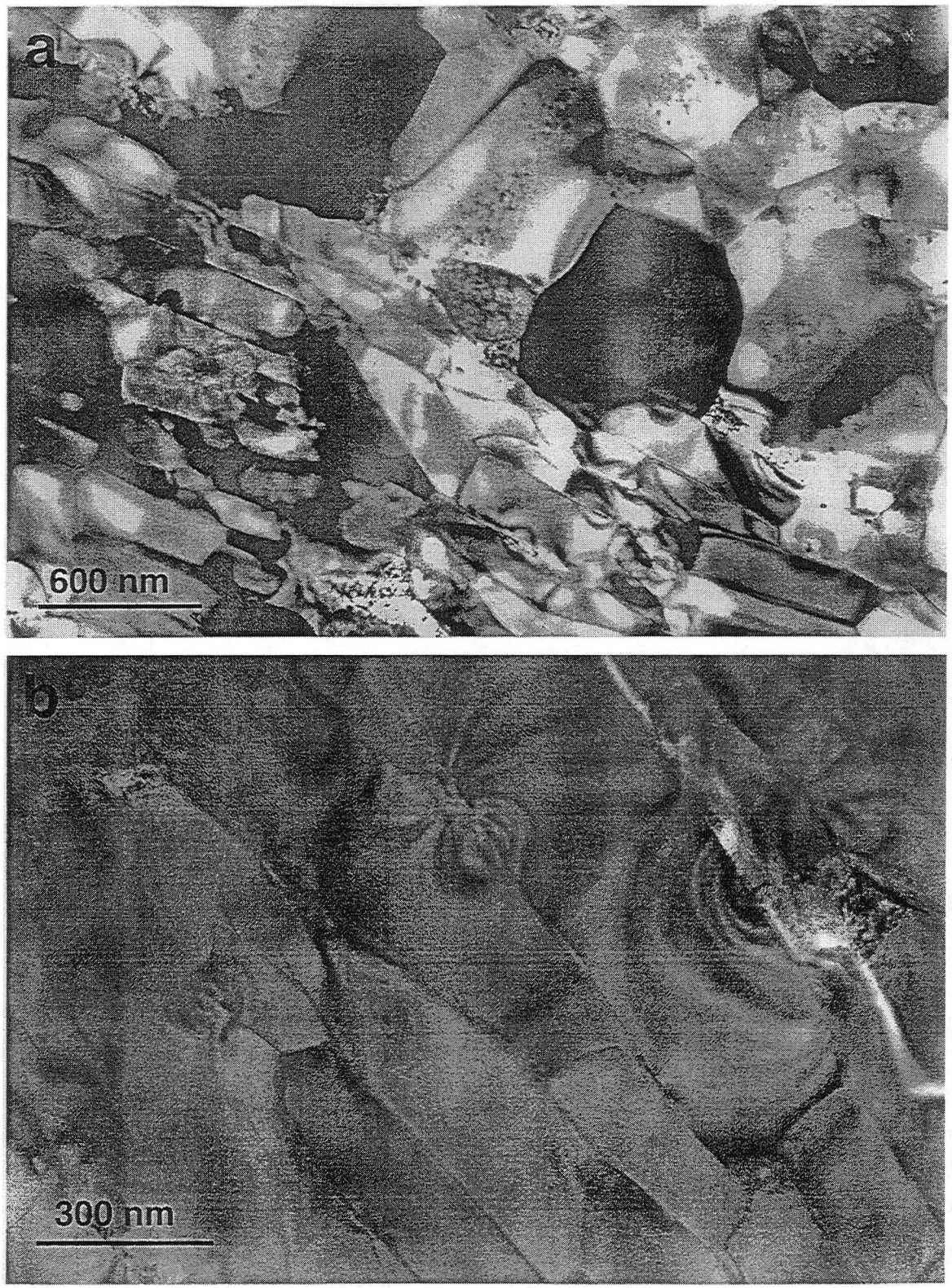

Figure 3. a) Grain structure of the die-upset sample showing both plate-like and equiaxed grains, and b) high magnification TEM of the plate-like grains showing the strain contrast around the second phase pockets.

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