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Surface studies on activated and hydrided $CaNi_5$ alloy

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X-ray photoelectron spectroscopic studies on the activated pure $CaNi_5$ alloy as well as the hydride formed at 1 atm pressure and room temperature, $CaNi_5H_{4.8}$, showed that on activation calcium segregates to the surface and forms the oxide, whereas most of the nickel on the surface is present in the metallic form. This indicates that the coexistance of the oxide phase and the metal phase is essential for the facile hydriding behaviour of $CaNi_5$.

1. Introduction

Of the available alloy materials for hydrogen storage applications as "rechargeable metal hydrides", AB_5 type systems have received considerable attention [1] because of their ability to form hydrides at modest hydrogen pressures and room temperature. Among the AB_5 type systems, $CaNi_5$ appears to be one of the promising materials for hydrogen storage. There are various conflicting reports on the $CaNi_5$–H system [2–5]. Van Mal *et al.* [3] reported a plateau pressure of 15 atm for absorption at room temperature but have not identified the composition of the hydride. Sandrock *et al.* [2] have observed two plateau pressures at 0.5 and 25 atm for hydrogen sorption at 25° C with the corresponding compositions approximating to $CaNi_5H_5$ and $CaNi_5H_6$. Shinar *et al.* [5] also report a hydride with the composition $CaNi_5H_8$.

Although there are numerous studies on $LaNi_5$, a prototype of AB_5 alloys, studies pertaining to $CaNi_5$ are rather limited. The aspects on which information is particularly required include:

1. the exact composition of the hydride formed at low pressures;
2. the surface segregation effects [6, 7], since in the case of $LaNi_5$ it is known that lanthanum diffuses to the surface and superparamagnetic nickel precipitates are formed; and
3. the process of activation of $CaNi_5$ and the validity of models involving the separation of surface oxides or different surface segregation effects.

The present communication, therefore, concerns these aspects with respect to $CaNi_5$ alloy by means of equilibrium hydrogen sorption mesurements as well as by X-ray photoelectron spectroscopic method.

2. Experimental procedure

The sample $CaNi_5$ (supplied by Ergenics Corporation, USA as HYSTOR 201) was activated by the following procedure.

The alloy was heated at 300° C under vacuum for a period of 90 min. Then keeping the temperature the same, hydrogen gas was admitted to a pressure of 150 torr. The sample was left in contact with hydrogen for 2 h and then evacuated completely at 300° C until a pressure of 10^{-6} torr was obtained. It was cooled and the absorption measurements were carried out.

The X-ray photoelectron spectroscopic analysis was performed on a Vacuum Generators ESCALAB spectrometer at a base pressure of 10^{-8} torr. The absorption measurements were carried out in an all-glass volumetric unit which can operate up to 1 atm pressure.

3. Results and discussion

3.1. Equilibrium hydrogen sorption measurements

Fig. 1 shows the hydrogen absorption/desorption hysteresis loop at 25° C for $CaNi_5$ up to 1 atm pressure. The plateau pressure (0.5 atm at 25° C) agrees with the report of Sandrock *et al.* [2] who have reported three absorption plateau pressures around 0.03 to 0.04, 0.5 and 25 atm at 25° C.

Fig. 2 shows the pressure–composition–temperature (P–C–T) behaviour of the system for absorption isotherms in the temperture range 0 to 35° C. Sandrock *et al.* [2], from a complete analysis of the P–C–T isotherms, deduced that the pseudo-binary system $CaNi_5$–H_2 contains four phases, an α-solution of hydrogen in $CaNi_5$, and three compound hydrides of average compositions approximating to $CaNi_5H$, $CaNi_5H_5$ and $CaNi_5H_6$, and designated them as β, γ and δ phases, respectively. In the present experiment, because of the restriction of the upper limit to the pressure range, the phases that can be identified are α, β and γ. The α-solution, with small values of x (~ 0.2), should be caused by initial chemisorption and trapping regions. However, the β and γ phases exhibit considerable hydrogen solubility with compositions at 25° C extending for the β-phase between $CaNi_5H_{0.6}$ to $CaNi_5H_{0.9}$, while the γ-phase composition range is $CaNi_5H_{4.4}$ to $CaNi_5H_{4.8}$. The values of plateau pressures were used in the plots of $\ln p$ against $1/T$ (Fig. 3) for obtaining the values of standard enthalpies of formation. The values of standard enthalpies for the formation of β and γ hydrides are 50 and 32 kJ (mol H_2)$^{-1}$, respectively. These values are comparable with those reported in literature [2].

