ELSEVIER

Journal of Alloys and Compounds 330–332 (2002) 215–218

Journal of
ALLOYS
AND COMPOUNDS

www.elsevier.com/locate/jallcom

Stability of $CaNi_5H_x$ stored at temperatures between 20 and 150°C

J.O. Jensen*, T.S. Møller, N.J. Bjerrum

Department of Chemistry, Building 207, Technical University of Denmark, DK-2800 Lyngby, Denmark

Abstract

The stability of $CaNi_5H_x$ stored at different temperatures was studied as a function of time. In general AB_5 metal hydrides are known to be metastable with a tendency to disproportionate at elevated temperatures. In the present study samples of $CaNi_5$ were stored in the hydrided state (as $CaNi_5H_{\sim 4.7}$) at temperatures between 20 and 150°C. After different periods of time, up to 120 days, the hydrogen absorption capacity was measured electrochemically. Significant capacity decays were observed at temperatures of 40°C and higher. The capacity decay with storage time tended to stop at a level of 147 mAh/g corresponding to 1.83 hydrogen atoms per calcium atom. X-ray diffraction revealed that the $CaCu_5$ structure was preserved after the degradation. A mathematical model for the decay is proposed.

Keywords: $CaNi_5$; Metastability; Metal hydride; Disproportionation; Stability

1. Introduction

It is well known that AB_5 alloy hydrides (AB_5H_x) are in general metastable [1]. Formation of binary hydrides (AH_y) and B metal is thermodynamically favoured. Disproportionation will eventually take place, especially at elevated temperatures. $CaNi_5$ is said to be more prone to disproportionation than $LaNi_5$, but the picture has been far from clear so far. Sandrock [2] briefly cites most results available in 1982. He expects the reaction

$$CaNi_5 + H_2 \rightarrow CaH_2 + 5Ni \qquad (1)$$

to be the ultimate result, but imagines that intermediate stages like $Ca_2Ni_7H_x$ are possible.

Substantial capacity losses of $CaNi_5$ are reported by Goodell [3] after gas cycling at 85°C. After 200 cycles the capacity was less than half the initial value. By subsequent annealing in vacuum at 500°C most of the capacity was recaptured. Oesterreicher et al. [4] stored $CaNi_5H_{5.5}$ for about one year in air at room temperature. After that and a reactivation treatment (vacuum/200°C) the hydrogen capacity had decreased to a value corresponding to $CaNi_5H_{2.1}$. However, X-ray diffraction showed that after storage the sample had predominantly returned to the un-hydrided state. We therefore find that it is somewhat uncertain whether the capacity loss was due to disproportionation of the hydride in a sense relevant here or simply a result of severe passivation during the storage period. Later Bawa et al. [5] stored 1 kg of $CaNi_5H_{3.4}$ for one year, presumably at room temperature. Periodical measurements of isotherms did not show any sign of disproportionation. Sheft et al. [6] reported a substantial capacity loss when $CaNi_5$ was contained in a hydrogen atmosphere for several years. No information was given on the storage temperature. X-ray diffraction and measurements of magnetic moment showed a small increase in free nickel and the presence of some Ca_2Ni_7, but not enough to account for the capacity loss.

On the other hand, Grant et al. [7] cycled several $CaNi_5$ samples up to 8 times with hydrogen and deuterium at temperatures from 0 to 40°C. Pressure–compositions isotherms showed perfect closure and X-ray diffraction showed only $CaNi_5$ and nickel at the levels initially present. The authors concluded that disproportionation rates are negligible at temperatures below 40°C. Bennett et al. [8] measured pressure–composition isotherms at 80°C, but could not measure desorption at 95°C afterwards. They explained this by disproportionation and based on the scarce literature available they suggested a lower threshold for the effect at 60°C. Bawa et al. [5] performed 5436 absorption cycles between 75 and 80% capacity. Absorption in the 20–40°C range and desorption in the 50–60°C range. Based on experiments and literature they concluded that below 60°C the system has adequate stability and lifetime.

