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Hydrogenation and structural properties of Gd_2Ni_7 with superlattice structure

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ABSTRACT

The crystal structure and hydrogenation properties of Ce_2Ni_7-type Gd_2Ni_7 were investigated by X-ray diffraction (XRD) and the hydrogen pressure–composition (*P*–*C*) isotherm. Ce_2Ni_7-type Gd_2Ni_7 was obtained by annealing at 1523 K for 12 h and quenching in ice water. Two superlattice reflections (002 and 004) of the Ce_2Ni_7-type were clearly observed at $2\theta = 7.3°$ and 14.6° in the XRD profile. The refined lattice parameters were $a = 0.49662(9)$ nm and $c = 2.4255(3)$ nm, respectively. Two plateaus were clearly observed during the absorption–desorption process in the *P*–*C* isotherm. The first and second plateaus were at 0.015 and 0.13 MPa, respectively, in the first desorption. The maximum hydrogen capacity reached was 1.13 H/M. The enthalpy and entropy were calculated as −20 kJ/mol H_2 and −80 J/mol H_2 K, respectively, from the van't Hoff plot. After the *P*–*C* isotherm, the $GdNi_5$ cell expanded by 2.15%, but the Gd_2Ni_4 cell shrank by 2.83%.

1. Introduction

The intermetallic compounds $RNi_{3-3.8}$ (R = rare earth) [1–7] and $(RMg)Ni_{3-3.8}$ [8–14] with superlattice structure have been investigated as a hydrogen storage material. These compounds consist of cells with $MgZn_2$- and $CaCu_5$-type cells stacked along the *c* axis.

The phase diagram of the Gd–Ni system shows nine phases in the equilibrium state: Gd_3Ni_1, Gd_3Ni_2, GdNi, $GdNi_2$, $GdNi_3$, Gd_2Ni_7, $GdNi_5$, and Gd_2Ni_{17} [15–19]. Recently, we reported the existence of Gd_5Ni_{19}; its crystal structure was determined by X-ray diffraction (XRD) and scanning transmission electron microscopy (STEM) [20]. Gd_2Ni_7 has two types of crystal structures as shown in Fig. 1: a hexagonal Ce_2Ni_7-type structure (space group $P6_3/mmc$) at high temperature and a rhombohedral Gd_2Co_7-type structure (space group $R\text{-}3m$) at low temperature [16,17]. They consist of cells with $MgZn_2$- and $CaCu_5$-type structures stacked along the *c* axis at ratios of 1:2. The lattice parameters of the Ce_2Ni_7-type structure are $a = 0.4953$ nm and $c = 2.421$ nm. The Ce_2Ni_7-type structure can be described as a stacking of two subunits (2H) that stacks a $MgZn_2$-type cell and two $CaCu_5$-type cells along the *c* axis. The Gd_2Co_7-type structure has lattice parameters of $a = 0.4953$ nm and $c = 3.641$ nm and is formed by stacking the three subunits (3R).

The crystal structure and hydrogenation properties of Ce_2Ni_7 were investigated by Denys et al. [3]. The refined lattice parameters were $a = 0.494131(3)$ nm and $c = 2.45136(2)$ nm. The hydrogen pressure–composition (*P*–*C*) isotherm was measured at several temperatures between 293 and 333 K. The plateau region was clearly observed, and hysteresis between the absorption and desorption was small. The maximum hydrogen storage capacity below 1 MPa was found to be 0.52 H/M at 293 K.

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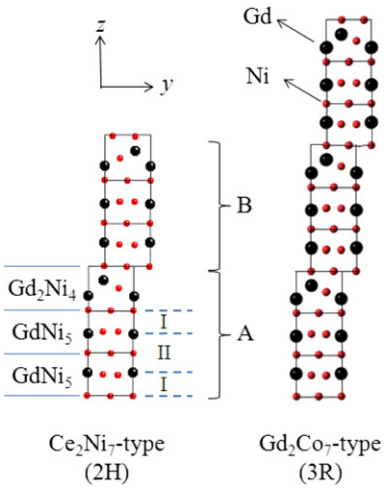

Fig. 1 – Ce_2Ni_7-type (2H) and Gd_2Co_7-type (3R) crystal structures.

