Composition design for Laves phase-related BCC-V solid solution alloys with large hydrogen storage capacities

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Abstract. This paper analyzes the alloy composition characteristics with large hydrogen storage capacities in Laves phase-related BCC solid solution alloy systems using the cluster line approach. Since a dense-packed icosahedral cluster \( A_6B_7 \) characterizes the local structure of \( AB_2 \) Laves phases, in A-B-C ternary system, such as Ti-Cr(Mn, Fe)-V, where A-B forms \( AB_2 \) Laves phases while A-C and B-C tend to form solid solutions, a cluster line \( A_6B_7-C \) is constructed by linking \( A_6B_7 \) to C. The alloy compositions with large hydrogen storage capacities are generally located near this line and are approximately expressed with the cluster-plus-glue-atom model. The cluster-line alloys \( (Ti_{66}Cr_{70})_{100-x}V_x \) (\( x = 2.5-70 \) at.\%) exhibit different structures and hence different hydrogen storage capacities with increasing V contents. The alloy \( (Ti_{66}Cr_{70})_{95}V_5 \) as well as \( Ti_{30}Cr_{40}V_{30} \) with BCC solid solution structure satisfy the cluster-plus-glue-atom model.

1. Introduction

Hydrogen storage (H-storage) alloys have been enthusiastically investigated for fuel cells and many other applications [1-3]. The Lave phase-related V-based BCC solid solution alloys [4-10], like Ti-Cr-V, Ti-Fe-V, Ti-Mn-V and Ti-Cr-Mn-V, have been developed rapidly as a new generation of H-storage alloys due to their large H-storage capacities and favorable kinetic characteristics for hydrogen absorption and desorption. However, it is difficult to determine the optimum alloy composition with large H-storage capacity in multi-component alloy systems where large H-storage capacities are generally achieved by multiple alloying of simple binary alloys with tedious trial-and-error methods. Therefore, the composition design is of great importance for developing new complex alloys with large H-storage capacities.

The \( AB_2 \) Laves phases, including three types of crystalline phases: \( cF24-MgCu_2 \), \( hP12-MgZn_2 \) and \( hP24-MgNi_2 \), are common topologically closed-packed structures [11]. We analyzed the local structures of these Laves phases and found that they contain a dense-packed icosahedral cluster \( A_6B_7 \) centered by smaller B atom. Taking the MgCu_2 phase for instance, figure 1 gives the unit cell of this phase where a Cu-centered icosahedral cluster \( Mg_6Cu_7 \) is identified. From the viewpoint of atomic cluster, it is easy to understand that the MgCu_2 phase composition can be decomposed into one \( Mg_6Cu_2 \) cluster plus five Cu atoms, i.e. \( Mg_6Cu_2 + 5Cu = Mg_6Cu_{12} = MgCu_2 \). If the five atoms are regarded as the pseudo third element, then the straight composition line can be defined by linking the
icosahedral Mg₆Cu₇ cluster composition with Cu in pseudo-ternary Mg-Cu-Cu system, as shown in figure 1. Such a cluster line refers to a straight composition line in a ternary system linking a binary topologically dense-packed cluster to the third element. In other words, this is a cluster-plus-glue-atom model where the third element serves as glue atoms linking atomic clusters. As a practical approach for composition design, the cluster line has guided successfully the composition analysis of quasicrystals and bulk metallic glasses [12-14], where often the local structures exhibit icosahedral short-range order.

Figure 1. Schematic composition chart of pseudo ternary Mg-Cu-Cu system and an MgCu₂ unit cell structure where the icosahedron Mg₆Cu₇ is derived.

The formation of atomic clusters is originated from the negative enthalpy of mixing of constituent elements, thus both the cluster line rule and the cluster-plus-glue-atom model should be general phenomena in other types of alloy phases as well. Therefore, in the present paper, we attempt to analyze the composition characteristics of alloys with large H-storage capacities in the Laves phases-related BCC-V solid solution alloy systems by using the cluster line approach, and to investigate H-storage capacities of cluster-line alloys in Ti-Cr-V ternary system.

