Hydrogen Absorption Characteristics of Crystalline $LaNi_5$ Prepared by Mechanical Alloying

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Crystalline $LaNi_5$ powder was synthesized by mechanical alloying of constituent metals preceding annealing at lower than a melting point of the alloy. The structure of the sample as mechanically alloyed was amorphous. After two-step heat treatments at 723 K in a stream of hydrogen and at 1273 K in helium, the crystalline sample was obtained. The hydrogen absorption characteristics of the crystalline sample were in fair agreement with those of the alloy prepared by a conventional melting technique.

$LaNi_5$ is one of most useful hydrogen storage alloys. Production of the alloy has been performed using melting methods, such as arc-melting.[1] The methods of production need high temperatures more than a melting point of the alloy, 1623 K, and the product obtained has to be ground to powder for its practical use. Furthermore, it is necessary to pay attention the composition of raw materials mixture to obtain the alloy of desired composition because of different vapor pressures of constituent metals, and to carefully control temperatures during a cooling process of molten metals to avoid a peritectic reaction.

On the contrary, mechanical alloying (MA) has advantages of simplicity as a preparing technique and a free choice for various kinds of alloys.[2-4] In addition, the technique can mass-produce nonequilibrium phases of alloys in the wide range of composition.

In the present study, we succeeded in synthesizing crystalline $LaNi_5$ powders using MA and the subsequent heat treatment. Furthermore, the hydrogen absorption characteristics of the mechanically alloyed sample which has an amorphous structure and the corresponding crystalline sample were investigated, and were compared with those of the sample prepared by the conventional melting method. An attempt to synthesize $MmNi_{4.5}Al_{0.5}$ alloy (Mm : mischmetal) by MA was previously performed.[5] The study was, however, nothing but suggestions for possibilities of the synthesis. It has never been obtained a single phase in this kind of alloy.

Elemental powders (ca. 5 g) of La (maximum size 3 mm - minimum size 1 mm, 99.5% pure, Santoku Metal Industry) and Ni (200 mesh, 99.95%, Koch Chemicals) were put into a stainless steel vial (45 ml) with five stainless steel balls (15 mm in diameter) and a solvent of n-heptane (10 ml) in an argon atmosphere. The composition of raw materials mixture was Ni/La=5.0. The ball-to-powder weight ratio was about 15 : 1. The vial was sealed with a viton O-ring. MA was carried out in a high-energy planetary ball mill (Fritsch P7) under an argon gas at room temperature. n-heptane was used as a grinding fluid to prevent agglomeration and adhesion between materials and the vial (or balls). The rotating speed was 400-600 r.p.m. and the total milling period was 360 ks.

Two-step heat treatment was carried out on the mechanically alloyed sample in a stream of hydrogen at 723 K for 180 ks and then in helium at 1273 K for 86.4 ks. The former heat treatment was needed to remove carbon impurity arising from n-heptane, while the latter was performed to raise crystallinity.

The determination of composition for the samples obtained was performed with a Rigaku System 3270A X-ray fluorescence spectrometer. To confirm phases formed and crystallinity, X-ray diffraction (XRD) work was done on the samples with a MAC Science M18XHF-SRA X-ray diffractometer. The thermal stability of the MA sample was studied by means of differential scanning calorimetry (DSC).

The amount of hydrogen in the samples was determined using a Sieverts-type apparatus and pressure-concentration-temperature (PCT) curves were prepared.

The composition of the sample as mechanically alloyed was $LaNi_{5.0}$ (31.1 wt% La, 66.1 wt% Ni). The concentrations of impurities in the sample were as follows : 0.33 wt% Fe, 0.038 wt% Cr, 0.12 wt% O, 0.11 wt% N and 2.0 wt% C. The concentrations of Fe and Cr were small, indicating that n-heptane used as a grinding fluid serves to prevent the contamination from the stainless steel vial and balls. The sample was contaminated obviously with carbon which came from n-heptane. After the heat treatment in a stream of hydrogen at 723 K, the carbon concentration decreased less than 10^{-3} wt%. The oxygen concentration slightly increased to 0.41 wt% after two-step heat treatments of 723 K in a stream of hydrogen and 1273 K in helium.

The sample powders as mechanically alloyed have an average particle size of 5 μm and some particles were condensed. After heat treatment, the powders were partially sintered.

Figure 1(a) illustrates a XRD pattern for the MA sample before annealing. No peak belongs to starting materials, such as La and Ni metals, was observed and a broad band peak newly appeared in the range of 2θ=40-45°. In a DSC curve of the MA sample before annealing, a distinct exotherm begins at a temperature about 530 K and is centered at 673 K. A similar result was obtained for amorphous $LaNi_5$ films prepared by sputtering.[6] After annealing the MA sample in vacuo at 673 K for 3.6 ks, as shown in Fig. 1(b), the peaks assigned only to the $LaNi_5$ phase were confirmed, so that the sample as prepared by MA appears to have an amorphous structure. The heat of

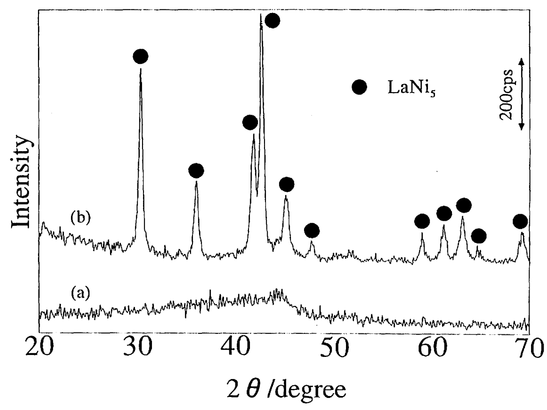

Figure 1. X-ray diffraction patterns for the MA samples before and after annealing.
(a) The MA sample before annealing.
(b) The MA sample after annealing in vacuo at 673 K for 3.6 ks.

