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Development of V-rich V-Ti-Cr and V-Ti-Cr-Al Alloys with High Hydrogen Desorption Pressure for High Pressure MH Tank

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1 Introduction

Recently, high-pressure metal hydride (MH) tanks attract many attentions for on-board usage due to its high volumetric hydrogen storage density and easiness of heat management(1). In order to enhance its merits, especially improving of cold-starting capability, increment of hydrogen desorption pressure of MH at ambient temperature is strongly required(2). Besides, from viewpoint of materials as on-board fuel storage media, durability or cyclic properties are quite important issue. V-Ti-Cr alloys with BCC crystal structure are known to its relatively high volumetric hydrogen capacity(3), in addition, alloys with high V content possess good cyclic properties. Therefore V-Ti-Cr alloys are regarded as one of the most promised candidates for on-board hydrogen storage media. In this ternary system, reducing of Ti and increasing of Cr content in alloys lead to increment of hydrogen desorption pressure of alloys. But excess substitution of Ti by Cr causes declination of hydrogen capacity of alloys(4)(this compositional restriction is called as “limitation line”). Therefore, to overcome this limitation, introduction of adequate substitutional element(s) into this system is one of the effective techniques to increase hydrogen desorption pressure. In addition, recently, it was revealed that in V-Ti-Cr system, not only Ti/Cr ratio but also V content is important factor to make alloys high hydrogen desorption pressure with high hydrogen capacity(5). Al and Mo are known to its effectiveness of increasing of hydrogen desorption pressure of V-based alloys. In our previous study, introducing of Al or Mo into alloys reduces the minimum optimum content of Ti in alloys with high hydrogen capacity. But degree of increment of hydrogen desorption pressure of Al substitution is higher than that of Mo substitution.

In this study, effects of Ti/Cr on 75at%V and substitutional element of Al in 75at%V-Ti-Cr-Al alloys were investigated with prospect of increment of hydrogen desorption pressure for improvement of cold starting capability of high-pressure MH tanks.

2 Experimental Procedures

Purity of starting materials was as follows. V : 99.95%(N200, provided by TAIYOKOKO co.,LTD), Ti:99.99% ,Cr:99.995%, Al:99.999%, respectively. The samples of approximately 13.5g were weight out and then arc-melted four times in order to improve its homogeneity. In this study, composition of the samples is described by atomic%. Crystal structure and lattice parameter were measured by X-ray diffraction with Cu-Kα radiation. Pressure composition isotherms (PCT curves) were measured by Sieverts-type apparatus (Suzuki-shoukan). First, sample was crushed into particles, weighted out about 1g and placed into pressure vessel for PCT measurement. Then the vessel was connected to PCT apparatus and flushed with hydrogen for three times. Each time, before commencing of PCT measurement, sample was evacuated with rotary pump for 2hrs at measuring temperature, and beginning point (or zero-point) of PCT curves were adjusted. Effective hydrogen capacity is defined as difference between amount of hydrogen stored at 9MPa in absorption step and remained in the sample at 0.1MPa in desorption step.

3 Results

3.1 Hydrogen storage properties of 75at%V-Ti-Cr alloys

Figure 1 shows PCT curves of 75at%V-xat%Ti-Cr as-cast samples (x=3 to 5) measured at 273K. The 75at%V-5at%Ti-Cr sample showed flat plateau region and relatively large hydrogen storage capacity. But 75at%V-4at%Ti-Cr sample showed declination of hydrogen storage capacity and 75at%V-3at%Ti-Cr sample showed quite small or almost no hydrogen storage capacity. This declination of hydrogen storage capacity with inclination of Cr content is regarded as Cr content is exceeding limitation line of corresponding V content and causing of reduction of hydrogen storage property(3). In this study, all the samples were confirmed as BCC single phase.

