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Preparation of $LaNi_5$ Films and Effects of Hydrogen Absorption on Electrical Resistivities of the Films

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Thin films of $LaNi_5$ have been prepared by means of a flash evaporation-deposition technique. Electric resistivity measurements on these films were carried out in an atmosphere of hydrogen. The films formed on quartz substrates were amorphous. Resistivities initially increased and then decreased during the absorption of hydrogen. During the desorption process, the reverse phenomenon was observed. The effect of the thickness of the films on the electric properties, during the hydrogen absorption-desorption process, was also studied. Sample pulverization could be avoidable by using films of less than 10 μm in thickness. The hydrogen contents of the films were determined by the quartz-crystal mass-monitoring (QCMM) method.

Technical applications of hydrogen absorption in intermetallic compounds have been eagerly pursued in some aspects,[1–8] such as energy storage, heat pumping and hydrogen purification. The $LaNi_5$ hydrides have been the most throughly investigated of all the hydrides of interest,[9–16] and the structure and phase relations have been well established.

A serious drawback regarding the practical use of $LaNi_5$ is the fact that the material pulverizes during hydrogen charging. The volume increase associated with the formation of the hydrides leads to stresses in the hydride envelope on the unhydrided core material.[9] This stress causes cracks which pulverize the hydride.[17] For $LaNi_5$ subjected to several charging-decharging cycles, the particle diameter was measured to be about 10^2 μm, though there was a broad distribution in size.[18,19]

An amorphous alloy which is prepared by rapid cooling is known to have a considerable resistance to a stress since a strain can be relaxed by the free volume existing in an alloy. The amorphous alloy is, therefore, a promising material for hydrogen storage.

A thin film of an alloy is sometimes amorphous[20] and is worth being investigated for possible applications. The preparation of a thin film of an alloy or an intermetallic compound is difficult owing to the difference in the vapour pressures of component metals. Nevertheless, the following methods have been proposed for the preparation of a thin film of an alloy: (1) ion sputtering;[21] (2) ion plating;[22] (3) vacuum vapour deposition at a temperature sufficiently high that component metals can be vaporized quickly and completely (flash evaporation-deposition).

We prepared some thin films of $LaNi_5$ by the third method and measured their electric properties under several atmospheres of hydrogen. This article is a full account of our preliminary papers.[23,24]

Experimental

Preparation of Films. $LaNi_5$ (La 32.16, Ni 67.84 wt%) powder was supplied by Santoku Metal Industry Co. Ltd., Kobe. Substrates were quartz plates, porous sintered glass discs (pore sizes; 3, 8, 50, and 100 μm) and porous sintered stainless steel discs (SUS304, pore sizes; 0.5 and 1 μm, Shoketsu Kinzoku, Tokyo). Samples for electric measurements were deposited on quartz plates. The substrates (except for a porous sintered stainless-steel discs) were first soaked in a $HCl–HNO_3$ mixed solution for 1 d and were then washed with a neutral detergent and rinsed with deionized water. The plate was cleaned with an ultrasonic washing machine filled with deionized water before drying in a desiccator. The porous sintered stainless-steel discs were first washed with acetone and next with methanol. The discs were then treated in an ultrasonic washing machine. The vacuum-deposition procedure was as follows. The $LaNi_5$ powder was placed on a tungsten boat which was preheated to a temperature of 2.3×10^3 K. Both components of $LaNi_5$ evaporated immediately (at this temperature) and were deposited onto a substrate which was placed just above the tungsten boat. The alloy powder was supplied by a conveyor belt equipped with a hopper. The vacuum during deposition was *ca.* 10^{-3} Pa. After deposition, pure helium gas was allowed into the chamber to prevent the formation of an oxide on the films. The thicknesses of the obtained films were determined by the direct observation of the cross sections of the samples using a Hitachi Scanning Electron Microscope S-405. The composition of the film bulk was determined with a Rigaku X-ray Energy Spectrometer equipped with an Si(Li) detector. The XPS measurement was carried out with a Shimazu Electron Spectrometer ESCA 650B mounted with a Mg target.

