

4-7 Mechanism of Performance Improvement of Hydrogen Storage Materials — Structural Determination of Additives by X-ray Absorption Spectroscopy —

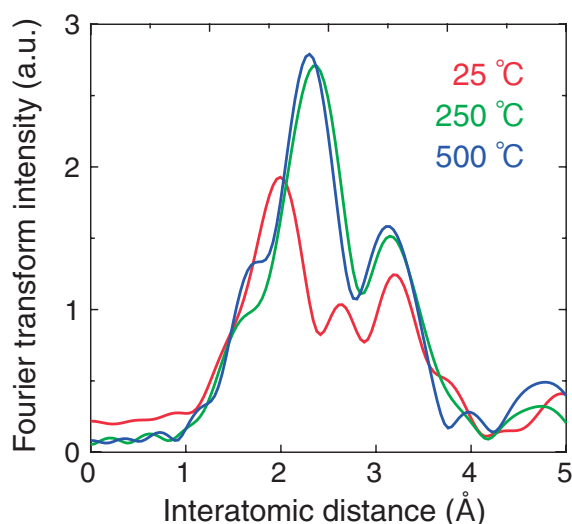


Fig.4-13 Local structure around Ti

The X-ray absorption fine structure (XAFS) technique is a powerful tool for the element-selective determination of the local structure. This figure shows the local structure of the Ti additive in $\text{Mg}(\text{BH}_4)_2$. The Fourier transform spectrum shows a large peak corresponding to the location of the coordination atoms. This provided element-selective information about the local structure.

Development of advanced onboard hydrogen storage materials with high hydrogen gravimetric density is urgently required. Magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$), which has a hydrogen density of 14.9 wt%, has been regarded as one of the potential hydrogen storage materials. Its potential applications are, however, restricted by its high dehydrogenation temperature ($>300\text{ }^\circ\text{C}$). In a recent study, it has been observed that Ti additives lower the initial dehydrogenation temperature of $\text{Mg}(\text{BH}_4)_2$. This result motivated us to clarify the effect of the addition of Ti on the dehydrogenation reaction of $\text{Mg}(\text{BH}_4)_2$.

In this study, we observed the local atomic structure around Ti compounds by the X-ray absorption fine structure (XAFS) technique. Local structural analysis of Ti additives in $\text{Mg}(\text{BH}_4)_2$ indicated that structural transformation occurs between 25 and 250 $^\circ\text{C}$ (Fig.4-13). It was important to confirm whether this structural transformation was related to the dehydrogenation reaction.

In order to study the correlation between the structure and the dehydrogenation properties, the XAFS and the dehydrogenation intensity were simultaneously observed (Fig.4-14). The Ti *K*-edge energy shift showed an abrupt change in the range 100~150 $^\circ\text{C}$, indicating a structural

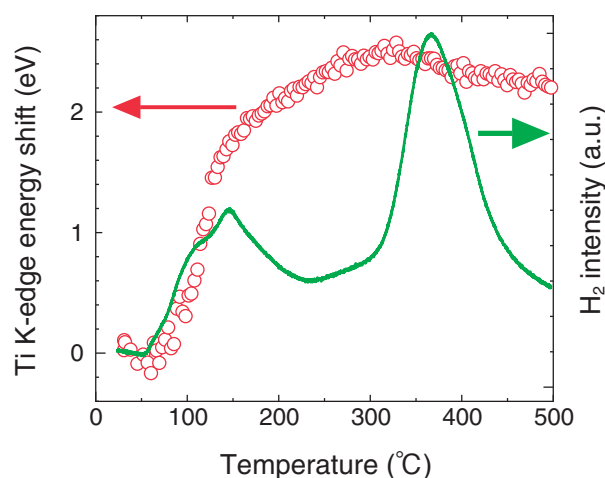


Fig.4-14 Ti *K*-edge energy shift and dehydrogenation curve

Continuous XAFS measurement enables us to simultaneously observe the local structural change in Ti additives and the dehydrogenation curve. This figure shows that the structural change in Ti additives is directly related to the first dehydrogenation peak.

change in the Ti compound. This temperature range was almost the same as the width of the first peak in the dehydrogenation curve. On the other hand, the *K*-edge energy shift did not show any change at around 360 $^\circ\text{C}$, where the main peak in the dehydrogenation curve was observed. As a result, we wholly concluded that the local structural change in the Ti compound was directly related to the first dehydrogenation peak, which appeared in the range 100~150 $^\circ\text{C}$ and was not strongly influenced by the main dehydrogenation peak at 360 $^\circ\text{C}$. The dehydrogenation peak in the range 100~150 $^\circ\text{C}$ was revealed to be due to the dehydrogenation reaction of $\text{Ti}(\text{BH}_4)_3$. For this reason, addition of the Ti compound brought about a decrease in the dehydrogenation temperature. $\text{Ti}(\text{BH}_4)_3$ was converted to TiB_2 , which is more stable.

Simultaneous measurement of the local structure of the Ti compound and the dehydrogenation curve for the hydrogen storage material clearly demonstrates the correlation between the structural change in the additive and the chemical reaction. We believe that such simultaneous measurements would reveal the key component for the development of more efficient hydrogen storage materials.

Reference

Matsumura, D. et al., Correlation between Structure of Titanium Additives and Dehydrogenation Reaction of Magnesium Borohydride Studied by Continuous Observation of X-ray Absorption Spectroscopy, *Materials Transactions*, vol.52, no.4, 2011, p.635-640.