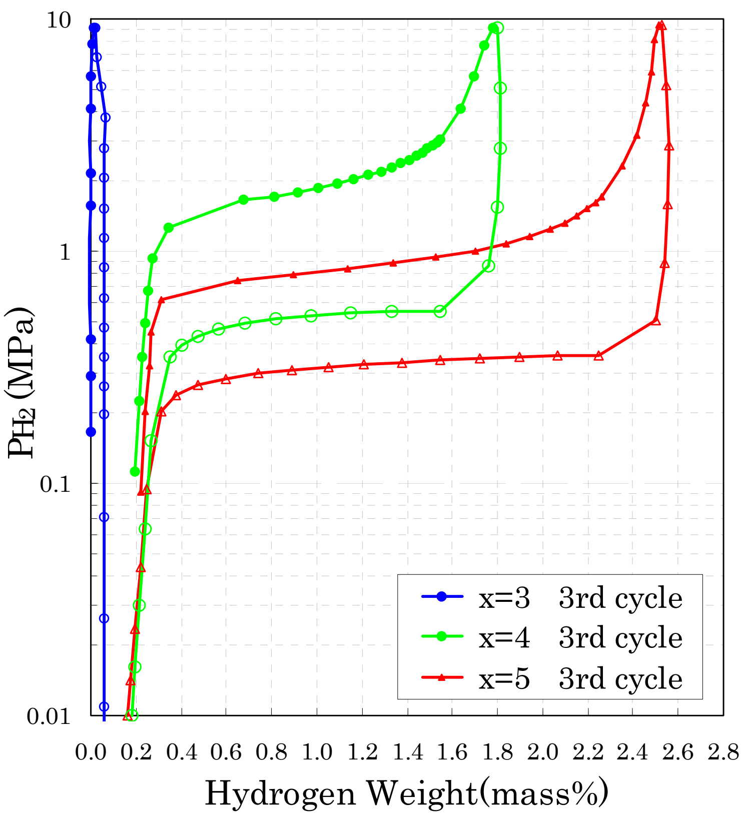

Figure 1: PCT curves of 75at%V-xat%Ti_Cr as-cast samples (x=3 to 5) measured at 273 K.

Figure 2 shows PCT curves of 75at%V-5at%Ti-Cr as-cast sample measured at 243K to 313K. At 273K, effective hydrogen capacity was about 2.3mass% (at 10th cycle). Hydrogen desorption pressure was 0.35MPa at 273K and 0.107MPa at 253K, respectively. From 243K through 313K, amount of hydrogen uptake maintained almost the same value.

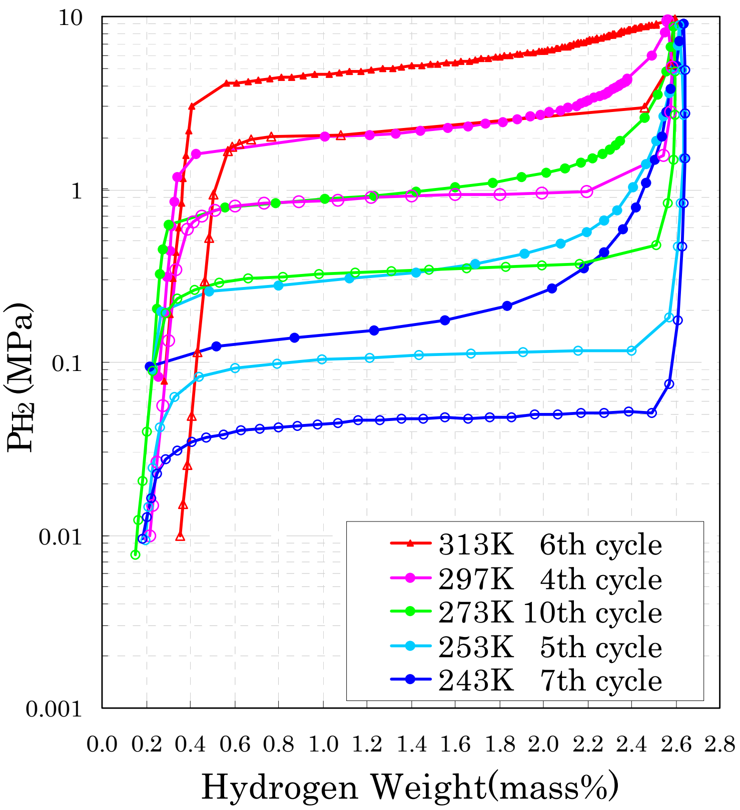

Figure 2: PCT curves of 75at%V-5at%Ti-Cr as-cast sample measured at 243 K to 313 K.

