

## Average and Local Structures in Hydrogen Absorbing Ti–Cr–Mo Alloy

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The average and local structures in the (Ti<sub>0.45</sub>Cr<sub>0.35</sub>Mo<sub>0.20</sub>)–D system have been investigated by neutron powder diffraction and total neutron scattering. From the result of neutron powder diffraction, the crystal structure of the system was found to change from CaF<sub>2</sub>-type structure to bcc structure in the hydrogen desorption process, and the D atoms occupy the tetrahedral (T) sites in both CaF<sub>2</sub>-type and bcc phases. The D–Ti, D–Cr, D–Mo and D–D correlation lengths and the nearest neighbor coordination number around a D atom have been obtained by the RDF analysis of total neutron scattering data. The D atoms occupy the T sites surrounded mainly by the Ti atoms in both CaF<sub>2</sub>-type and bcc phases.

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### 1. Introduction

Neutron diffraction can directly determine hydrogen atomic positions in metal hydrides. Using neutron powder diffraction, Nakamura *et al.* showed that Ti–Mn–V bcc solid solution alloys exhibit two hydride phases with NaCl-type and CaF<sub>2</sub>-type structure<sup>1</sup> and the crystal structure changes from bcc to CaF<sub>2</sub>-type with increasing hydrogen content. From the result of Rietveld refinement, the D atoms occupy the octahedral (O) sites in the NaCl-type phase and the T sites in the CaF<sub>2</sub>-type one. In the Rietveld refinement, three metal elements, Ti, Mn and V were assumed to be distributed randomly on the 4a site in the CaF<sub>2</sub>-type phase, and the particular bond lengths, D–Ti, D–Mn and D–V, in the solid solution alloy deuteride were not be distinguished.

The radial distribution function (*RDF(r)*) analysis of total neutron scattering data is useful to discriminate individual bond lengths. In fact, the *RDF(r)* has been used for amorphous metal hydrides.<sup>2,3</sup> In this study, we focus on the Ti<sub>0.45</sub>Cr<sub>0.35</sub>Mo<sub>0.20</sub> bcc solid solution alloy in the hydrogen absorption-desorption process, and study the local structure obtained by the *RDF(r)* analysis as well as the crystal structure by the Rietveld analysis. The change in the crystal structure, the D atomic position, the correlation length and the coordination number around a D atom in hydrogen absorption-desorption process is presented.

### 2. Experiment

The Ti<sub>0.45</sub>Cr<sub>0.35</sub>Mo<sub>0.20</sub> alloy was prepared by arc melting of the constituent elements in Ar atmosphere. Heat treatment was carried out at 1673 K for 3.0 h and quenched into ice water. *P–C* isotherms were measured by the Sieverts method.

The samples, Ti<sub>0.45</sub>Cr<sub>0.35</sub>Mo<sub>0.20</sub>D<sub>0.60</sub> and Ti<sub>0.45</sub>Cr<sub>0.35</sub>Mo<sub>0.20</sub>D<sub>1.9</sub>, were investigated by neutron diffraction at room temperature. High resolution neutron powder diffraction data were collected at room temperature (RT) on a time-of-flight (TOF) neutron diffractometer, Sirius,<sup>4</sup> at Neutron Science Laboratory (KENS) of High Energy Accelerator Research Organization (KEK). For neutron diffraction experiments, deuterides were used instead of hydrides because of the large incoherent scattering cross section of H. The sample was put into a vanadium cylindrical cell. Neutron diffraction data were analyzed by the Rietveld method.<sup>5</sup> Coherent scattering lengths used in the refinements are 6.67 fm (D), –3.438 fm (Ti), 3.64 fm (Cr) and 6.71 fm (Mo).<sup>6</sup>