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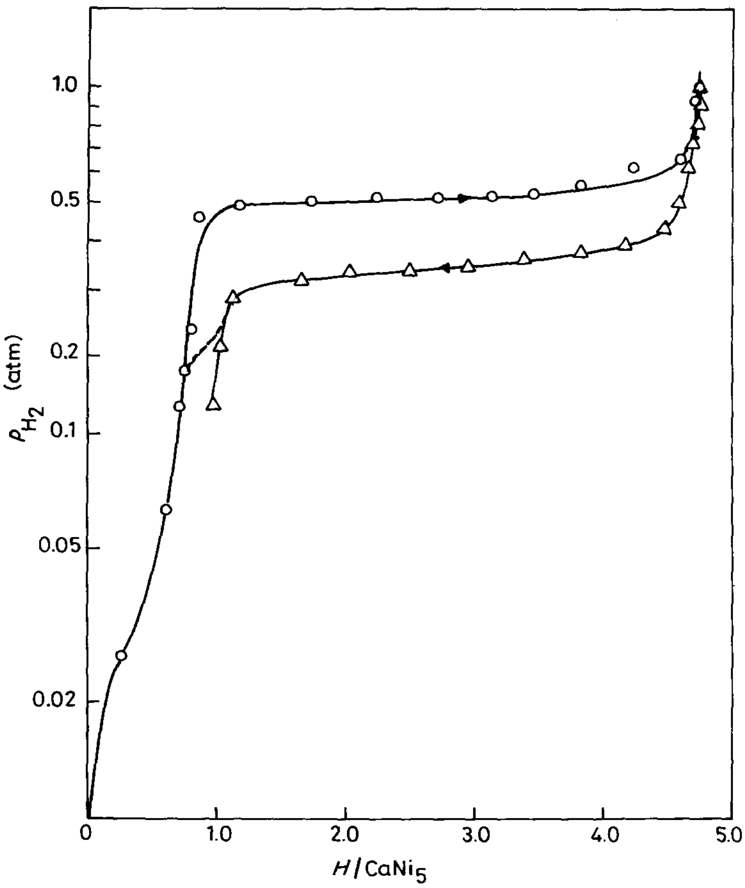

Figure 1 Hydrogen absorption/desorption hysteresis loop for $CaNi_5$ alloy at 25° C. (△) Adsorption, (○) desorption.

3.2. X-ray photoelectron spectroscopic analysis

The X-ray photoelectron spectra of core levels of Ni $2p_{3/2}$, Ca $2p_{3/2}$ and O 1s were recorded for the activated (by high temperature evacuation) as well as the hydrided sample (after evacuation the $CaNi_5$ alloy was hydrided at 760 torr hydrogen at 25° C resulting in a composition approximating to $CaNi_5H_{4.8}$). The observed XPS peak intensities were used for the evaluation of the relative concentrations of the various species on the surface using appropriate values for the photoionization cross sections. Fig. 4 shows the spectra obtained for both samples, and the data extracted from these spectra are assembled in Table I. For

