ELSEVIER

Journal of Alloys and Compounds 293–295 (1999) 872–876

Journal of ALLOYS AND COMPOUNDS

Ga site occupancy in HDDR-treated $Nd_2Fe_{14}B$-based alloy by XAFS

Makoto Matsuura[a,*], Ahmad Ashfaq[a,1], Masaki Sakurai[b], Tosiro Tomida[c], Naoyuki Sano[c], Satoshi Hirosawa[d]

[a] *Miyagi National College of Technology, Nodayama Natori Miyagi 981-1239, Japan*
[b] *Institute for Materials Research, Katahira-cho Sendai 980, Japan*
[c] *Sumitomo Metal Industries Ltd., 1–8 Fuso-cho, Amagasaki 660, Japan*
[d] *Sumitomo Special Metals Co., Ltd., 2-15-17, Mishima-gun, Osaka, 618, Japan*

Abstract

The changes of local structure for Ga in $Nd_{13.0}Fe_{68.2}Co_{10.8}Ga_{1.0}Zr_{0.1}B_{6.9}$ during hydrogenation, disproportionation, desorption and recombination (HDDR) process are studied by fluorescence XAFS in order to understand the evolution of magnetic anisotropy by HDDR process. Comparing the observed Ga XAFS data with the calculated ones, using ab initio calculation (FEFF), Ga is proved to occupy preferentially an Fe(c) site in the $Nd_2Fe_{14}B$ structure before disproportionation and dissolves in α-Fe after the disproportionation. In the recombined state Ga redistributes into two phases, i.e. $Nd_2Fe_{14}B$ and a Nd-rich phase. The behavior of Ga during the HDDR process differs from Zr which occupies $Fe(j_2)$ sites before disproportionation and after the disproportionation. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: $Nd_2Fe_{14}B$; HDDR; XAFS; Site occupancy; Ga-additive

1. Introduction

By utilization of hydrogen, high coercivity has been achieved in $Nd_2Fe_{14}B$-based magnets [1,2]. The HDDR (Hydrogenation Disproportionation, Desorption and Recombination) process refines originally coarse grains of $Nd_2Fe_{14}B$ to about 0.3 μm which significantly increases its coercivity. Moreover, when a small amount of additives like Ga, Zr, Nb and Hf are included together with Co in a $Nd_2Fe_{14}B$-based alloy, the crystalline axes of recombined $Nd_2Fe_{14}B$ grains are aligned parallel to those of the original coarse grains resulting in higher magnetic anisotropy [3,4]. Recently, only a single additive (Zr) was reported to be able to produce magnetic anisotropy in $Nd_2Fe_{14}B$-based alloy by HDDR process [5]. One of the controversial points about this HDDR process is why and how the original crystalline axis of coarse grains is inherited by the recombined $Nd_2Fe_{14}B$ fine grains after addition of such elements. From microscopic studies, Uehara et al. have proved that very fine $Nd_2Fe_{14}B$ particles less than 50 nm in diameter are embedded in the decomposed phases of α-Fe and Fe_2B [6] in the disproportionated state. Tomida et al. observed by HRTEM that these fine $Nd_2Fe_{14}B$ particles have the same crystalline axis as that of the original coarse grains [7]. From these observations they concluded that these fine $Nd_2Fe_{14}B$ grains are likely to act as recombination centers during dehydrogenation process. Uncertainties remain, however, about the details of the growing process of recombined $Nd_2Fe_{14}B$ from the decomposed phases.

It is important that this crystallographic memory effect in the HDDR process occurs when small amounts of such elements like Ga, Zr, Nb and Hf are added to the $Nd_2Fe_{14}B$-based alloys. The roles of such additives on the magnetic anisotropy in the HDDR process have not yet been clarified. In the present work we focus our attention on the behavior of Ga in $Nd_{13.0}Fe_{68.2}Co_{10.8}Ga_{1.0}Zr_{0.1}B_{6.9}$(hereafter abbreviated as NdFeCoGaZr) during the HDDR process by means of fluorescence XAFS. Information on the local structures for such additives in NdFeCoGaZrB before and after hydrogenation is of great importance for revealing the roles of the additives on the crystallographic memory effects.

