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Correlation between hydrogen absorption properties and homogeneity of Ti–Cr–V alloys

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Abstract

The factor affecting the hydrogen storage capacity of Ti–Cr–V b.c.c. solid solution alloys was investigated and a method to increase the capacity was proposed. The concentration of each element of the Ti–Cr–V alloy did not become very uniform by the heat treatment. The degree of fluctuation in vanadium concentration between higher and lower vanadium area content exceeds 5 wt.%, even after the conventional heat treatment. But we successfully made a more homogeneous alloy by the application of the floating zone (FZ) melting process. The degree of fluctuation in the vanadium concentration in this alloy diminished to under 2.5 wt.%. The flatness of the plateau and the rechargeable hydrogen storage capacity were drastically improved by this homogenizing process. The rechargeable hydrogen storage capacity of FZ melted alloy reached 2.7 wt.%, although that of the heat-treated alloy remained at 2.1 wt.%.

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Keywords: Hydrogen absorbing alloy; Vanadium; Microstructure; Floating zone melt

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1. Introduction

Ti–Cr–V, which has a body centered cubic structure and a wide solid solution range, is one of the hydrogen absorbing alloys with a high hydrogen storage capacity. Maximum hydrogen storage capacity of these alloys reaches about 3.7 wt.%, but the rechargeable hydrogen storage capacity is limited to only about half of that. Recently, many researchers are interested in Ti–Cr–V b.c.c. alloys because the hydrogen storage capacity of these alloys is larger than that of intermetallic compound alloys. It has been reported that the hydriding properties of the b.c.c. structured Ti–Cr–V alloy are influenced by the melting methods and thermal history [1,2]. On the other hand, it was reported that the hydrogen storage capacity of these alloys has been improved by optimizing the heat-treating condition [3] and by additional elements [4]. It is necessary to further increase the rechargeable hydrogen storage capacity, in order for this alloy to be used more generally. So, we aimed to increase the hydrogen storage capacity by adding the homogenizing process without the heat treatment. In this study, the floating zone melting method was tried as a homogenizing process, and the effect on the microstructure and hydriding properties of Ti–Cr–V alloy were compared with those obtained by conventional methods.

2. Experimental details

Ti–Cr–V alloys were prepared by arc-melting under argon atmosphere in a water-cooled Cu crucible. The target composition of the arc-melted alloy was $Ti_1Cr_1V_1$. Two ordinary specimens were processed. One was an as-cast alloy, hereafter referred to as AC, the other underwent heat treatment under argon atmosphere, hereafter referred to as HT. The HT sample was water-quenched after the heat-treatment at 1573 K for 10 min. The floating zone melting method was adopted as another homogenizing process. A part of the cylindrical AC alloy was re-melted in the argon atmosphere and the melting zone was moved along the axis at the speed of 20 mm/h or 12 mm/h, hereafter referred to as FZ20 and FZ12, respectively. Each sample was investigated by X-ray diffraction analysis, pressure–composition isotherm (P–C–T) measurements and ob-

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servation of the microstructure. Powder X-ray diffractions were measured with Cu Kα radiation. The measurements of hydrogen capacity and *P–C–T* characteristics were carried out at 323 K and in the range of hydrogen pressure 0.001–5 MPa after one activation and following degassing treatment with R.P. at 357 K for 1 h. The activation of alloys was performed with cycling absorption at 297 K under 5 MPa hydrogen and desorption at 357 K under vacuum. The microstructure was observed using an optical microscope and an electronic microscope.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the tested alloys. All alloys have b.c.c. structure with 0.306 nm of lattice constant. Although X-ray diffraction patterns of HT, FZ20, and FZ12 are single phase, X-ray diffraction patterns of AC have a small peak of chromium. It means that as-cast alloy is poor in homogeneity. Comparing the half width of XRD peaks, FZ alloys showed sharper peaks than that of AC or HT. Although the b.c.c. structure is thought to be stable at higher temperatures in Ti–Cr–V from the phase diagram, the single phase b.c.c. structure with good crystallinity was obtained in the $Ti_1Cr_1V_1$ alloy even through the gradual solidification.

