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BRITTLE FRACTURE IN $Nd_2Fe_{14}B$ INTERMETALLIC MAGNETS

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Abstract

Efforts to understand and improve the fracture toughness of $Nd_2Fe_{14}B$ permanent magnets require an understanding of the fracture process itself. Cleavage plane orientations in $Nd_2Fe_{14}B$ were identified by X-ray diffraction and found to be rather random. Cleavage fracture surfaces often exhibited smooth curvatures with no evidence for cleavage steps. The small grain sizes of less than 100 nm in Magnequench MQ material preclude an easy assessment of the fracture mode by scanning electron microscopy. Auger electron spectroscopy showed that much of the surface is covered with a 1 nm thick layer of a neodymium-rich phase, presumably the 70Nd-30Fe eutectic phase, suggesting that the hard $Nd_2Fe_{14}B$ grains do not cleave but instead failure is at or in the grain boundary phase.

Introduction

Efforts to understand and improve the fracture toughness of $Nd_2Fe_{14}B$ permanent magnets require an understanding of the fracture process itself. It has been known that $Nd_2Fe_{14}B$ has no deformation modes and therefore is completely brittle. Earlier studies have measured toughness and strength but have not addressed the fracture process [1-3]. Generally, low symmetry, large-unit-cell intermetallics fail by cleavage. Even at hot pressing temperatures of 750°C, when the low melting point eutectic phase forms and serves as a sintering aid, no slip deformation is thought to occur. Cleavage during this step in processing may aid development of anisotropy much as slip does in texture development in many metal alloys. Because of the small grain sizes (less than 100 nm) in the melt spun Magnequench MQ magnets, it is difficult to conclude much about the fracture process based on images from a scanning electron microscope (SEM) of the fracture surface.

In this paper, orientations of cleavage faces formed from fracture of single crystals of $Nd_2Fe_{14}B$ were identified by x-ray diffraction (XRD). Auger electron spectroscopy (AES) analysis was used to measure the composition of the fracture surface as a function of depth in order to confirm the presence of the expected grain boundary phases.

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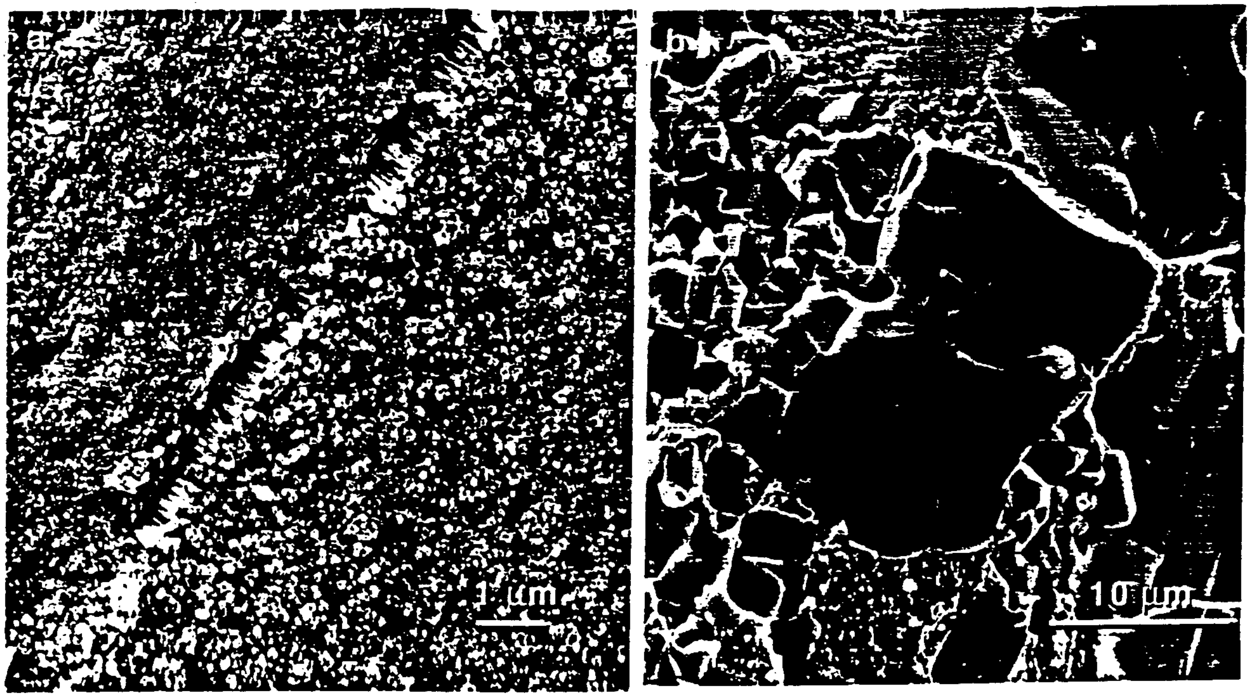


Figure 1: SEM micrographs of fracture surfaces in a MQII magnet showing (a) the small grain size and difficulty in assessing the fracture mode and (b) a similar sample after a 4 hr anneal at 800°C.

