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Hydrogen absorbing properties and structures of Ti–Cr–Mo alloys

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Abstract

Ti–Cr–Mo alloys show different hydrogenation properties to Ti–Cr–V and Ti–Mn–V hydrogen absorbing alloys with b.c.c. structure. Ti–Cr–Mo alloys have a smaller solid solution range (<0.5 wt.%) than Ti–Cr–V (<1.3 wt.%). In order to understand this difference, crystal structure and hydrogenation behaviors were investigated by X-ray diffraction and pressure–composition isotherms (P–C–T) measurements. Most of the alloys investigated were single bcc phase. The relation of the plateau pressure vs. lattice volume of Ti–Cr–Mo alloys was opposite to Ti–Cr–V and many of conventional intermetallic alloys. The new parameter, the radius of tetrahedral hydrogen site, is introduced. This new parameter gives a linear relationship with the plateau pressure for both Ti–Cr–Mo and Ti–Cr–V alloys. Hydrogen capacity of Ti–Cr–Mo and Ti–Cr–V are the same in a hydrogen to metal ratio basis. Slight addition of V to Ti–Cr–Mo alloys leads to dramatic increase of solid solution range.

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Keywords: Ti–Cr–Mo alloy; Ti–Cr–V alloy; Hydrogen site; Plateau pressure; Hydrogen solid solution region

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1. Introduction

Large hydrogen absorbing capacity is one of the most important characteristics for hydrogen absorbing alloys utilized for hydrogen storage, heat pump, MH batteries and many other applications. Most of the hydrogen-absorbing alloys for practical use have been intermetalic compounds such as $LaNi_5$, TiFe and $TiMn_{1.5}$. However, in recent years, study of Ti-based b.c.c. alloys, particularly Ti–Cr–V, has been promoted in several laboratories since Iba and Akiba reported ‘‘Laves phase related BCC solid solution alloys’’ and their remarkable hydrogen capacity [1]. Although Ti–Cr–V shows large hydrogen absorbing capacity over 3.0 wt.% at the first hydrogen absorption, rechargeable hydrogen capacity near room temperature is limited to about 2.3 wt.%. This alloy also shows remarkable hysteresis and poor durability, which are disadvantages for applications. Considering the situation above, the authors are interested in Ti–Cr–Mo b.c.c. alloys [2] as well as Ti–Cr–V. As has been reported by some of the authors [3], Ti–Cr–Mo showed wide plateau region similar to Ti–Cr–V. However Ti–Cr–Mo showed different hydrogen absorption–desorption cycling properties from Ti–Cr–V. The present study was carried out to clarify the properties of Ti–Cr–Mo and to compare them with those of Ti–Cr–V in order to understand the hydrogen absorbing mechanism and stability of b.c.c. alloys.

2. Experimental details

Ti–Cr–V and Ti–Cr–Mo alloys were prepared by arc melting in water-cooled Cu crucible. The size of alloy is approximately φ40 mm×22 mm (50 g). The target compositions of arc-melted alloys were $TiCr_{1.8-x}M_x$ ($x=0.2$–0.5, M=V, Mo) and $TiCr_{1.5}V_{0.3-y}Mo_y$ ($y=0$–0.3). Following the heat-treatment for 60 s at 1723 K under an argon atmosphere, alloys were water-quenched in order to freeze the high temperature phase. Every specimen was examined using X-ray diffraction and P–C–T measurements. Powder X-ray diffraction was measured with CuKα radiation. The measurements of hydrogen capacity and P–C–T characteristics were carried out between 233 and 293 K under hydrogen pressure of 0.001–5 MPa. Plateau

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pressure was defined as the pressure at the center of plateau region.

3. Results and discussion

3.1. Ti–Cr–M (V or Mo) ternary alloy

From the results of X-ray diffraction analysis, all the alloys except $TiCr_{1.6}V_{0.2}$ alloy showed b.c.c. single phase. The second phase observed in $TiCr_{1.6}V_{0.2}$ alloy was identified as C15 Laves phase. Authors have reported that heat-treatment at 1673 K for 60 s achieves single b.c.c. phase and excellent plateau property in $Ti_{30}Cr_{50}V_{20}$ alloy, which is written in the formula of $TiCr_{1.667}V_{0.667}$ [4]. It is easily understood that the C15 Laves phase tends to appear with decreasing V or Mo content because the composition become too close to $TiCr_2$. In this study, Ti–Cr–Mo alloy showed b.c.c. single phase even at the Mo content of $x=0.2$, while second phase can be observed in Ti–Cr–V alloy at the V content of $x=0.2$. It is concluded that Mo atom has superior ability to stabilize the b.c.c. structure than V.