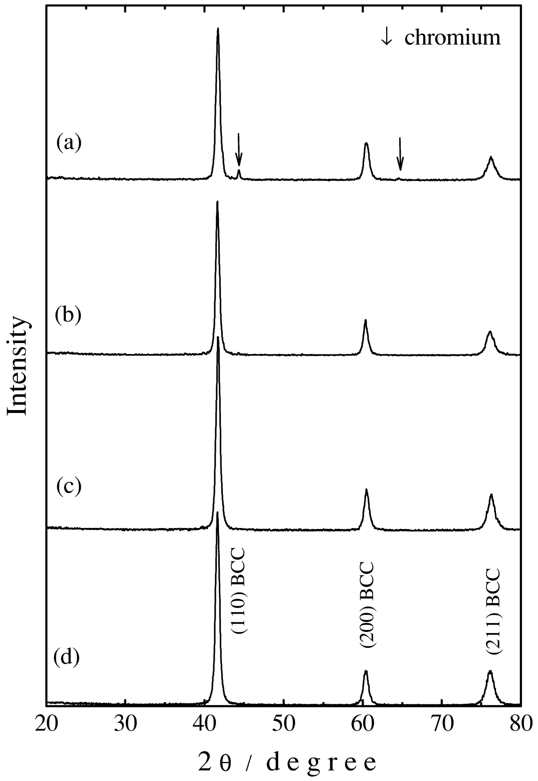

Fig. 1. X-ray diffraction patterns of the Ti–Cr–V samples: (a) AC; (b) HT; (c) FZ20; and (d) FZ12.

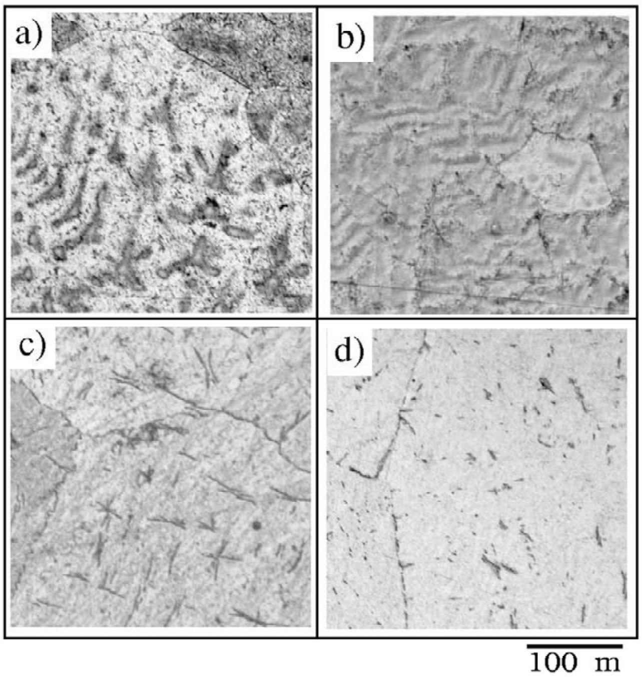

Fig. 2. Optical microstructures of Ti–Cr–V samples: (a) AC; (b) HT; (c) FZ20; and (d) FZ12.

Fig. 2 shows the typical optical microstructures of the samples. In the case of AC, a lot of blackish parts of dendrite were observed in the crystal grain. These parts seem to be corroded strongly with the segregation. In the case of HT, the segregation was reduced because of the homogenization by heat treatment. But the blackish parts were observed in the crystal grain though they were not as deep as in AC because the segregation did not disappear completely. On the other hand, the blackish parts of dendrite were not observed in FZ alloys. This means that the segregation does not exist in matrix. But needle shaped precipitations were observed in FZ alloys. These precipitations have directionality in the crystal grain and are observed more in FZ20 than in FZ12. By measurement with X-ray microanalysis (EPMA) it was understood that these precipitations were enriched with titanium. The crystal grain of FZ alloys grew up to the size of 1000–5000 μm. The size was considerably large compared with AC and HT, whose size is only in the range of 100–500 μm.