Experimental Procedure

Single crystals of $Nd_2Fe_{14}B$ were grown at Ames Laboratory by the slow cooling of a Nd-rich ternary melt. Crystals as large as $10 \times 10 \times 2$ mm^3 can be grown using this technique. These crystals were crushed to obtain cleavage faces. XRD orientations of crystals with fairly flat cleavage faces were made using a 4-circle x-ray diffractometer. After orientation in the goniometer, reflected laser light was used to measure the angular curvature of the face. Stereo images were made of these cleavage faces in a field emission SEM. Surface imaging was also performed in the contact mode in a Park Scientific AutoProbe XL atomic force microscope (AFM). To measure grain boundary compositions, a series of alloys, all processed by the normal MQII route, were analyzed by AES. After specimen insertion and bake out, the specimens were fractured under UHV conditions inside the spectrometer immediately before analysis. The AES data were collected using a PHI Model 590 Scanning Auger Microprobe with a beam energy of 5 keV and a current of ~140 nA. The data were collected in a voltage to frequency conversion mode.

Results and Discussion

Figure 1a shows a fracture surface of a Magnequench MQII magnet. The grain size is generally less than 100 nm and much too small to determine orientations. Figure 1b shows a similar specimen after an anneal for 4 h at 800°C. Attempts were made to orient the larger faces using electron backscattered patterns (EBSP) also called backscattered Kikuchi patterns (BKP) in a SEM. However, due to the low symmetry, large unit cell and the low incidence angle (the specimen was tilted nearly parallel to the incident electron beam) and the roughness of the fracture surface, images could not be obtained that were analyzable.

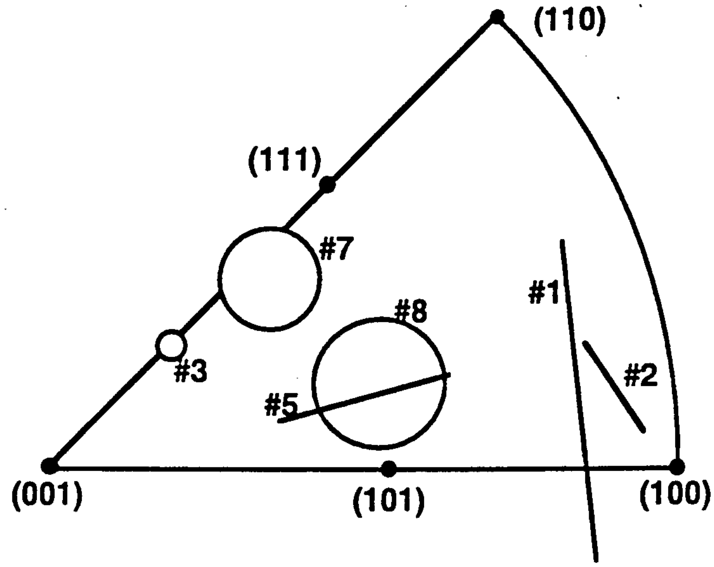


Figure 2: Stereographic triangle with marked cleavage face orientations as measured by XRD. Faces labelled 1, 2, and 5 are drawn as lines since they were curved in one direction. The length of the line represents the angular range. The areas labelled 3, 7, and 8 were hemispherical and the circle covers the angular range of the cleavage faces.

The orientations of cleavage plane normals measured on single crystals are listed in Table I and shown graphically on a stereographic triangle in Fig. 2. The circles in Fig. 2 represent the approximate angular range of the hemispherical faces oriented by XRD. The lines in Fig. 2 represent the approximate cylindrical angular range of the other faces analyzed. Note that $Nd_2Fe_{14}B$ has a tetragonal unit cell and so the stereographic triangle shown consists of what looks like two regular cubic stereographic triangles. Even though these orientations appear in a band, they cover such a large fraction of the stereographic projection that they therefore are quite random.

