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Hydrogen absorption–desorption properties and crystal structure analysis of Ti–Cr–Mo alloys

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Abstract

We investigated that heat treatment condition, hydrogen absorption–desorption properties and crystal structure of Ti–(55 − *x*)Cr–*x*Mo alloys by the use of X-ray diffraction (XRD) and *PCT* measurement. We found that the quenching treatment was effective to synthesize bcc single phase alloys in comparison with annealing treatment. The lattice parameter, *a*, of bcc phase in the quenched alloys showed linear relationship with increasing the Mo content. The as-cast alloys had a sloping plateau, while the quenched alloys had a flat plateau. The alloys showed the equilibrium pressure increased with increasing the Mo content. The hydrogen reversible capacity of the alloys reached 1.33–1.39 H/M (2.34–2.68 mass%) under hydrogen pressure 8.0 MPa at 313 K.

Keywords: bcc solid solution alloy; X-ray diffraction; Hydrogen storage materials; Crystal structure and symmetry

1. Introduction

Metal hydride (MH) can store hydrogen safely and compactly. Metal hydrides based on AB_5, AB_2 and bcc alloys have been investigated extensively. AB_5-type alloys are used as an anode of Ni-MH battery. bcc alloys are expected to be applied for hydrogen storage tank, because its storage hydrogen capacity reaches about 3 mass% at ambient conditions.

Iba and Akiba reported the Laves phase related bcc solid solution including Ti–Cr–V and Ti–Mn–V alloys [1–3]. The as-cast 25Ti–35Cr–V alloy had a sloping plateau but the alloys annealed at 1473 K for 2 h exhibited a flat plateau and reached about 2.2 mass% (1.1 H/M) at 313 K [2]. The alloy annealed at 1573 K for 1 min showed about 2.6 mass% of capacity. However, hydrogen capacity decreased after annealing times of up to 50 h [4]. It means that the hydrogen capacity depends very much on the heat treatment condition.

Nakamura and Akiba studied the crystal structures of Ti–Cr–V and Ti–Mn–V alloys by neutron and X-ray powder diffraction; they found that Ti–V–Mn alloy had three hydride phases with a bcc, NaCl-type and CaF_2-type structures [5–7].

Since V is an expensive element, the effect of substitution of other elements such as Mo, W, Nb, etc. for V has been investigated. There are few reports concerning the crystal structure of Ti–Cr–Mo alloys [8] whereas several reports are available for alloys and hydrides of Ti–Cr–A (A = V, Mo or other transition metal) [9–11].

In this study, we will focus on the relation between heat treatment and hydrogen capacity of Ti–Cr–Mo hydrogen absorbing alloy with bcc structure. Because Mo has higher melting point than other constituent elements, Ti and Cr, the as-cast alloy is considered to be inhomogeneous. We measured X-ray diffraction (XRD) after various heat treatments, which provides information of crystal structure of each phase and the phase abundance. We also investigated the optimum heat treatment condition to maximize the hydrogen capacity of Ti–Cr–Mo alloys.

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2. Experimental

The alloys were prepared by arc melting of the elements in Ar atmosphere. The purities of elements were Ti (99.6%), Cr (99.9%) and Mo (99.95%). Heat treatment was carried out at 1673 K for 3.0 h and quenched into ice water. Before *PCT* measurements, the samples were evacuated at 313 K for 1 h. *P–C* isotherms were measured by the Sieverts method at 313 K and under hydrogen up to 8.0 MPa. X-ray powder diffraction data were taken with a Bragg–Brentano type diffractometer, Rigaku RINT-2500V. Cu Kα radiation monochromatized with a curved graphite was used. X-ray data were analyzed by the Rietveld method [12].

3. Results and discussion

Fig. 1 shows *P–C* isotherms of as-cast Ti–(55 − *x*)Cr–*x*Mo ($5 \leq x \leq 20$) alloys at 313 K. Hydrogen desorption of 1.14–1.29 H/M ratio were observed and the plateaus are sloping. The 45Ti–Cr–5Mo alloy showed the smallest desorption capacity among the alloys studied. All the alloys could absorb hydrogen without activation. Since Mo has a higher melting point than that of Ti and Cr, it is difficult to synthesize homogeneous bcc phase without heat treatment. Fig. 2 shows the XRD patterns of as-cast, annealed and quenched alloys. The annealing treatment was carried out under an Ar atmosphere at 1673 K for 3.0 h. We obtained single bcc phase in Ti–(55 − *x*)Cr–*x*Mo ($15 \leq x \leq 20$) alloys, but Laves phases were found in Ti–(55 − *x*)Cr–*x*Mo ($7.5 \leq x \leq 10$) alloys as shown in Fig. 2. Single bcc phase alloys formed with increasing the Mo contents. The quenching treatment was carried out to make homogeneous bcc phase for all the alloys. X-ray diffraction patterns of Ti–(55 − *x*)Cr–*x*Mo ($5 \leq x \leq 20$) which were heat-treated at 1673 K for 3.0 h and quenched into ice water are shown in Fig. 2. The alloys were composed mainly of bcc phase but Laves phase was found about 2.0 mass% estimated by Rietveld refinement. Ti–(55 − *x*)Cr–*x*Mo ($15 \leq x \leq 20$) alloys with the bcc structure were prepared by annealing and