Fig. 3 shows the concentration in vanadium analyzed by EPMA. For AC, the degree of fluctuation in vanadium concentration, which was defined as the difference of vanadium concentration between the higher and lower vanadium area, was very large, and reached about 10 wt.%. Even after the heat treatment at high temperatures, the degree of fluctuation remained about 5 wt.% and a completely homogenous alloy was not obtained. Therefore, a chromium peak was observed in the XRD pattern of AC, and it was observed that the XRD peaks of AC and HT were broad. On the contrary, the matrix of FZ alloys shows the degree of fluctuation in vanadium concentration to be

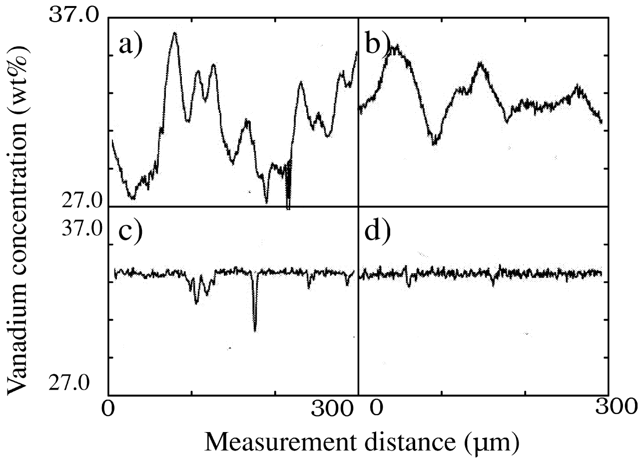

Fig. 3. Vanadium distribution of the Ti–Cr–V samples with EPMA: (a) AC; (b) HT; (c) FZ20; and (d) FZ12.

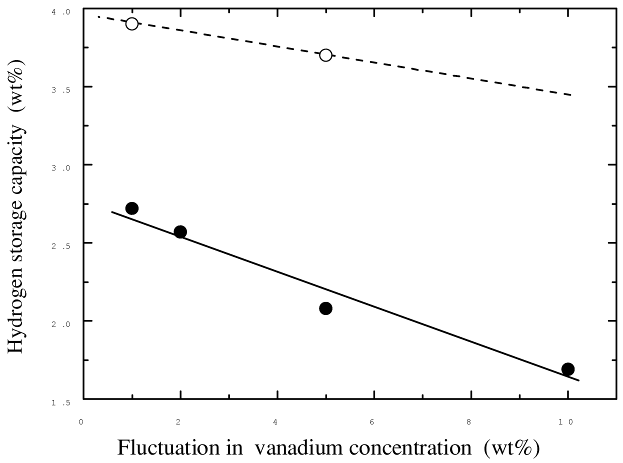

Fig. 5. Correlation of the effective hydrogen capacity with the fluctuation in vanadium concentration. ○, Maximum hydrogen capacity; ●, Effective hydrogen capacity.

only 2 wt.% or less. For FZ20, some sharp peaks were observed. These peaks were precipitations observed in Fig. 2. In all alloys, the distribution of chromium was similar to the vanadium, and that of titanium was the opposite.

Fig. 4 shows the *P–C–T* (Pressure–composition isotherms) diagram of the alloys tested. In this *P–C–T* diagram, the *X*-axis starting point in these *P–C–T* lines was shifted by the dissolved hydrogen to compare the effective hydrogen capacity. Heat-treatment makes the plateau slope flat and enlarges the hydrogen capacity. FZ melting makes the plateau slope even more flat and enlarges the hydrogen capacity further. The rate of zone melting affects these properties, and the lower rate is especially desirable. The effective hydrogen capacity of FZ12 increased about 0.6 wt.% compared with HT. Although titanium rich phases were observed in FZ20, the hydrogenation properties, such as the effective hydrogen capacity and the flatness of the plateau of the Ti–Cr–V alloys, were excellent in FZ alloys. The reason for this seems to be that the hydrogenation properties are influenced by the homogeneity of the matrix rather than the existence of precipitations. Moreover, the volume ratio of precipitations was too low to show any peak in the XRD pattern. Therefore, precipitations hardly influence the hydrogenation properties.