Figure 3 shows relationship of hydrogen desorption pressure and Ti content of 75at%V-Ti-Cr samples at 273K along with those of 60at%V-Ti-Cr and 80at%V-Ti-Cr. Open diamond marks in Fig.3 refer to samples with poor hydrogen storage capacity. This deterioration of hydrogen storage capacity for alloys with low Ti content might be attributed that Cr content of the sample might have exceeded "limitation line" as mentioned above. From the results of Fig.3, in V-Ti-Cr alloys, further increment of hydrogen desorption pressure without declination of hydrogen storage capacity is quite difficult without introducing of substitutional element(s).

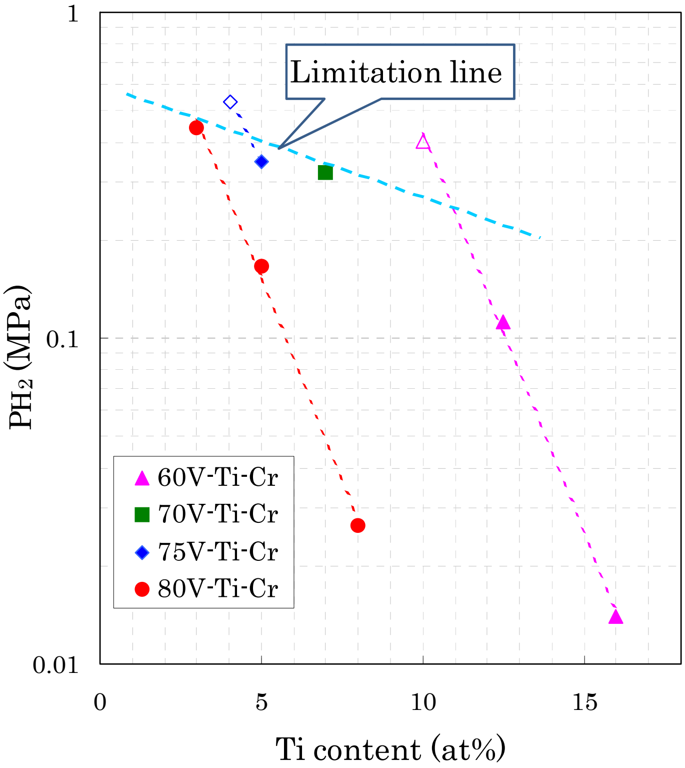

Figure 3: Relationship of hydrogen desorption pressure and Ti content of 75at%V-Ti-Cr samples at 273 K along with those of 60at%V-Ti-Cr and 80at%V-Ti-Cr. (Open marks refer to sample with poor capacity)

3.2 Hydrogen storage properties of 75at%V-Ti-Cr-Al alloys

Figure 4 shows PCT curves of 75at%V-xat%Ti-Cr-1Al% samples (x=3 to 5) measured at 273K. Compared to 75at%V-4at%Ti-Cr sample, hydrogen storage properties of 75at%V-4at%Ti-Cr-1at%Al, such as hydrogen storage capacity and hydrogen desorption pressure, were improved significantly. But declination of hydrogen storage capacity is observed in this sample, so, in the case of 75at%V-Ti-Cr-1at%Al samples, limitation line lies between 75at%V-4at%Ti-Cr-1at%Al and 75at%V-5at%Ti-Cr-1at%Al samples. 75at%V-3at%Ti-Cr-1at%Al showed further declination of hydrogen storage capacity along with increment of hydrogen desorption pressure. This deterioration of hydrogen storage capacity might be attributed to exceeding of “limitation line”.