Fig. 1 shows the *P–C–T* diagrams of $TiCr_{1.8-x}V_x$. Plateau pressure of these alloys was near atmospheric pressure at room temperature. With increasing V content, plateau pressure became lower and solid solution region increased. Maximum hydrogen capacity was 3.49 wt.% ($H/M=1.76$) and rechargeable hydrogen capacity exceeded 2.05 wt.% at the composition of $TiCr_{1.5}V_{0.3}$.

Fig. 2 shows the *P–C–T* diagrams of $TiCr_{1.8-x}Mo_x$. Plateau pressure of these alloys was higher than Ti–Cr–V alloys and near atmospheric pressure at 233 K. With increasing Mo content, plateau pressure rose and solid solution region decreased. Maximum hydrogen capacity was 2.85 wt.% ($H/M=1.53$) and rechargeable hydrogen capacity exceeded 2.05 wt.% at the composition of $TiCr_{1.6}Mo_{0.2}$. It should be pointed out that rechargeable hydrogen capacity is identical in both Ti–Cr–V and Ti–Cr–Mo alloys though maximum hydrogen capacity differs considerably. This was caused by the difference of maximum hydrogen capacity and solid solution region between Ti–Cr–V and Ti–Cr–Mo. This suggests that the number of hydrogen occupiable site of Ti–Cr–Mo is smaller than that of Ti–Cr–V, even though the number of effective hydrogen site is almost same. It is known that Mo atom is the element which narrowed solid solution region of b.c.c. alloy.

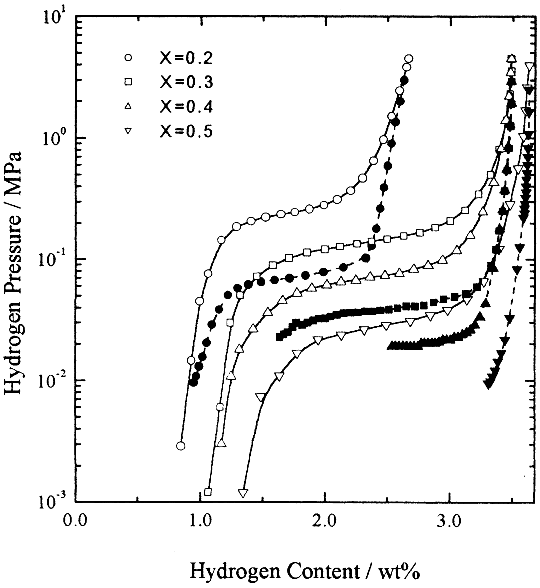

Fig. 1. *P–C–T* diagrams of $TiCr_{1.8-x}V_x$ ($x=0.2$–0.5) at 293 K. Open symbols, open absorption; filled symbols, close desorption.

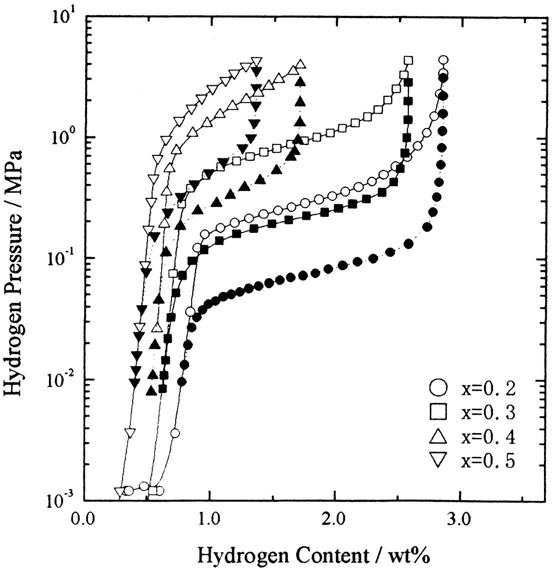

Fig. 2. *P–C–T* diagrams of $TiCr_{1.8-x}M_x$ ($x=0.2$–0.5) at 233 K.

