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Exfoliation of $LaNi_5$ Thin Film from Substrate by Hydrogenation

Shingo Tsubuteishi, Yoshitake Nishi and Haru-Hisa Uchida*
Dept. of Materials Science, Tokai University, Kitakaname 1117, Hiratsuka, Kanagawa, 259-1292 Japan
e-mail: 1aamm019@keyaki.cc.u-tokai.ac.jp
*Dept. of Human Development, Tokai University, Kitakaname 1117, Hiratsuka, Kanagawa, 259-1292 Japan
Fax: +81-463-50-2208, e-mail: hhuchida@keyaki.cc.u-tokai.ac.jp

Hydrogen storage alloy is expected as an intelligent material. The volume expansion of $LaNi_5$ accompanied by hydrogen absorption may amount to not less than 25%. $LaNi_5$ is, therefore, expected as a functional material in the application of actuator, disconnection technology, etc. The cracks and exfoliation from substrate become a serious problem when $LaNi_5$ is used as thin film form. In this paper, we report effect of parameters, such as film thickness, deposition temperature, film composition, oxidation of film and the kind of substrate material. $LaNi_5$ thin film samples deposited on glass and polyimide substrate were prepared by flash evaporation method. The conditions of film deposition were changed variously. The cracks and exfoliation of $LaNi_5$ thin film from substrate were strongly dependent on the kind of substrate. The oxidation of $LaNi_5$ thin film was expected to accelerate occurrence of the cracks and exfoliation from substrate. It is very important to determine the parameters important for the use conditions when $LaNi_5$ is applied as thin film form.
Key words: hydrogen storage alloy, thin film, flash evaporation, pulverization behavior, $LaNi_5$

1. INTRODUCTION

Hydrogen storage alloy is expected as useful and smart material for storage and transportation of hydrogen as energy carrier in the renewable energy systems. Today, hydrogen storage alloy is applied to not only storage and transportation of hydrogen but also actuator, chemical heat pump, etc. using pressure change or reaction heat accompanied by hydrogen sorption cycles. Many of hydrogen storage alloys are, however, pulverized to several micron meters by hydrogen sorption cycles [1]. Pulverization of hydrogen storage alloy influences hydrogen absorption property, such as smaller absorption rate by decrease of thermal conductivity. Because the volume expansion caused by hydrogen absorption may amount to not less than 25%, therefore, $LaNi_5$ is expected for the application of actuator, disconnection technology, etc [2-4]. While thin film form may enlarge the application of hydrogen storage alloys, degradation of film, such as cracks and exfoliation from substrate, become on the other hand a serious problem.

In this paper, at first, we investigated the critical diameter of $LaNi_5$ bulk powder, which significantly decelerated pulverization. The critical diameter of $LaNi_5$ powder was expected to 2 μm or less. The critical thickness of $LaNi_5$ thin film, with which the cracks and exfoliation from substrate, therefore, was expected to about 2 μm. We report the effect of parameters of film thickness, deposition temperature, film composition, oxidation of film and the kind of substrate material on film degradation.

2. EXPERIMENTAL

2.1 Observation of pulverized $LaNi_5$ powder

The sample of $LaNi_5$ was prepared by arc melting process and subsequently annealed at 1073 K for 8 h for the homogenization. The block sample was pulverized by 30 times of 2 MPa hydrogen sorption cycles using high-pressure volumetric apparatus (Fig. 1) and placed under dry air for longer than 1 month before use. The powder sample was divided by a sieve to particle size smaller than 45 μm.

The initial activation was carried out with the applied hydrogen pressure of 3 MPa. The absorption (300 s) and desorption (300 s) cycles were carried out 300 times with the applied hydrogen pressure of 2 MPa at room temperature. The sample particles of initial and after 300 times of hydrogen sorption cycles were observed using scanning electron microscope (SEM). The samples of 300 particles were randomly chosen for measurements of the particle size. The mean value of the length in short and long axes of each particle was taken as its diameter.

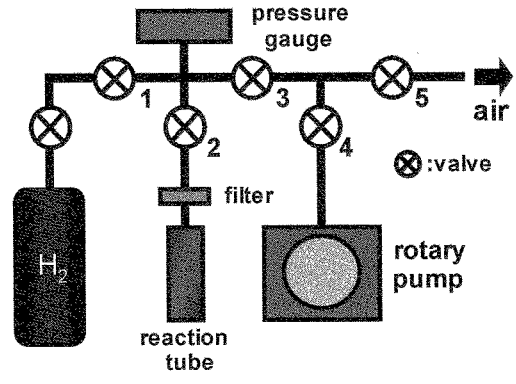

Fig. 1 Schematic diagram of high-pressure volumetric apparatus.

