Zr site determination and origin of magnetic anisotropy in HDDR processed Nd2Fe14B-based magnets

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It has been a controversial prospect about the roles of small additives such as Zr, Hf and Ga for the evolution of magnetic anisotropy in the HDDR (Hydrogenation, Dispropotionation, Desorption and Recombination) treated $Nd_2Fe_{14}B$-based magnets. XAFS measurements of the Zr K-edge were carried out for the $Nd_{16}Fe_{75.5}Zr_{0.5}B_8$, $Nd_{1.6}Zr_{0.4}Fe_{14}B$ and $Nd_2Fe_{13.6}Zr_{0.4}B$ magnets. Zr, in the as-cast $Nd_{16}Fe_{75.5}Zr_{0.5}B_8$ ingot, is found to occupy $Fe(j_2)$ sites in $Nd_2Fe_{14}B$ structure. Small changes of the Zr XAFS spectra after disproportionation and recombination suggest that local portion of $Nd_2Fe_{14}B$ phase including Zr at $Fe(j_2)$ sites is stabilized against disproportionation. Effects of concentration, i.e. ratio of Nd to Fe, on Zr site occupancy are presented.

K eywords: $Nd_2Fe_{14}B$, Magnetic anisotropy, HDDR, XAFS, Zr impurity.

1. Introduction

In recent years the Hydrogenation Disproportionation Desorption Recombination (HDDR)-process has been recognized as a suitable method for the production of NdFeB–based hard magnets. The process converts the coarse grains of homogenized or as-cast alloys into submicrometer grains; a heat treatment in hydrogen disintegrates of $Nd_2Fe_{14}B$-phase into mixture of Nd-hydride, α-Fe, Fe_2B and a subsequent heat treatment in vacuum recombines the mixture into fine $Nd_2Fe_{14}B$ grains (Gutfleisch & Harris, 1994 and Hirosawa et al, 1997). Furthermore, HDDR process results in high magnetic anisotropy by adding Co, Ga and/or Zr in NdFeB–based alloys (Takeshita & Morimoto, 1996). However controversy exists about the roles of these additives for the evolution of magnetic anisotropy. Several possible explanations have been proposed to account for the origin of magnetic anisotropy (Buschow, 1994; Tomida et al, 1996, 1997; Harris, 1992).

The purpose of present study is to investigate the site occupancy of Zr and its role on the orientational memory mechanism by means of X-

ray Absorption Fine Structure (XAFS) analysis.

2. Experimental Procedure

The alloy ingots of off-stoichiometric composition $Nd_{16}Fe_{75.5}Zr_{0.5}B_8$ and stoichiometric compositions $Nd_2(Fe_{13.6}Zr_{0.4})B$ and $(Nd_{1.6}Zr_{0.4})Fe_{14}B$ were prepared by arc-melting constituent elements in an argon gas atmosphere.

For HDDR treatment, the ingots were crushed into small pieces and those of 10g were located in a sample chamber for processing. Disproportionation was carried out under 1 bar of hydrogen by heating from room temperature up to 800°C with holding for two hours and subsequently evacuating for one hour for recombination.