2. Experimental procedure

An ingot of NdFeCoGaZrB alloy was prepared in an induction furnace. The ingot was pulverized (about 100

---

*Corresponding author.

[1] JSPS postdoctoral fellowship for foreign researchers.

0925-8388/99/$ – see front matter © 1999 Elsevier Science S.A. All rights reserved.

PII: S0925-8388(99)00381-3

μm) and homogenized at 1140°C for 16 h. HDDR was carried out by exposing the powder samples under 0.1 MPa hydrogen gas at 850°C for 3 h (disproportionation) followed by subsequent evacuation for 1 h (recombination) and cooling to room temperature. These HDDR conditions were reported as the optimum one for NdFeCoGaZrB to have the highest coercivity [7].

XAFS measurements of the Ga K-edge and the Zr K-edge were carried out at room temperature using synchrotron radiation at BL7C in the KEK photon factory. Incident energy was selected by using a Si(111) monochromator using a total reflection mirror in order to cut off the higher order harmonics. A Zn filter was used to eliminate elastic scattering for the Ga K-edge. A Lytle-type collimating slit combined with an ion-chamber was used as a detector of the fluorescence X-ray. The Zr concentration (0.1 at%) in NdFeCoGaZrB is one tenth of that for Ga, so the XAFS signal-to-background ratio of the Zr K-edge was much lower compared to Ga. Hence, we could not make a quantitative analysis of the Zr K-edge XAFS results for the present alloy.

3. Results

After the usual background subtraction and normalization $\chi(k)$ was deduced by using program AUTOBK [8]. Fig. 1 shows the results of $\chi(k)$ curves for the Ga K-edge of NdFeCoGaZrB represented by $k^2\chi(k)$ vs. k for the homogenized (a), disproportionated (b) and recombined (c) states. Fig. 2 represents the Fourier transformed curves $F(r)$ of these $k^2\chi(k)$ vs. k curves in the k-range between 3.0 A^{-1} and 11.0 A^{-1}.

These XAFS results of the Ga K-edge clearly indicate that the local structure around Ga changes significantly during the HDDR process. In order to determine the site occupancy of Ga, the XAFS data for the Ga K-edge was analyzed using FEFF6 [9]. Before hydrogenation, the NdFeCoGaZrB sample was heat-treated at 1140°C for 16 h in order to homogenize it as described before. After the heat treatment of as-cast samples, at least two phases have been shown to exist, i.e. $Nd_2Fe_{14}B$ and $CoNd_3$ [10]. XAFS calculation of the Ga K-edge for $CoNd_3$ was done using FEFF assuming Ga atoms to occupy Co sites. The calculated result differs significantly from the observed one. Therefore, we can exclude the case of Ga atoms in the $CoNd_3$ phase in the homogenized state.

Tetragonal $Nd_2Fe_{14}B$ structure ($P4_2/mnm$ in space group) consists of crystallographically inequivalent six Fe, two Nd and one B sites [11]. The calculations of $\chi(k)$ curves of the Ga K-edge were done using FEFF for the $Nd_2Fe_{14}B$ structure with Ga occupying one of those inequivalent Fe and Nd sites. Fig. 3 shows these calculated $k^2\chi(k)$ results of the Ga K-edge together with the observed one for the homogenized sample. Fig. 4 represents the Fourier transformation of the calculated $k^2\chi(k)$ results of the Ga K-edge along with observed one for the same k-range i.e. 3.0–11.0 A^{-1}. The calculated results for Fe(c) and Fe(k_2) sites are also shown as broken lines in Figs. 1(a) and 2(a). The calculated $k^2\chi(k)$ curves for Fe(c) and Fe(k_2) fit well with the observed one but the calculated curves for other sites do not. The result for the Fe(c) site fits closer to the observed one than that for the Fe(k_2) site. Furthermore, because the nearest neighbor distance at a k_2-site in $Nd_2Fe_{14}B$ structure is shorter (2.39 A) than that for a c-site (2.50 A), Ga atoms (2.7 A in atomic diameter) should more favorably occupy c-sites than k_2-sites in the homogenized state.