2.2 Preparation and observation of $LaNi_5$ thin film

$LaNi_5$ thin film samples were prepared by flash evaporation using $LaNi_x$ (x=2.26-5.03) powder with particle size of smaller than 45 μm. The film samples were deposited on glass (borosilicate glass, 18 x 18 x 0.12-0.17 mm, young's modulus: 71.5 GPa, Matsunami glass Ind., Co., Ltd) and polyimide (Kapton, 18 x 18 x 0.125 mm, young's modulus: 3.4 GPa, Toray-Du Pont Co., Ltd) substrate. All the substrates were washed first with acetone and then with methanol in the ultrasonic washing machine. The film samples were deposited on substrates situated above a tungsten heater, maintained at 2273 K, on which the alloy powder was continuously dropped (Fig. 2).

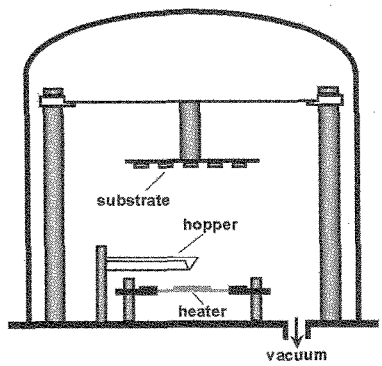

Fig. 2 Schematic diagram of flash evaporation apparatus.

Table I shows conditions of film deposition. The substrate temperatures were changed in the range of 299-573 K. The vacuum conditions were fixed at 10^{-5} Pa. The thicknesses of the film samples were 0.74-2.38 μm. The deposited films were observed using SEM. Energy-dispersive X-ray spectrometer (EDX) analysis of the deposited films showed an alteration in composition from $LaNi_x$ (x=2.26-5.03) for the powder to be evaporated to $LaNi_x$ (x=2.53-7.07) for the deposited film. The X-ray diffraction (XRD) spectra of the samples were measured using CuKα radiation. The hydrogenation of film samples was carried out with the applied hydrogen pressure of 5 MPa for 10 h by high-pressure volumetric apparatus at room temperature. Additionally, the film samples, exposed to the atmosphere immediately after film deposition, were prepared for investigation of the influence of oxidation.

Table I Conditions of film deposition.

Vacuum	**$2.4 \sim 7.8 \times 10^{-5}$ Pa**
Powder Composition	**$LaNi_{2.26 \sim 5.03}$**
Heater Temp.	**2273 K**
Substrate	**Glass, Polyimide**
Substrate Temp.	**299 ~ 573 K**
Thin Film Composition	**$LaNi_{2.53 \sim 7.07}$**
Thickness of Thin Film	**0.74 ~ 2.38 μm**

3. RESULTS AND DISSCUSSITON

3.1 Pulverization behavior of $LaNi_5$ powder

The pulverization behavior of $LaNi_5$ powder before and after 300 times of hydrogen sorption cycles are shown in Fig. 3. The median and mode diameter of initial grain were 12.5 and 9.60 μm, respectively. After 300 times of hydrogen sorption cycles, the median and mode diameter were 6.96 and 8.30 μm, respectively. After 300 times of hydrogen sorption cycles, the minimum particle diameter was 2.15 μm. The critical diameter of $LaNi_5$ powder, with which the pulverization was decreased significantly, was expected to 2 μm or less. Therefore, the thickness of $LaNi_5$ thin film, which does not generate cracks and exfoliation from substrate, was also expected to 2 μm or less.