Structural analysis was done by x-ray diffraction using Cu Kα radiation with a curved LiF (111) monochromator. XAFS measurements were carried out at BL7C in the KEK Photon Factory, Tsukuba, using a Si(111) double crystal monochromator at the temperature 20K.
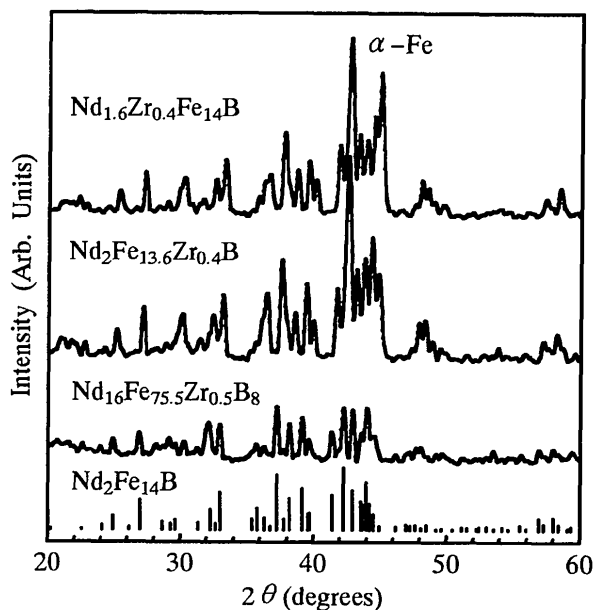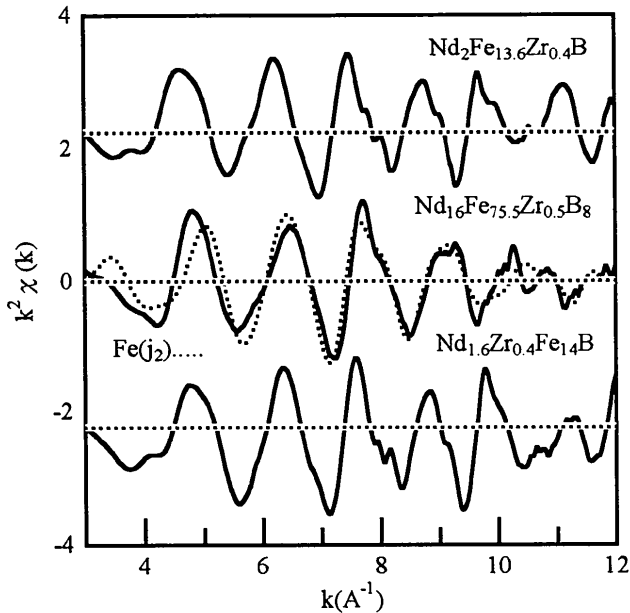

Figure 1
X-ray powder diffraction patterns of the as-cast ingots for stoichiometric and off-stoichiometric $Nd_2Fe_{14}B$-based alloys along with $Nd_2Fe_{14}B$ phase.

3. Results and Discussion

Fig. 1 shows the x-ray diffraction patterns of the as-cast ingots $Nd_{16}Fe_{75.5}Zr_{0.5}B_8$, $Nd_2(Fe_{13.6}Zr_{0.4})B$ and $(Nd_{1.6}Zr_{0.4})Fe_{14}B$ along with the $Nd_2Fe_{14}B$ phase (Shoemaker & Shoemaker, 1984). Dominant x-ray peaks are in good agreement with the $Nd_2Fe_{14}B$ phase for $Nd_{16}Fe_{75.5}Zr_{0.5}B_8$ while additional peaks of α -Fe, are observed for the stoichiometric compositions $Nd_2(Fe_{13.6}Zr_{0.4})B$ and $(Nd_{1.6}Zr_{0.4})Fe_{14}B$. The higher Nd content in off-stoichiometric ingot compared to stoichiometric

composition may suppress the appearance of free iron.

Background subtraction and normalization procedure was achieved for the observed XAFS data using AUTOBK (Newville, 1995). The results for the Zr K-edge of the as-cast off-stoichiometric and stoichiometric ingots are presented in Fig. 2.
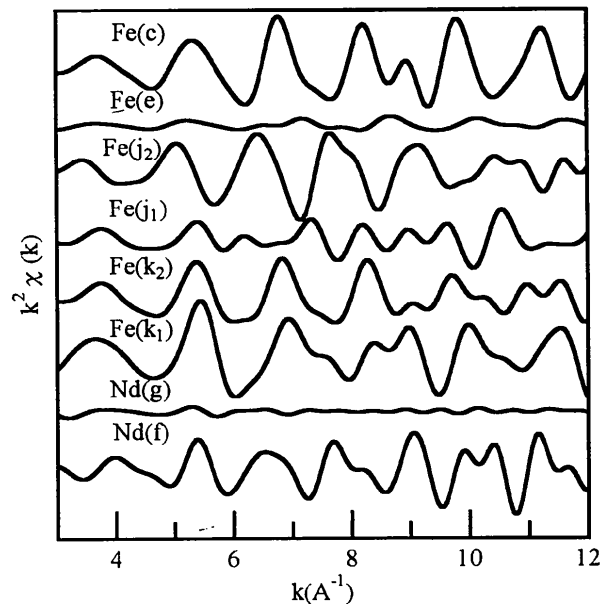

Figure 2

Observed XAFS data (solid line) of the Zr K-edge of the as-cast ingots and the calculated one (broken line) for Zr occupying $Fe(j_2)$ site using FEFF.