Measurements of Properties. Electric-resistivity measurements were performed under a hydrogen atmosphere. A sample with attached leads and a thermocouple were installed in a reactor which was made of 316 stainless steel (Fig. 1). The reactor was connected to a high-pressure manifold with connections to a pressure gauge, a vacuum pump and a high-pressure hydrogen gas cylinder. The resistivity of the film was measured by the four-probe technique.[25,26] The voltage drop across the film for a constant current was recorded as a function of time. Then hydrogen gas was quickly admitted to the vacuum reactor. The resulting changes in voltage drop due to absorption were monitored on a recorder.

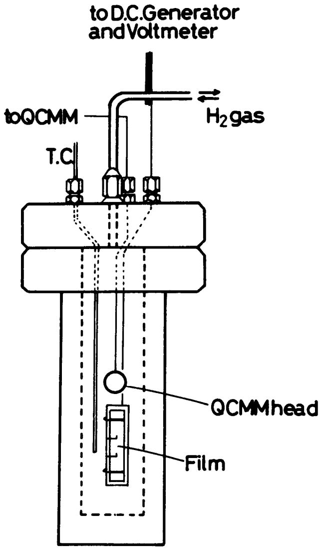

Fig. 1. The apparatus used for the electrical resistivity measurements and the QCMM frequency measurements.

A QCMM apparatus (NICHIDEN ANELVA EVM 32B) was used to determine the quantity of hydrogen absorbed in the films. The apparatus and procedure were as follows. Flash vacuum evaporation was also used to form an $LaNi_5$ film. A crystal monitor head with a quartz disk was placed 0.2 m above a tungsten filament to recieve the metal vapor. The vessel for setting the $LaNi_5$ deposited QCMM head was the same one that was used to measure the electrical resistivity. All the QCMM measurements were done at 333 K. After the vacuum system had reached thermal equilibrium, hydrogen was then introduced into the vessel. The change in the frequency of the quartz was recorded as a function of pressure change.

Results and Discussion

Characterization of Deposited $LaNi_5$ Films: Obtained films were amorphous, at least as determined from X-ray diffraction results. Faint dots were observed in some electron-diffraction patterns. These dots, however, did not originally seem to be due to the presence of any crystalline phase, but due to the oxidation of the film or crystallization by the electron beam in the electron microscope.[27]

The chemical composition of the films (determined by the X-ray fluorescence method) was the same as the original $LaNi_5$ supplied in the hopper. X-ray photoelectron spectroscopy revealed that the La $3d_{2/3}$ peak was split into two components (1.367×10^{-6} and 1.372×10^{-6} J) because of the oxide.[28–33] However, the peak at 1.372×10^{-6} J disappeared after bombardment with argon ions for 30 min. Therefore, the oxide was considered to have formed only on the top surfaces of the films.

The homogeneity of the chemical composition for the whole surface of the films was confirmed by EPMA (Electron Probe Micro Analysis).

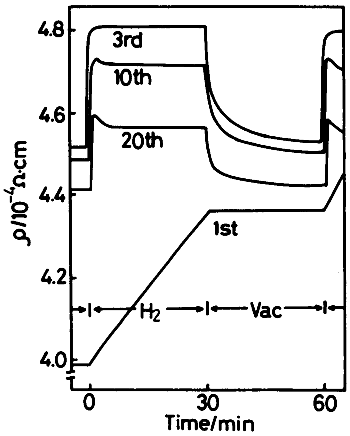

Fig. 2. Variation of resistivities as a function of time for thicker $LaNi_5$ film (thickness *ca.* 0.63 μm) in the activation process (at 313 K for 1st and 2nd cycle, at 363 K for other cycle. H_2 2.5×10^6 Pa).

The density of the film was 4.44 g/cm³. This was estimated from the weight, area, and thickness of a film (1.33 μm thick). This value is considerably smaller than the bulk value, *i.e.* 8.28 g/cm³.[34]

Stability of the Films during Hydrogen Absorption-desorption Cycles: Intermetallic compounds, such as $LaNi_5$, are brittle materials and break up into fine particles because of their volumetric expansion during hydrogen absorption. The thin films obtained, however, do not form powders even after 150 cycles of the absorption-desorption of hydrogen. This is because that the films are amorphous, *i.e.* hydrogen enters the film just like a hand put into water.