---

*Corresponding author. Tel.: +45-45-25-23-14; fax: +45-45-88-31-36.

E-mail address: joj@kemi.dtu.dk (J.O. Jensen).

0925-8388/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0925-8388(01)01481-5

Sridar Kumar et al. [9] have observed formation of CaH_2 when $CaNi_5$ was subjected to hydrogen at temperatures above 350°C, none of the authors cited above have reported any sign of CaH_2 at lower temperatures. In a more recent study concerning the iso-structural hydrogen storage alloy $LaNi_5$ Grey et al. [10] stated that LaH_x is usually not seen despite severe degradation. Based on the literature they suggest that more stable La–Ni hydrides beginning with $La_2Ni_7H_x$ are initially formed. In general a relative increase in A metal (La or Ca respectively) results in a more stable hydride and in the ultimate consequence pure binary hydride (LaH_2, LaH_3 or CaH_2 respectively). Moreover, the disproportionation products may be more or less amorphous.

In this work the stability of fully charged $CaNi_5$ was studied after storage at different temperatures.

2. Experimental

The $CaNi_5$ used was HYSTOR 201 produced by Ergenics and obtained via Aldrich Chemical Company. Samples of about 0.7 g of coarse $CaNi_5$ was loaded into steel/brass pressure vessels and activated with 20–25 bar hydrogen (99.9999% pure). The first absorption was followed by three additional absorption/desorption cycles ending with absorption and the pressure was adjusted to about 20 bar. With this amount of hydrogen the gas pressure would be above the broad medium plateau (0.5 bar/25°C) and below the smaller high absorption plateau (22 bar/25°C) within the whole temperature range, 20–150°C (calculated using the van't Hoff relationship and the ideal gas equation; for 25°C isotherms see [2]). The sample vessels were closed by a valve and placed in heating cupboards in baths of silicone oil to buffer the temperature fluctuations. The charged samples were then stored for different periods of time ranging from 1 to 120 days at constant temperatures between 20 and 150°C. After storage each vessel was opened and only samples with an audible overpressure maintained was used. The hydrogen storage capacity was measured electrochemically in 6 M KOH. Before electrode preparation the powder was sieved below 45 μm to ensure that only activated and thus pulverized particles were used. 0.2 g alloy was mixed with 0.8 g copper powder (<45 μm) and cold-pressed at 4 ton/cm^2. The electrodes were cycled at 100 mA/g, charged for 5 h and discharged at the same current density to a cut-off potential of -0.6 V vs. Hg/HgO. Charge and discharge were both followed by a resting period of 30 min. The reported capacity of each sample was the highest value obtained within the first number of cycles. Selected samples were subjected to X-ray powder diffraction with a Philips PW 1729-1820-1710 powder diffractometer with Cu–K_α radiation. Calculations of 2θ values were performed with the program REFBASE.

3. Results and discussion

The reversible hydrogen storage capacities of the $CaNi_5H_x$ samples as a function of storage temperature and storage time are shown in Fig. 1. According to the pressure–composition isotherm at 25°C [2] the equilibrium composition is about $CaNi_5H_{4.7}$ at atmospheric pressure. All samples stored at 20°C had capacities corresponding to compositions close to this, and no significant decay was observed from the 20°C graph. At higher temperatures the capacity clearly decreased with time of storage and the effect was more pronounced at higher temperatures. It also appeared that the degradation had a lower limit at about

