学位論文の要旨

論文題目 （英文）Critical conditions of degradation during thermochemical hydrogen compression by $V_{20}Ti_{32}Cr_{48}$ alloy
（和文）$V_{20}Ti_{32}Cr_{48}$合金による熱化学水素圧縮中の劣化の臨界条件

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論文の要旨

Hydrogen as a clean energy attracted a lot of attentions and becoming a promising technology to help us to build a sustainable and renewable society in the future. The development of excellent hydrogen storage materials and the evaluation of their hydrogen storage behaviors are very important steps for establishing basic infrastructure and hydrogen industrial chain. Disproportionation and phase separation of hydrogen storage materials are big issues that occurred under extreme pressure and temperature conditions during prolonged hydrogen compressor cycles, which make metal hydrides inactive and reduce their compression efficiency. Thus, it is important to identify boundary conditions to avoid such unwanted phase separation. However, no investigation related to this problem has been carried out by practical experiment so far. Thus, in this thesis, systematically investigations were conducted to find the critical conditions of hydrogen compressor cycle test for $V_{20}Ti_{32}Cr_{48}$ alloy as a model system for the first time.

The initial hydrogen amount was precisely fixed according to pressure composition isotherm(PCI) measurements of $V_{20}Ti_{32}Cr_{48}$ alloy: four different points were selected as starting points according to different hydrogen content on desorption curve, namely, solid solution (0% β-phase), half saturated (50% β-phase), 75% saturated (75% β-phase), and fully saturated (100% β-phase). Hydrogen compressor cycle tests were conducted for 25 cycles with same amount of $V_{20}Ti_{32}Cr_{48}$ alloy with various hydrogen content and temperature conditions individually. Main finding and results are summarized as follows:

First of all, the influence of hydrogen content on the cyclic durability of $V_{20}Ti_{32}Cr_{48}$ alloy was given the priority to be studied. It was found that after 25 hydrogen compressor cycles up to higher temperature (100% saturated up to 240 ^{o}C, others up to 260 ^{o}C), the hydrogen storage properties of $V_{20}Ti_{32}Cr_{48}$ alloy with fully and 75% saturated H_2 were deteriorated a lot and 20.2% and 22.7% reduction in hydrogen storage capacity was observed respectively with sloppy plateau region. The increased slope indicated the possibility of multiple phases present in the sample, which dramatically reduced hydrogen compression efficiency. On the other hand, $V_{20}Ti_{32}Cr_{48}$ alloy with 50% saturated H_2 and solid solution, the hydrogen storage capacity losses were found to be negligible, 5.0 and 4.0% respectively, with similar slope in PCI curves, indicating the intact hydrogen compression efficiency during cycling. Structure and morphology changes measured by XRD and SEM provided the direct evidence that the disproportionation and phase separation occurred in the sample of $V_{20}Ti_{32}Cr_{48}$ alloy with fully saturated H_2 from the appearance of multiple and overlapped peaks in forms of $VH_{0.88}$ and $TiH_{0.66}$. In addition, the sample with initial 75% saturated H_2 for hydrogen compressor at 260 ^{o}C undergone through a reduction in capacity, however no big changes in peaks position was observed except the alteration in peak width and intensity which might be caused by stress/strains. Thus it is concluded that the phase separation is not the only reason for capacity fading, but the stress/strain generated in the material during the compressor test may also be responsible for this degradation. Based on the above results, lower hydrogen content was found to be better for hydrogen compressor cyclic durability of $V_{20}Ti_{32}Cr_{48}$ alloy whereas the large amount of stored hydrogen in alloy led to the reduction of reversible hydrogen storage capacity during hydrogen compression process for practical usage. This resulted in lowering compression efficiency and the increase in the maintenance cost.

Besides the hydrogen content influence on the cyclic durability of $V_{20}Ti_{32}Cr_{48}$ alloy, temperature impact should also not be negligible. Thus, temperature influence on the cyclic durability for $V_{20}Ti_{32}Cr_{48}$ alloy employed for compressor was also investigated for the maximum temperature as 240, 200, 175, 150, and 100 °C individually. The PCI curves of $V_{20}Ti_{32}Cr_{48}$ alloy, fully saturated with H_2 and cycled for hydrogen compressor up to 240 °C and 200 °C showed significant hydrogen storage capacity loss up to 20.2% and 17.9% respectively, revealing the disproportion and degradation of the materials. On the other hand, the same alloy cycled up to 175, 150 and 100 °C showed little hydrogen capacity losses around 4 to 5% with similar PCI slope and stable hydrogen storage capacity. The appearance of the new phases, $VH_{0.88}$ and $TiH_{0.66}$ in XRD pattern, and the Ti-rich phase found by SEM-EDS results clearly showed the disproportionation of $V_{20}Ti_{32}Cr_{48}$ alloy with fully saturated H_2, which is caused by thermodynamically favored reactions. In addition, 200 °C may not be high enough to lead such kind of reaction but could generate lattice stress / strains in the alloy which causes the reduction in hydrogen storage capacity after compressor cycling test. Thus lower temperature was found better for the compressor cyclic durability of $V_{20}Ti_{32}Cr_{48}$ alloy. Whereas, higher temperature resulted in the degradation of this alloy and reduced the hydrogen storage capacity during practical usage.

In summary, hydrogen content as well as temperature both play an important role in the disproportionation processes. The threshold about hydrogen content and temperature of $V_{20}Ti_{32}Cr_{48}$ alloy for hydrogen compressor without disproportionation were identified as 75% and 200 °C respectively. Operation conditions should not be beyond these threshold values if we want to use $V_{20}Ti_{32}Cr_{48}$ alloy for hydrogen compressor safely and efficiently. This methodology can be employed to be used with other materials to identify the critical conditions required for their safer and stable operation during hydrogen compressor cycling.