

The role of Fe on the improvement of hydrogen absorption and desorption cyclic stability in $V_{0.65-x}Ti_{0.12}Cr_{0.23}Fe_x$ ($x=0, 0.01$)

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Summary

It has been known that materials with poor hydrogen absorption and desorption cyclic properties show a significant diffraction peak broadening over cycles. This indicates that the development of structural defects or disorders or reduction in crystallite size is somehow closely related to degradation in reversible hydrogen capacity. However, detailed mechanism behind this phenomenon hasn't been unraveled yet. In this study, we are particularly interested in elucidating the origin of the poor cyclic properties of V-based bcc alloys and provide a possible way to improve them by investigating the local structure of $V_{0.65-x}Ti_{0.12}Cr_{0.23}Fe_x$ ($x=0, 0.01$) using a powerful local structural probing techniques, X-ray absorption fine structure (XAFS).

key words:

Hydrogen storage materials, local structure, V-based bcc alloys, XAFS

1. Objectives

V-based bcc alloy is considered as one of the most realistic hydrogen storage materials for on-board application because of higher volumetric density of hydrogen. Considering the relatively high cost of V, it is more favorable to reduce the amount of V in alloys. In general, however, low-V containing alloys show a considerable reduction in reversible hydrogen capacity over hydrogen absorption and desorption cycles. Although an excellent cyclic stability is one of important prerequisites for fuel cell application, the origin of such poor cyclic stability in V-based bcc alloys hasn't been fully elucidated yet.

It has been recently reported that the hydrogen absorption-desorption cyclic stability of $V_{0.65}Ti_{0.12}Cr_{0.23}$ was dramatically improved by substituting a small amount of Fe (1 at.%) for V [1]. After 100 cycles, the hydrogen capacity of $V_{0.64}Ti_{0.12}Cr_{0.23}Fe_{0.01}$ remained 97% of the initial value while that of $V_{0.65}Ti_{0.12}Cr_{0.23}$ dropped to 88% despite the fact that Fe is the unfavorable element for hydrogen storage. This would be an excellent model system for our study. By using XAFS, we would like to resolve difference in the local environment of each composed element in $V_{0.65}Ti_{0.12}Cr_{0.23}$ and $V_{0.64}Ti_{0.12}Cr_{0.23}Fe_{0.01}$ including the coordination number. We are particularly interested in difference between the local environment of Fe from that of other composed elements (V, Ti, Cr) and the evolution of their local environment over cycling. At the end, we would like to combine information obtained from other local probing techniques such as the atomic pair distribution function (PDF) [2] to elucidate the role of Fe in the improvement of the cyclic stability.

2. Methods

XAFS experiments were carried out at the bending magnet beamline BL14B1 at SPring8. The V, Ti and Cr *K*-edge XAFS spectra of 1st and 10th cycled $V_{0.65}Ti_{0.12}Cr_{0.23}H_2$ and $V_{0.64}Ti_{0.12}Cr_{0.23}Fe_{0.01}H_2$ were collected in a transmission mode. The Fe *K*-edge spectrum was measured in a fluorescence mode using a 19-element pure-Ge solid state detector (SSD). All measurements were conducted at room temperature. Extended X-ray absorption fine structure (EXAFS) data reduction was done by using the ATHENA program [3].

3. Results and Discussion

Figure 1 shows the Fourier transform (FT) intensities of k^3 -weighted EXAFS function for $V_{0.65}Ti_{0.12}Cr_{0.23}H_2$ and $V_{0.64}Ti_{0.12}Cr_{0.23}Fe_{0.01}H_2$. Only the first peak was shown. This peak provides the information of the first nearest neighbors of each element. FT intensities of EXAFS spectrum clearly show that the first nearest neighbor atoms of Ti is slightly further apart than those of Cr and V and Cr and V has a similar average nearest neighbor distance. This tendency was observed in all samples regardless of cycling numbers. For the case of $V_{0.64}Ti_{0.12}Cr_{0.23}Fe_{0.01}H_2$, Fe has the shortest average nearest neighbor distance and seems to have a wide inter-atomic distance distribution. Although no appreciable difference between $V_{0.65}Ti_{0.12}Cr_{0.23}H_2$ and $V_{0.64}Ti_{0.12}Cr_{0.23}Fe_{0.01}H_2$ was seen by eyes, more detailed analysis would provide much more information of these materials.