2. Cluster line phenomenon in typical BCC-V solid solution alloy systems

2.1. Ti-Cr-V ternary system
The Ti-Cr-V ternary system is a typical BCC solid solution-forming system [5, 6]. The enthalpies of mixing between constituent elements are respectively \( \Delta H_{\text{Ti-Cr}} = -7.5 \text{ kJ/mol} \), \( \Delta H_{\text{Cr-V}} = -2 \text{ kJ/mol} \), \( \Delta H_{\text{V-Ti}} = -2 \text{ kJ/mol} \) [15]. So binary Ti-V and Cr-V are solid solution-forming systems while Ti-Cr forms TiCr₂ Laves phases of the \( \varepsilon-F\)-MgCu₂ type (low temperature) and the \( hP\)-MgNi₂ type (high temperature). The Cr-centered icosahedral TiCr₇ cluster characterizes the local structure of the TiCr₂ Laves phase. According to the topologically efficient cluster-packing structural model [16], the critical ratio \( R' \) of ideally dense-packed icosahedral cluster is 0.902, which is defined as the ratio of the radius of the center atom \( r_0 \) to that of the nearest-neighbor shell atom \( r_1 \). Here, the Goldschmidt radii of Cr and Ti atoms are respectively 0.128 nm and 0.146 nm, and then the ratio \( R \) of the Ti₆Cr₇ cluster is \( R = r_0/r_1 = \)
0.128 / [(0.128*6+0.146*6)/12] = 0.934, where \( r_1 \) is the average atomic radius of the nearest-neighbor shell atoms Cr_6Ti_6. The difference represented by \( \Delta=(R-R^*)/R^* \) between the actual \( R \) and the ideal \( R^* \) is 3.5 %, which indicates that the icosahedral cluster Ti_6Cr_7 is quite dense-packed.

Thus the cluster line Ti_6Cr_7-V is constructed in the Ti-Cr-V ternary system by linking binary cluster Cr_7Ti_6 with V as shown in figure 2. In figure 2, the black circles and neighboring numbers represent the Ti-Cr-V alloy compositions and the H-storage capacities (H/M) of the designed alloys, respectively [5]. It is noted that the icosahedral cluster line Ti_6Cr_7-V traverses exactly the composition range with large H-storage capacities, which verifies the validity of the cluster line approach in the Ti-Cr-V H-storage alloy system. Furthermore, the best experimental alloy composition Ti_30Cr_40V_30 with the largest H-storage capacity (H/M=1.69) is approximately expressed with the cluster-plus-glue-atom model of (Ti_6Cr_7)V_5 (=Ti_{33.3}Cr_{38.9}V_{27.8}, i.e. one Ti_6Cr_7 cluster glued by five V atoms, where, the number of glue atom V is same to that of glue atom Cu in the MgCu_2 Laves phase.

**Figure. 2** Composition chart of the Ti-Cr-V ternary system. The cluster line Ti_6Cr_7-V is plotted and the H-storage capacities (H/M) of some Ti-Cr-V alloys at 303 K [5] are also listed.

### 2.2. Ti-Mn-V ternary system

The cluster line approach in this ternary system is similar to that in the Ti-Cr-V system. The enthalpies of mixing between Ti-Mn and Mn-V are respectively \( \Delta H_{Ti-Mn} = -8 \) kJ/mol, \( \Delta H_{Mn-V} = -0.8 \) kJ/mol [15]. Therefore Ti and Mn tend to form the TiMn_2 Laves phase while V forms solid solutions both with Ti and Mn. The TiMn_2 Laves phase has an \( hP-MgZn_2 \) structure and is characterized by Mn-centered dense-packed icosahedral cluster Ti_6Mn_7 (\( \Delta=2.7 \% \), \( r_{Mn}=0.126 \) nm). The cluster line Ti_6Mn_7-V is then constructed in the Ti-Mn-V system as is shown in figure 3. Experimental results indicate that the TiMnV alloy consisting of ternary Laves alloy distributed in BCC-V solid solution matrix has a large H-storage capacity [9]. It can bee seen from figure 3 that this ternary alloy is located near the cluster line Ti_6Mn_7-V and also close to the (Ti_6Cr_7)V_5 composition, indicating that the alloys near the cluster line may have large H-storage capacities.
2.3. Ti-Fe-V ternary system
The large enthalpies of mixing between Ti-Fe and Fe-V ($\Delta H_{Ti-Fe} = -17$ kJ/mol, $\Delta H_{Fe-V} = -8$ kJ/mol) favor formation of intermetallics. Similarly, the Fe-centered dense-packed icosahedral cluster $\text{Ti}_6\text{Fe}_7$ ($\Delta = 3.1 \%$, $r_{Fe}=0.127$ nm) exists in the local structure of MgZn$_2$-type TiFe$_2$ Laves phase. In Ti-Fe-V ternary system, the V-rich alloy compositions with large H-storage capacities [8] (represented by full-circle points in figure 3) are also located near the cluster line $\text{Ti}_6\text{Fe}_7$-V.