We thought the difference of vanadium concentration was one of the parameters to show homogeneity of the alloy, because vanadium is a base metal of the b.c.c. solid solution alloy. So we showed the relation between the difference of the vanadium concentration and the hydrogenation properties in Figs. 5 and 6. In Fig. 5, the

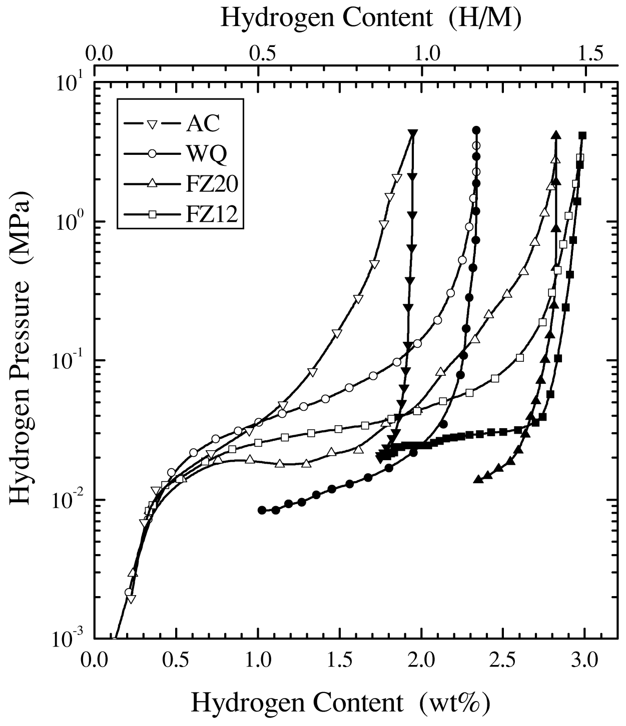

Fig. 4. *P–C–T* diagrams of TiCrV alloys at 323 K.

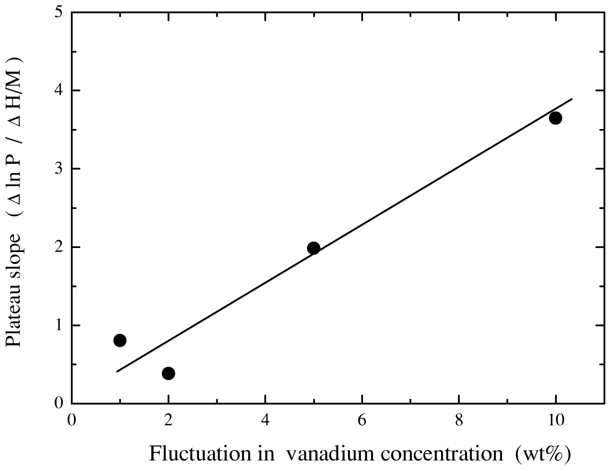

Fig. 6. Correlation of the Plateau slope with the fluctuation in vanadium concentration.

maximum hydrogen capacity of FZ12 increased slightly (about 0.2 wt.%) compared with HT, though the effective hydrogen capacity of FZ12 increased about 0.6 wt.%. This shows the dissolved hydrogen area narrowed about 0.4 wt.%. In other words, an increase of the effective hydrogen capacity of FZ alloys was not caused by an increase of maximum hydrogen capacity but by a decrease of dissolved hydrogen. The reason for this is not yet clear. In Figs. 5 and 6, the smaller the degree of fluctuation in the vanadium concentration, the better are the hydrogenation properties. Hydrogenation properties can be expected to improve even more by homogenizing the vanadium concentration further.

4. Conclusion

Hydrogen absorption properties of the Ti–Cr–V alloy with b.c.c. structure from various histories were investigated. It was found that melting methods highly influence the hydrogen absorbing properties of the Ti–Cr–V system b.c.c. alloy. Although many titanium rich precipitations were observed in the floating zone melted alloys, these alloys showed higher homogeneous matrix in vanadium than heat-treated alloys did. The alloys prepared by the floating zone melting increased in the hydrogen absorbing capacity and in the plateau flatness according to the increase in homogeneity. As a result, the effective hydrogen capacity of 2.7 wt.% was achieved. The possibility of increasing the hydrogen capacity in the Ti–Cr–V system may still remain if manufacturing methods to obtain the complete homogeneity are improved.

Acknowledgements

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