

Structure of nano-crystalline FeTiD_x by neutron and X-ray diffraction

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Abstract

Complementary studies by neutron and X-ray diffraction were performed to elucidate the location of deuterium atoms in nano-crystalline FeTiD_x. Remarkable rearrangement of the metal atoms due to the deuterium absorption was observed in the pair distribution functions, $g(r)$, obtained by X-ray diffraction. The result indicates that disordered grain boundary is developed through the deuterium absorption. The $g(r)$ function obtained by neutron diffraction indicates the occurrence of two types of deuterium sites located inside the grains and in the grain boundaries, respectively. The deuterium atoms in the grain boundaries occupy tetrahedral sites consisting mainly of Ti atoms.

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1. Introduction

FeTi alloys have considerable potential for technological application as a hydrogen storage material [1–8]. A large number of investigations have been performed not only on the hydrogen absorption properties of these alloys [1–5] but also on the structure of their hydrides (deuterides) [3,6–8]. Recently, interest has been focused on nano-crystalline FeTi hydrides because of their excellent hydrogen sorption properties [9–11]. It is very important to investigate the structural changes accompanying the decrease in the grain size and to determine the local environments of hydrogen (deuterium) atoms in the grain boundaries of nano-crystalline materials.

In this work, the structure of nano-crystalline FeTi produced by mechanical milling and the location of deuterium atoms in nano-crystalline FeTiD_x were examined by neutron and X-ray diffraction.

2. Experimental procedure

A 3 g sample of 99.9% FeTi powder (High Purity Chemistry Research Institute, the average grain size 25 μm) was put into a 80 cm³ steel vial with 10 steel balls of 10 mm in diameter. After evacuating for 12 h below 10⁻⁴ Pa by a turbomolecular pump, the vial was filled with a high-purity 99.999% Ar gas. After a 5 h milling in a planetary ball mill Fritsch P-5 at 300 rpm, the FeTi sample was reacted with high-purity deuterium (99.999%) at a pressure of 1 MPa for 24 h. The concentration of deuterium in the sample was measured at the Center for Organic Elemental Microanalysis, Kyoto University.

The X-ray diffraction measurements were carried out using the RIGAKU RINT-Ultima with Mo-Kα radiation and also using the horizontal two-axis diffractometer with a photon energy of 113.68 keV on the BL04B2 beam line at SPring-8. The neutron diffraction measurements were carried out by using the High Intensity Total Scattering spectrometer (HIT-II) installed at the pulsed neutron source at the High Energy Accelerator Research Organization (KEK, Tsukuba, Japan). The scattering intensities were converted to the structure factors, $S(Q)$, after various kinds of corrections [12,13]. The pair distribution functions, $g(r)$, can be derived from the Fourier transformation of $S(Q)$.

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3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns for FeTi before milling and after 1 and 5 h of milling. The Bragg peaks associated with the CsCl-type structure are clearly visible for the FeTi before milling. These peaks decrease in intensity with increasing milling time, indicating that the crystalline grain size decreases. The grain size of FeTi after 5 h of milling was calculated to be 10 nm by using Scherrer equation.

The $g(r)$ functions for FeTi after 5 h of milling and for nano-crystalline FeTiD_{0.97} obtained by X-ray diffraction with a photon energy of 113.68 keV are shown in Fig. 2. The $g(r)$ of FeTi after 5 h of milling shows a distinct first peak at 0.256 nm. This peak is attributed to the Fe–Ti nearest neighbour correlation and it is shifted to larger r with the deuterium absorption. In contrast, a second peak, which is attributed to the Fe–Fe and Ti–Ti correlations, is slightly shifted to smaller r . Moreover, new correlation peaks appear at around 0.35 nm. The remarkable change in the $g(r)$ after the deuterium absorption evidences a rearrangement of metal atoms in the grain boundaries as well as a lattice expansion of the crystalline grains. This leads us to anticipate the existence of a new type of deuterium sites in the grain boundaries, different from the octahedral sites in polycrystalline β -FeTiD.

Figs. 3 and 4 show $S(Q)$ and $g(r)$, respectively, for the nano-crystalline FeTiD_{0.97} studied by neutron diffraction. A strong peak can be found at 20.7 nm^{-1} in the $S(Q)$ and this peak corresponds to diffraction peaks of (0 1 1) and (1 0 0) planes of β -FeTiD [7]. Diffraction peaks of γ -FeTiD_x phase [3] are not found in the $S(Q)$. Hence, a contribution from the γ -phase can be negligible. The $g(r)$ shows a positive peak around 0.17 nm and a negative peak around 0.21 nm.