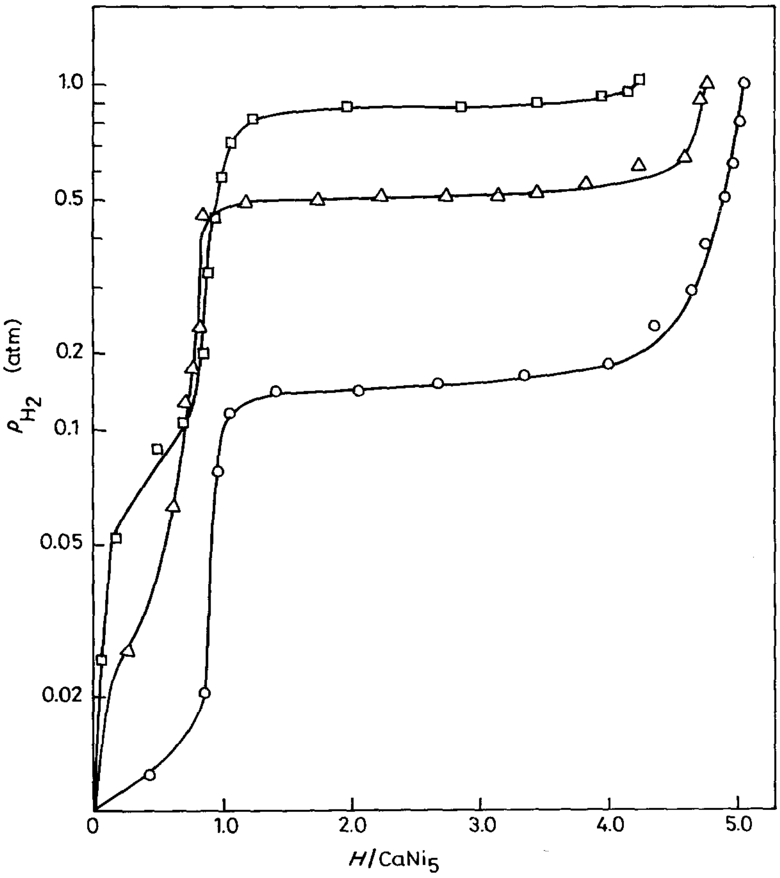

Figure 2 P–C–T behaviour of the $CaNi_5$ system for hydrogen absorption in the temperature range 0 to 35° C. (□) 35° C, (△) 25° C, (○) 0° C.

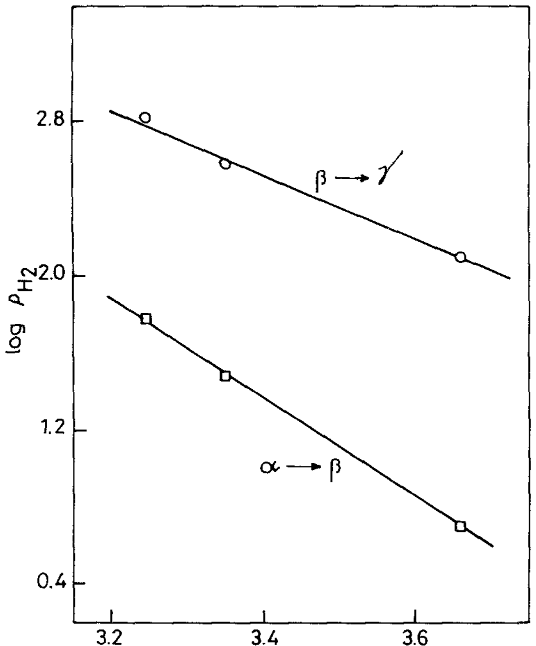

Figure 3 Vant Hoff plots for the $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ phase transitions.

comparative purposes, the 2s region of calcium was also scanned and the data obtained are also included in Table I. The points that emerge from these results are:

1. the values of binding energy of calcium $2p_{3/2}$ in the unhydrided and hydrided forms are 347.3 and 347.1 eV and the values of $2p_{3/2}$–$2p_{1/2}$ separation is around 3.4 eV;
2. in the case of nickel, peak in the $2p_{3/2}$ region of nickel can be resolved by deconvulsion into two peaks with binding energy values 852.1 and 853.6 eV in the case of the hydrided sample while in the case of the unhydrided sample only the high binding energy peak was obtained.

Schlapbach and co-workers [8-12] studied the chemisorption-induced surface segregation in $LaNi_5$ and $ThNi_5$ and concluded that lanthanum or thorium diffuses to the surface and reacts with impurities in hydrogen gas forming the oxide, while nickel precipitates as super paramagnetic particles of elemental nickel. Von Waldkirch and Zurcher [13] have provided Auger electron spectroscopic evidence for the surface segregation induced by oxygen.

Recently Schlapbach and Reiesterer [14] analysed the surface properties of $Fe_2Ti_4O_x$ and of FeTi before and after activation by means of X-ray photoelectron spectroscopy and showed that on activation of FeTi at 650 K the passivating layer of the alloy is converted into titanium(IV) and iron(0) resulting in decomposition into two phases by surface segregation and chemical reduction. From the analysis of hydrogen sorption data by binary FeTi metallic alloys, Amano and Sasaki [15–17] postulate that alloys consisting of stoichiometric FeTi and oxide phase were not hydrided without any activation treatment. They have therefore decided that the presence of excess of titanium plays an important role in the first activation sequence and the co-existance of excess titanium and the oxide phase probably promotes the activation and hydriding process. These recent developments on the elucidation of the effect of activation of the alloys and its consequences in hydriding behaviour, provide scope for analysis of the X-ray photoelectron spectroscopic results presented in this paper, in a broader perspective.