Table I: XRD Determined Cleavage Plane Normals

Area #	Cleavage Plane Normals		
	h	k	l
1	4.0	0.4	0.7
2	4.0	0.6	0.5
3	1.5	1.4	4.8
5	3.2	0.7	3.4
7	2.4	1.9	3.7
8	2.8	0.7	2.6

Often, curved cleavage fracture surfaces in intermetallic alloys are actually stepped. Stereo SEM micrographs of specimens in this study showed curved faces with no evidence of stepping. Figure 3 shows two SEM micrographs of two flat areas that were oriented and had adjacent chipped areas with highly curved surfaces. AFM scans, Fig. 4, also indicated that curved surfaces were present. Cleavage in intermetallic alloys is often planar with particularly "weak" planes favored. In tetragonal structures, the c-face is often the cleavage plane. The unit cell of $Nd_2Fe_{14}B$ is a layered structure with a mixed layer on the c plane followed by two iron-only layers. Because of this structure, cleavage on (001) was expected. However, no calculations of weak bonding directions have been performed on this structure as has been done on several other intermetallic alloys. The lack of preferred cleavage planes and the curved nature observed here suggest a fracture similar to that expected in amorphous or glassy materials.

The $Nd_2Fe_{14}B$ magnets consist of a mechanically-hard, nondeforming boride phase sintered together with a metallic Nd-rich phase at the grain boundaries. Transmission electron microscopy (TEM) images of the MQII material show very little grain boundary phase mainly due to the near stoichiometric composition used. Detailed TEM analyses of these materials have described the presence of several grain boundary phases from 1 to 10 nm thick [4-5]. The thinner areas were

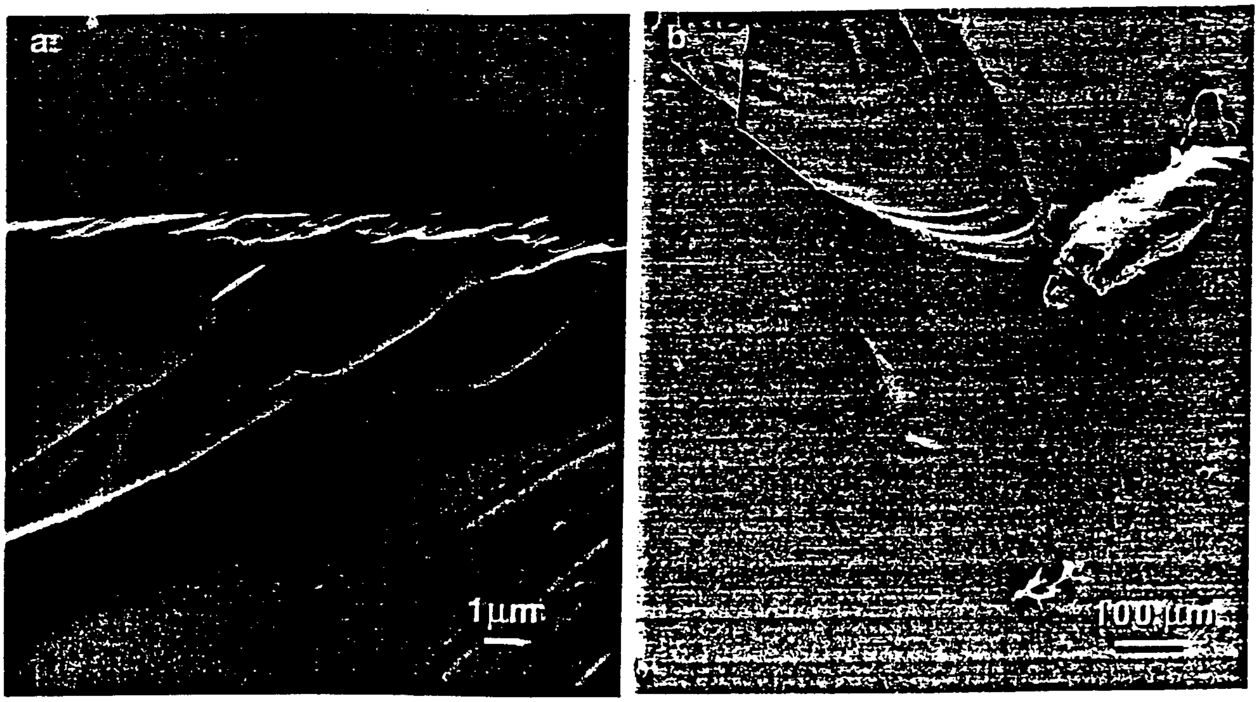


Figure 3: SEM micrographs of cleavage fracture surfaces in $Nd_2Fe_{14}B$ single crystals. Flat fracture surfaces were oriented by XRD. The top of figure 3a is looking obliquely at an almost flat region analyzed as area 1, while the lower half of the figure is a chipped edge showing the smoothly curved fracture surfaces. Figure 3b is looking down on a relatively flat region analyzed as area 2.

found to have a composition of $NdFe_3$, the thicker areas were neodymium rich and 70Nd-30Fe was present at grain boundary junctions. However, these results covered a limited number of boundaries and areas analyzed. AES was used first to help confirm that the fracture surface was intergranular and secondly to gain an estimate of the area fraction covered by grain boundary phase and a confirmation to the composition. So far, similar analysis by atom probe has failed on bulk MQII material due to the difficulty in specimen preparation.