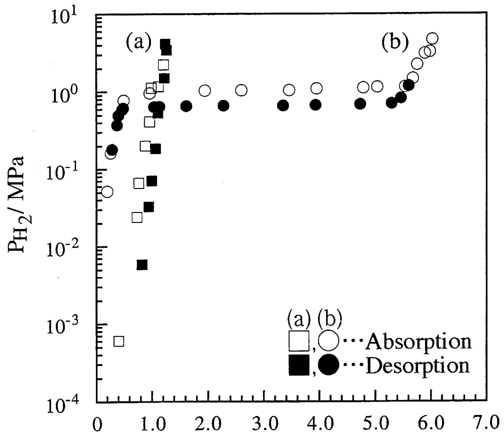

Figure 2. Pressure-composition-temperature curves at 333 K for the MA samples before and after annealing.
(a) The amorphous sample prepared by MA.
(b) The crystalline sample prepared by MA and the subsequent two-step heat treatment at 723 K in a stream of hydrogen and 1273 K in helium.

crystallization estimated by the DSC measurement was about 12 kJ mol^{-1}.

For $Ni_{70}Zr_{30}$ alloy, it was reported that the accumulation of Fe and Cr impurities arising from the stainless steel plays a role in triggering the crystallization when the impurities are substantially contained in the sample (13.7 at%).[7] The concentration of Fe and Cr impurities in the $LaNi_5$ sample obtained were, however, both less than 1 at% (0.38 at% Fe, 0.047 at% Cr). In addition, the crystallization temperatures are not so different between the amorphous MA sample and amorphous sputtered film which is free from the impurities.[6] Therefore, in the present experiment, the influence of impurities on the crystallization of amorphous $LaNi_5$ appears to be weak.

A PCT curve for the MA sample at 333 K is given in Fig. 2(a). On a hydrogen pressure of 5 MPa at 333 K, hydrogen concentration ($H/LaNi_5$) in the MA sample was about 1.3 which is no more than one fourth that in the crystalline bulk. As for the pressure dependence on hydrogen concentration, the concentration increases monotonically with the hydrogen pressure, i.e. absence of a pressure plateau. The results are analogous to those for the sputtered amorphous $LaNi_5$ films.[6,8-10] The relationship between structures and hydrogenation characteristics is described elsewhere.[11-13]

From the XRD pattern, the heat treated MA sample was found to have a high crystallinity. Figure 2(b) shows a PCT curve for the sample at 333 K. In the isotherm, a distinct pressure plateau having a good flatness and a wide range was observed. The hydrogen concentration in the sample under 5 MPa H_2 atmosphere at 333 K was 6.0 which is equivalent to that of the sample prepared by conventional melting techniques.[14] A van't Hoff-type plot obtained from equilibrium pressures on desorption isotherms at 313 K, 333 K and 353 K is shown in Fig. 3. A good linear relationship between ln P_{H_2} and T^{-1} could be obtained. The standard enthalpy, ΔH, and entropy, ΔS, of formation of the $LaNi_5$ hydride phase were estimated at - 33.6 kJ $mol^{-1}H_2$ and -116 J K^{-1} $mol^{-1}H_2$ respectively. The values were found to be nearly equal to those of the alloy prepared by melting, which are -32 kJ $mol^{-1}H_2$ for ΔH and -108 J K^{-1} $mol^{-1}H_2$ for ΔS.[14]

In conclusion, a crystalline $LaNi_5$ alloy having the same

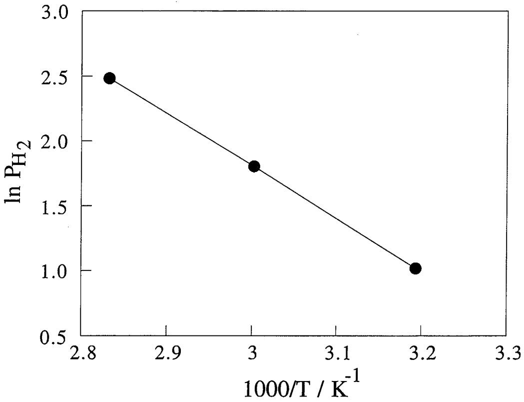

Figure 3. A van't Hoff - type plot for the crystalline sample prepared by MA and the subsequent two-step heat treatment at 723 K in a stream of hydrogen and 1273 K in helium.

hydrogen concentration and thermodynamic properties for hydride formation as the alloy prepared by the conventional melting method was synthesized by MA and the subsequent heat treatment. Advantages of the technique are the low temperature of synthesis much less than the melting point of the alloy, and no need of grinding for practical use because the alloy is obtained as a form of powder.

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