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Resistance change during cyclic hydrogen charging and discharging in $LaNi_5$ thin films

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Abstract : Hydrogen storage alloys are very important due to their variety of technological applications Bulk alloys have been studied extensively and research field of thin film hydride is relatively new. In present work thin film of $LaNi_5$ of thickness 1300Å were obliquely deposited at θ = 0°, 30°, 45°, 60° and 75° by flash evaporation technique onto glass substrate at a pressure 2×10^{-5} Torr and at room temperature. It was found that the activation of $LaNi_5$ thin films for hydrogen absorption is fairly easy compared to the bulk material. The effect of number of hydrogen absorption desorption cycles on the resistance of $LaNi_5$ increases during hydrogen absorption and decrease during desorption The resistance change in subsequent cycles was found to decrease and finally reaches equilibrium state denoting the saturation stage of thin films due to hydrogen absorption

Keywords : Hydrogen storage, absorption / desorption, thin film

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Introduction

The $LaNi_5$ alloys is a hydrogen attractive intermetallic compound in the field of renewable energy research [1-2], which can reversibly store hydrogen for the technological application. The kinetics of hydrogen absorption in bulk form, were extensively studied [3-6]. These studies relate to change in hydrogen characteristic of the metal hydrides under cyclic condition [7-9]. The use of thin film for hydrogen storage has become very important [10-14], since the main process of hydrogen absorption /desorption takes place on the surface of the material [13-14], and also depends upon the defect structure of films [12].

The hydrogen content of thin film is less, compared to the bulk [16-19]. The electrical resistivity of bulk hydride material has been studied by many workers [15-18]. Adachi *et al* [10, 19] have studied the effect of hydrogen absorption on the electrical resistivity of $LaNi_5$ and $LaCo_5$ films deposited by flash evaporation at 90°C under vacuum condition for 30 min. for several cycles. Uchida and Fromm [20] have investigated the resistivity change during hydrogen absorption in tantalum wire and have measured the content of hydrogen absorbed. Welter [21] have measured and monitored the concentration of hydrogen absorbed with the resistivity variation in FeTi-H system. Upadhyay *et al* [22] have studied the effect of resistance of cyclic hydrogen charging and discharging of obliquely deposited FeTi thin films. Recently Jain *et al* (23, 24) have studied the hydrogen absorption characterisation of obliquely deposited $MmNi_{4.5}al_{0.5}$ and $LaNi_5$ thin films and their results are in agreement with results of Suzuki [15].

In this paper, we have investigated the resistance change during cyclic hydrogen charging and discharging of obliquely deposited $LaNi_5$ thin film for four cycles.

2. Experimental technique

2.1 Thin film preparation :

The $LaNi_5$ thin film (size 1 cm × 1 cm) of thickness 1300Å were deposited by flash evaporation method at a pressure of 2×10^{-5} Torr at room temperature at different angles (θ = 0°, 30°, 45°, 60°, 75°) on the glass substrate (size of 2.54 cm × 2.54 cm) by obliquely deposited technique [25]. In the flash evaporation technique, the tungsten boat was heated upto 1500°C, material was allow to fall on the heated boat and it was deposited on to the glass substrate. The substrates were kept equal distance from the tungsten boat in order to get the uniform thickness maintaining the different angle of deposition θ = 0°, 30°, 45°, 60°, 75° with respect to base plate. The thickness of the sample was measured by quartz crystal thickness monitors and weighing method. After deposition, all samples were exposed to the dry

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hydrogen (purity 99.95%) at a pressure of 1 atm and left for 12 hours. The hydrogenated samples were transformed to the measurement chamber one by one. The temperature of hydrogenated $LaNi_5$ thin film was measured with the help of copper constantan thermocouple with accuracy ± 2°C.