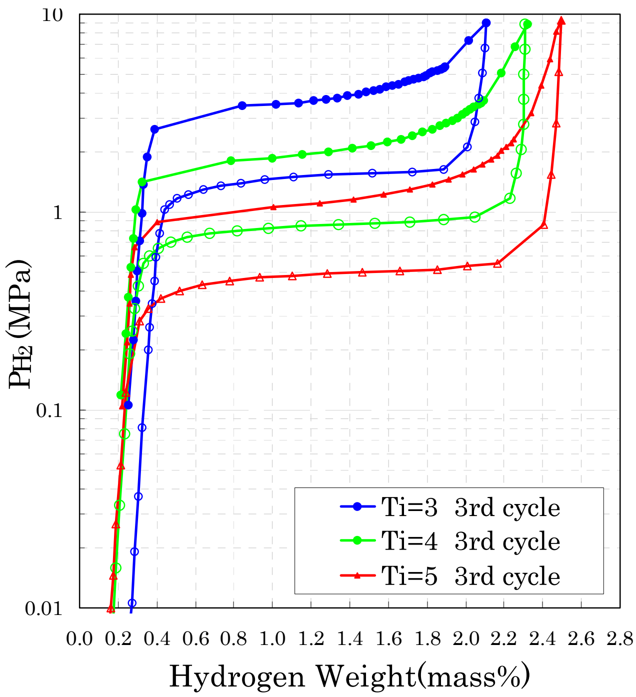

Figure 4: PCT curves of 75at%V-xat%Ti-Cr-1Al% samples (x=3 to 5) measured at 273 K.

Figure 5 shows PCT curves of 75at%V-xat%Ti-Cr-2at%Al samples (x=3 to 5) measured at 273K. 75at%V-4at%Ti-Cr-2at%Al sample shows high hydrogen capacity and improvement of hydrogen desorption pressure. In this 75at%V-Ti-Cr-2at%Al series, limitation line is raised between 75at%V-3at%Ti-Cr-2at%Al and 75at%V-4at%Ti-Cr-2at%Al samples.

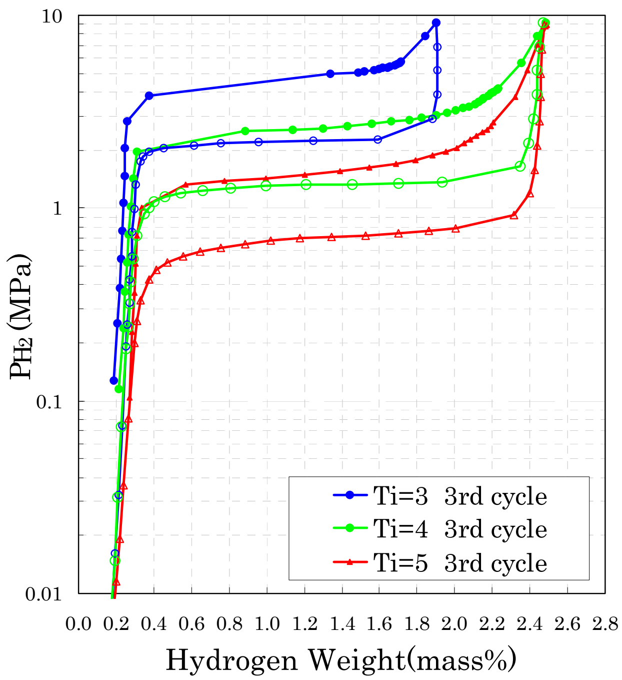

Figure 5: PCT curves of 75at%V-xat%Ti-Cr-2at%Al samples (x=3 to 5) measured at 273 K.

Figure 6 shows PCT curves of 75at%V-xat%Ti-Cr-3at%Al samples (x=3 to 5) measured at 273K. It is quite unique and clearly confirmed that 75at%V-3at%Ti-Cr-3at%Al sample shows high hydrogen capacity and improvement of hydrogen desorption pressure. In this 75at%V-Ti-Cr-3at%Al series, limitation line is raised above 75at%V-3at%Ti-Cr-3at%Al sample.