The unit cell of $Nd_2Fe_{14}B$ crystal ($P4_2/mmm$ space group) consists of 68 atoms (Herbst et al, 1984) where Nd atoms occupy two inequivalent sites ($4f$ & $4g$), Fe atoms six inequivalent sites ($16k_1$, $16k_2$, $8j_1$, $8j_2$, $4e$ & $4c$) and B atoms one site ($4g$). The calculation of $\chi(k)$ of the Zr K-edge for cases of Zr substituting one of these two Nd and six Fe sites in $Nd_2Fe_{14}B$ structure were carried out using FEEF6 (Rehr et al, 1991) and results are shown in Fig. 3.

The calculated $k^2 \chi(k)$ curve for the case with Zr substituting $Fe(j_2)$ site fits very well with the observed one for the off-stoichiometric ingot but does not for the stoichiometric one. Calculated results for other sites do not fit with the stoichiometric one as shown in Fig. 2. Unlike the off-stoichiometric case, stoichiometric ingots consist of at least two phases. Furthermore , Zr content for the stoichiometric ingot is much higher (~2.4 at.%) than the off-stoichiometric one (~0.5 at.%). Therefore, Zr can not simply substitute one of the $Nd_2Fe_{14}B$ sites and it seems to be distributed into multi phases (Gao et al, 1997).
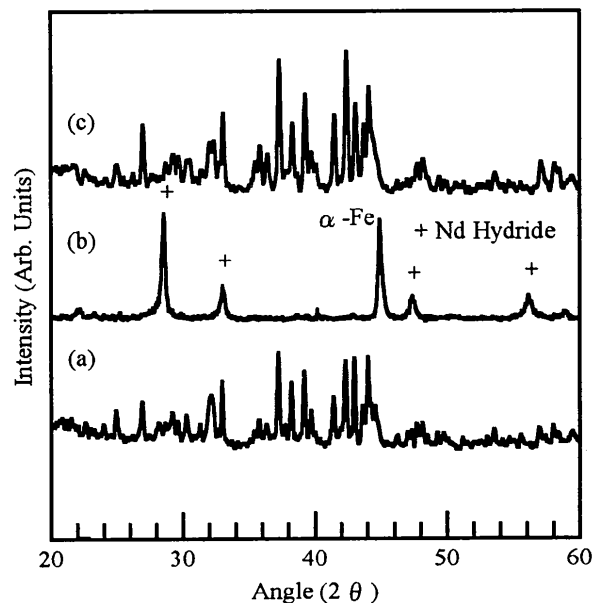
Fig.4 shows the x-ray patterns of the disproportionated and the recombined states of the off-stoichiometric composition. The result confirms

the formation of Nd-hydride, α-Fe and Fe_2B in the disproportionated stage and $Nd_2Fe_{14}B$ in the recombined one.

Figure 3

Calculated $k^2 \chi(k)$ results using FEFF of the Zr K-edge for the $Nd_2Fe_{14}B$ structure with Zr substituting one of the six Fe-sites and two Nd-sites.

Figure 4

X-ray diffraction patterns of the (a) as-cast (b)disproportionated and (d) recombined state of off-stoichiometric composition $Nd_{16}Fe_{75.5}Zr_{0.5}B_8$.