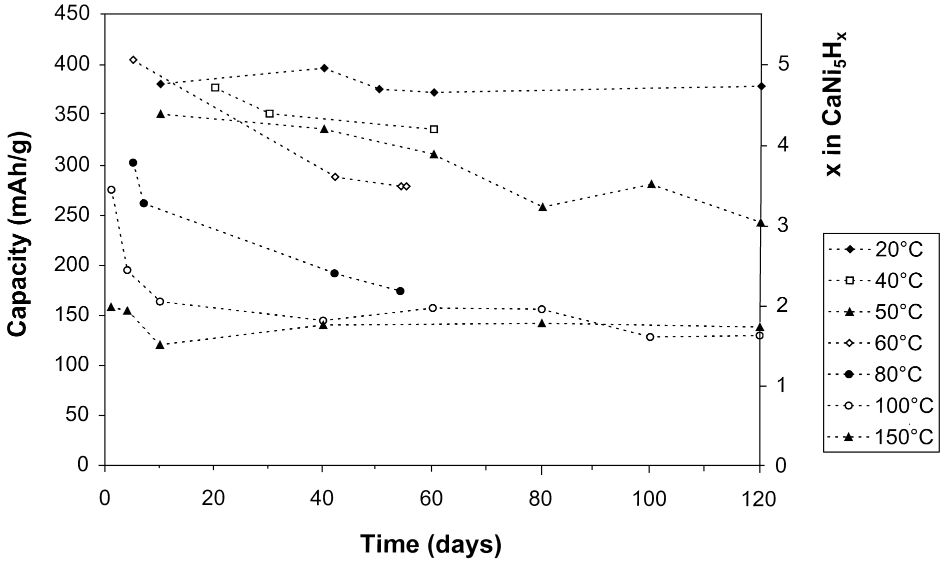

Fig. 1. Measured electrochemical hydrogen absorption capacities of $CaNi_5$ as a function temperature and time of storage.

150 mAh/g (or a little less than 2 hydrogen atoms pr. calcium atom). Apparently when this capacity was reached a more stable material was formed. A similar behaviour was seen in reference [3] during cycling at 85°C where an almost steady capacity of about 30% of the initial capacity was reached after about 400 cycles.

X-ray diffraction patterns of different samples stored for 60 days are shown in Fig. 2. The pattern for 20°C matches the pattern for un-hydrided $CaNi_5$ but with the peak positions shifted to lower values of 2θ (i.e. higher lattice constants). The shift of peaks is explained by the expansion of the unit cell caused by the hydrogen absorption. The peaks for temperatures of 50°C and higher were all broad, indicating small crystallites in the nano-crystalline regime. The X-ray patterns for samples stored for 60 days at 100°C and 150°C respectively are very similar indicating that basically the same material was formed at the two different temperatures. From Fig. 1 it can be seen that after 60 days both the 100°C and the 150°C curves have reached the approximate constant capacity of about 150 mAh/g. Thus both X-ray and capacity measurements support the idea of a more or less stable material formed. The X-ray patterns for 100 and 150°C are very similar to the original $CaNi_5$ pattern but with shifted values of 2θ and some broadening. The unit cell of $CaNi_5$ (hexagonal $CaCu_5$ structure) was fitted to the 150°C pattern with good agreement. The calculated peak positions are plotted just below the 150°C pattern on Fig. 2. I contrast to the patterns for 20°C and pure $CaNi_5$ the (001) peak is seen. The peak marked ‘x’ is probably due to remaining un-hydrided $CaNi_5$. The X-ray study shows that despite the substantial capacity decrease during storage at elevated temperatures, the $CaCu_5$ structure is maintained. The calculated unit cell dimensions are listed in Table 1. The X-ray pattern for the sample stored for 60 days at 50°C appears more compound. This is probably owing to an only partial transformation with two or more phases present. Correspondingly, the capacity is between the 60 day-values for 20 and 100°C respectively.

Table 1
Calculated unit cell dimensions for pure un-hydrided $CaNi_5$ and the sample stored for 60 days at 150°C. Both samples with hexagonal $CaCu_5$ structure

	a (Å)	c (Å)	Volume (Å^3)
Pure $CaNi_5$	4.942	3.940	83.33
150°C sample	5.094	4.058	91.19
Expansion (%)	3.0	2.9	8.6