TABLE I Values of core-level binding energies for the various species in activated and hydrided $CaNi_5$ alloy

	Core-level binding energy (eV)	
	Activated alloy	Hydrided alloy ($CaNi_5H_{4.8}$)
Ni $2p_{1/2}$	872.1	869.6, 872.1
Ni $2p_{3/2}$	853.6	852.1, 853.6
Ca $2p_{1/2}$	350.6	350.6
Ca $2p_{3/2}$	347.3	347.1
Ca 2s	439.1	439.6

The results presented in Table I and Fig. 4 show that the metals are predominently present in the oxidized state in the activated form. These results are similar to those reported by Yoshikawa and Yagisawa [18] except that they have recorded a lower concentration of Ni^{2+} as compared to the results obtained in the present study. However, in the hydrided form, a considerable amount (about 60%) of the nickel is reduced to the metallic state although the presence of the oxidized form of calcium is still discernable on the surface of the hydrided alloy. The ratio of calcium to nickel as deduced from the intensities of the XPS $2p_{3/2}$ peaks shows that in the activated alloy, as well as in the hydrided alloy, there is an enrichment of calcium on the surface. Similar surface segregation of the A element of AB_5 alloys, for example $LaNi_5$ and $ThNi_5$, has been observed as a result of oxygen chemisorption [10–12]. However, the segregation of calcium appears to be less in the case of hydrided alloy as compared to the activated alloy (in the ratio of 1 : 2). This may arise due to the preferential reduction of nickel and its separation on the hydrided sample where it can promote the dissociative adsorption of hydrogen. The excessive segregation of calcium to the surface and its easy oxidation in the activated alloy show that the presence of oxide phase in co-existance with metallic phase capable of dissociating hydrogen molecules is the favourable situation for the observation of facile hydriding behaviour.The presence of a high density of defects at the interface and the differences in the structures of the surface film in the interface may facilitate rapid hydrogen diffusion through the film on the interface. However, nucleation and the subsequent hydride growth will take place only after the hydrogen is permeated into the interior of the alloy. The possibility of easy formation of cracks in the multiphase systems due to differences in the surface tension values may be favourable for hydride growth. In the case of FeTi alloy, hydriding has been shown to be facile when the alloy contained a slight excess of β-Ti and the titanium(IV) oxide phase coexists with the alloy [18] (the incubation time has been shown to be considerably reduced). It is therefore deduced that the activation of $CaNi_5$ alloy by heating in vacuum and subsequent treatment with hydrogen at 300° C results in surface segregation of calcium followed by its oxidation.