Electric Resistivities: Figures 2, 3, and 4 show the variation in electric resistivity as a function of the time that hydrogen pressure was applied to $LaNi_5$ films of various thicknesses during the activation process.

The resistivity change in a thicker film (*ca.* 0.63 μm thick) is shown in Fig. 2. In the first cycle, the resistivity for the film keeps rising when hydrogen gas is allowed into the system. After the evacuation of the system, the resistivity maintains a constant value. In the third cycle, the resistivity of the film increases immediately and then attains a constant value during the absorption process. During the desorption process, the resistivity decreases rapidly at first and then gradually. During the tenth cycle the variation in the resistivity was almost the same as that during the third cycle. The corresponding increase and decrease was, however, quicker than that for the third cycle. After the first sudden increase, the resistivity decreased slightly. This behaviour suggests that the following steps take place during hydrogen absorption. Hydrogen molecules are adsorbed on the surface of the film and then dissociate into atoms. The dissociated hydrogen atoms reach the underlying $LaNi_5$ by diffusion in monatomic form along the La_2O_3–Ni interface.[35] The hydrogen atoms take on the conduction electrons of $LaNi_5$ and become the hydrogen anions. This reaction is represented by the formula $H+e^- \rightarrow H^-$. The number of electrons in the conduction band of the $LaNi_5$ decreases and, consequently, the resistivity of the $LaNi_5$ film increases. The second step (the formation of a highly conductive hydride) then, occurs. For a thicker film, the resistivity is maintained at a constant value since the formation of the hydrogen anion is balanced by the formation of the highly conductive hydride. In the hydrogen-desorption process, the dissolved hydrogen anions are removed as hydrogen molecules, releasing their electrons to the conduction band of the metal. Since the number of electrons in the conduction band of the $LaNi_5$ increases, the resistivity of the film decreases. Subsequently, hydrogen which has formed the highly conductive metal hydride, slowly desorbs. The decrease in the resistivity of the film becomes slow.

Figure 3 illustrates the change in resistivity of a thinner film (*ca.* 0.20 μm thick). The behavior during the first cycle is similar to that of the third cycle for a thicker film. As the cycle is repeated, the rate of decrease in the resistivity (which occurs after the increase when hydrogen is first admitted into the system) becomes faster. This is because the quantity of the highly conductive hydride increases. When the system is evacuated (as seen from the results of the 10th cycle in the thicker film) there occurs a sudden decrease in the resistivity because of the removal of the residual hydrogen anions in the film. Then, the resistivity gradually increases due to the decomposition of the highly conductive hydride.

Figure 4 displays the resistivity change in the thinnest film (*ca.* 3.8×10^{-2} μm thick). During the 10th cycle, there was no increase caused by introduction of hydrogen into the system because all of the dissolved hydrogen anions formed highly conductive hydride. As mentioned above, the resistivity change differs depending on the thickness of the film. The thickness of the highly conductive hydride layer seems to be almost the same even though the film thickness is different. For the thicker film, the thickness of the H^- dissolved slightly conductive $LaNi_5$ layer was quite large and the effect of this layer was predominant rather than that of the highly conductive hydride layer. For the thinner film, the effect of the highly conductive hydride was forcible and the electric resistivity fell immediately.

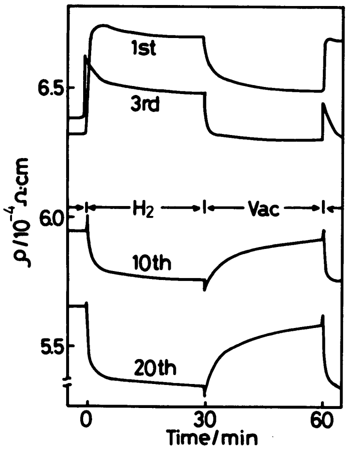

Fig. 3. Variation of resistivities as a function of time for thinner $LaNi_5$ film (thickness *ca.* 0.20 μm) in the activation process (at 313 K for 1st and 2nd cycle, at 363 K for other cycle. H_2 2.5×10^6 Pa).