![Composition charts of Ti-Mn-V, Ti-Fe-V and Ti-(Cr,Fe)-V ternary systems.](image)

**Figure. 3** Composition charts of Ti-Mn-V, Ti-Fe-V and Ti-(Cr,Fe)-V ternary systems.

2.4. Ti-Cr-Fe(Mn)-V quaternary systems
In Ti-Cr-Fe-V and Ti-Cr-Mn-V quaternary systems, Cr - Fe and Cr - Mn can be regarded as a pseudoelement M due to their similar atomic radius and similar enthalpies of mixing with Ti or V. Thus, the quaternary Ti-Cr-Fe-V alloy composition $\text{Ti}_{35}\text{Cr}_{25}\text{Fe}_{10}\text{V}_{30}$ [17] with a large H-storage capacity can be expressed as a pseudo ternary composition $\text{Ti}_{33}\text{M}_{35}\text{V}_{30}$, which is located near the icosahedral cluster line $\text{Ti}_6\text{M}_{7}$-V in the pseudo ternary alloy system (see in figure 3) and also close to the $(\text{Ti}_6\text{M}_7)_5\text{V}_5$ composition.
A general characteristic existing in the above Laves phase-related BCC-V solid solution alloy systems A-B-C is that the absolute value of \( \Delta H_{A,B} \) is larger than \( \Delta H_{B,C} \) and \( \Delta H_{A,C} \) and the latter two are close to zero. A-B then forms an AB\(_2\) Laves phase while A-C and B-C tend to form solid solutions. Thus, the dense-packed icosahedral cluster line A\(_6\)B\(_7\)-C can be applied into these ternary and pseudo ternary systems and alloy compositions with large H-storage capacities are located near the cluster line.

In the present work, the Ti-Cr-V alloy compositions are designed along the icosahedral cluster line Cr\(_7\)Ti\(_6\)-V and the H-storage capacities of these cluster-line alloys are investigated.

3. Experimental

Ingots of the (Ti\(_6\)Cr\(_7\))\(_{100-x}\)V\(_x\) (x = 2.5-70 at. %) alloys were prepared by using arc melting the mixtures of constituent elements under argon atmosphere. The purities of elements are 99.9 wt% for Cr, 99.99 wt% for Ti and 99.5 wt% for V, respectively. Alloy rods with a diameter of 3 mm were prepared by means of copper mould suction casting. Structural identification of these alloys was carried out by means of X-ray diffractometry (XRD) with the Cu \( K_\alpha \) radiation (\( \lambda = 0.15406 \) nm). The alloy ingots and rods were mechanically crushed into powders under 300 \( \mu \)m. The activation treatment was carried out as follows. The sample powders, about 2 g, were put into the reactor and evacuated for 30 min at 673 K. The hydrogen with a pressure of 5 MPa was introduced into the reactor for 30 min. The reactor was subsequently quenched in water and was again evacuated for 30 min at 673 K. This processing is repeated for 3-4 times. At last, the P-C isotherms (PCT curves) of the samples were measured at 288 K and 313 K under a hydrogen pressure of 5 MPa.

4. Results and discussions

![Figure 4](image-url)

**Figure 4** XRD patterns of the (Ti\(_6\)Cr\(_7\))\(_{100-x}\)V\(_x\) (x = 2.5-70 at. %) cast alloy ingots and suction-cast rods.
Figure 4 shows the XRD results of the cast (Ti<sub>6</sub>Cr<sub>7</sub>)<sub>100-x</sub>V<sub>x</sub> (x = 2.5-70 at. %) alloy ingots and rods. For the alloy ingots at V contents x=2.5 and 5 at. %, the Cr<sub>2</sub>Ti phase is formed; with increasing V contents, dual-phase TiCr<sub>2</sub> - BCC solid solution appear in the range of x = 10-20 at. %; then upon further increasing in the V contents, only BCC solid solution phase is maintained in the range of x = 20-70 at. %. While for the alloy rods prepared by suction casting with x=2.5 and 5 at. %, the TiCr<sub>2</sub> phase is absent but instead is replaced by single BCC structure. Note that only the cluster-line alloys of x=2.5 and 5 at. % can be suction-cast as rods.

The H-storage capacities of the cluster-line alloys vary with temperatures. Figures 5 (a) and (b) show the PCT curves of four typical cast (Ti<sub>6</sub>Cr<sub>7</sub>)<sub>100-x</sub>V<sub>x</sub> (x = 2.5, 10, 40, 60 at. %) alloy ingots at different temperatures. At 288 K (figure 5(a)), the hydrogen absorbing capacity of the alloy x = 2.5 at. % containing the pure TiCr<sub>2</sub> phase is weak and no plateau appears in the PCT curve. With increased V contents, the hydrogen absorbing capacities of the BCC solid solution alloys along the cluster line are enhanced and the alloys x = 40 at. % and x = 60 at. % can absorb at maximum about 2.5 wt. % of hydrogen. While the H-storage capacities at a higher temperature of 313 K are larger (figure 5 (b)). The maximum hydrogen contents of these alloys are all larger than 3 wt. %. Although the alloy (Ti<sub>6</sub>Cr<sub>7</sub>)<sub>90</sub>V<sub>10</sub> absorbs 3.32 wt. % of hydrogen, the PCT curve is steep and the effective H-storage capacity is weak. The BCC solid solution alloy x = 40 at. % has the largest effective hydrogen storage capacity and can absorb about 3.19 wt. % of hydrogen, which is consistent with the reported value in the literature [5].