Another important behavior is the opposite tendency of plateau pressure change with the V or Mo content. Table 1 shows lattice constants of b.c.c. phases obtained from X-ray diffraction analysis. Both Ti–Cr–V and Ti–Cr–Mo show a tendency that lattice expands with the increase of Mo or V content. Atomic radius of V and Mo were larger than that of Cr, so the tendency that lattice constant increase with V or Mo content is appropriate. Fig. 3a shows the change of plateau pressure with lattice volume of Ti–Cr–V, and Fig. 3b shows the change of plateau pressure with lattice volume of Ti–Cr–Mo. Plateau pressure of

Table 1
Lattice constants of $TiCr_{1.8-x}M_x$ (M=V, Mo)

	$x=0.2$	$x=0.3$	$x=0.4$	$x=0.5$
M=Mo	3.023(5)	3.029(4)	3.039(4)	3.048(5)
M=V	3.029(5)	3.035(4)	3.038(4)	3.042(5)

Lattice constant, *a* (Å).

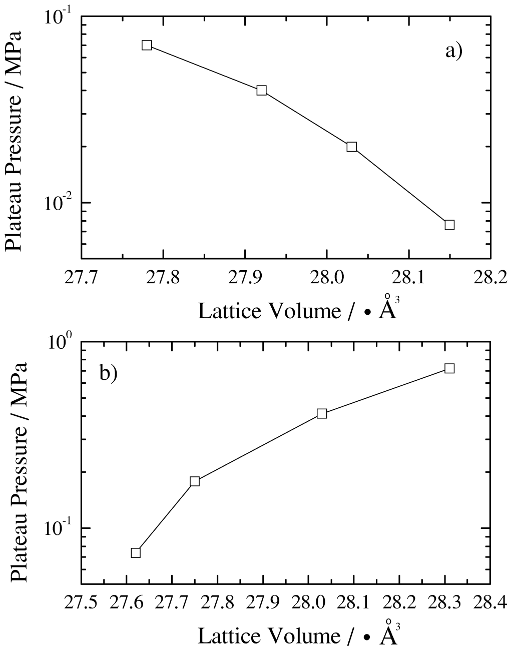

Fig. 3. Reverse relationship of plateau pressure to lattice volume: (a) Ti–Cr–V alloys, (b) Ti–Cr–Mo alloys.

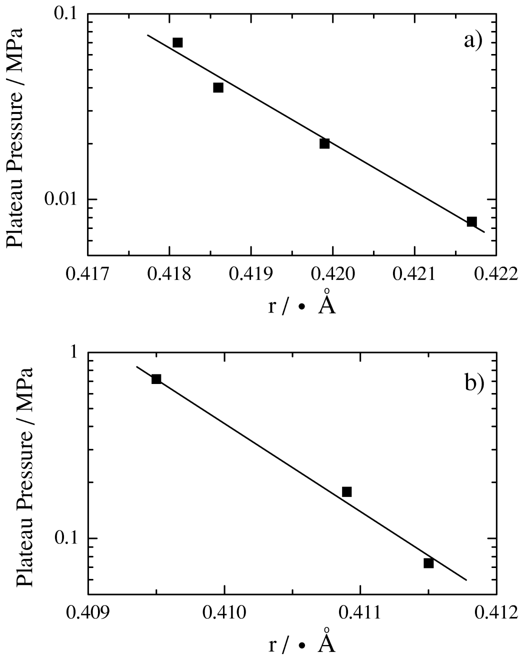

Fig. 4. Relationship of plateau pressure to radius of hydrogen site: (a) Ti–Cr–V alloys; (b) Ti–Cr–Mo alloys.

Ti–Cr–V decreased with increasing lattice volume, but plateau pressure of Ti–Cr–Mo alloys rose with increasing lattice volume. In the case of conventional intermetalic compounds, lattice expansion by adding large radius elements generally lowers plateau pressure [5,6]. The change of plateau pressure in Ti–Cr–V system can be explained by the empirical rule mentioned above, but in Ti–Cr–Mo system, the change of plateau pressure can not be explained.