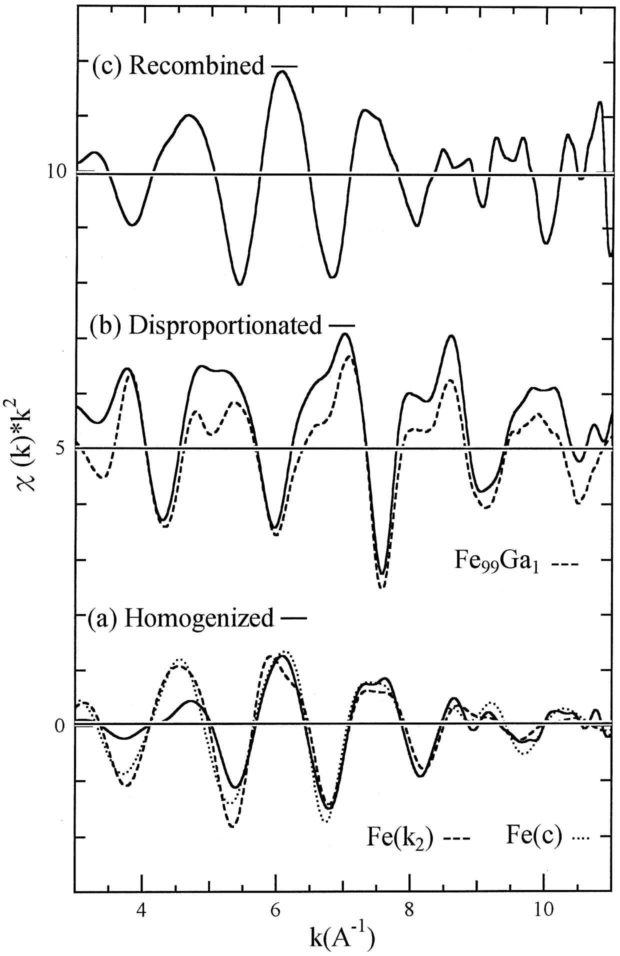

Fig. 1. XAFS spectrum of the Ga K-edge for (a) homogenized (b) disproportionated and (c) recombined states for $Nd_{13.0}Fe_{68.2}Co_{10.8}Ga_{1.0}Zr_{0.1}B_{6.9}$. The calculated results for $Nd_2Fe_{14}B$ with Ga substituting for Fe at Fe (c) and Fe(k_2) sites and the observed Ga K-edge for $Fe_{99}Ga_1$ are also shown in (a) and (b) respectively.

NdFeCoGaZrB is decomposed into three phases by disproportionation, i.e. α-Fe, Fe_2B and Nd-hydrides with very small $Nd_2Fe_{14}B$ particles. Because of a strong bonding between Nd and H, Ga is not likely to substitute for Nd in NdH_2. Therefore Ga will appear in the two main phases (α-Fe and Fe_2B) and $Nd_2Fe_{14}B$ particles. In the previous work, we measured the XAFS spectrum of the Ga