**Figure.** 5 PCT curves of the (Ti<sub>6</sub>Cr<sub>7</sub>)<sub>100-x</sub>V<sub>x</sub> (x = 2.5-60 at. %) alloy ingots and rods (after Copper mould suction casting, 3 mm in diameter).
For the same composition, the H-storage capacity varies with the alloy structures. As shown in figure 5 (c), the H-absorbing contents of the alloy rods are larger than those of the alloy ingots. Taking (Ti<sub>6</sub>Cr)<sub>75</sub>V<sub>5</sub> for instance, the maximum H-absorbing content of the alloy ingot with pure TiCr<sub>2</sub> phase reaches 1.8 wt. %, while the alloy rod with BCC-V solid solution structure can absorb at most 3.14 wt. % of hydrogen. Furthermore, the H-absorbing capacity of this alloy in both ingot and rod forms is larger than that of the (Ti<sub>6</sub>Cr)107.5V<sub>2.5</sub> alloys. The hydrogen absorption and desorption capacity of the (Ti<sub>6</sub>Cr)<sub>75</sub>V<sub>5</sub> alloy rod is comparable to that of (Ti<sub>6</sub>Cr)<sub>70</sub>V<sub>40</sub> alloy ingot. Although two alloys possess BCC-V solid solution structure, the former contains a much less V content, which reduces the material cost.

From the viewpoint of the cluster-plus-glue-atom model, the alloy composition (Ti<sub>6</sub>Cr)<sub>70</sub>V<sub>5</sub> (Ti<sub>32.8</sub>Cr<sub>51.2</sub>V<sub>5</sub>) with large H-storage capacity is approximately expressed with (Ti<sub>6</sub>Cr)<sub>70</sub>V<sub>1</sub> (=Ti<sub>42.9</sub>Cr<sub>50</sub>V<sub>1.1</sub>), which is consistent with those optimum quasicrystals and bulk metallic glasses also determined by the (cluster)<sub>1</sub>(glue atom)<sub>1</sub> model [12-14]. This is supported by the efficient cluster packing model proposed by Miracle [18]: dense-packed clusters centered by primary solute atoms are packed in a close-packing face-centered-cubic (fcc) like structure and the secondary solute atoms (or glue atoms as we call them) are located in the interstitial sites. An fcc unitcell includes four lattice sites, four octahedral interstices and eight tetrahedral interstices. Thus the ratio of the number of atoms to that of octahedral and tetrahedral interstices is 1:3. The ratio 1:1 for the number of clusters to that of glue atoms indicates that glue atoms only occupy the octahedral interstices, while the ratio 1:3 indicates the glue atoms takes all the octahedral and tetrahedral interstices. Ma et al [19] further revised the efficient cluster packing model and pointed out that double atoms can fill into an interstitial sites. If double atoms fill into an octahedral interstice, the number of clusters to that of glue atoms will be 1:5, which is consistent with cluster-glue-atom expression of the Laves phase and V solid solution alloys with large H-storage capacities.

5. Conclusions

The hydrogen storage characteristics in ternary Laves phase-related BCC solid solution alloys Ti-Cr, Mn, Fe)-V have been analyzed by using the cluster line approach. It is revealed that the alloy compositions with large hydrogen capacities are located near the dense-packed icosahedral cluster line Ti(x)(Cr,Mn,Fe)-V. In Ti-Cr-V ternary system, the structures of the cluster-line (Ti<sub>6</sub>Cr)<sub>x</sub>V<sub>y</sub> (x = 2.5-70 at. %) alloy ingots prepared by conventional casting evolves with increasing V contents from pure Laves phase, then to dual-phase TiCr<sub>2</sub> - BCC solid solution structures, and finally to the BCC solid solution. Upon suction casting, the alloy rods all contain single BCC solid solution. Among them, the (Ti<sub>6</sub>Cr)<sub>75</sub>V<sub>5</sub> BCC alloy after suction casting exhibits a high hydrogen storage capacity of 3.14 wt. %, which is comparable with the best known alloy but V-richer Ti<sub>6</sub>Cr<sub>40</sub>V<sub>30</sub> prepared by conventional casting. Moreover, these two alloy compositions can be expressed according to the cluster-plus-glue-atom model as (Ti<sub>6</sub>Cr)<sub>75</sub>V<sub>5</sub> ≈ (Ti<sub>6</sub>Cr)<sub>1</sub>V<sub>1</sub> and Ti<sub>30</sub>Cr<sub>40</sub>V<sub>30</sub> ≈ (Ti<sub>6</sub>Cr)<sub>1</sub>V<sub>5</sub>.

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