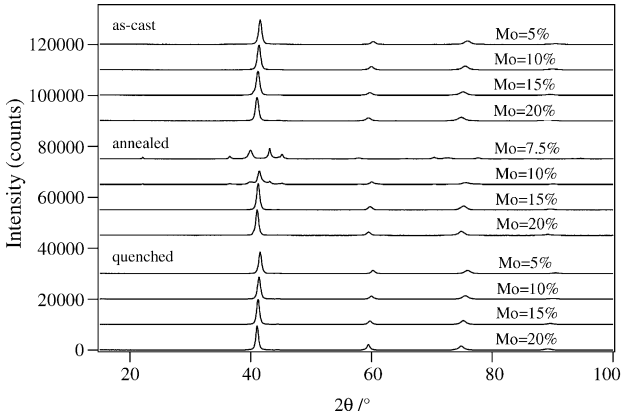

Fig. 2. X-ray diffraction patterns of heat-treated Ti–(55 − *x*)Cr–*x*Mo ($5 \leq x \leq 20$) alloys and as-cast ones. Laves phases were found in annealed Ti–(55 − *x*)Cr–*x*Mo ($7.5 \leq x \leq 10$) alloys. As-cast Ti–(55 − *x*)Cr–*x*Mo ($5 \leq x \leq 20$) alloys and quenched ones were composed mainly of bcc phase.

quenching treatments. From the Rietveld refinement, full width at half maximum (FWHM) of all Bragg reflections of the quenched alloys was smaller than the annealed and as-cast ones (Table 2). The quenched alloys have better crystallinity than annealed and as-cast ones. The relationship between the Mo contents and lattice parameters of the quenched bcc phases is shown in Fig. 3. Lattice parameter, *a*, of the alloys linearly increases with increasing the Mo contents or decreasing the Cr contents. Goldschumidt atomic radius of Ti, Cr and Mo are 0.147, 0.128, 0.140 nm, respectively. Increase of the amount of Mo results increase of lattice parameter but increase of the amount of Cr reduces the lattice parameter. The results of XRD suggest that quenching treatment is effective to form single bcc phase alloys with better crystal as compared with annealing treatment.

Fig. 4 shows *P–C* isotherms of quenched Ti–(55 − *x*)Cr–*x*Mo ($5 \leq x \leq 20$) at 313 K and under hydrogen up to 8.0 MPa. The as-cast alloys (Fig. 1) had a sloping plateau but the quenched alloys showed a flat plateau. Quenched alloys could absorb hydrogen without activation. Hydrogen capacity and equilibrium pressures of Ti–(55 − *x*)Cr–*x*Mo

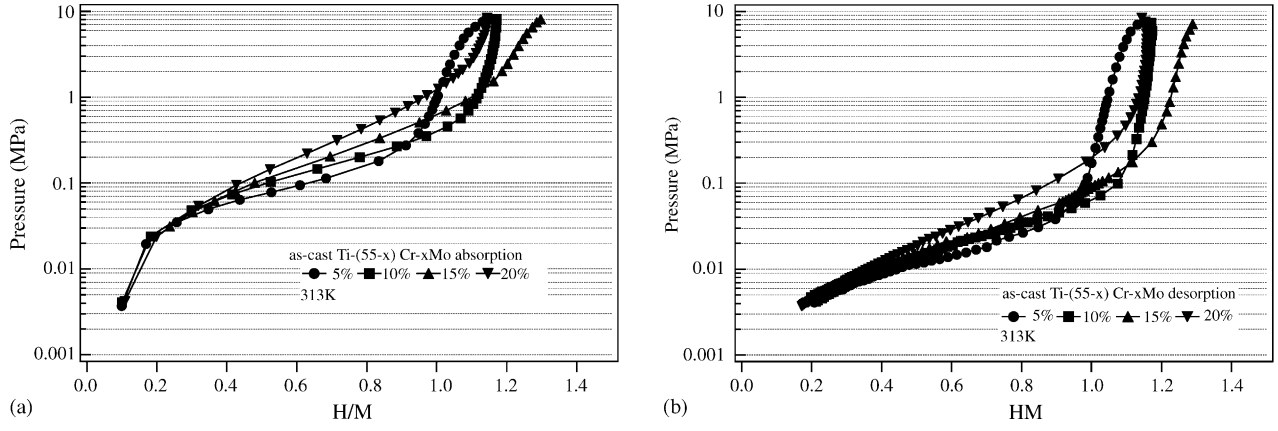

Fig. 1. *PCT* diagram of as-cast Ti–(55 − *x*)Cr–*x*Mo ($5 \leq x \leq 20$) alloys: (a) absorption and (b) desorption at 313 K.