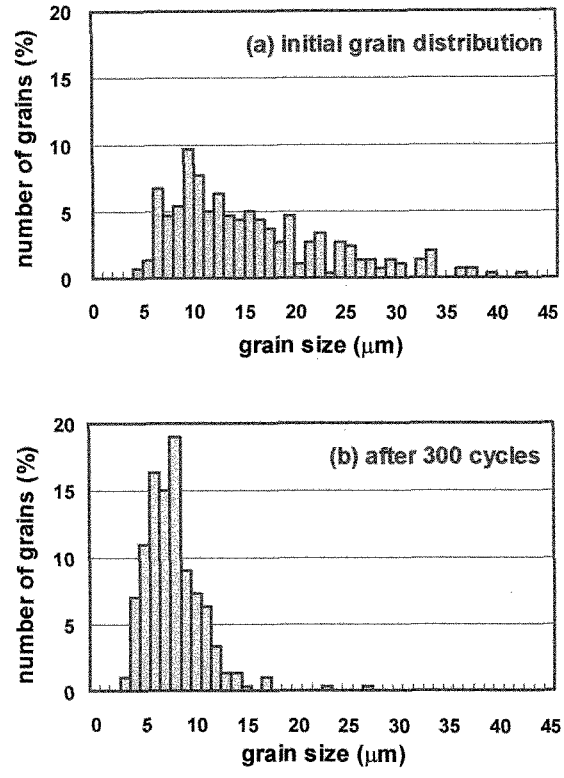

Fig. 3 Histogram of the particle size of $LaNi_5$ powder, (a) initial and (b) after 300 times of hydrogen sorption cycles.

3.2 Influence of film composition, film thickness, film crystallinity and kind of substrate material on the film degradation

The X-ray diffraction patterns of film samples deposited on glass and polyimide substrates at 373, 573 K displayed broadened but distinct X-ray diffraction peaks typical for $LaNi_5$. However, for the film samples deposited on glass and polyimide substrates at 299 K no clear diffraction peaks was not observed. Therefore, the former seem the crystallized structure, and the latter seem the amorphous-like structure.

Figure 4 shows the effect of parameters on the cracks and exfoliation from substrate.

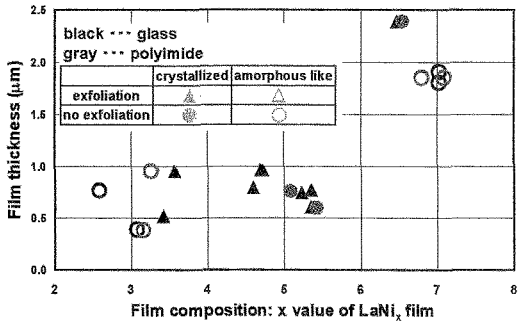

Fig. 4 Effect of film thickness, film composition, film crystallinity and the kind of substrate material on the cracks and exfoliation of $LaNi_x$ thin film from substrate.

In this figure, the film samples with the cracks and exfoliation from substrate accompanied by hydrogenation are denoted by triangles. Similarly, circles denote the film samples without the cracks and exfoliation from substrate. The film samples deposited on glass and polyimide substrate are denoted by black and gray symbols, respectively. Additionally, the crystallized and amorphous-like film samples are denoted by painted and outline symbols, respectively. In case of the crystallized film samples deposited on glass substrate, the cracks and exfoliation from substrate occurred, regardless of film thickness and film composition (see Fig. 5). However, in case of the amorphous-like film samples, the cracks and exfoliation from substrate did not occur. The amorphous-like $LaNi_5$ sample, such as film, does not have plateau slope on P-C-isothermal curve and indicate much smaller amount of hydrogen absorption [5-6], that is, the partial volume expansion accompanied by hydrogenation does not occur. Accordingly, in case of the amorphous-like film samples, the cracks and exfoliation from substrate did not occur even the film absorbed hydrogen. In case of film samples deposited on polyimide substrate, the cracks and exfoliation from substrate did not occurred, regardless of film crystallinity, film thickness and film composition. This may be also attributed to the elastic deformation of polyimide substrate accompanying volume expansion of $LaNi_5$ thin film by hydrogenation (see Fig. 6).

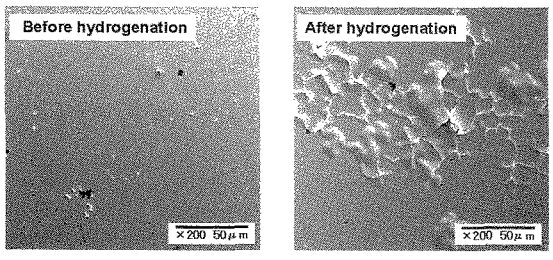

Fig. 5 Scanning electron micrographs of the $LaNi_{3.18}$ thin film sample (0.95μm thick) with crystallized structure deposited on glass substrate at 573 K before and after hydrogenation.

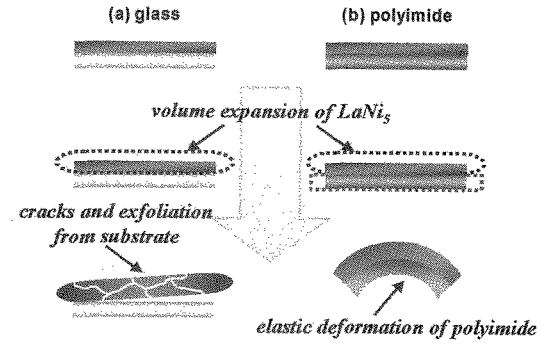

Fig. 6 Model of deformation of $LaNi_5$ thin film accompanying hydrogenation, (a) glass and (b) polyimide substrate.