The local structure of the alloy was investigated using a high intensity total scattering spectrometer, HIT-II,<sup>7</sup> installed at KENS. The sample was put in a cylindrical cell made of the zero-scattering Ti<sub>67.56</sub>Zr<sub>32.44</sub> alloy (the coherent neutron scattering lengths of titanium and zirconium atoms are –3.438 and 7.16 fm, respectively).<sup>8</sup> The radial distribution function, *RDF(r)*, was derived from the Fourier transformation of the structure factor, *S(Q)*, up to *Q* = 350 nm<sup>–1</sup>, where *Q* is a momentum transfer (= 4π sin θ/λ). The *S(Q)* was derived by applying various kinds of corrections to the background, absorption<sup>9</sup> and multiple scattering<sup>10</sup> and normalizing with an incident neutron beam profile. In the Fourier transformation of the *S(Q)*, the *RDF(r)* is defined as follows:

$$RDF(r) = 4\pi r^2 \rho_0 g(r), \quad (1)$$

$$g(r) = 1 +$$

$$(1/2\pi^2 r \rho_0) \int_0^\infty Q \{S(Q) - 1\} \sin(Qr) dQ, \quad (2)$$

where *g(r)* is the pair distribution function and  $\rho_0$  is the average number density of atoms. Coordination number,  $N_{ij}$ , is defined by the equation:

$$N_{ij} = W_{ij}(b)^2 / \xi C_i b_i b_j, \quad (3)$$

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where  $\xi$  is constant number of 1 or 2. In case of homogeneous atomic pair,  $\xi$  is 1. While  $\xi$  is 2 in case of inhomogeneous atomic pair.

$$\langle b \rangle = \sum_i C_i b_i, \quad (4)$$

where  $C_i$  is the concentration and  $b_i$  is the neutron coherent scattering length and  $W_{ij}$  is the integral of Gaussian distributions.

### 3. Result and Discussion

Figure 1 shows  $P$ - $C$  isotherms of the  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}$  alloy at 313 K. The alloy absorbs hydrogen without activation treatment. The alloy hydride exhibits a flat plateau and the maximum storage capacity of 1.9 H/M.

In  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{1.9}$ , all reflections in X-ray and neutron diffraction data could be indexed with a  $\text{CaF}_2$ -type structure model. No superlattice reflection is observed, indicating that transition metals, Ti, Cr and Mo, are not ordered in the long-range scale. Then, in the Rietveld refinement, Ti, Cr and Mo were assumed to be located at the 4a site (hereafter M site) with the ratio of 0.45:0.35:0.20. D atoms were found to be located at the tetrahedral site. Figure 2 shows the Rietveld refinement pattern of neutron powder diffraction data for the  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{1.9}$  sample. The refined lattice and structural parameters are listed in

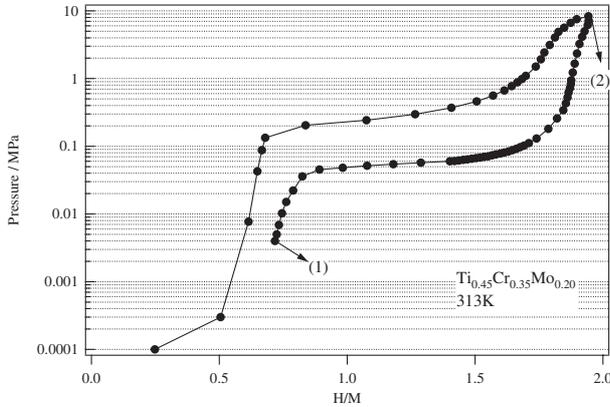


Fig. 1  $P$ - $C$  isotherm of the  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}$  alloy at 313 K.

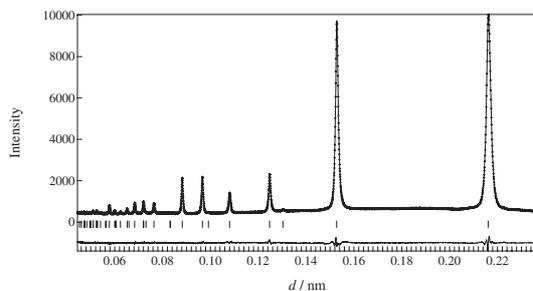


Fig. 2 Rietveld refinement pattern of  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{1.9}$ . The plus marks are the observed intensities and the solid line is the calculated intensities. The tick marks below the patterns indicate the position of allowed Bragg reflections. The difference between the observed and calculated intensities are shown in the bottom.