An attempt to model the capacity decay was made assuming first order kinetics and consequently an exponential dependence of time. The temperature dependence of the rate constant was assumed to follow the Arrhenius relationship (ln k depending linearly on $1/T$) as usual for activation energy controlled kinetics. The model was fitted by minimizing the sum of the squares of the deviations from the model. 390 mAh/g was set as the zero-time capacity. The following model is proposed:

$$C(T,t) = a\exp(-kt) + C_\infty \tag{2}$$

With $a = 243$ mAh/g and $C_\infty = 147$ mAh/g. t is time (in days), T is temperature (in K), $C(T,t)$ is the electrochemical capacity (in mAh/g) after storage for the time t at temperature T. The rate constant, k, can be expressed as

$$k = k_\infty \exp(-E_A/RT) \tag{3}$$

were $k = 3.62 \cdot 10^9$ days^{-1}, E_A is the activation energy

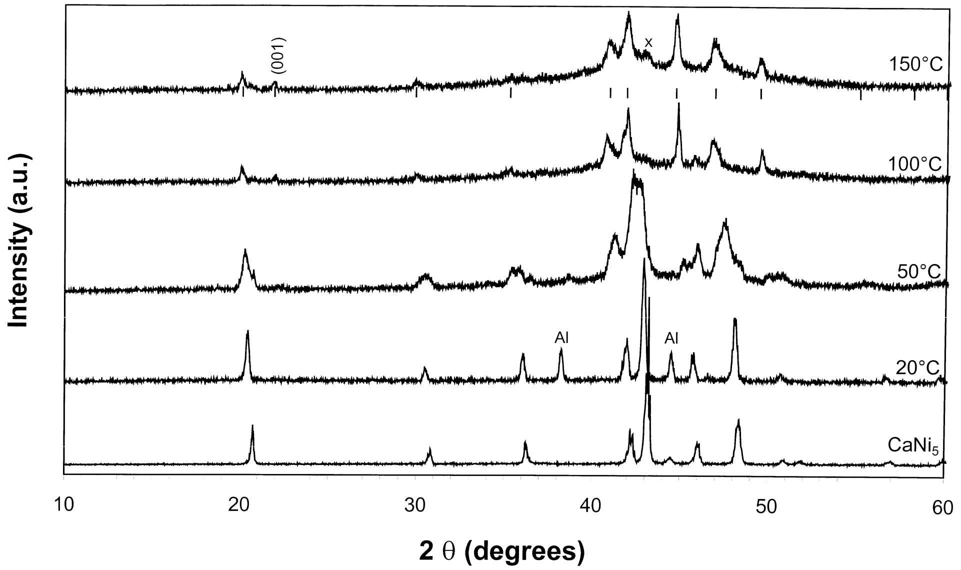

Fig. 2. X-ray diffraction patterns of four samples stored for 60 days at various temperatures from 20 to 150°C. The pattern for un-hydrided $CaNi_5$ is included for comparison. Calculated 2θ positions are shown below the 150°C pattern, see text for further details. The peaks marked ‘Al’ on the 20°C pattern are assigned to aluminium from the sample holder in the X-ray apparatus.

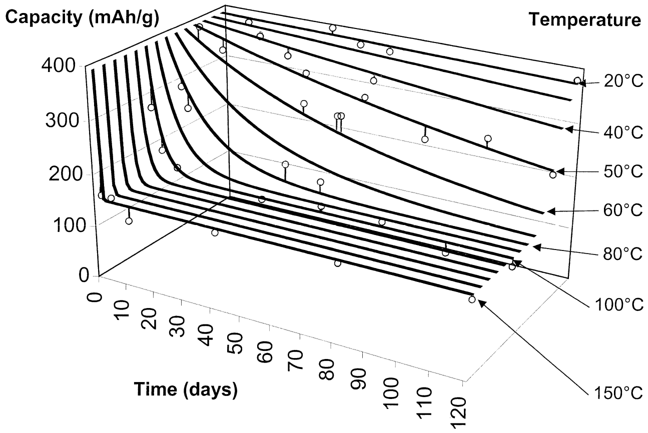

Fig. 3. The exponential model for the capacity decay as a function of temperature and time. The measured values are plotted as ○ connected to the appropriate curves.