2.2 *Hydrogenation of $LaNi_5$ thin films :*

The $LaNi_5$ thin films were activated at 300°C for 30 min. at a pressure of 2×10^{-5} Torr. The samples were cooled to room temperature and again hydrogenated at 1 atmosphere hydrogen pressure for hydrogen absorption. For discharging, the samples were heated slowly and gradually by varying power in a heater. The dry hydrogen (99.9% purity) was flushed into the vacuum chamber for charging the sample for second cycle.

Each sample was charged with hydrogen and discharged by heating under vacuum conditions. For each subsequent charging cycle, all samples in turn, were exposed to hydrogen under similar condition. The charging and discharging cycles of $LaNi_5$ sample were monitored by measuring the resistance variation with the help of a digital multimeter having input impedance of about $\approx 10\ M\Omega$.

2.3 *Composition of $LaNi_5$ thin films :*

The $LaNi_5$ thin films were characterised by X-ray fluorescence (XRF) technique to study the composition. From the XRF spectrum, the composition of the thin films was found to be almost same as that of bulk $LaNi_5$.

3. Result and discussion

3.1 *Effect of deposition angle on resistance of $LaNi_5$ thin films :*

Figure 1 shows the variation of resistance with angle of deposition of $LaNi_5$ thin films. It can be seen from the Figure that resistance of thin film increases with angle of deposition. Thickness of all thin films are almost same therefore the large variation in the resistance of thin films is due to large variation

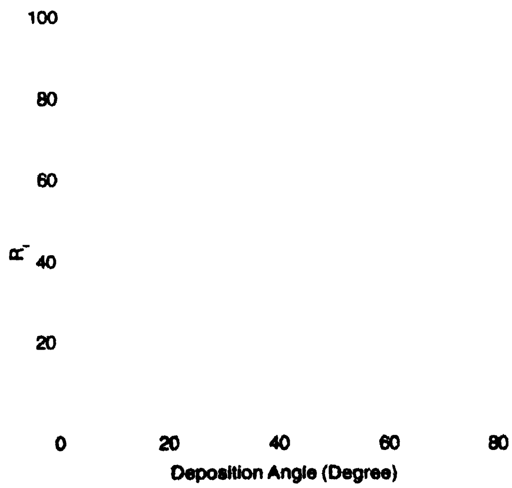

Figure 1. R_θ / R_0 *vs* angle of deposition.

during deposition. In oblique deposition, the growth of film is in the direction of vapour beam ; hence crystal grows in the direction of vapour beam, casting shadow behind, resulting in vacant spaces known as "Self Shadowing Effect" (26, 27). In such type of growth, due to Self Shadowing Effect, porosity of thin film increases. This porosity increases with increase in deposition angle [28], resulting in larger surface area than normally deposited film.

3.2 *Effect of hydrogen charging and discharging cycle :*

The charging and discharging of $LaNi_5$ thin films deposited at different angles (θ = 0°, 30°, 45°, 60°, 75°) were studied for four hydrogen charge and discharge cycles are shown in Figure 2-7.