Table 1 Refined structure parameters of the  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{1.9}$  phase: space group  $Fm\bar{3}m$ .  $B$  is the isotropic displacement parameter and  $g$  is the occupation factor of each site.

Atom	Site	$g$	$x$	$y$	$z$	$B$ ( $10^{-2} \text{ nm}^2$ )
M	4a	1.0	0	0	0	0.50(2)
D	8c	0.95(1)	1/4	1/4	1/4	1.01(1)

$R_{wp} = 2.74$ ,  $R_p = 2.36$ ,  $S = 1.66$ . Lattice parameter  $a = 0.432153(3)$  nm.

Table 2 Refined structure parameters of the  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{0.6}$  phase: space group  $Im\bar{3}m$ .  $B$  is the isotropic displacement parameter and  $g$  is the occupation factor of each site.

Atom	Site	$g$	$x$	$y$	$z$	$B$ ( $10^{-2} \text{ nm}^2$ )
M	2a	1.0	0	0	0	0.65(2)
D	24g	0.055(3)	0.3528(8)	0	1/2	1.7(2)

$R_{wp} = 1.72$ ,  $R_p = 1.49$ ,  $S = 1.83$ . Lattice parameter  $a = 0.31937(3)$  nm.

Table 1, D atoms occupy the tetrahedral site with an occupancy of  $g(\text{D}) = 0.95(1)$ .

By the similar argument, it is safely concluded that  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{0.6}$  adopts bcc structure with the three metal elements located at the 2a site (M site) with the ratio of 0.45:0.35:0.20. In the preliminary Rietveld analysis, D atoms were put at the T site. However, the atomic displacement parameter of the D atom was large in accordance with that in the Ti-V-Mn deuteride system.<sup>1)</sup> Considering the difference of atomic radii among the three metal elements, Ti, Cr and Mo, the deuterated Ti-Cr-Mo alloy with bcc structure may have a deformed tetrahedral interstitial site. Then, the 24 g site is used instead of the T site for the occupation site of the D atom. The final results of refined lattice and structural parameters in  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{0.6}$  are listed in Table 2. The occupancy of the D atoms was found to be 0.055(3) with an isotropic thermal displacement parameter of  $B = 1.70(2) 10^{-2} \text{ nm}^2$ .

It is noteworthy to compare the crystal structures of the deuterated phases in Ti-Cr-Mo and Ti-Mn-V systems. In the D atom content of 1.8–1.9, both systems adopt the  $\text{CaF}_2$ -type structure. In the D atom content around 0.6, however,  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{0.6}$  adopts the bcc structure while  $\text{Ti}_{0.33}\text{Mn}_{0.3}\text{V}_{0.37}\text{D}_{0.66}$  adopts the NaCl-type structure.

As mentioned above, no superlattice reflection is observed in both  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{1.9}$  and  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{0.6}$ . It implies transition metals are disordered in long-range scale (average structure). However, in short-range scale, it does not mean transition metals are located randomly at the same atomic position. The short-range ordering is generally expected, and it can be measured through diffuse scattering experiments. Since usual Rietveld analysis codes only deal with Bragg reflections, the local structure related to D-Ti, D-Cr and D-Mo bonds cannot be clarified.

It is widely accepted that since the total neutron scattering includes both Bragg reflections and diffuse scattering, it gives us information on the local structure as well as the average crystal structure. In order to investigate the local structure of the deuterated Ti-Cr-Mo system, the total neutron scattering data  $S(Q)$  were measured. Figure 3 shows  $S(Q)$  of  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{1.9}$  and  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{0.6}$ . As is easily

