Hydrogenation-induced microstructure changes of AB$_2$ Laves compounds
(水素化による **AB$_2$** ラーベス化合物の微細構造変化)

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Abstract

Laves compounds have been considered as one of the prominent candidates of hydrogen storage materials, since they have relatively good hydrogen capacity compared to AB$_5$ type compounds such as LaNi$_5$ and also can charge/discharge hydrogen under ambient conditions. Laves AB$_2$ structures are effectively viewed as tetrahedral close-packing of constituent A and B atoms, where their atomic size ratio, i.e., R$_A$/R$_B$ (R denotes the relevant atomic radius) plays a critical role for a stability of the compounds. Empirically, hydrogen storage AB$_2$ compounds are designed toward less-dense packing conditions in order to incorporate hydrogen atoms into interstitial spaces within the structure. However, there is a definite limit for this strategy; it is a well-known phenomenon that the Laves structures are transformed into amorphous during hydrogenation when the R$_A$/R$_B$ exceeds critical value of approximately 1.37. This is referred to as hydrogen-induced amorphization (HIA), which was indeed confirmed for a large number of AB$_2$ compounds with C15-type cubic structure. Therefore, understanding microscopic origin of the HIA phenomenon is an important key to improve furthers the hydrogen-storage ability of the Laves compounds. So far, HIA have been studied mostly by X-ray diffraction. In the present study, we investigate the details of microstructural changes of Laves RENi$_2$ (RE = Pr, Gd, La) compounds using mainly conventional transmission electron microscopy observation (CTEM) and scanning transmission electron microscopy (STEM) equipped with electron energy loss spectrum (EELS) detector.

In chapter 1, general background of the present study is introduced. Metal hydride the most prominent type of hydrogen storage is explained briefly. Characteristics of Laves and pseudo-Laves compounds are elucidated including HIA.

In chapter 2, experimental procedures are described. For sample synthesis, arc-melting was used for RENi$_2$ (RE = Pr, Gd, La) and induction melting for pseudo-Laves (Pr$_{1-x}$Mg$_x$)Ni$_2$ compounds. Sieverts apparatus was used to measure hydrogen capacities of each compound. To investigate the structural changes of Laves and pseudo-Laves compounds, (S)TEM observation was performed mainly.

In chapter 3-5, the main results of the present study are described. Chapter 3 contains investigation of microstructure changes of Laves $RENi_2$ (RE = Pr, Gd, La) compounds. It is turned out that hydrogenation-processed microstructures of $RENi_2$ compounds, supposed to be amorphized according to their R_A/R_B, are not pure amorphous structure but composed of Ni nanocrystals embedded in an amorphous matrix of PrH_2. On this basis, we propose hydrogenation-induced micro-phase separation (HIMPS), which provides a more precise/correct view of the phenomenon that has so far been referred to as HIA.

For hydride properties, the amounts of hydrogen absorption of Laves $RENi_2$ compounds were proportional to the atomic size ratio (R_A/R_B), since the interstitial space increases with R_A/R_B. But most of absorbed hydrogen cannot be desorbed due to HIA (i.e, HIMPS in the present study). It seems that the entire amorphization occurred based on X-ray diffraction patterns of Laves $RENi_2$ compounds. However, the electron diffraction patterns reveal significant features, which are hardly detected by X-ray diffraction. For the hydrogenated Laves $RENi_2$ compounds, the patterns are not single halo-ring typical of amorphous structure but definitely composed of multiple rings even after the disappearance of distinct Bragg reflection in the X-ray patterns. This immediately suggests that the structure is not pure amorphous but perhaps microcrystalline states responsible for generating the powder diffraction pattern (i.e., Debye-Scherrer rings). In fact, the multi-rings can be successfully indexed by the crystalline Ni with face-centered-cubic (fcc) structure and the amorphous hydride REH_2. Based on the results, HIMPS can be described as follow;

$$(RENi_2) \xrightarrow{H_2} REH_2 + 2Ni$$

Dark field images obtained from hydrogenated $RENi_2$ compounds directly shows HIMPS phenomenon in Laves phase. By imaging with the several parts of the innermost strong-ring indexed as $(111)_{REH2}$ in the dark field image obtained from $RENi_2$ compound, the contrast always appear to be homogeneous all over the matrix. On the contrary, when the DF images are formed with the second strong-ring indexed as $(111)_{fcc-Ni}$ in the same manner, there appear to be significant variations with strong diffraction contrast. On the basis of these DF-TEM observations, it can be concluded that the microstructure is not pure amorphous but composed of nano-crystals embedded in an amorphous matrix, and they are reasonably identified as fcc-Ni crystals and REH_2 amorphous by indexing the relevant peaks in the electron diffraction pattern. Atomic-resolution TEM/STEM images also confirmed the presence of Ni nanocrystals embedded amorphous structure of hydrogenated Laves $RENi_2$ compounds. Additionally, chemical analysis using EELS was performed to support HIMPS phenomenon. The nanocrystals are identified to be almost pure Ni whose plasmon peak appears at ~25.0 eV. The amorphous matrix reveals two peaks in EEL spectra, which are basically interpreted as due to plasmon excitations (~ 15 eV for Pr as an example) and excitations of the 5p electrons (~ 30 eV

for Pr) of rare-earth metals. It is empirically known that, after hydrogenation (i.e., forming hydrides), the plasmon peak of rare-earth metals generally reveal upward shift about 2~3 eV, a tendency of which is qualitatively understood as a mean increase of valence electrons provided by hydrogen atoms based on nearly free electron approximations. For the present amorphous matrix, the relevant peak shift is in fact observed when compared with the peaks from the original $RENi_2$ compound, supporting that the amorphous matrix is composed of PrH_2.