Table 1
Hydrogen desorption capacity and equilibrium pressures of the Ti–(55 − x)Cr–xMo (5 ≤ x ≤ 20) alloys

	As-cast		Quenched			
Mo%	H/M	Mass%	H/M	Mass%	P (MPa) of absorption	P (MPa) of desorption
5	1.14	2.20	1.39	2.68	0.07	0.01
10	1.17	2.17	1.39	2.57	0.12	0.02
15	1.29	2.30	1.33	2.36	0.20	0.03
20	1.15	1.95	1.37	2.34	0.34	0.06

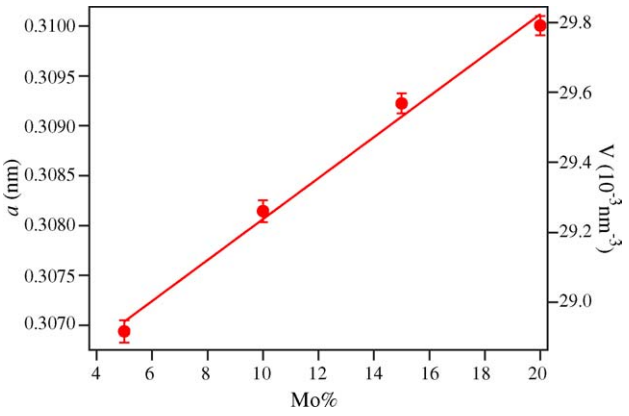

Fig. 3. Relation between Mo at% and lattice parameter for quenched Ti–(55 − x)Cr–xMo (5 ≤ x ≤ 20) alloys.

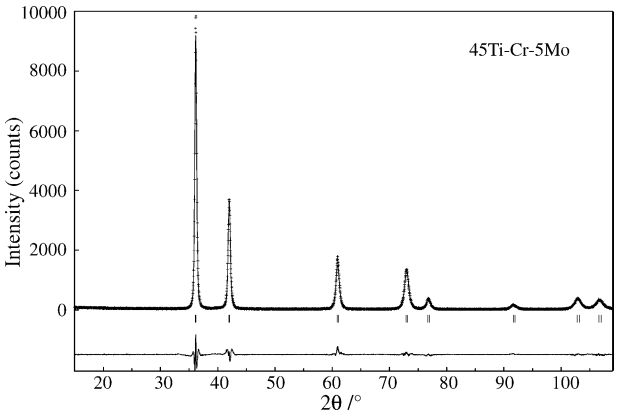

Fig. 5. Rietveld refinement of the saturated hydride 45Ti–Cr–5Mo alloy from the X-ray diffraction data.

Table 2
FWHM (full width at half maximum) of the as-cast, quenched and annealed Ti–(55 − x)Cr–xMo (15 ≤ x ≤ 0) alloys with bcc structure FWHM (°)

	Mo = 15%			Mo = 20%		
hkl	As-cast	Quenched	Annealed	As-cast	Quenched	Annealed
110	0.6966	0.5393	0.5771	0.6231	0.4649	0.5307
200	1.0115	0.7792	0.8080	0.9203	0.6602	0.7510
211	1.3416	1.0653	1.1084	1.2225	0.8629	1.0298
220	1.7262	1.3724	1.4836	1.5696	1.0983	1.3705
310	2.2243	1.7687	1.9849	2.0147	1.1655	1.8145

(5 ≤ x ≤ 20) alloys are listed in Table 1. Hydrogen capacity was calculated by the width of plateaus at 313 K. Equilibrium pressures were estimated from the middle point of plateaus at 313 K. The quenched alloys exhibited a larger hydrogen capacity than that of the as-cast alloys. When the Mo content varied, the equilibrium pressure was changed evidently. The quenched 45Ti–Cr–5Mo alloy reversibility absorbed and desorbed hydrogen in 1.39 H/M ratio and showed the maximum value in H/M ratio among the alloys studied, while the as-cast alloy showed minimum H/M ratio. Quenching treatment was effective for all compositions studied and H/M ratio was little affected by the Mo contents as far as the quenched alloys were concerned. It should be noted that heat-treated condition of influence very much in homogeneity, phase abundance, crystallinity and hydrogenation properties.