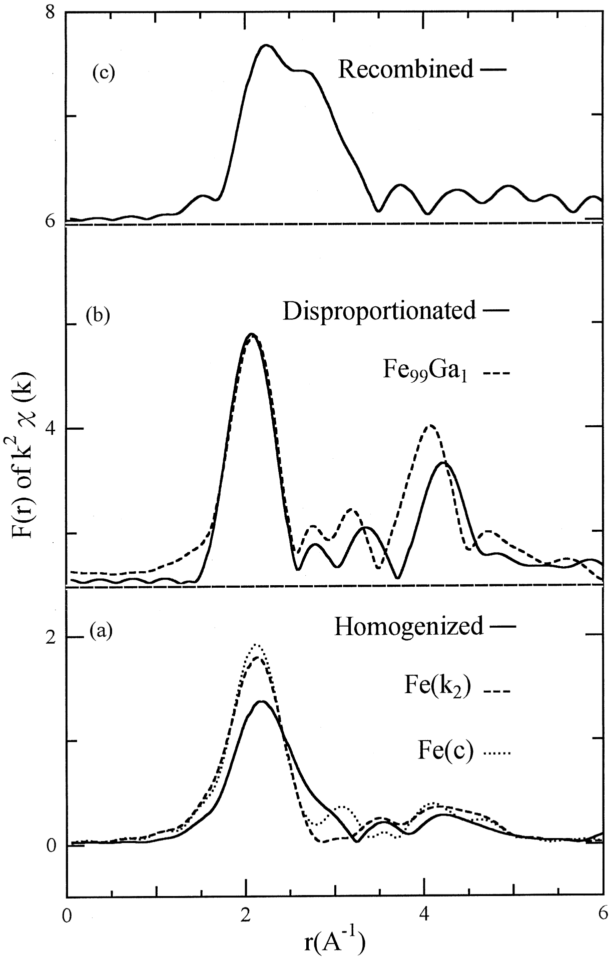

Fig. 2. Fourier transformation of $k^2\chi(k)$ of the Ga K-edge for those shown in Fig. 1.

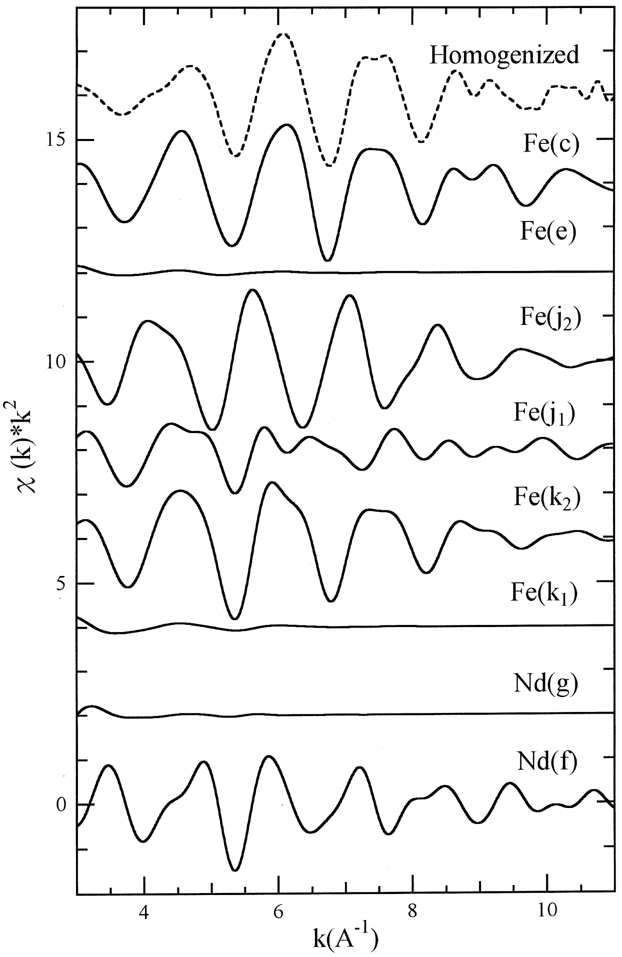

Fig. 3. Calculated $k^3\chi(k)$ results using FEFF of the Ga K-edge for the $Nd_2Fe_{14}B$ structure with Ga substituting for Fe or Nd atoms at six Fe-sites and two Nd-sites, respectively together with the observed one (homogenized) for the comparison.

K-edge for α-Fe supersaturated with Ga ($Fe_{99}Ga_1$) and showed that Ga substitutes an Fe site of α-Fe [12]. In Figs. 1(b) and 2(b) the observed results of the Ga K-edge for $Fe_{99}Ga_1$ are shown as broken lines. Agreement of the $k^2\chi(k)$ and its Fourier transforms between the observed NdFeCoGaZrB (disproportionated) and that for $Fe_{99}Ga_1$ is excellent. Poor agreement is found between the observed and calculated curves of the Ga K-edge for Fe_2B where one Ga atom sits at an Fe site. From these results, Ga is shown to dissolve in α-Fe in the disproportionated state.

