界面に着目した 金属-水素系の材料設計
ー Mg、Y および Zr 基複合材料の生成と水素化特性ー*

折茂慎一**

広島大学大学院生物圏科学研究科

Interfacial Materials Design for Metal-Hydrogen System
— formation and hydriding properties of the Mg-, Y- and Zr-based composite materials —

Shin-ichi Orimo

Graduate school of Biosphere Sciences, Hiroshima University,
Higashi-Hiroshima 739, Japan

要　旨

Much attention have been paid to the design of composite materials to achieve some requirements on material properties, especially in researches on structural materials. Thus the interface science and engineering on structural materials have been developed to microscopically understand the interface-phenomena; e.g. diffusion of composed elements, formation of interface phases, or phase transformation at interfaces.

For the metal-hydrogen system as functional materials, the design like compaction with binding phases (mainly pure metals such as Cu, Al or Ni) were practically studied so far. Unfortunately, almost all researchers have not focused on the studies about relations between the interface-phenomena and the hydrogen-related reactions. Such relations have been mainly treated only as fundamental problems of "hydrogen trapping" or "hydrogen embrittlement".

However, the current studies both on the composite (multi-phase) materials for hydrogen storage and on the processing of the advanced materials with hydrogen indicate that the interface-phenomena dominantly affect their functional and structural properties. The relations between the interface-phenomena and the hydrogen-related reactions should be investigated in details as a new direction of materials design technique; to effectively

---

広島大学総合科学部紀要Ⅳ理系編、第21巻（1995）

*広島大学審査学位論文
　口頭発表日：1995年２月15日、学位取得日　1995年３月24日

**現在の所属　日本学術振興会特別研究員（P.D.広島大学総合科学部助手）

improve the material properties of the metal-hydrogen system.

In the present thesis, therefore, the interfacial materials design focused on the solid-solid interface was applied to the investigation of the metal-hydrogen system. The purposes of the thesis are as follows:

Ⅰ) Study on the composite materials for hydriding reactions;
to clarify the interface-phenomena during heat treatment, and moreover, to investigate the effects of their interface-phenomena on "kinetical and thermodynamical properties for hydride formation", "interdiffusion of hydrogen atoms" and "practical durability for cyclic hydriding reactions".

Ⅱ) Study on the hydrogen induced interface-phenomena;
to clarify the mechanism of "hydrogen enhanced powder reaction" and "reactive mechanical grinding" under hydrogen atmospheres, and moreover, to investigate the hydriding properties of the composite particles synthesized by their induced phenomena.

Through the characterizations of the composite materials relating to the Mg-, Y- and Zr-based intermetallic compounds, the interfacial materials design for/by the hydrogen-related reactions was investigated under the above purposes. The results obtained are summarized as follows:

In chapter 3, the composite materials (Zr-based compound/Mg), composed of $ZrCr_2$ or $ZrFe_{1.4}Cr_{0.6}$ as a host hydriding phase and elemental Mg as a chemical binding phase, were prepared under various heat treatment conditions. The formation/reduction of host-Mg interface oxides, the diffusion of composed elements across the host-Mg interface, and their effects on the hydriding properties of the host phases were investigated. Microscopic observations indicate that the heat treatment at 773 K not only promotes the reduction of host phase oxides at the interface owing to the MgO formation, but also helps to form the diffusion-bonded interfaces. Because of these interface-phenomena, the host phases in the composite materials promptly react with gas phase hydrogen without any activation treatments. Furthermore, they exhibit high durabilities for cyclic hydriding reactions. The mechanism for improving the hydriding properties of the host phases can be also applied for the Ti-based multi-component system. The hydrogen dissolved phases of $ZrCr_{0.6}Fe_{1.4}$ in the composite materials are continuously unstabilized with increasing the heat treatment temperatures.

Next in chapter 4, the Cu-doped composite material ($ZrCr_{1.8}Cu_{0.3}$/Mg) was prepared to study both the formation of the interface Mg_2Cu phase and its effect on the low-temperature hydriding of the Mg phase. As a result of the diffusion of Cu mainly in grain boundaries of the host compound phase, the Mg_2Cu phases are formed along the host-Mg interface with the layer-like microstructure by the heat treatment at 773 K; while with the rod-like eutectic microstructure at 873 K. The MgH_2 formation owing to the interdiffusion of hydrogen atoms from the host compound phase is confirmed from both in-situ thermal and crystallographical analyses. Moreover, this interdiffusion is found to be enhanced in the eutectic interface. Consequently, the interphase boundaries of Mg_2Cu/Mg eutectic are deduced to act both as diffusion passes for hydrogen atoms from the host compound into the Mg phases, and as stable nucleation sites for MgH_2.