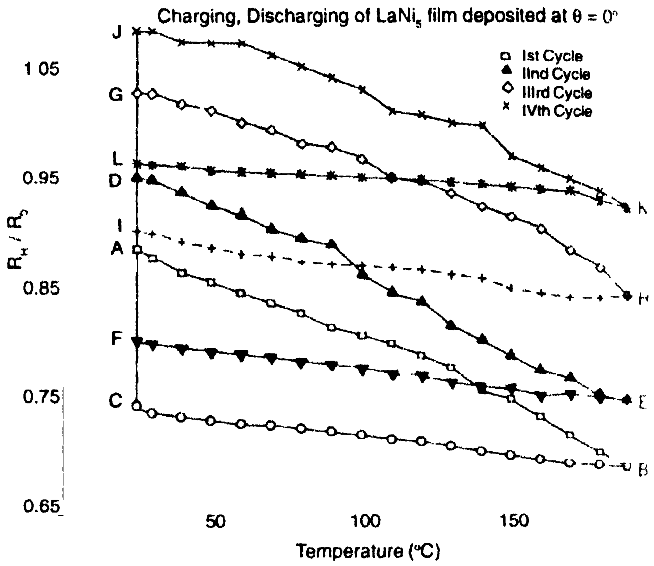

Figure 2. R_H/R_0 *vs* Temperature for θ = 0°

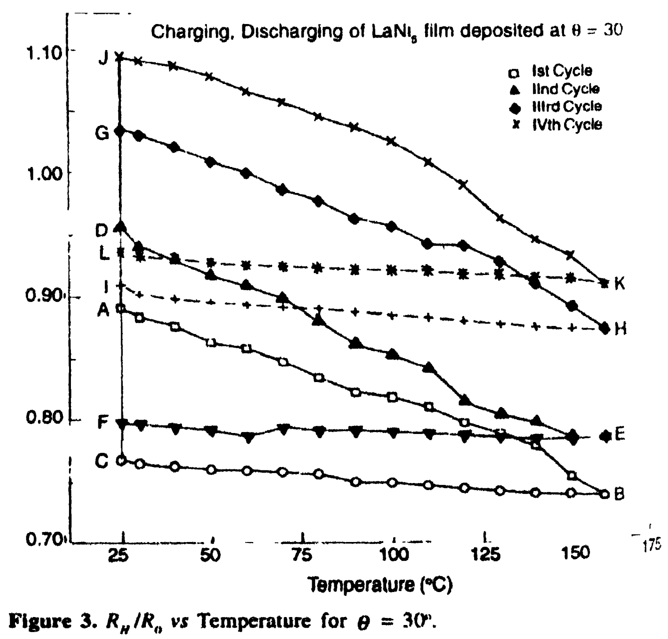

Figure 3. R_H/R_0 *vs* Temperature for θ = 30°.

In the Figures 2-6, R_H/R_0 is plotted as a function of temperature, where R_H is the resistance activation of hydrogenated $LaNi_5$ film and R_0 is the resistance of hydrogen exposed as deposited thin film. The charging of all sample was carried out at 1 atmosphere of hydrogen pressure and at room temperature, and discharging was carried out in the temperature range 30 to 170°C. The charging of all samples by hydrogen is shown in Figures 2-6 by the relative change in resistance (R_H/R_0) on the left side of vertical line marked with points A, D, G and J and hydrogen discharging by the points B, E, H and K including the curves. The increase in resistance of $LaNi_5$ thin film on charging with hydrogen is due to hydrogen atom taking one electron from the conduction band of $LaNi_5$ in agreement with Adachi *et al* [10].

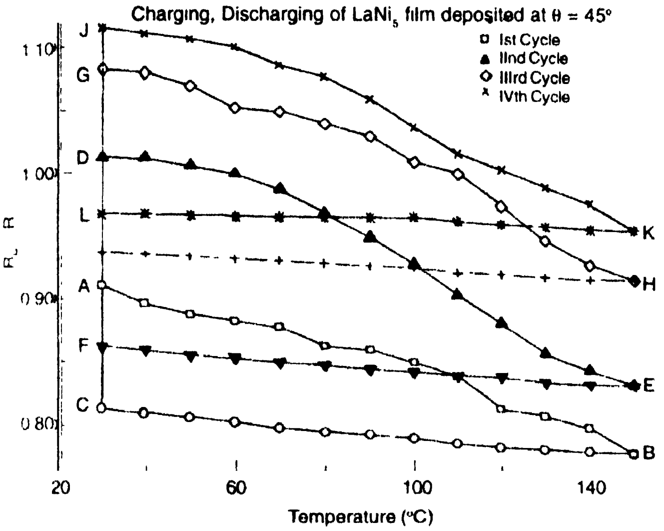

Figure 4. R_H/R_0 *vs* Temperature for θ = 45°

Ist cycle :

The hydrogenated film was heated upto 170°C at a pressure of 2×10^{-5} Torr and found that the ratio of resistance (R_H/R_0) of $LaNi_5$-H thin film decreases with increasing the temperature as shown in the portion A-B in Figures 2-6. On cooling the sample at room temperature, the ratio of resistance is stabilised indicated by the portion B-C. At this stage, the thin film sample was exposed to hydrogen at 1 atmosphere and left for 12 hours, for next cycle.

