平成 17 年 1 月 11 日

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論　文　要　旨(博士)

論文題目	Phase Relation, Thermodynamic Properties and Electronic Structure of Hydrogen Storage Alloys (水素吸蔵合金の相関係、熱力学特性及び電子構造)

Zirconium-based AB_2 alloys with C14 Laves phase structures have been brought into focus of attention recently due to their potential ability as hydrogen storage media and electrode materials for Ni-MH batteries. $ZrMn_2$ is a representative one among them, but its hydride is too stable to be of practical significance owing to low equilibrium pressures. Although many studies have been conducted to increase the equilibrium pressures by partial substitution of the A(Zr) or B(Mn) element and substitution of both the elements to form $Ti_xZr_{1-x}(Fe_yMn_{1-y})_z$, some interesting aspects still remain unanswered both experimentally and theoretically. This thesis is intended to provide a survey of the effects of element substitution on the thermodynamic stability of $ZrMn_2$ trough discussing the correlations of systematical experimental results and theoretical calculations.

This thesis comprises six chapters. Chapter 1 introduced the background and fundamental theory of hydrogen storage alloys. Past researches were reviewed and the objectives of this thesis were then presented. Chapter 2 dealt with effects of partial substitution of B element (Mn) by Fe to form $Zr(Fe_yMn_{1-y})_2$ with y = 0, 0.2, 0.5, 0.7, 0.8. Change of equilibrium pressures, differential heats on hydriding and the variation of crystal structure with the iron content were studied by isothermal-calorimetric measurement and X-ray diffraction with the samples in an inert atmosphere. Then, effects of partial substitution of A element (Zr) by Ti to form $Ti_xZr_{1-x}Mn_2$ with x = 0, 0.1, 0.2 and 0.3 were discussed in Chapter 3, where the crystallographic and thermodynamic aspects were characterized by the XRD Rietveld analysis and isothermal measurement. The best fitting in the Rietveld analysis revealed that Ti atoms preferentially occupied the Zr sites. In order to theoretically elucidate the relation between element substitutions and hydrogen absorption characteristics, accurate crystal data on $Ti_xZr_{1-x}Mn_2$ alloys and relevant hydrides, which were determined by the XRD Rietveld analysis and experimental thermodynamic data in Chapter 3, were used to discuss the thermodynamic stability of the hydrides in terms of the bond order differences between the alloys and the hydrides calculated by the DV-X_α cluster method as presented in Chapter 4. Thermodynamic stability of $Ti_xZr_{1-x}Mn_2$ hydrides was able to be predicted using a proposed ratio, *R*, of the sum of Zr(Ti)-Mn and Zr(Ti)-Zr(Ti) bond order differences to the Mn-Mn bond order difference, where the differences were taken between the alloys and the corresponding hydrides. It was found that experimental enthalpy changes on hydriding linearly increased (absolute values decreased) with *R*. Approximate values for *R*, which were calculated with lattice expansion on hydriding neglected, were also discussed in Chapter 4. B site (Mn site) substitution effects were similarly discussed by the same method in Chapter 5 with the clusters somewhat varied. Thermodynamic stability of $Zr(Fe_yMn_{1-y})_2$ hydrides was fairly interpreted by the DV-X_α method using the proposed parameter *R*. Finally, Chapter 6 summarized the results obtained in the present research.