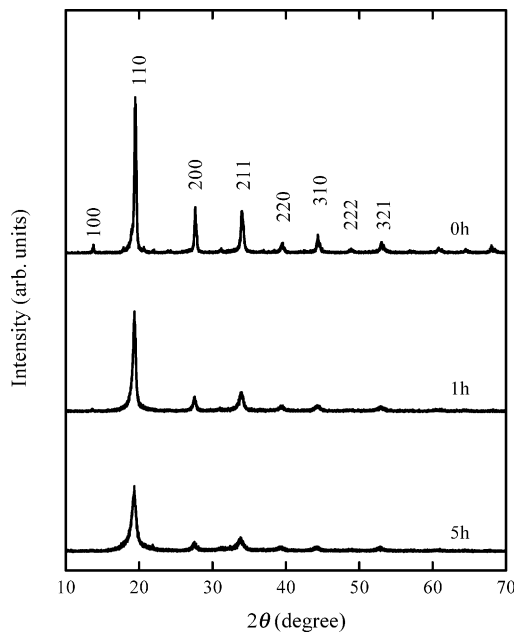


Fig. 1. X-ray diffraction patterns for FeTi before milling and after 1 and 5 h of ball-milling under an argon atmosphere.

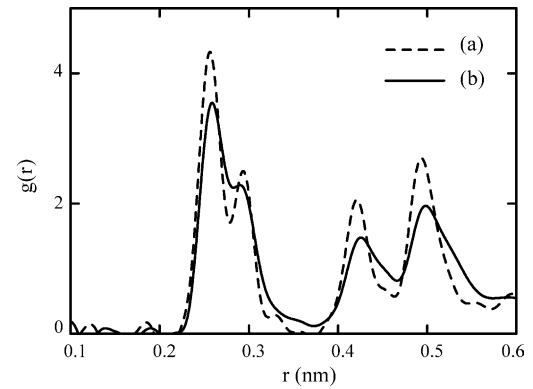


Fig. 2. Pair distribution functions, $g(r)$, obtained by X-ray diffraction with a photon energy of 113.68 keV: (a) FeTi after 5 h of milling; (b) nano-crystalline FeTiD_{0.97}.

There are no peaks in this region in the $g(r)$ obtained by X-ray diffraction (Fig. 2) therefore the peaks in the neutron $g(r)$ should correspond to correlations involving deuterium atoms. Since titanium has a negative coherent neutron scattering length, the positive and negative peaks in the $g(r)$ obtained by neutron diffraction should be attributed to the Fe–D and Ti–D correlations, respectively. In the polycrystalline β -FeTiD, deuterium atoms occupy octahedral sites with two iron atoms and four titanium atoms, the mean Fe–D and Ti–D distances being equal to 0.172 and 0.214 nm, respectively [7]. As the positive and negative peak in the neutron $g(r)$ function have these very positions, these peaks mostly originate from the Fe–D and Ti–D correlations inside the grains. There is also a shoulder at the left side of the positive peak, which indicates another correlation. The position of the shoulder is close to the Fe–D distances observed in other amorphous alloys [12,13]. Consequently, this shoulder can be ascribed to the Fe–D correlation in the grain boundaries.

To understand the local environments of deuterium atoms in the grain boundaries, $g(r)$ for the nano-crystalline FeTiD_{0.97} was fitted with Gaussian distribution functions. The Fe–D and Ti–D distances and the coordination numbers in the grains were taken from the previous work on polycrys-

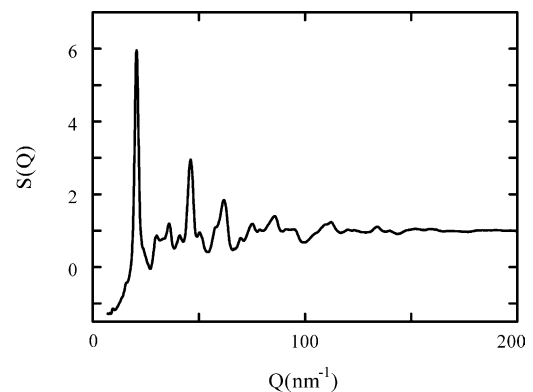


Fig. 3. Structure factors, $S(Q)$, obtained by neutron diffraction for nano-crystalline FeTiD_{0.97}.