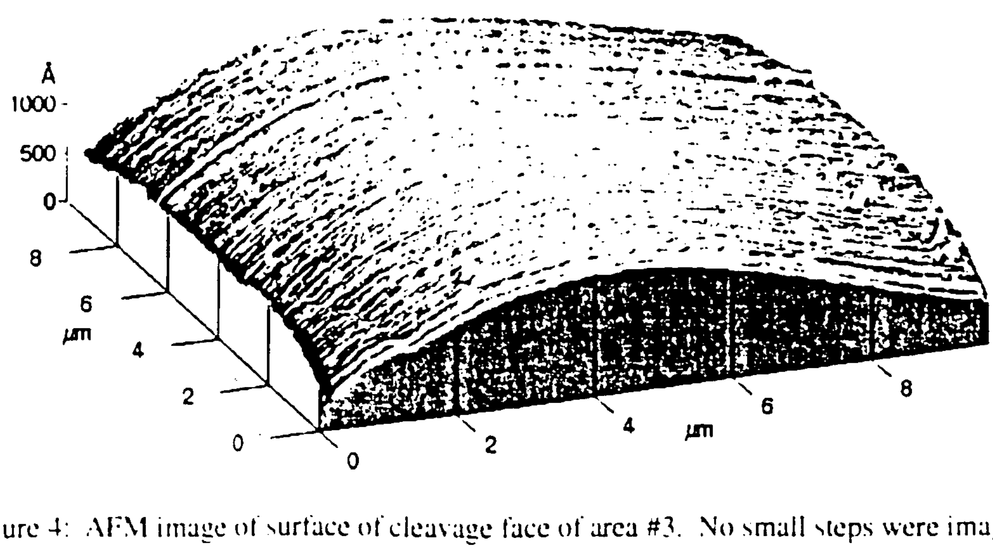
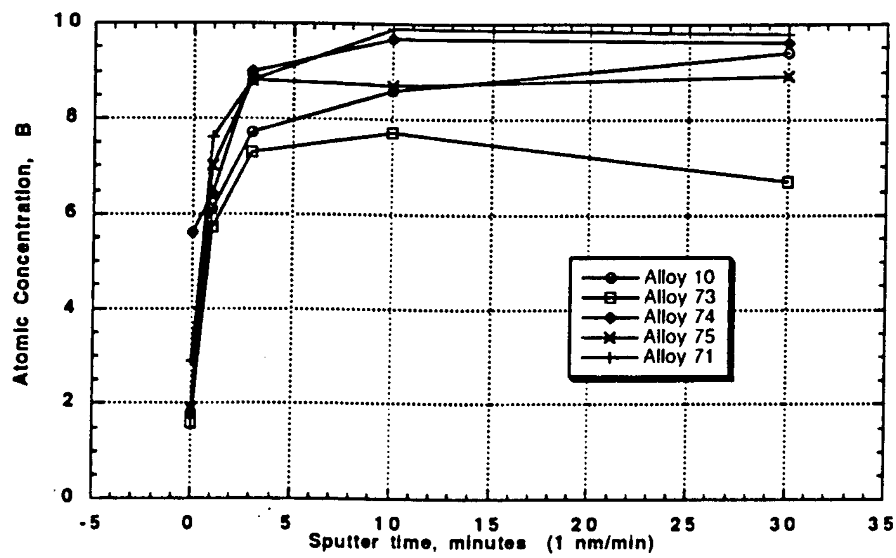


Figure 4: AFM image of surface of cleavage face of area #3. No small steps were imaged.

Figure 5 shows AES data for 5 alloys analyzed, all processed similarly. The data plotted are averages of more than 5 scans on each alloy. The curve labelled 10 is a normal E grade MQII magnet. Base compositions are given in Table II. Note, the boron compositions after 30 mins (~30 nm removed) of argon sputtering from the lowest data point on the graph to the highest are in the correct order, 0.81, 0.87, 0.89, 0.97, and 1.01 wt.%, suggesting that the measurement technique is relatively accurate. The neodymium concentration after 30 m of sputtering are almost in order. From the lowest to highest curve on the graph, the data points are from alloys with 29.4, 29.9, 30.9, 32.2 and 31.9 wt.% total rare earth. However, the absolute bulk composition from the AES analysis is high. The surface concentration of neodymium is more than twice the bulk concentration. The iron concentration curves, not shown, are opposite that of the neodymium. The neodymium

Table II Compositions of alloys analyzed by AES.