Figure 5 shows the effect of temperature on the electric resistivity of an $LaNi_5$ film (0.3 μm thick) during a hydrogen-desorption process. The rate of released hydrogen which is formed the highly conductive hydride increases with a rise in temperature.

Hydrogen Pressure Dependence on Resistivities: Figure 6 illustrates the pressure dependence of the saturated electric resistivity for hydrogen absorption in the film. The saturated resistivity reaches a constant value at about 1.2×10^6 Pa. Regarding the effect of the temperature on the electric resistivity and the hydro-

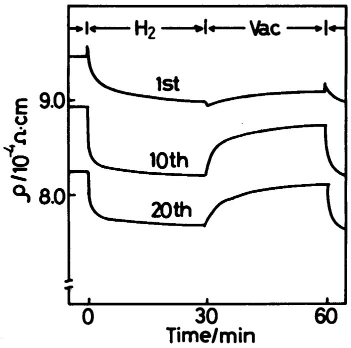

Fig. 4. Variation of resistivities as a function of time for thinnest $LaNi_5$ film (thickness *ca.* 3.8×10^{-2} μm) in the activation process (at 313 K for 1st and 2nd cycle, at 363 K for other cycle. H_2 2.5×10^6 Pa).

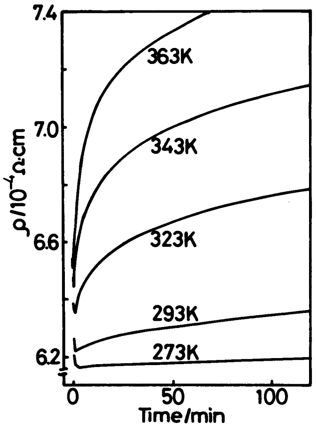

Fig. 5. Effect of temperature on electrical resistivity of an $LaNi_5$ film (thickness *ca.* 0.30 μm) in hydrogen desorption process.

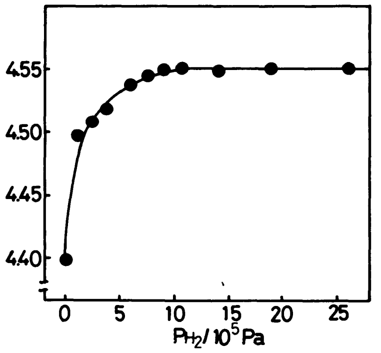

Fig. 6. Electrical resistivity *vs.* Hydrogen pressure for an $LaNi_5$ film (thickness *ca.* 0.63 μm) at 363 K.

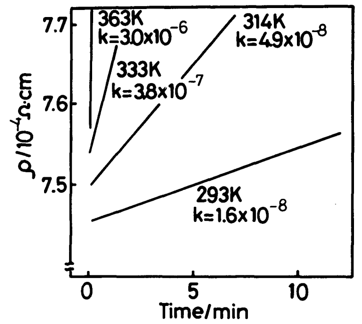

Fig. 7. Variation of resistivities *vs.* Time at various temperatures for an $LaNi_5$ film (thickness *ca.* 0.35 μm).

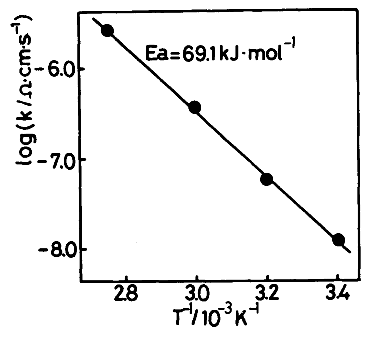

Fig. 8. Arrhenius plot of the rate constant for hydrogen absorption in an $LaNi_5$ film (thickness *ca.* 0.35 μm).

gen pressure dependence on resistivities, some typical results since the behavior of the resistivity is unrelated to the film thickness.