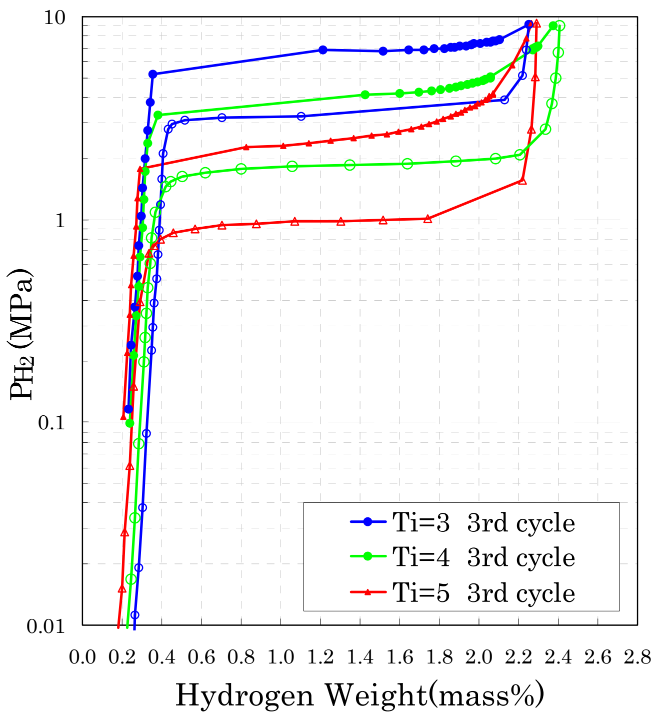

Figure 6: PCT curves of 75at%V-xat%Ti-Cr-3at%Al samples (x=3 to 5) measured at 273 K.

4 Discussion

Figure 7 shows relationship of hydrogen desorption pressure at 273K and Ti content for 75at%V-Ti-Cr, 75at%V-Ti-Cr-1at%Al, 75at%V-Ti-Cr-2at%Al and 75at%V-Ti-Cr-3at%Al samples of this study (open marks in Fig.7 refer to samples with poor hydrogen storage capacity). In 75at%V-5at%Ti-Cr-yat%Al samples (y=0 to 3at%), raising of hydrogen desorption pressure with increment of Al content is observed and thus, introduction of Al of adequate amount is effective method for improvement of hydrogen desorption pressure in this system. Without Al substitution, minimum adequate Ti amount for 75at%V-Ti-Cr is around 5at%. But with introducing and increasing of amount of Al substitution, minimum optimum content of Ti reduced. In the case of sample with 3at%Al substitution, minimum optimum Ti content reduced to around 3at%. From these results mentioned above, introducing of adequate amount of Al substitution are effective for not only raising hydrogen desorption pressure by Al substitution effect itself but also for enhancing limitation, in resulting in enabling alloys with more less Ti composition. With this latter effect, further improvement of hydrogen desorption pressure of V-Ti-Cr-Al alloys could be possible.

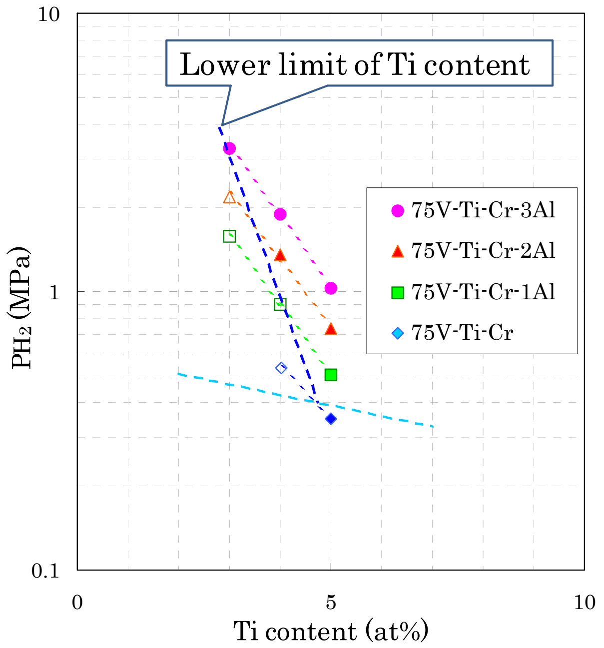

Figure 7: Relationship of hydrogen desorption pressure and Ti content for 75at%V-Ti-Cr, 75at%V-Ti-Cr-1at%Al, 75at%V-Ti-Cr-2at%Al and 75at%V-Ti-Cr-3at%Al samples for 273 K. (Open marks refer to sample with poor capacity)