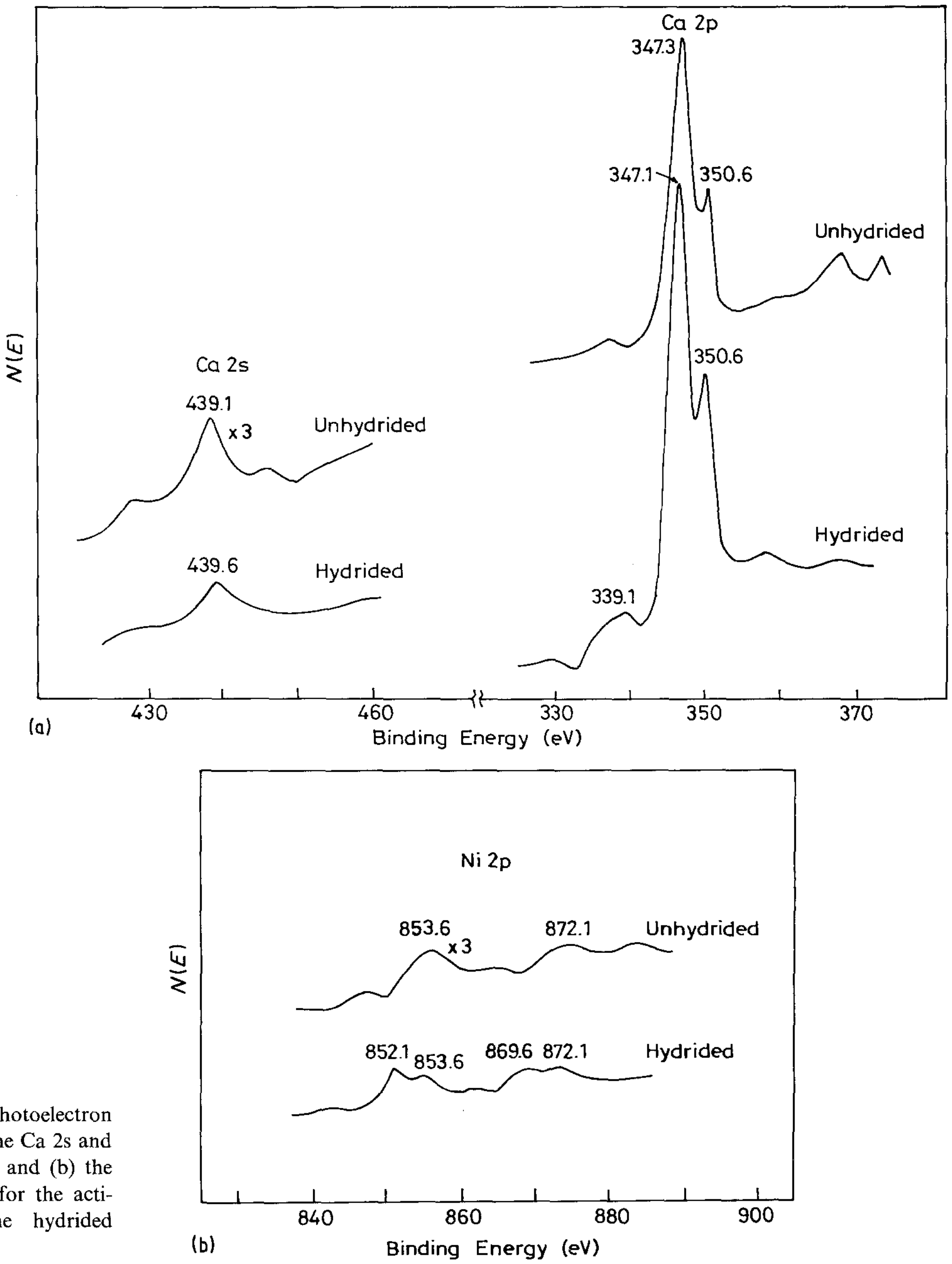

Figure 4 Photoelectron spectra in (a) the Ca 2s and Ca 2p regions, and (b) the Ni 2p region, for the activated and the hydrided alloys.

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References

1. G. G. LIBOWITZ and G. D. SANDROCK (Eds), Metal Hydrides, 1980, *J. Less-Common Met.* **73**, **74** (1980).
2. G. D. SANDROCK, J. J. MURRAY, M. L. POST and J. B. TAYLOR, *Mat. Res. Bull.* **17** (1982) 887.
3. H. H. VAN MAL, K. H. J. BUSCHOW and A. R. MAIDEMA, *J. Less-Common Met.* **35** (1974) 65.
4. C. E. LUNDIN, F. E. LYNCH and C. B. MAGEE, *ibid.* **56** (1977) 19.
5. J. SHINAR, D. SHALTIEL, D. DAVIDOV and A. GRAGEVSKY, *ibid.* **60** (1978) 209.
6. A. YOSHIKAWA and K. YAGISAWA, *Proc. JIMIS* **2** (1979) 393.
7. L. SCHLAPBACH, A. SEILER, H. C. SEIGMANN, Th. VON WALKDKIRCH and P. ZURCHER, *Int. J. Hydrogen Energy* **4** (1978) 21.
8. L. SCHLAPBACH, A. SEILER and F. STUCKI, *Mat. Res. Bull* **14** (1979) 785.
9. L. SCHLAPBACH, A. SEILER, F. STUCKI and H. C. SEIGMANN, *J. Less-Common Met.* **73** (1980) 145.
10. L. SCHLAPBACH, *Solid Stat. Commun.* **38** (1981) 117.
11. L. SCHLAPBACH and C. R. BRUNDLE, *J. Phys.* **42** (1981) 1025.
12. H. C. SEIGMANN, L. SCHLAPBACH and C. R. BRUNDLE, *Phys. Rev. Lett.* **40** (1978) 972.
13. Th. VON WALDKIRCH and P. ZURCHER, *Appl. Phys. Lett.* **33** (1978) 689.
14. L. SCHLAPBACH and T. REIESTERER, *J. Less-Common Met.* **101** (1984) 453.
15. M. AMANO and Y. SASAKI, *Trans. JIM Suppl.* **21** (1980) 329.
16. M. AMANO, T. HITARA, T. KIMMA and Y. SASAKI, *Trans. Jpn. Inst. Met.* **25** (1984) 657.
17. Y. SASAKI and M. AMANO, International Symposium on Metal Hydrogen Systems, Miami, April, edited by T. N. Veziroglu (Pergamon, Oxford, 1981) p. 551.
18. A. YOSHIKAWA and K. YAGISAWA, *Trans. Jpn Inst. Met.* **21** (1980) 383.

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