The XAFS result for the recombined state is quite different from the disproportionated one and rather similar to the homogenized one. It is quite possible that Ga atoms dissolve in the recombined $Nd_2Fe_{14}B$ phase. The first peak of the $F(r)$ curve splits into two, in contrast to single peak for the homogenized one, as shown in Fig. 2. Since there are no sites in $Nd_2Fe_{14}B$ crystal which show such a splitting of the first peak in the $F(r)$ curves (Fig. 4), Ga in the recombined state is probably distributed into phase besides the recombined $Nd_2Fe_{14}B$. The peak positions of the first peak correspond to that of Fe-sites in $Nd_2Fe_{14}B$, i.e. 2.0 A~2.2 A as estimated from Fig. 4. Therefore some of Ga atoms substitute for Fe in the $Nd_2Fe_{14}B$ structure and the rest resolve in other phase. From the longer r-distance of the second peak(~2.7 A) it is plausible that Ga is surrounded by Nd. From these results it can be inferred that Ga dissolves not only in recombined $Nd_2Fe_{14}B$ phase but also in Nd-rich phase in the recombined state.

4. Discussion

The present XAFS results show that Ga atoms move from Fe(c) sites in $Nd_2Fe_{14}B$ phase in the homogenized state into α-Fe at the disproportionated state. In the recombined state Ga redistributes into two phases, i.e. recombined $Nd_2Fe_{14}B$ and possibly the Nd-rich phase. Because Ga substitution for Fe in $Nd_2Fe_{14}B$ leads to an increase in Curie temperature and coercivity like the Si case, it is interesting to investigate the site occupancy of Ga and Si. For the as-cast state, Ga was reported to sit at

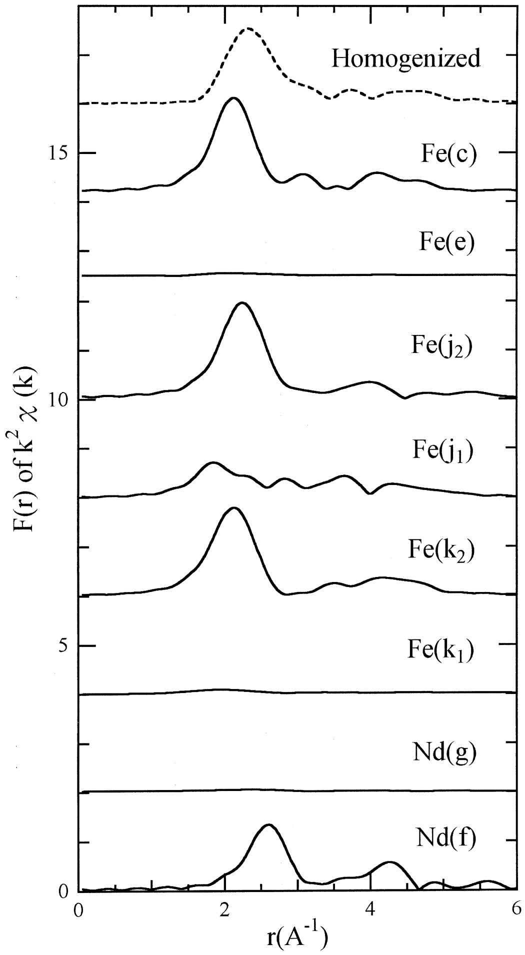

Fig. 4. Calculated Fourier transformation of $k^2\chi(k)$ of the Ga K-edge for those shown in Fig. 3.

$Fe(j_1)$ and Fe(c) sites by Quan using neutron diffraction [13]. The resolution of spectrum, however, is not high enough to decide the site occupancy of Ga conclusively. Xie et al. reported that preferential site occupancy of Ga in $Nd_2Fe_{14-x}Ga_xB$ depends on the concentration of Ga; k_2-site for $x \leqslant 1$ and k_1 and j_1 sites in addition to k_2 site for $x > 1$ [14]. Preferential Fe(c) site occupancy for Si was reported from neutron diffraction by Pringle et al. [15]. Fe(c) preferential occupancy of Ga in the $Nd_2Fe_{14}B$ structure in the present results is consistent with the Si case. Present XAFS results proved that most part of Ga moves into decomposed α-Fe in the disproportionated state. This results seem to disagree with the results by Uehara et al. [6] which show that Ga is concentrated in $Nd_2Fe_{14}B$ particles embedded in the decomposed phases. But since the volume of α-Fe is far larger than undecomposed $Nd_2Fe_{14}B$ particles, our conclusion does not necessary conflict with their results. In the recombined state Ga is distributed into two phases; $Nd_2Fe_{14}B$ and probably the Nd-rich phase. It is interesting that the same behavior is observed for Zr in $Nd_{16}Fe_{75.5}Zr_{0.5}B_8$; Zr at the recombined state shows two splitting peaks in the Fourier transform of $\chi(k)$ [16]. From these results small additives like Ga and Zr can substitute for Fe in $Nd_2Fe_{14}B$ in the homogenized or as-cast state while in the recombined state not all of them can desolve in the recombined $Nd_2Fe_{14}B$ phase and are included in other phases such as Nd-rich. Though at the present stage it is difficult to clarify the role of Ga for the evolution of magnetic anisotropy, Ga plays different roles from Zr. As reported in other papers, Zr remains at an $Fe(j_2)$ site even after disproportionation, which means that the local portions of $Nd_2Fe_{14}B$ phase in which Zr are included are stabilized against decomposition [16]. More extensive research is necessary on the local Ga structural changes in the case of a single additive in $Nd_2Fe_{14}B$, i.e. $Nd_2Fe_{14-x}Ga_xB$ and on the effects of concentration: whether stoichiometric or off-stoichiometric composition.