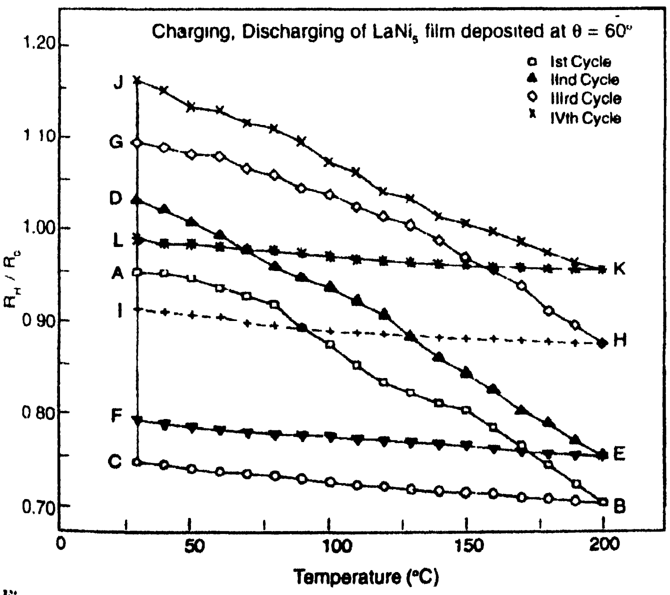

Figure 5. R_H/R_0 *vs* Temperature for θ = 60°.

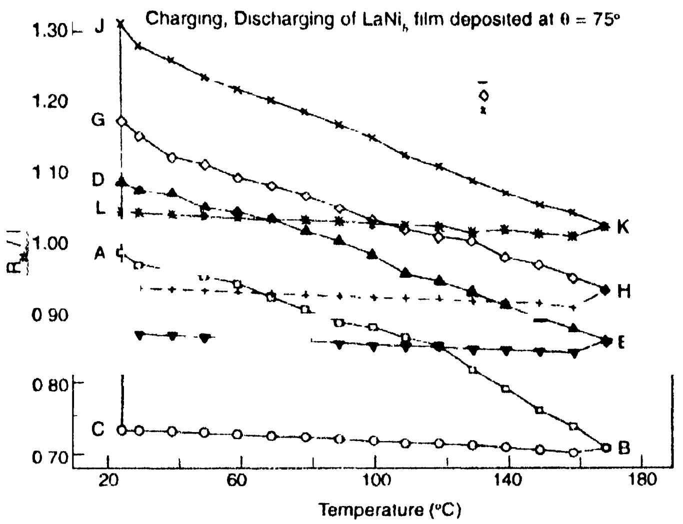

Figure 6. R_H/R_0 *vs* Temperature for θ = 75°

IInd cycle :

In second hydrogenated cycle, the increase in the ratio of resistance (R_H/R_0) of film is found to be more than Ist charging cycle as shown by the vertical line C-D. In desorption cycle, the films is heated upto 170°C, the ratio of resistance R_H/R_0 is found to decrease with temperature as shown the portion D-E in Figures 2-6. On cooling the sample at room temperature at pressure 2×10^{-5} Torr, the ratio of resistance is stabilised indicateds by the points E-F. Again thin film is exposed to a pressure 1 atmosphere of hydrogen and left for 12 hours for third cycle.

IIIrd cycle :

In the third hydrogen charging cycle, the change in the ratio of resistance is more than IInd cycle shown by vertical line F-G in Figures 2-6 and desorption cycle shows the portion G-H in Figures 2-6. Again thin films were left in hydrogen environment at 1 atmosphere for 12 hours, and for fourth cycle.