Alloy #	RE level		B level	
	wt.%	at.%	wt.%	at.%
75	29.4	13.3	0.87	5.3
74	29.9	13.5	0.97	5.9
10	30.9	14.1	0.89	5.4
73	31.9	14.7	0.81	5.0
71	32.2	14.8	1.01	6.2



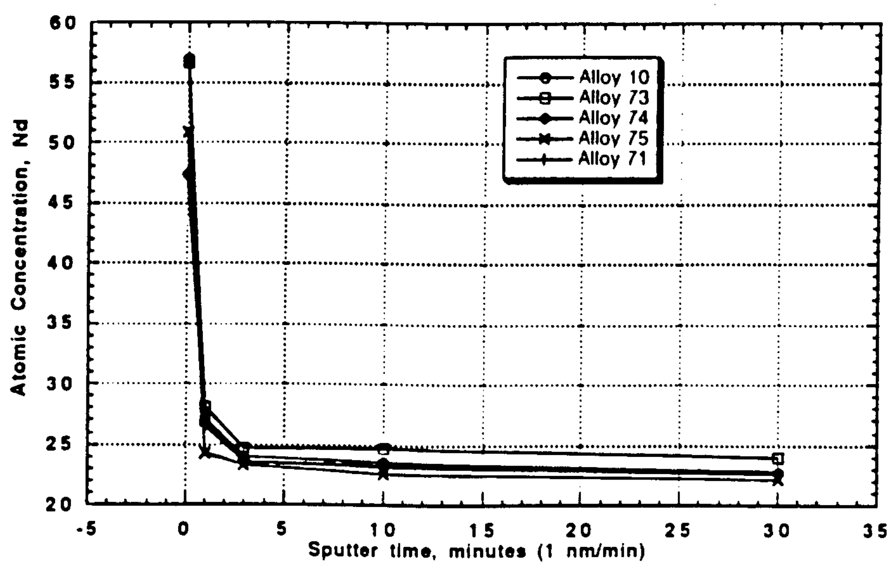


Figure 5: Averaged AES scans for neodymium and boron levels as a function of depth for the 5 alloys listed in Table II. The surface composition was close to that of the low melting point eutectic 70Nd-30Fe phase suggesting that a substantial fraction of the fracture surface was covered with a 1 nm thick layer of the eutectic phase.

enrichment levels observed suggest that up to 3/4 of the surface is coated with a 1 nm thick layer of the 70Nd-30Fe phase. After 3 min of sputtering (3 nm removed) bulk compositions are reached.

Summary and Conclusions

Fracture in the small-grained $Nd_2Fe_{14}B$ MQII magnets is intergranular with a 1 nm thick layer of the eutectic 70Nd-30Fe phase over possibly 3/4 of the fracture surface. While brittle intermetallics usually cleave on preferred planes, $Nd_2Fe_{14}B$ appears to be non-directional when cleaving.

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References

1. J. A. Horton, J. L. Wright, and J. W. Herchenroeder, "Fracture Toughness of Commercial Magnets," *IEEE Trans. on Magn.* **32**, (5), (1996), 4374-4376.

2. Yu. M. Rabinovich, V. V. Sergeev, A. D. Maystrenko, V. Kulakovsky, S. Szymura, and H. Bala, "Physical and Mechanical Properties of Sintered Nd-Fe-B type Permanent Magnets," *Intermetallics* **4** (1996), 641-645.

3. P. A. Withey, H. M. Kennett, P. Bowen and I. R. Harris, "The Magnetic and Mechanical Properties of NdFeB Type Permanent Magnets and the Effect of Quenching," *IEEE Trans. on Magn.* **26** (5) (1990), 2619-2621.

4. T. D. Nguyen, K. M. Krishnan, L. H. Lewis, Y. Zhu, and D. O. Welch, "Microstructure and Composition in Rapidly Quenched NdFeB-Based Hard Magnet Alloys," *J. Appl. Phys.* **79** (8) (1996), 4848-4850.

5. L. H. Lewis, Y. Zhu, and D. O. Welch, "Ferromagnetic Grain Boundary Signature in Die-Upset RE-Fe-B Magnets," *Scripta Met.* **33** (10/11) (1995), 1775-1780.

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