predicted by the model, 72.4 kJmol^{-1}, and R is the gas constant, 8.314 J(mol K)$^{-1}$. The model is shown graphically in Fig. 3. According to the model the steady capacity obtained at high temperatures is 147 mAh/g corresponding to 1.83 hydrogen atoms per calcium atom. The standard deviation of the difference between the 36 measurements and the model was 20.6 mAh/g. We believe this is the order of magnitude of the general experimental error judging from the pronounced fluctuations at 100 and 150°C where constant capacity is expected. Also the curves for 20 and 50°C show fluctuations which are hardly explained except by the experimental error. Two factors might have influenced the accuracy of the capacity measurements. During initial activation and subsequent gas cycling the reaction heat heated the samples in an un-controlled manner, and some decay may have taken place already at this stage. Moreover, the samples stored at low temperatures obtained the maximum capacity within the first charge/discharge cycle while the samples stored at high temperatures required about three cycles to reach maximum capacity. Since the capacity decay of these materials (during electrochemical cycling) is generally rapid, the electrodes may have lost some capacity during the electrochemical activation (i.e. after storage).

The fact that a substantial decay in the reversible capacity was seen with the $CaCu_5$ structure basically preserved makes it possible that the first step in the degradation is formation of a more stable $CaNi_5H_x$ with hydrogen trapped in irreversible sites not capable of being discharged (under the present conditions). The remaining reversible capacity was about 1.8 hydrogen atoms. With x of about 4.7 before degradation almost 3 hydrogen atoms were either trapped or by other means unavailable.

In this study only passive storage was addressed. Cycling of $CaNi_5$ with hydrogen may affect the disproportionation process as well and the degradation kinetics significantly due to the contraction/expansion work.

4. Conclusion

$CaNi_5H_x$ was stored at different temperatures and the decay of the reversible hydrogen storage capacity was measured electrochemically as a function of storage time. It can be concluded that the decay was severe even at storage temperatures as low as 40°C. The decay tended to stop when a capacity value of about 147 mAh/g ($x=1.83$) was reached. Apparently a more stable material was then formed. X-ray diffraction patterns revealed that the hexagonal $CaCu_5$ structure was basically preserved after the loss of reversible capacity during storage. The decay rate was modelled assuming activation energy control and first order kinetics. The activation energy according to the model was 72.4 kJ mol^{-1}.

Acknowledgements

The authors wish to thank the European Commission for the financial support of the present work.

References

[1] K.H.J. Buschow, A.R. Miedema, in: A.F. Andresen, A.J. Maeland (Eds.), Proceedings of an International Symposium held in Geilo, Norway, 14–19 August 1977, Hydrides for Energy Storage, Pergamon Press, Oxford, 1978, pp. 235–249.
[2] G.D. Sandrock, J.J. Murray, M.L. Post, J.B. Taylor, Mater. Res. Bull. 17 (1982) 887–894.
[3] P.D.J. Goodell, Less-Common Met. 99 (1984) 1–14.
[4] H. Oesterreicher, K. Ensslen, A. Kerlin, E. Bucher, Mater. Res. Bull. 15 (1980) 275–283.
[5] M.S. Bawa, E.A. Ziem, Int. J. Hydrogen Energy 7 (1982) 775–781.
[6] I. Sheft, D.M. Gruen, G.J. Lamich, J. Less-Common Met. 74 (1980) 401–409.
[7] D.M. Grant, J.J. Murray, M.L.J. Post, Chem. Thermodynam. 19 (1987) 1217–1226.
[8] L.G.I. Bennett, S.D. Arguner, J.S. Hewitt, Int. J. Hydrogen Energy 11 (1986) 577–582.
[9] M.P. Sridhar Kumar, B. Viswanathan, C.S. Swamy, V. Srinivasan, Mater. Chem. Phys. 20 (1988) 245–253.
[10] E.M. Gray, T.P. Blach, C.E. Buckley, J. Alloys Comp. 293–295 (1999) 57–61.