In chapter 5, the composite particles (Mg_2Ni/Y-based compounds) were synthesized as a result of the phase modification in the size of micrometer by the "hydrogen induced powder reaction" of the Mg-YNi_2 mixture. The synthesis processes and hydriding properties of synthesized particles were investigated. Consequently, the following phenomenon is confirmed to be essential: YNi_2 is first activated by the disproportionation reaction under hydrogen atmospheres; and then the evaporated Mg, which occurs during the dehydriding, adheres to the surface of the activated YNi_2 and accelerates the powder reaction to form the Mg_2Ni phase at their interface. In the synthesized particles, Mg_2NiH_4 is formed even at low temperatures less than 373 K, indicating both the reduction of host phase oxides owing to the Y_2O_3 formation and the spillover phenomenon of hydrogen atoms.

Finally in chapter 6, the Zr-based composite particles were synthesized by the "reactive mechanical grinding" of ZrNi under hydrogen atmospheres. Each particle was composed of amorphous and crystalline hydride phases as a result of the structural modification in the size of nanometer. In addition to the grinding processes, spacious characterizations and the interface-phenomena of the synthesized particles were investigated. Depending on partial pressures of hydrogen, the hydride phases (ZrNiH and/or $ZrNiH_3$) are formed to lower the free energy of the compound and particle sizes are reduced at the beginning of the grinding. Then, the amorphous phase grows up with progression of the grinding. The measurements of small angle neutron scattering indicate that the fine structures of nearly 6 nm are formed in the particles ground under 1. 0 MPa of pure hydrogen even 20 hours. The grinding also enhances the decomposition to form ZrH_2. In the synthesized fine particles, the dehydriding of the ZrH_2 phase progresses even at low temperatures around 750 K, which is caused by the preferential crystallization accompanied by the recombination reaction of the amorphous hydride phase in each particle.

On the basis of the findings above summarized, the interfacial materials design in present thesis will be further progressed as a new direction of materials design technique for the metal-hydrogen system. Parts of this thesis were already (will be) published as follows: Chapter 3 ; (1), (2), (3) :
Chapter 4 ; (3), (6) : Chapter 5 ; (4) : Chapter 6 ; (5).

関 連 文 献

(1) "Development of new composite material for hydrogen storage using Mg as a binder" S. Orimo, H. Fujii, K. Yamamoto, K. Yoshimoto and T. Ogasawara, *J. Jpn. Inst. Met.*, *54* (1990) 1154 (in Japanese).

(2) "New composite materials for hydrogen storage using magnesium as a binder" H. Fujii, S. Orimo, K. Yamamoto, K. Yoshimoto and T. Ogasawara, *J. Less-Common*

Met., 175 (1991) 243.

(3) "Low temperature formation of MgH_2 in $Ti_{0.6}Zr_{0.4}Mn_{0.8}CrCu_{0.2}/Mg$" S. Orimo, M. Tabata and H. Fujii, *J. Alloys Comp., 203* (1994) 61.

(4) "Synthesis of fine composite particles for hydrogen storage, starting from $Mg\text{-}YNi_2$ mixture" S. Orimo, H. Fujii and M. Tabata, *J. Alloys Comp., 210* (1994) 37.

(5) "Reactive mechanical grinding of ZrNi under various partial pressures of hydrogen" S. Orimo, H. Fujii and M. Yoshino, J. *Alloys Comp., 217* (1994) 287.

(6) "Investigation of interfacial materials design - the effect of interface microstructure in $ZrCr_{1.8}Cu_{0.3}/Mg$ on hydrogen interdiffusion for MgH_2 formation - " S. Orimo, H. Fujii and S. Horie, *International Symposium on Metal-Hydrogen Systems, Fujiyoshida, Yamanashi, Japan, Nov. 1994, J. Alloys Comp.*, (1995) in press.