Table 1

Nearest-neighbour coordination numbers, N_{i-j} , and interatomic distances, r_1 , in the grains and in the grain boundaries of nano-crystalline FeTiD_{0.97} calculated from the pair distribution function, $g(r)$, obtained by neutron diffraction

	D–Fe		D–Ti		$N_{D-Fe} + N_{D-Ti}$ (atoms)
	N_{D-Fe} (atoms)	r_1 (nm)	N_{D-Ti} (atoms)	r_1 (nm)	
Polycrystalline β -FeTiD [7]	2	0.172	4	0.214	6
In grain	2.1	0.178	4.0	0.215	6.1
In grain boundaries	0.7	0.165	3.4	0.184	4.1

talline β -FeTiD [4]. The components of the fit for the Fe–D and Ti–D correlations in the grains and in the grain boundaries are plotted in Fig. 4 together with the residual. The peak at 0.22 nm in the residual can be identified as arising from the D–D correlation, as its position well agree with the position of such a peak for polycrystalline β -FeTiD [7] and amorphous metal hydrides [12,13]. From the fitting result, it was found that about 50% of deuterium atoms are situated in the grain boundaries. The nearest neighbour coordination number, N_{i-j} , and the interatomic distance, r_1 , which were derived from the areas and peak positions of the Gaussian distribution functions are summarized in Table 1. It is noteworthy that the value of $N_{D-Fe} + N_{D-Ti}$ in the grain boundaries is about four. This suggests that the deuterium atoms sit on tetrahedral sites. The occurrence of tetrahedrally coordinated deuterium in the grain boundaries of ball-milled FeTi is consistent with the structural changes of the Ni–V powder [14], in which the octahedral units in the FCC crystal structure are destroyed and transformed into tetrahedral ones when the amorphization due to milling proceeds.

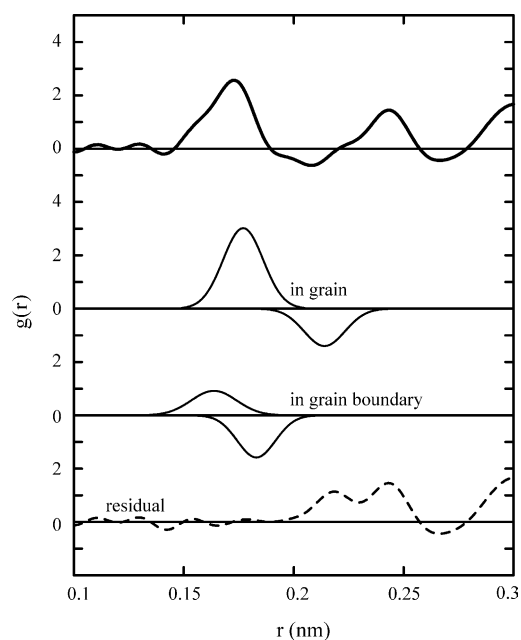


Fig. 4. Pair distribution functions, $g(r)$, obtained by neutron diffraction for nano-crystalline FeTiD_{0.97} and the components of the fit for the Fe–D and Ti–D correlations in the body of the grain and in the grain boundaries. The dashed line is the difference between the experimental $g(r)$ and these two components.

It is of interest to note that N_{D-Ti} in the grain boundary is considerably larger than N_{D-Fe} . This result indicates that deuterium atoms occupy tetrahedral sites consisting mainly of Ti atoms, i.e. the 4Ti and 3Ti+1Fe tetrahedral sites. This is because of the strong affinity between deuterium and titanium atoms. Similar results are reported for amorphous NiZrD_x [15] and TbFe₂D_x [12].

4. Conclusion

Neutron and X-ray diffraction measurements were carried out to elucidate the location of deuterium atoms in nano-crystalline FeTiD_x. X-ray diffraction data definitely indicate that the region of the grain boundary with the disordered arrangement grew up during the milling and deuterium absorption processes. The $g(r)$ obtained by neutron diffraction for nano-crystalline FeTiD_{0.97} indicates that deuterium atoms occupy two types of sites, in the grains and in the grain boundaries, respectively. It is found that about 50% deuterium atoms are situated in the grain boundaries and occupy tetrahedral sites consisting mainly of Ti atoms. Since a lot of defects and strain may accumulate not only in the grain boundary but also in the grains during the milling, the metal atoms can move over a short distance with the strong affinity of deuterium for titanium as the driving force. Hence, the result allows us to conclude that the interaction between deuterium and titanium draws the rearrangement of metal atoms in the grain boundary and the growth of the boundary regions due to the deuterium absorption.

Acknowledgments

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