

The kinetics of Cr layer coated on TiNi films for hydrogen absorption

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Abstract. The effect of hydrogen absorption on electrical resistance with temperature for TiNi and TiNi–Cr thin films was investigated. The TiNi thin films of thickness 800 Å were deposited at different angles ($\theta = 0^\circ, 30^\circ, 45^\circ, 60^\circ$ and 75°) under 10^{-5} Torr pressure by thermal evaporation on the glass substrate at room temperature. A layer of Cr of thickness 100 Å was coated on the TiNi thin films. The changing rate of hydrogen absorption increases after Cr layer coating because Cr enhances the catalytic properties of hydrogen absorption in thin films. The rate of hydrogen absorption increases with temperature at lower range but at higher range of temperature it was found to decrease and also it was found that the hydrogen absorption increases with angle of deposition.

Keywords. Hydrogen absorption; protective layer; catalytic layer; electronegativity; oblique deposition.

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1. Introduction

TiNi is a very useful material for advanced technology. The nickel titanium alloy Ti_2Ni and TiNi have been used by [1–3] as electrode materials for reversible hydrogen electrode in nickel hydrogen system. The reversible hydrogen electrodes of this type have been studied in great detail by a number of workers [4–6] because of their increased energy density, number of charge discharge cycles and efficiency. One major problem is that traditional electrode materials for aqueous service are made of noble metals and are expensive and electrodes made of hydrides of intermetallic phases have been studied in the last few years only. The hydride batteries with hydride anodes on the prototype stage exhibit superior low-temperature behaviour, good cycling life and energy density. One should also draw attention to the possibility of developing hydride-based ‘Super Batteries’ with energy density far beyond established cell systems. Hydrides permit the design of some special energy packages which combine advantages offered by fuel cells and storage batteries [7].

The thin film metal hydrides for hydrogen storage are a new and emerging field of research because hydrogen absorption is a surface phenomenon rather than a bulk phenomenon. The large area of thin films gives fast charging–discharging rates of hydrogen absorption [8]. Study of the effect of sulfur and selenium layer coating on FeTi and TiNi thin film hydride was carried out by Singh *et al* [9,10] and they suggested that sulfur layer coating on FeTi and selenium coating on TiNi thin films produced a marked improvement in properties of thin films for hydrogen storage and charging rate becomes faster in comparison to FeTi and TiNi thin films. The formation of surface oxide layer can be prevented by the usage of a thin layer of palladium as a coating [11] and absorption of hydrogen on FeTi surface covered by palladium monolayer was investigated by Kulkova *et al* [12] and they suggested that coating is helpful for hydrogen adsorption. Hence, one can see that the activation of metal hydride is very important and one of the methods for activation is coating of certain catalytic elements to the alloy to improve the activation performance while retaining its inherent character. In this paper, we are presenting the kinetics of hydrogen absorption at low pressure and temperature to check the suitability of the material for battery hydride electrodes.

2. Experimental

The TiNi thin films were obliquely deposited at angle ($\theta = 0^\circ, 30^\circ, 45^\circ, 60^\circ$ and 75°) onto a glass substrate by thermal evaporation (resistive heating of a wire of Ti and Ni (purity 99.99%) layer by layer at 10^{-5} Torr pressure and room temperature. The evaporation technique to deposit thin films of an oblique deposition angle is described elsewhere [9]. The samples were placed at equal distance from the boat spiral assembly in order to get samples of the same thickness. The size of the glass substrate used was 2.54×2.54 cm and thin films of 1×1 cm were deposited on this substrate. The thin-film electrode of Al was deposited on all the samples for providing electrical contacts to the samples before depositing TiNi thin films. The thickness 800 Å of the films was measured with the help of quartz crystal thickness monitor supplied by Hind High Vacuum Co. (India). A layer of chromium (Cr) (purity 99.99%) of thickness 100 Å was deposited on TiNi thin films using a tungsten spiral filament for evaporation. Dry hydrogen at room temperature and atmospheric pressure was introduced into the vacuum chamber for the hydrogenation of TiNi and TiNi–Cr thin films. The DC resistance of TiNi and TiNi–Cr thin films was measured by the two-probe method with the help of a digital multi-meter of input impedance of 10 M Ω and temperature dependence of hydrogen absorption was measured using a temperature controller.

3. Results and discussion

3.1 Kinetics of hydrogen absorption in TiNi and TiNi–Cr thin films

The samples under 10^{-5} Torr pressure were exposed to dry hydrogen at atmospheric pressure and room temperature which resulted in change in the value of resistance

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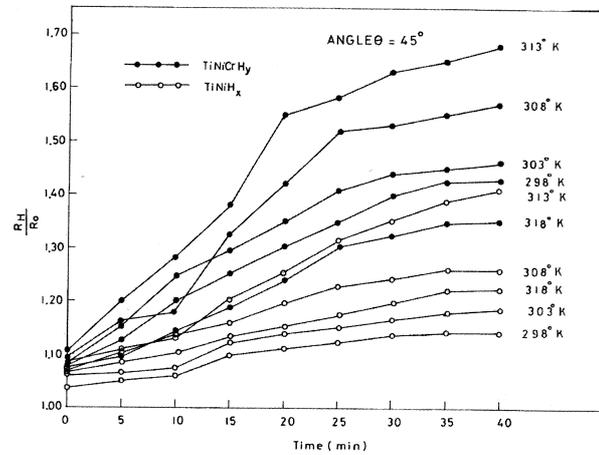