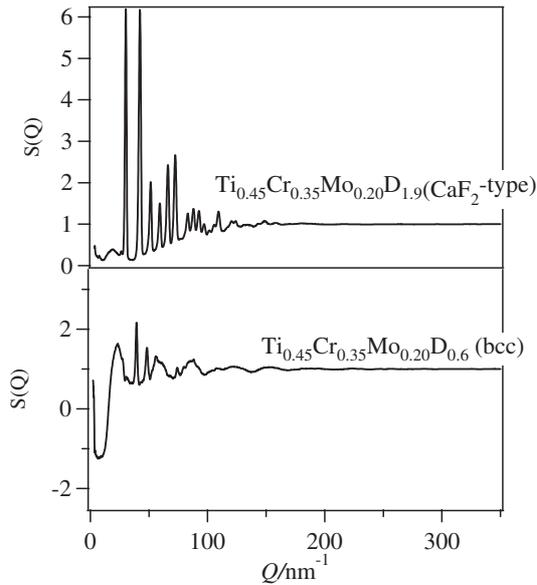


Fig. 3 Structure factors,  $S(Q)$ , of  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{0.6}$  and  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{1.9}$  taken by the total neutron scattering technique.

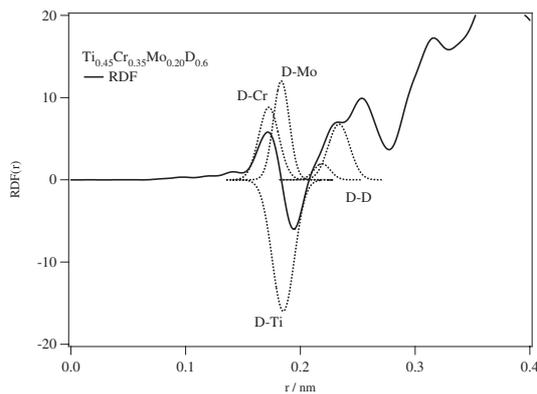


Fig. 4 Radial distribution function,  $RDF(r)$ , for  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{0.6}$  taken by the total neutron scattering technique. Dashed lines show the Gaussian functions of the D–Ti, D–Cr, D–Mo and D–D correlations.

recognized,  $S(Q)$  of  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{1.9}$  is rather different from that of  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{0.6}$ . The Bragg peaks associated with the  $\text{CaF}_2$ -type structure of the  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{1.9}$  are clearly observed in  $S(Q)$  while those of  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{0.6}$  are not obviously separated. Figure 4 shows  $RDF(r)$  of  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{0.6}$  with bcc structure. The distribution of the nearest neighbour atoms can be divided into partial correlations of D–Ti, D–Cr, D–Mo and D–D pairs by Gaussian distribution functions; each pair is plotted by a dashed line. The first positive peak in the  $RDF(r)$  can be separated into the signals of the D–Cr and the D–Mo correlations. In contrast, the second negative peak shows the D–Ti correlation, since titanium has a negative coherent scattering length. The third and fourth positive peaks are the D–D correlations.

The interatomic distance and the nearest neighbor coordination number calculated from the area of the Gaussian peaks are listed in Table 3. The tetrahedral interstitial site in the  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{0.6}$  phase is deformed. The value of

Table 3 Coordination number,  $N_{i-j}$ , and inter atomic distance,  $r$ , for  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{0.6}$  with the bcc structure and  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{1.9}$  with the  $\text{CaF}_2$ -type structure.

		$\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{0.6}$	$\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{1.9}$
D–Ti	$r/\text{nm}$	0.185(2)	0.185(2)
	$N_{\text{D-Ti}}$	2.36	1.96
D–Cr	$r/\text{nm}$	0.172(1)	0.183(1)
	$N_{\text{D-Cr}}$	1.07	1.14
D–Mo	$r/\text{nm}$	0.183(2)	0.184(2)
	$N_{\text{D-Mo}}$	0.63	0.90
1. D–D	$r/\text{nm}$	0.219(2)	0.218(1)
	$N_{\text{D-D}}$	0.24	5.66
2. D–D	$r/\text{nm}$	0.234(2)	
	$N_{\text{D-D}}$	1.03	

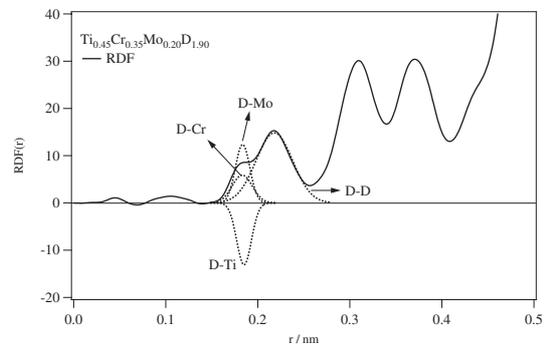


Fig. 5 Radial distribution function,  $RDF(r)$ , for  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{1.9}$  taken by the total neutron scattering technique. Dashed lines show the Gaussian functions of the D–Ti, D–Cr, D–Mo and D–D correlations.