Crystal structures of the alloys were studied using XRD data. Fig. 5 shows the results of Rietveld refinement for saturated hydride of 45Ti–Cr–5Mo alloy. The points are

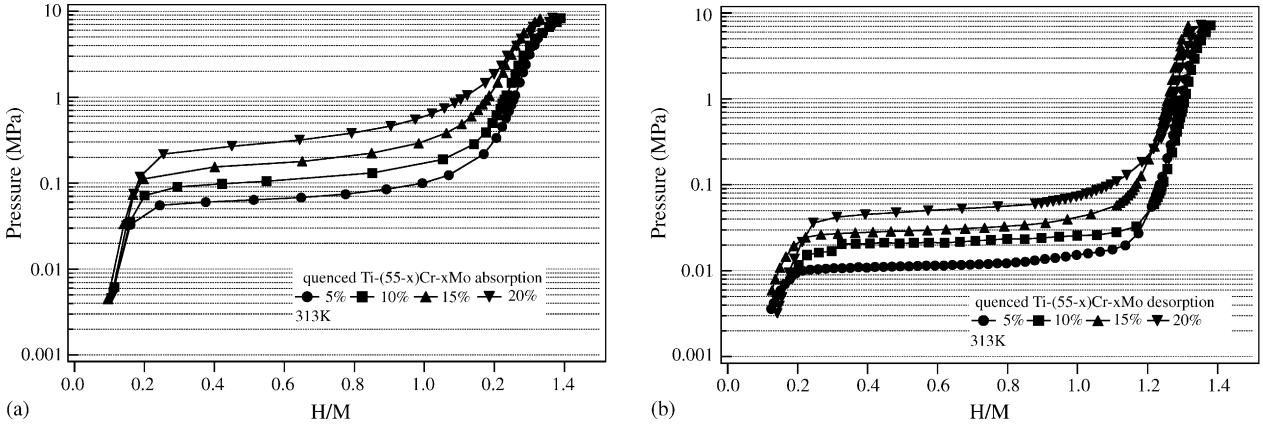

Fig. 4. *PCT* diagram of quenched Ti–(55 − x)Cr–xMo (5 ≤ x ≤ 20) alloys: (a) absorption and (b) desorption at 313 K.

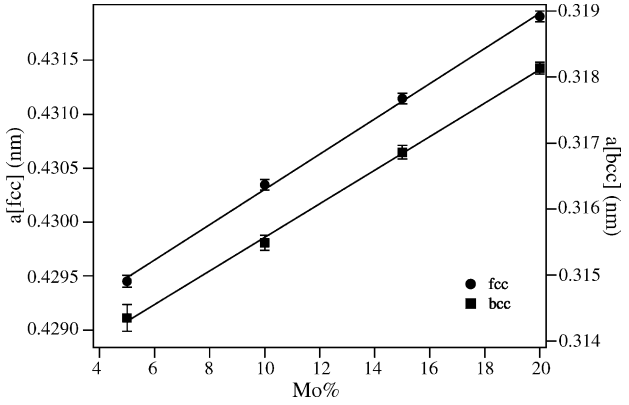

Fig. 6. Relation between Mo at% and lattice parameters.

observed intensities and the line is the calculated intensities. The tick marks below the profile indicate the position of all allowed Bragg reflections for the fcc phase. From the Rietveld refinement, it was found that the saturated hydride of Ti–(55 − x)Cr–xMo ($5 \leq x \leq 20$) alloys had a single fcc phase. The phases which were taken after *PCT* measurement of the alloys had a single bcc phase. Fig. 6 shows the lattice parameters, a, of the fcc and the bcc phases. Linear relations between lattice parameter and the Mo content are obtained for fcc and bcc phases as indicated with two lines in Fig. 6. These are the same tendencies that have been mentioned previously for the alloy phases (Fig. 3).

4. Conclusion

We investigated the heat treatment condition, the hydrogen capacity and crystal structure of Ti–(55 − x)Cr–xMo ($5 \leq x \leq 20$) alloys. The quenching treatment was effective. The nearly homogeneous alloys with bcc structure were prepared by quenching treatment. The linear relation between lattice parameter and the Mo content was obtained.

The *P–C* isotherms of quenched Ti–(55 − x)Cr–xMo ($5 \leq x \leq 20$) alloys exhibited flat plateau and desorption capacity of 1.33–1.39 H/M ratio at 313 K. The equilibrium pressure of the alloys depend on the Mo contents but H/M ratio was little affected when the Ti content was kept constant.

It is clarified that quenching treatment is indispensable for Ti–(55 − x)Cr–xMo ($5 \leq x \leq 20$) alloys to be improved hydrogen absorbing properties.

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