In order to explain the proper behavior of Ti–Cr–Mo, we introduced ‘the radius of hydrogen site’, as Westlake calculated the radii of various interstitial holes for $LaNi_5$ [7]. Hydrogen atoms occupy tetrahedral site in most of b.c.c. alloys [8], so we suppose that tetrahedral site is hydrogen site. The size of tetrahedral site was calculated as the radius of sphere, which is tangent to four metal atoms. Generally, metallic radius is defined as half of the distance between nearest neighbor atoms, so the radii of metal and tetrahedral site will be calculated as $\frac{\sqrt{3}}{4}a$ and $\frac{\sqrt{5}-\sqrt{3}}{4}a$ for bcc structure, respectively, where a is lattice constant. The model, we have applied, is based upon the following assumptions: (1) the spherical metal atoms do not need contact with each other; (2) the lattice constant from X-ray analysis determines the relative position of metal atoms; and (3) the metallic radius, r_M was calculated as the compositional average of the atomic radii for coordination number 8 [9]; they are $r_{Ti} = 1.314$ Å, $r_{Cr} = 1.249$ Å, $r_V = 1.309$ Å, $r_{Mo} = 1.363$ Å. The radius of hydrogen site is calculated as

$$\frac{\sqrt{5}}{4}a - r_M.$$

Fig. 4a and b show the relationship between plateau pressure and the radius of hydrogen site of Ti–Cr–V and Ti–Cr–Mo, respectively. From Fig. 4a, plateau pressure of Ti–Cr–V decreased with increasing radius of hydrogen site. From Fig. 4b, plateau pressure of Ti–Cr–Mo also decreased with increasing radius of hydrogen site. While, lattice volume showed reverse relationship to plateau pressure in Ti–Cr–V and Ti–Cr–Mo, but the radius of hydrogen site had the same relationship to plateau pressure in Ti–Cr–V and Ti–Cr–Mo. We conclude that change in plateau pressure can be explained by the radius of hydrogen site better than by lattice volume.

3.2. The effect of V addition to Ti–Cr–Mo alloy

The width of solid solution region is remarkably different in Ti–Cr–Mo and Ti–Cr–V alloys though rechargeable hydrogen capacity is equivalent. One of the methods to achieve the high rechargeable capacity in bcc alloy is transform the solid solution region into plateau region by combining small solid solution region like Ti–Cr–Mo alloy and large maximum hydrogen capacity like Ti–Cr–V. V metal less than 10 at.% was added to Ti–Cr–Mo alloy. Fig. 5 shows *P–C–T* diagrams of Ti–Cr–V–Mo alloys. From Fig. 5, all alloys except Ti–Cr–Mo ternary alloy had same solid solution region and almost same maximum hydrogen capacity. Thus, with a little addition of V, solid solution region and maximum hydrogen capacity increased largely but the rechargeable hydrogen capacity remains constant.

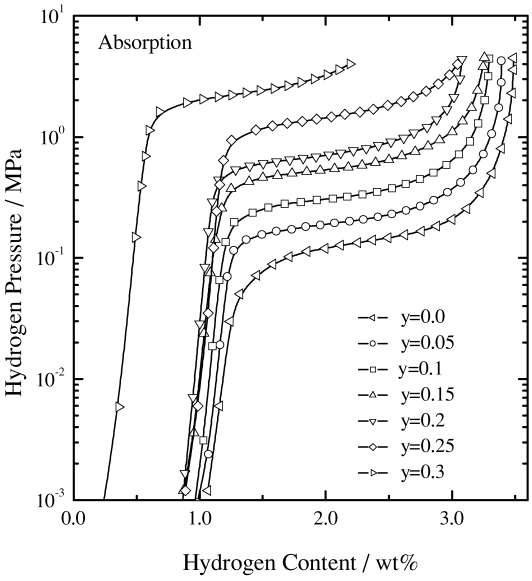

Fig. 5. *P–C–T* diagrams of $TiCr_{1.5}V_{0.3-y}Mo_y$ at 293 K.

4. Conclusion

Hydrogen absorbing properties such as *P–C–T* characteristics and crystal structure were investigated for Ti–Cr–M (M=V, Mo) alloys. The results obtained were as follows.

1. Ti–Cr–V and Ti–Cr–Mo alloys had an equivalent rechargeable hydrogen capacity, but they are different in maximum hydrogen capacity and the width of solid solution region.
2. The change of plateau pressure was not explained by lattice volume but by the radius of hydrogen site calculated from non-rigid spherical model in both Ti–Cr–V and Ti–Cr–Mo.
3. V addition to Ti–Cr–Mo made solid solution region large.

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