$N_{\text{D-Ti}} + N_{\text{D-Cr}} + N_{\text{D-Mo}}$  is about four, and  $N_{\text{D-Ti}}$  is two-times larger than  $N_{\text{D-Cr}}$  and  $N_{\text{D-Mo}}$ . These results indicate the D atoms occupy the T site surrounded by nearly two Ti atoms and Cr and Mo atoms.

Figure 5 shows  $RDF(r)$  of  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{1.9}$  with  $\text{CaF}_2$ -type structure. From the result of Rietveld refinement by neutron powder diffraction,  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{1.9}$  forms deuterides with an fcc metal sublattice in which the D atoms occupy the T site. The first positive peak with a shoulder around  $r = 0.16\text{--}0.25$  nm can be separated into the signals of the D–Ti, D–Cr, D–Mo and D–D correlations. No negative peak in  $RDF(r)$  implies intensities of the D–Cr, D–Mo and D–D correlation peaks are larger than that of the D–Ti correlation peak. The interatomic distance and the nearest neighbor coordination number for  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{1.9}$  are listed in Table 3. It is noted that refined correlation lengths are close to those obtained from the Rietveld analysis of powder diffraction data where (Ti, Cr, Mo)–D and D–D bond lengths are 0.18713(3) and 0.21608(3) nm, respectively. The value of  $N_{\text{D-Ti}} + N_{\text{D-Cr}} + N_{\text{D-Mo}}$  is about four in accordance with the result of crystal structure analysis. The D atoms occupy tetrahedral sites surrounded by nearly two Ti atoms and Cr and Mo atoms. The coordination numbers for D–D pair correlations in the  $\text{Ti}_{0.45}\text{Cr}_{0.35}\text{Mo}_{0.20}\text{D}_{1.9}$  is 6 with an occupation factor of  $g(\text{D}) = 1.0$ . From the result of Rietveld refinement, the occupation factor,  $g(\text{D})$ , equal 0.95(1) and the

coordination numbers for D–D pair correlations showed 5.7. This agrees with nearest neighbor coordination number,  $N_{D-D} = 5.66$ , of the result of total neutron scattering technique.

To clarify the crystal structure and the local environment of the D atoms, neutron powder diffraction and total neutron scattering experiments were carried out. For  $Ti_{0.45}Cr_{0.35}Mo_{0.20}D_{0.6}$  with bcc structure, it is determined that the D atoms occupy the T site. The nearest neighbor coordination number and interatomic distance around a D atom are determined by total neutron scattering technique. The D atoms occupy T sites surrounded by nearly two Ti atoms and Cr and Mo atoms. For  $Ti_{0.45}Cr_{0.35}Mo_{0.20}D_{1.9}$  with  $CaF_2$ -type structure, a D atom occupies the T site and the value of the occupation factor,  $g(D)$ , agrees with nearest coordination number,  $N_{D-D}$ . The D atoms occupy the T site surrounded mainly by the Ti atoms. The D–Ti, D–Cr, D–Mo and D–D correlation lengths determined by total neutron scattering technique are close to the (Ti, Cr, Mo)–D and D–D bond lengths refined by neutron powder diffraction.

#### 4. Conclusion

The crystal structure of the  $Ti_{0.45}Cr_{0.35}Mo_{0.20}$  alloy changes from  $CaF_2$ -type structure to bcc structure in hydrogen desorption process. From the Rietveld refinement of neutron powder diffraction data, it was obtained that the D atoms occupy the T site in both  $CaF_2$ -type and bcc phases. The nearest neighbor coordination numbers and correlation lengths were obtained by total neutron scattering technique.

The D atoms occupy the T sites surrounded by two Ti atoms and Cr and Mo atoms in both  $CaF_2$ -type and bcc phases.

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