Figure 1. The relative resistance R_H/R_0 for TiNi and TiNiCr thin films vs. time during hydrogen absorption, where H_x is the hydrogen content in TiNi thin films and H_y is the hydrogen content in TiNiCr thin films.

of TiNi and TiNi–Cr thin films as a function of time for different temperatures. Figure 1 shows the relative resistance for TiNi and TiNi–Cr thin films vs. time for the angle $\theta = 45^\circ$ for different temperatures. The behaviour for other angles resembles that in figure 1 for hydrogen absorption kinetics, where R_H represents the resistance of hydrogenated samples with time and R_0 is the resistance before it was exposed to hydrogen. The increases in resistivity of TiNi thin films during hydrogen absorption are due to charge transfer from Ni to hydrogen in hydrides. The process of charge transfer can be understood by the concept of electronegativity of elements. The electronegativity of Ti is smaller than that of Ni which is less electronegative than hydrogen. This produces charge transfer from Ti to Ni in the host compound and to hydrogen in the hydrides.

Consequently, we can expect decrease in the number of 3d electrons of Ni during hydrogen absorption in TiNi thin films. The abovementioned concept explained charge transfer phenomena also applied for TiNi–Cr thin films. The charge transfer occurs from Ti to Ni and also from Cr to Ni in host metal (because electronegativity of $Ti < Cr < Ni < H$) after the layer coating of Cr on TiNi thin films. This produces easy charge transfer from Ni to H because of majority charge on Ni elements. So, after Cr layer coating, hydrogen absorption was observed higher in TiNi–Cr thin films than in TiNi thin films. Similar concept was applied for $ZrMn_{2-x}Fe_x$ alloy by Fuji *et al* [13] and for FeTi–Mn by Singh [14] and it was found that hydrogenation leading to increase in resistivity occurred due to capture of electron by hydrogen absorption. After 40 min of hydrogen absorption, the resistance of the samples becomes a constant, indicating that the saturation of samples due to atmospheric equilibrium pressure of hydrogen occurs but hydrogen absorption increases with temperature.

3.2 Temperature effect on hydrogen absorption in TiNi and TiNiCr thin films

It is observed in figures 2a and 2b that the absorption of hydrogen increases with lower temperature and decreases at higher temperature at atmospheric pressure of hydrogen. In the case of the bulk hydrides, initial hydrogen absorption increases with temperature. Since the initial hydride formation raises the temperature and as a result of expansion of the metallic lattice, the surface layer cracks due to this reaction speed-up. The hydrogenation disintegrates the host metal, a fresh surface is produced and the reaction is further accelerated [15]. But at higher temperature the reaction of hydrogen with a metal is usually an exothermic process. That is, enthalpy (H) of formation is negative and so the plateau pressure increases with temperature [16]. It means a higher pressure is needed for further hydrogen absorption. Similar results were observed by Sakaguchi *et al* [17] and according to them the temperature dependence of the isotherm concerns the hydrogen content at higher temperatures but was less than that for a lower temperature under the same pressure for LaCO₅ films.

Figures 2a and 2b shows the graph between temperature vs. relative resistance for the time period of 20 and 40 min for hydrogen absorption. It is observed that hydrogen absorption increases with temperature at low temperatures but after a certain temperature hydrogen absorption decreases. It means that there is an optimal temperature around 313 K, and increasing the temperature above this value has an adverse effect and absorption of hydrogen decreases.

The higher the temperature the larger the heat effect. Excessively high temperature must be avoided in order to study intrinsic kinetics. Increasing the temperature above the moderate temperature shows adverse effect [18], the absorption of hydrogen decreases but at constant temperature the absorption becomes faster with increasing pressure. The layer coating of Cr on TiNi enhances the hydrogen absorption and it is also observed in figure 2b that as the absorption time increases hydrogen absorption also increases and it gets saturated with hydrogen equilibrium pressure. This is the optimum amount of hydrogen absorbed by TiNi and TiNiCr thin films at atmospheric pressure of hydrogen. Similar results were observed by Kulkova *et al* [12] also for the absorption of hydrogen on TiFi surface covered by palladium monolayer and it is suggested that coating is helpful for hydrogen adsorption.