Activation Energy for Hydrogen Absorption: The time dependence of the resistivities for the initial stages of absorption is shown in Fig. 7. The reaction-rate constants are obtained from the slopes of straight lines in the figure.[36] Figure 8 gives an Arrhenius plot of the rate constants for the hydrogen absorption of the film. An activation energy for the absorption, E_a, is evaluated from the slope, being 69.1 kJ mol^{-1}. The E_a is related to the reaction which is the formation of a hydrogen anion. This reaction is independent of the film thickness.

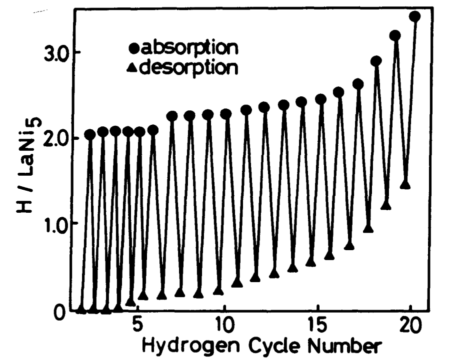

Fig. 9. Hydrogen concentration in an $LaNi_5$ film (thickness *ca.* 1.8 μm) in the hydrogen absorption-desorption cycle (in H_2 2.5×10^6 Pa—Vacuum cycle at 333 K).

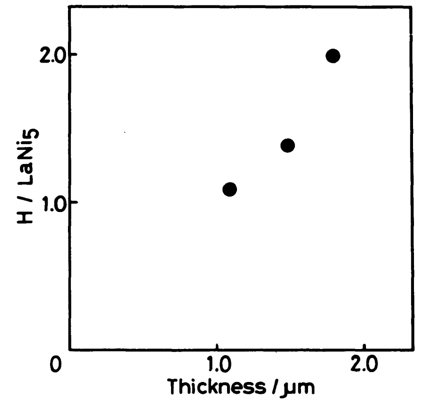

Fig. 10. Hydrogen concentration *vs.* $LaNi_5$ film thickness (in H_2 2.5×10^6 Pa—Vacuum cycle at 333 K).

Hydrogen Concentration in the Films: Figure 9 gives the hydrogen concentration in $LaNi_5$ films measured by the QCMM method[37] while repeating the hydrogen absorption-desorption cycle. The amounts of hydrogen taken up by the $LaNi_5$ film (*ca.* 1.8 μm thick) is about 2.0 H/$LaNi_5$. It is recognized that the amount of the hydride which is not desorbed from the film increases as the cycle repeats. This agrees with the measurements of the electrical resistivity. The amounts of hydrogen for other films are 1.1 and 1.4 for films of 1.1 and 1.5 μm thickness, respectively. The hydrogen content in their films is dependent on the film thickness and, as indicated in Fig. 10, the hydrogen concentration decreases with a decrease in film thickness. The hydrogen content for thinner films is at present under investigation. For a bulk sample, it is known that the amount of hydrogen taken up by $LaNi_5$ is about 7.[9] The smallness of hydrogen uptake by the films compared with the bulk is due to the amorphous state of the film structure and to the existence of a surface oxide as a dead layer for hydrogen absorption.

Figure 11 shows a pressure-composition isotherm for the $LaNi_5$ film (*ca.* 1.5 μm thick) at 333 K. The hydrogen concentration increases with an increase in

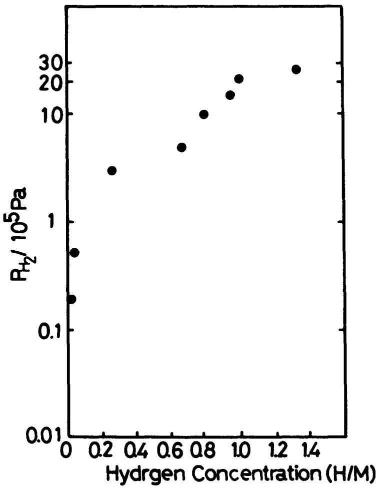

Fig. 11. Pressure-Concentration isotherm for an $LaNi_5$ film (thickness *ca.* 1.5 μm) at 333 K.

pressure. A pressure plateau (usually observed in a bulk sample) is absent. A result for an ZrNi amorphous alloy[38] is analogous to our result. It can be assumed that the absence of a pressure plateau is one of the features of an amorphous alloy.

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