The critical thickness of $LaNi_5$ film, with which the cracks or exfoliation from substrate does not occur, was significantly changed by the kind of substrate material. In case of the film deposited on glass substrate, the critical thickness was expected to under 0.5 μm or less. On the other hand, the critical thickness of the film deposited on polyimide substrate was expected to over 2.4 μm. However, the critical thickness of $LaNi_5$ film can be determined by additional parameters.

3.3 Influence of holes and foreign substances

Figure 7 shows electron micrograph of the thin film sample deposited on polyimide substrate.

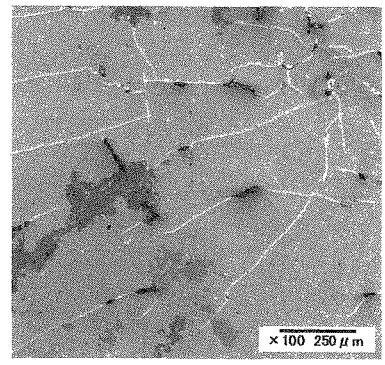

Fig. 7 Scanning electron micrograph of the thin film sample with stress deposited on polyimide substrate.

When the stress was applied to the thin film sample, the cracks occurred from hole. Therefore, the existence of holes and foreign substances, which are caused by inadequate substrate washing and/or blown up source powder sample during flash evaporation, has influence on generation of cracks.

3.4 Influence of oxidation

Figure 8 shows the photograph of the film samples after hydrogenation. (a) is the film sample, which was kept under 10^{-5} Pa for 2 hours in receiver after film deposition. (b) is the film sample, which was immediately exposed to atmosphere after film deposition.

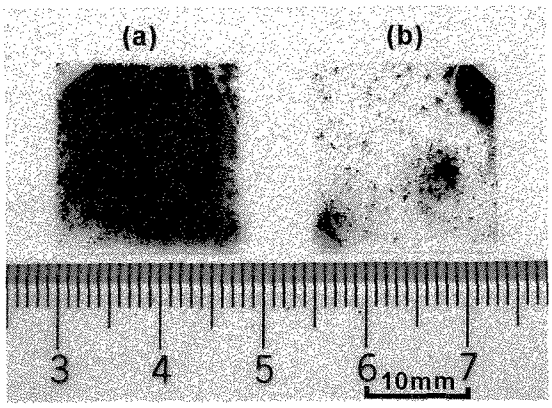

Fig. 8 Photograph of the film samples deposited on glass substrate after hydrogenation, (a) kept in vacuum and (b) exposed to air just after film deposition.

The exfoliation from substrate of the film sample (b) accelerated than the film sample (a). The thickness of the oxide layer was formed by exposure can be markedly reduced if air exposure is carried out only after the fast cooling to room temperature and kept for some time under high vacuum condition [7]. Therefore, it seems that the oxide layer of film sample (a) was thinner than the oxide layer of film sample (b). Pulverization behavior of $LaNi_5$ powder is significantly changed by alteration of surface condition by oxidation or alkaline pretreatment [1, 8-9]. Especially, the oxidation accelerates the pulverization of $LaNi_5$. The enhanced pulverization is generally considered to be the increased crack initiations attributed to dislocation stacking at the metal-oxide boundaries, which is yielded by the volume expansion in the course of hydrogen absorption [1]. Accordingly, the oxidation of film sample accelerates the exfoliation from substrate, like a powder sample.

4. CONCLUSION

In this paper, we report the effect of parameters on film degradation, such as cracks and exfoliation from substrate. The conditions, with which the cracks and exfoliation from substrate occur to $LaNi_5$ thin film, were glass substrate and crystallized structure. In case of the film samples deposited on polyimide substrate, the cracks and exfoliation from substrate did not occur. The cracks and exfoliation of $LaNi_5$ thin film from substrate were strongly dependent on the kind of substrate. The oxidation of $LaNi_5$ thin film showed a tendency to accelerate the cracks and exfoliation from substrate, like a $LaNi_5$ powder sample. It is very important to determine the parameters according to use conditions, when $LaNi_5$ is applied as thin film form. Especially, the thin film without the cracks and exfoliation from substrate is required when the $LaNi_5$ thin film is used for an actuator. It is important that the film sample do not have thick oxide layer.

5. REFERENCE

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