IVth cycle :

In fourth charging cycle, shown in the vertical line I–J, is the same variation as that of the Ist, IInd and IIIrd cycle with temperature. And in cooling, the resistance is shown by the portion H-I.

In first hydrogen charging cycle, small increase in the variation of resistance indicates that there exist an over layer of oxygen which is due to exposure of thin film to air during transfer of sample from one preparation chamber to one measurement chamber. This causes the less hydrogen absorption in first cycle than IInd cycle. But it seems that the effect of oxide layer is removed with number of hydrogen charging and discharging cycles shown in Figures 2-6. In fourth cycle the sample tends to acquire the stable state.

The measurement described above for four hydrogen charging and discharging cycles of $LaNi_5$ obliquely deposited films, can be understood with the help of another plot of percentage change in the ratio of resistance (R_H/R_0) due to hydrogen absorption with the angle of deposition (θ) which is shown in Figure 7. The large R_H/R_0 change with angle of deposition can be explained on the basis of "Self Shadowing Effect" introduced during the growth of thin film by obliquely deposition technique (26, 27).

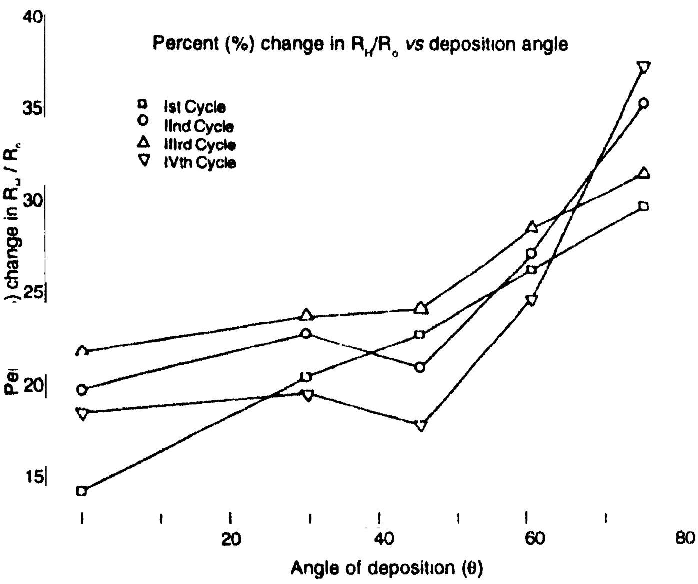

Figure 7. Percentage (%) change in R_H/R_0 *vs.* angle of deposition (θ).

The effect of cycle charging and discharging of films due to hydrogen tends to saturate the sample with hydrogen after fourth cycle. On cooling, the resistance of film increases which can be explained due to absorption of hydrogen by samples, which takes an electron from $LaNi_5$. In case of granular films, the electrical conduction is due to the hopping of electrons from one grain to another [31] which is easier at high temperature. Thus on heating the sample the resistance decreases due to increase in grain size and decreases in intergrannular distance. The different hysteresis curves obtained on heating and subsequent cooling for films deposited at different angles, (θ = 0°, 30°, 45°, 60°, 75°) could be explained on the basis of Grosky effect [29]. This is due to the inhomogeneous spatial distribution in a sample which causes strain gradients leading to deformities in the shape of samples, probably giving rise to different shapes of the curves. The results is in agreement with the results of Doyle *et al* [30] on Pd-8 at. % Y alloy, where they observed hysteresis type behaviour in the resistivity curves.

4. Conclusion

(i) The resistance of obliquely deposited $LaNi_5$ thin films increases with deposition angles.

(ii) During cyclic charging / discharging of hydrogen in $LaNi_5$ thin films, the resistance increases due to hydrogen charging and decreases while discharging it.

(iii) The amount of hydrogen absorbed increases with the number of charging and discharging cyclic and in four cycles, the sample becomes saturated with hydrogen.

(iv) The rate of charging and discharging increases with deposition angles of thin films.

(v) Percentage (%) change in variation in resistance with number of hydrogen charging and discharging increases with the number of cycles.

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