As summary, figure 8 shows PCT curves of 75at%V-Ti-Cr-Al alloys of various Al content measured at 243K. 75at%V-xat%Ti-Cr-3at%Al (x=3, 4) and 75at%V-4at%Ti-Cr-2at%Al alloys show desorption pressure higher than 0.23Mpa at 243K with large hydrogen capacity.

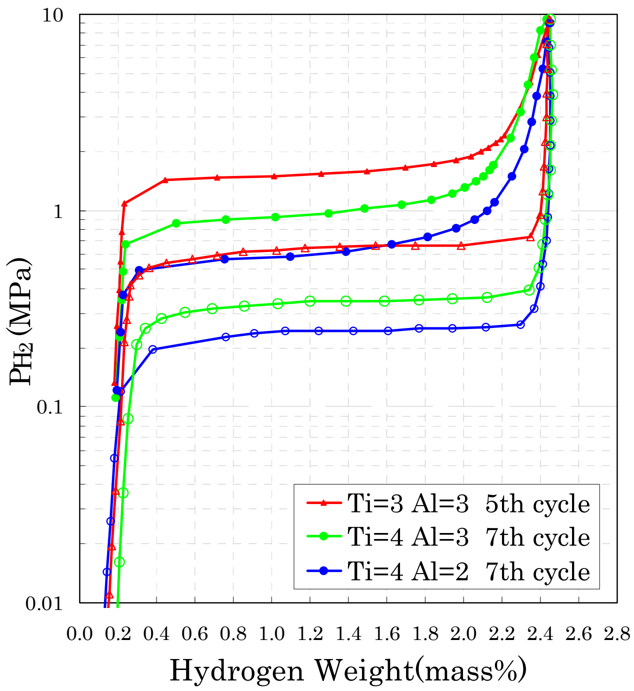

Figure 8: PCT curves of 75at%V-Ti-Cr-Al alloys of various Al content measured at 243 K.

5 Conclusion

In this study, effects of Ti/Cr on 75at%V and substitutional element of Al in 75at%V-Ti-Cr-Al alloys were investigated with prospect of increment of hydrogen desorption pressure for improvement of cold starting capability of high-pressure MH tanks.

The 75at%V-5at%Ti-Cr sample showed flat plateau region and relatively large hydrogen storage capacity. But 75at%V-4at%Ti-Cr sample showed declination of hydrogen storage capacity. So, limitation line is located between 4at%Ti and 5at%Ti in 75at%V-Ti-Cr series.

In 75at%V-5at%Ti-Cr-yat%Al samples (y=0 to 3at%), raising of hydrogen desorption pressure with increment of Al content is observed and thus, introduction of Al of adequate amount is effective method for raising hydrogen desorption pressure in this system. Without Al substitution, minimum adequate Cr amount for 75at%V-Ti-Cr is around 5at%. But with introducing and increasing of amount of Al substitution, minimum allowed Cr content reduced and in the case of sample with 3at%Al substitution, minimum optimum Ti content reduced less than 3at%. From these results mentioned above, introducing of adequate amount of Al substitution are effective for not only raising hydrogen desorption pressure but for also enhancing limitation and enabling alloys with more less Ti composition. With this latter effect, further increment of hydrogen desorption pressure of V-Ti-Cr-Al alloys could be possible. As V-Ti-Cr-Al system, introducing of adequate amount of Al is quite effective tactics to make alloys high hydrogen desorption pressure that would be effective for improvement of cold starting capability of high-pressure MH tank for on-board usage.

Acknowledgement

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