Fig.5 shows the results of $k^2 \chi(k)$ for the as-cast,

disproportionated and recombined states of the off-stoichiometric alloy. The XAFS spectra of the as-cast ingot and disproportionated states are similar as a whole except some details but somewhat different from the recombined one. Based on this observation it can be inferred that Zr atoms occupy $Fe(j_2)$ sites in $Nd_2Fe_{14}B$ crystal for the as-cast state and

Figure 5
Observed XAFS results of $k^2 \chi$ (k) of the Zr K-edge for the (a) as-cast (b) disproportionated and (c) recombined state of off-stoichiometric $Nd_{16}Fe_{75.5}Zr_{0.5}B_8$.

remain there even in the disproportionated stage with keeping $Nd_2Fe_{14}B$ structure unchanged at the local region containing Zr. The Zr substitution for Fe is also suggested by the magnetic measurements where incorporation of Zr into $Nd_2Fe_{14}B$ results in reduction of low-temperature magnetic moments (Jurczuk & Wallace, 1986). It seems strange that local structure of Zr in recombined stage is quite different from the as-cast one even though both of x-ray diffraction results show same patterns as that for $Nd_2Fe_{14}B$ structure. For this recombined state, more precise structure analysis using TEM is necessary.

In the $Nd_2Fe_{14}B$ structure $Fe(j_2)$ sites seem to have specific characters compared to other Fe sites; it connects hexagonal nets consisting of six Fe atoms and it is surrounded spherically by twelve Fe nearest neighbors. Because of strong bonding nature between Fe and Zr (Boer & Fettifor, 1988), Zr is likely to sit in a $Fe(j_2)$ site where all nearest neighbors are Fe. Furthermore $Fe(j_2)$ site seems to be a key position to construct this complex structure connecting hexagonal planes. It is very likely that a local portion of $Nd_2Fe_{14}B$ phase including Zr into

$Fe(j_2)$ sites is stabilized against disproportionation and stays undecomposed. Consequently it acts as a nucleation site of grain growth during recombination and recovers the original crystal orientation.
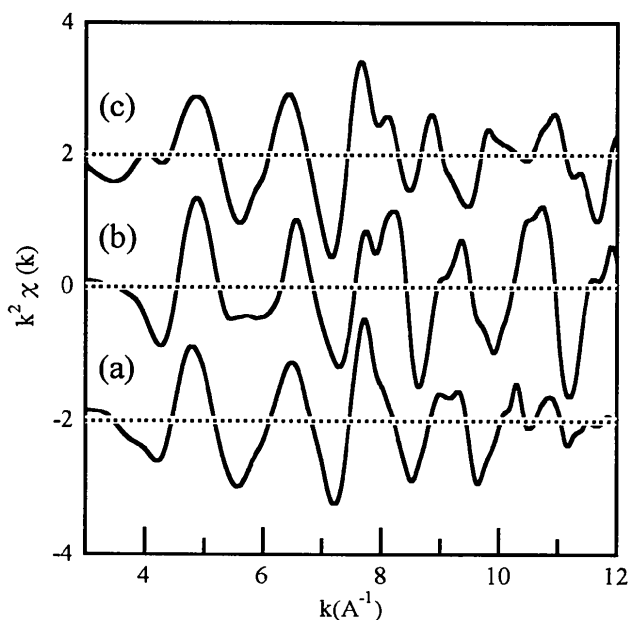
Conclusion
Site occupancy of Zr in the off- stoichiometric and stoichiometric NdFeB magnets was studied by XAFS. The results show that in case of the stoichiometric composition the presence of a large amount of α -Fe and/or other phases makes difficult to determine the specific site occupancy of Zr. The Zr in the off-stoichiometric composition $Nd_{16}Fe_{75.5}Zr_{0.5}B$ occupies an $Fe(j_2)$ site in the $Nd_2Fe_{14}B$ structure in the as-cast and in the disproportionated states. Because $Fe(j_2)$ site in the $Nd_2Fe_{14}B$ structure is situated at the position connecting the hexagonal nets, Zr in $Fe(j_2)$ site stablizes the $Nd_2Fe_{14}B$ structure due to strong Fe-Zr bonding. This helps to prevent the disproportionation with keeping as the nanoscale original grains which later can serve as seeds for grain growth and leads to the magnetic anisotropy.

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