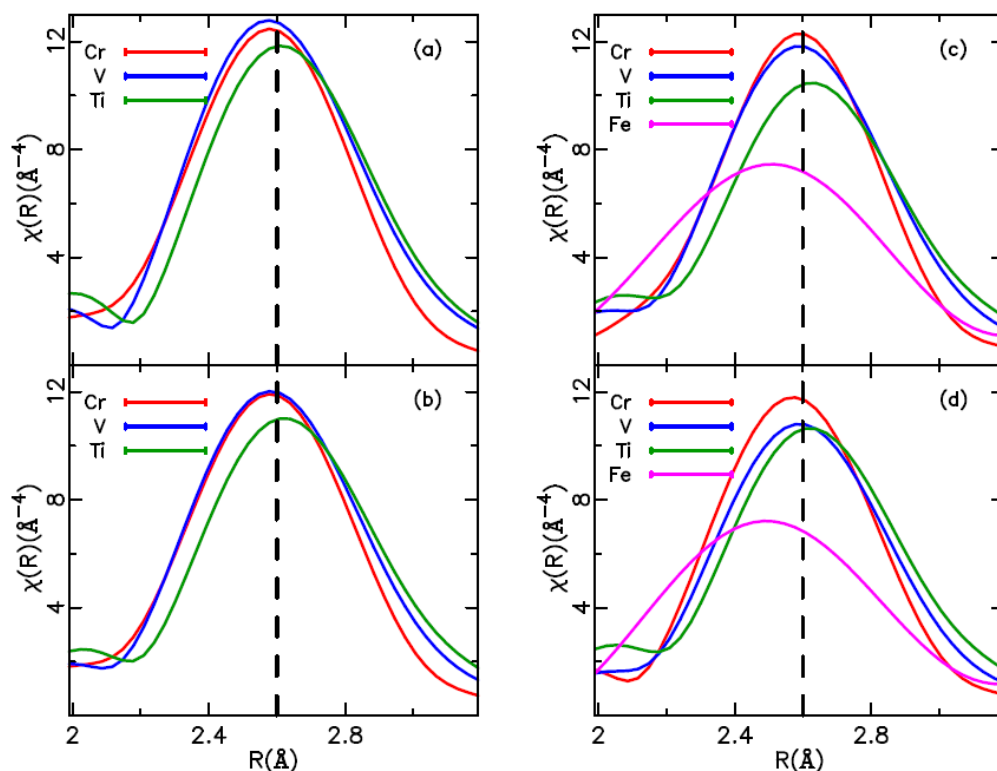


Figure 1 The 1st peaks of the Fourier transform intensities of k^3 -weighted EXAFS function for (a) 1st and (b) 10th cycled $V_{0.65}Ti_{0.12}Cr_{0.23}H_2$ and (c) 1st and (d) 10th cycled $V_{0.64}Ti_{0.12}Cr_{0.23}Fe_{0.01}H_2$. Dashed lines are for guidance.

Previously, we collected the synchrotron X-ray data of 1st and 10th cycled $V_{0.65}Ti_{0.12}Cr_{0.23}H_2$ and $V_{0.64}Ti_{0.12}Cr_{0.23}Fe_{0.01}H_2$ for the PDF study, which is another powerful local structural probing technique. From the

PDF study it was found that PDF peaks get broader with hydrogen cycling and this effect is especially significant for the non-Fe containing composition. We believe that the broadening of PDF peaks is due to the formation of structural defects such as dislocations. Other than broadening of peaks, no noticeable change in the local structure was observed. This can be seen from the almost unchanged first PDF peaks of the 1st (blue line) and 10th (red line) cycled samples in Figure 2. This suggests that Fe somehow suppresses the defect formation during cycling. Therefore, element-specific local structural information obtained from EXAFS spectra would help us to understand why the Fe-containing composition is more resistant to the defect formation and ultimately how this leads to improvement in the cyclic stability.

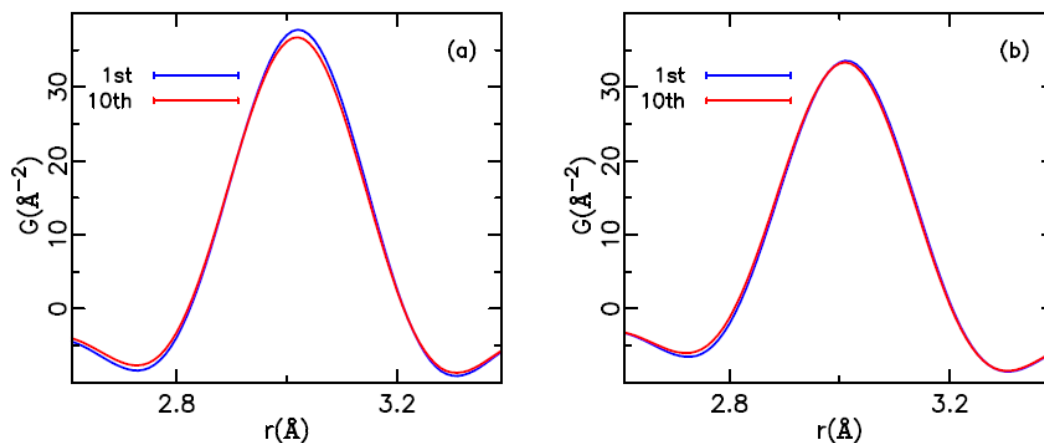


Figure 2 The first X-ray PDF peaks of (a) $V_{0.65}Ti_{0.12}Cr_{0.23}H_2$ and (b) $V_{0.64}Ti_{0.12}Cr_{0.23}Fe_{0.01}H_2$. Data of the first and 10th cycled samples were plotted in blue and red lines, respectively.

4. References

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