In chapter 4, we suggest new sight to interpret HIMPS (i.e., HIA in the previous study). So far, HIA phenomenon of Laves compounds has been well described by topological way (i.e., critical point of R_A/R_B, ~1.37). We confirmed that HIMPS occurs instead of HIA in Laves compounds in a previous chapter. Accordingly, the question arises how the micro-phase separation proceeds in Laves compounds. In the present study, we assume that a driving force for the phase separation may be related to enthalpy changes during hydride formation. Miedema's semi-empirical model was used to estimate the enthalpy changes of Laves compounds caused by HIMPS in Laves compounds. The relation of Miedema's model is as follow;

$$\Delta H \ (AB_2H_4) - \Delta H \ (AH_2) + 2\Delta H \ (BH) - (1-F)\Delta H \ (AB_2)$$

where "*1-F*" term is a correction term supplementing the original relation of Miedema's model. The detail explanation of the correction term is described in chapter 4. Since this relation seems to describe phase separation between A and B elements very well, we used this model to estimate the enthalpy changes of Laves compounds induced by HIMPS. As a consequence, we confirmed that the enthalpy change of HIMPS on Laves compounds correlates to the atomic size ratio. It is shown that out that the HIMPS phenomenon can be explained well by thermodynamic criteria as well as topological way. Additionally, we find a particular group of the hydrogenated Laves compounds, which can be explained by thermodynamic criteria but not by topological criteria. After the studies by Aoki *et. al*, which it was immediately pointed out that the R_A/R_B criterion cannot be applied for some of the AB_2 compounds. For some compounds of which atomic size ratio exceeds the critical point of R_A/R_B, HIMPS does not occur at room temperature, but occurs only with heat-assisted condition. We find that three groups of Laves compounds with occurrence of HIMPS are divided by different range of the enthalpy changes estimated by Miedema's model. Accordingly, we assume that HIMPS may occur when the phase separation is rather stable than hydride phase maintain C15 Laves structure. To ensure our assumption, estimation of possible enthalpy changes of the hydride phase with Laves structure is necessary. We use first principles calculation to estimate the enthalpy changes of Laves phase hydride and compare to those of HIMPS. There are three tetrahedral hydrogen sites with different chemical environment (B_4, AB_3, A_2B_2). Generally hydrogen atoms cannot be positioned in the B_4 site since "B" element is non-hydriding element. Thus, we considered two hydrogen sites

(AB_3, A_2B_2) for the calculation. The results were obtained with self-consistent density functional theory (DFT) calculation using the Vienna Ab initio Simulation package (VASP). As a result, we found that until the atomic size ratio up to ~ 1.37, the state of hydride phase maintaining Laves structure is more stable than the state of HIMPS in Laves compounds. In contrast, as the atomic size ratio exceeds the critical point, it reveals that the state of HIMPS is more stable than that of hydride Laves phase.

In chapter 5, we try to find the Laves compounds available for hydrogen charge-discharge. By choosing the element A and B, atomic-size ratio can be controlled. However, a precise control is difficult due to the selecting limitation of elements forming Laves phase. In pseudo-Laves compounds, a precise control of atomic-size ratio is possible by the composition change. Pseudo-Laves ($Pr_{1-x}Mg_x$)Ni_2 (x = 0.3, 0.5. 0.7) compounds were prepared. We checked the occurrence of HIMPS as increasing amounts of Mg in pseudo-Laves ($Pr_{1-x}Mg_x$)Ni_2 compound. When x reaches 0.5, the pseudo-Laves compounds firstly can desorb hydrogen. The atomic size ratio of pseudo-Laves ($Pr_{0.5}Mg_{0.5}$)Ni_2 is 1.37, the exact critical point in a topological criteria. In addition, we presume that at the critical point of HIMPS some microstructural changes may occur. It is found that the precursor structural changes already occur in the hydrogenation-processed ($Pr_{0.5}Mg_{0.5}$)Ni_2 compound. From a combination of STEM and EELS analysis, Ni-rich regions and Pr-rich regions were observed in the ($Pr_{0.5}Mg_{0.5}$)Ni_2 compound. It seems that fcc Ni clusters were formed in the matrix of the ($Pr_{0.5}Mg_{0.5}$)Ni_2. It is assumed that hydrogen atoms may be captured at Pr-rich regions. Accordingly, we investigated ($Pr_{0.5}Mg_{0.5}$)Ni_2 compound as increasing a cycle of hydrogen charge-discharge. We confirmed that amount of captured hydrogen gradually increases with hydrogen charge-discharge cycles from the upward shift of plasmon peaks of Pr.

Finally, in chapter 6, we summarize the present thesis: Hydrogen-induced microstructure changes of Laves compounds, i.e., the previous HIA should be replaced with HIMPS. The HIMPS phenomenon can be successfully described by enthalpy changes during the hydrogenation. Energetically, the HIMPS state is more stable than of hydride state Laves phase for Laves compounds, whose R_A/R_B exceeds the critical point.