5. Conclusion

In conclusion, Ga in $Nd_{13.0}Fe_{68.2}Co_{10.8}Ga_{1.0}Zr_{0.1}B_{6.9}$ alloy exhibits preferential Fe(c) occupancy in $Nd_2Fe_{14}B$ structure in the homogenized state and moves into α-Fe in the disproportionated state. In the recombined state not all of Ga redistributes into the recombined $Nd_2Fe_{14}B$ phase but part are included in other phases, probably in Nd-rich phase.

Acknowledgements

Thanks are due the Japan Society for the Promotion of Science for the provision of research funds.

References

[1] I.R. Harris, in: Proceedings of the 12th International Workshop on Rare-Earth Magnets and their Applications, Canberra, Australia, July 1992, p. 327.
[2] T. Takeshita, R. Nakayama, in: Proceedings of the 12th Int. Workshop on Rare Earth Magnets and their Applications, Canberra, Australia, July 1992, p. 670.
[3] T. Takeshita, R. Nakayama, in: Proceedings of the 11th Int. Workshop on Rare Earth Magnets and their Applications, Pittsburgh, 1990, p. 49.
[4] R. Nakayama, T. Takeshita, J. Alloys Comp. 193 (1993) 259.
[5] C.L. Short, P. Guegan, O. Gutfleisch, O.M. Ragg, I.R. Harris, IEEE Trans. Mag. 32 (1996) 4368.
[6] M. Uehara, P. Choi, T. Tomida, H. Tomizawa, S. Hirosawa, Y. Maehara, IEEE. Trans. Magn. 31 (1995) 3632.
[7] T. Tomida, P. Choi, Y. Maehara, M. Uehara, H. Tomizawa, S. Hirosawa, J. Alloys Comp. 242 (1996) 129.
[8] M. Newville, Program ‘‘AUTOBK’’ Ver. 2.61(University of Washington, 1995)
[9] J.J. Rehr, J. Mustre de Leon, S.I. Zabinsky, R.C. Albers, Phys. Rev. B4 (1991) 4146.
[10] S. Hirosawa, private communication.
[11] J.F. Herbst, J.J. Croat, P.E. Pinkerton, Phys. Rev. B29 (1984) 4176.

[12] M. Matsuura, M. Sakurai, S.-H. Kim, K. Suzuki, T. Tomida, J. Phys. Condens. Matter 7 (1995) 7087.
[13] C.R. Quan, J.G. Zhao, Y.Z. Wang, L. Yin, B.G. Shen, Z.X. Cheng, Y.F. Cheng, S.W. Niu, Phy. Rev. 42 (1990) 6697.
[14] J.Q. Xie, C.H. Wu, Y.C. Chuang, F.M. Yang, J. Appl. Phys. 68 (1990) 4208.
[15] K.H.J. Buschow, G.K. Marasingle, G.J. Long, W.J. James, D. Xie, W.B. Yelon, Rep. Prog. Phys. 54 (1991) 1123.
[16] A. Ashfaq, M. Matsuura, M. Sakurai, Appl. Phys. Lett. 73 (1998) 2512.