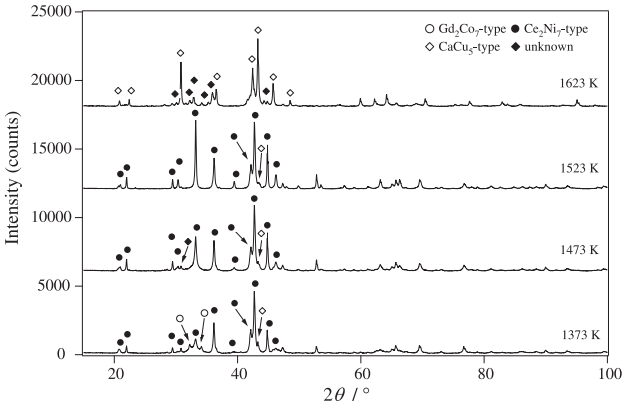

Fig. 2 – XRD profiles of Gd_2Ni_7 quenched at several temperatures.

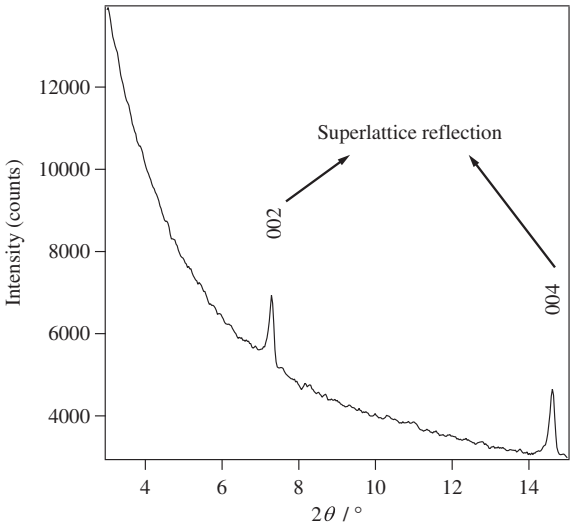

Fig. 3 – XRD pattern for Gd_2Ni_7 in a low-angle region.

The crystal structural change of La_2Ni_7 with a Ce_2Ni_7-type structure along the *P*–*C* isotherm was investigated by using in situ XRD [21]. The starting material with $P6_3/mmc$ (Ce_2Ni_7-type) transformed to *Pbcn* (orthorhombic) and *C*2/*c* (monoclinic) with increasing hydrogen content in the first absorption. The *P*–*C* isotherm showed a plateau between 0.8 and 1.2 H/M, and the maximum hydrogen storage capacity reached 1.24 H/M at 273 K. Hysteresis of La_2Ni_7 was larger than that of Ce_2Ni_7.

This study focused on Ce_2Ni_7-type Gd_2Ni_7 to study the hydrogen absorption–desorption property. Our interest was in the differences in hydrogenation properties among Gd_2Ni_7, Ce_2Ni_7, and Ce_2Ni_7-type La_2Ni_7. The hydrogenation properties of Gd_2Ni_7 have not yet been fully elucidated. The behavior of the $MgZn_2$- and $CaCu_5$-type cells during hydrogenation should be closely related to the hydrogenation properties. We attempted to synthesize Ce_2Ni_7-type Gd_2Ni_7 to understand the hydrogen absorption–desorption properties by using XRD and the *P*–*C* isotherm. This paper presents the *P*–*C* isotherm of Ce_2Ni_7-type Gd_2Ni_7 and the structural parameters and volume

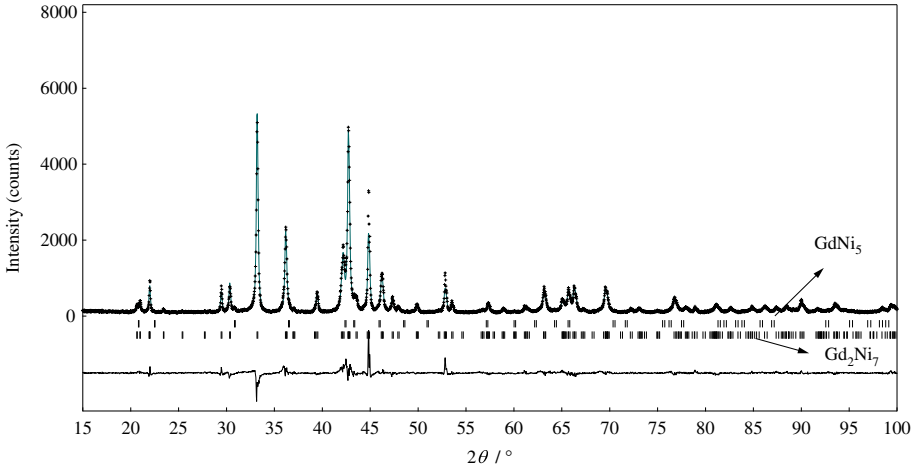

Fig. 4 – Rietveld refinement of XRD data for the Gd_2Ni_7. A model containing Ce_2Ni_7-type Gd_2Ni_7 and $CaCu_5$-type $GdNi_5$ was applied.