3.3 Kinetics of hydrogen absorption in TiNi and TiNiCr thin films with angle of deposition

Figure 3 shows that the resistance of TiNi and TiNiCr obliquely deposited thin films increases with angle of deposition. This is due to structural variations [19,20] in obliquely deposited thin films. At large angle of deposition granular thin films are deposited, where growing islands are bigger in size and they are separated by vacant spaces due to self-shadowing effect [21,22]. The hydrogen absorption increases with the angle of deposition suggesting that the structure becomes more porous as the angle of deposition increases [19]. The resistance of thin films increases on exposure to hydrogen in vacuum chamber as reported by Adachi *et al* [23,24] for LaNi₅

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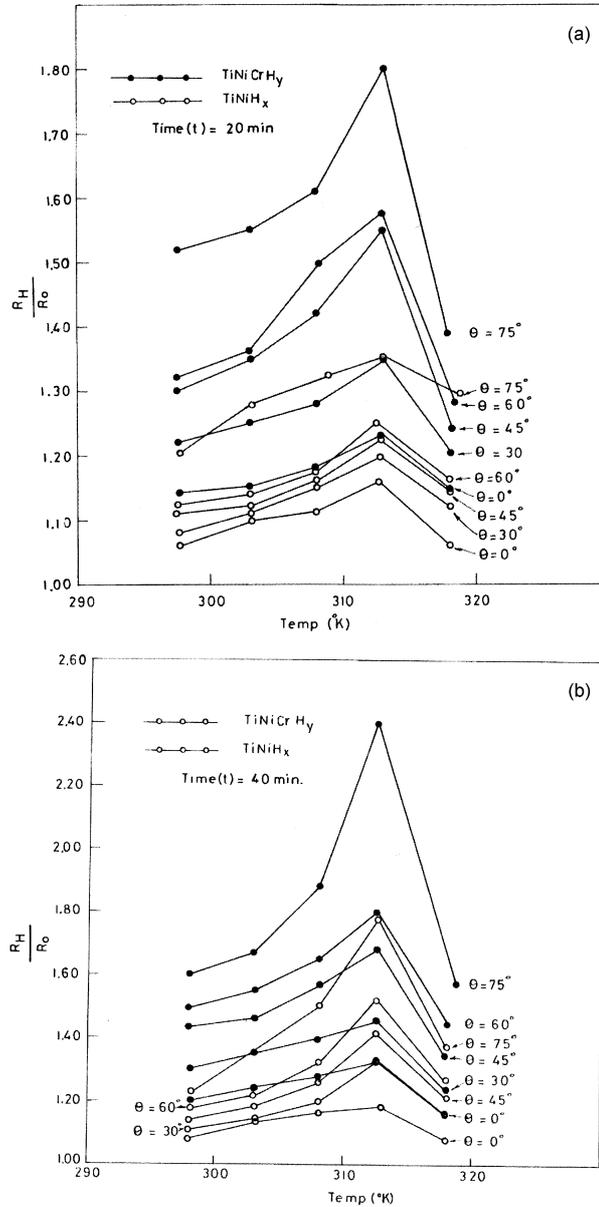


Figure 2. (a) The kinetic curves of TiNi and TiNiCr thin films with temperature for different angles at a time period of 20 min. (b) The kinetic curves of TiNi and TiNiCr thin films with temperature for different angles at a time period of 40 min.

films. The increase in resistivity is due to the formation of hydrogen anions [H] during hydrogen absorption [24]. Another explanation for the resistivity change on

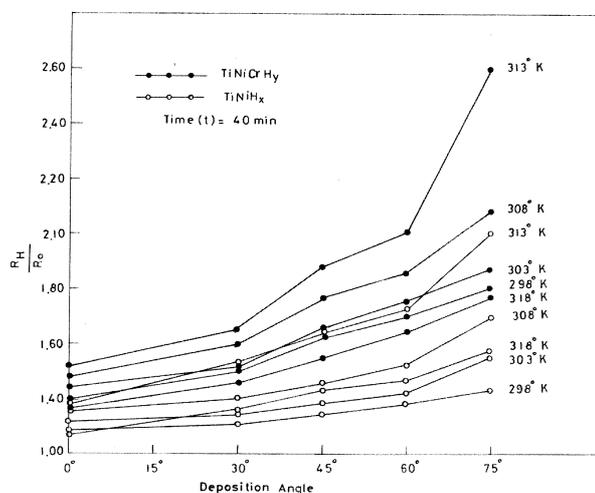


Figure 3. The hydrogen absorption mechanism of TiNi and TiNiCr thin films with angle of deposition at different temperatures for a time period of 40 min.

hydrogenation is that the band structure itself might be changed [25]. Hence the fact that hydrogen absorption increases with angle of deposition supported our earlier work [26]. The absorption increases with temperature also and found maximum absorption of hydrogen at 313 K with angle of deposition. After this temperature, absorption decreases with the angle of deposition because higher temperature needs a higher pressure for more absorption of hydrogen. The hydrogen absorption also found to increase with layer coating in Cr on TiNi thin films. The samples reach saturation at 40 min due to equilibrium pressure of hydrogen. It was suggested that low pressure and temperature of hydrogen absorption is very useful in battery hydrides to remove encasement problem in cells.

4. Conclusion

- (1) Hydrogen absorption increases with the angle of deposition.
- (2) The charging rate becomes faster after coating the TiNi thin films with Cr.
- (3) The critical temperature is 313 K for TiNi and TiNi–Cr films to maximum hydrogen absorption at the atmospheric hydrogen pressure.
- (4) The coating of catalytic layer of Cr enhances the hydrogen absorption.

Acknowledgements

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