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HYDRIDES AND DEUTERIDES OF CaNi_5

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ABSTRACT

CaNi_5 is unique among the known AB_5 hydrogen storage compounds in that three distinct hydride phases can be formed at room temperature and modest H_2 pressures. These hydrides have average compositions of approximately CaNi_5H , CaNi_5H_5 and CaNi_5H_6 , designated herein as β , γ and δ hydride respectively. Deuteride phases of identical composition can be formed but the isotopic pressure effects are different for each of the three phases. Thermodynamics of the β and γ hydrides are presented along with comments on the tendency for CaNi_5 to disproportionate when hydrided.

Introduction

The AB_5 family of intermetallic compounds represents a popular class of hydrogen storage compounds or "rechargeable metal hydrides". As can be seen from recent symposia proceedings (1,2) and elsewhere, much research on AB_5 -hydride theory, properties, and applications has been done. The best known AB_5 hydrogen storage compound is LaNi_5 , which forms a hydride of the approximate composition LaNi_5H_6 at modest H_2 pressures and room temperature (3). Almost all of the AB_5 storage compounds consist of A-elements that are either lanthanides or actinides and B-elements that are either Ni or Co. One exception to the first half of this general rule is CaNi_5 , the subject of this paper.

The fact that CaNi_5 can be reversibly hydrided has been independently observed at least four times (4-7). Van Mal et al (4) reported a plateau pressure of 15 atm (1.5 MPa) at room temperature but did not report any compositions. Sandroock (1,5) reported two plateaus: about 0.5 and 25 atm (0.05 and 2.5 MPa) at 25°C, corresponding to approximately CaNi_5H_5 and CaNi_5H_6 . Lundin et al (6) reported the 0.5 atm (0.05 MPa) plateau and hydride stoichiometry CaNi_5H_5 . Finally, Shinar et al (7), whose equipment was limited in pressure capability, also reported only CaNi_5H_5 . Structural studies have been done on CaNi_5H_5 (8), and show an orthorhombic distortion of the CaCu_5 -type hexagonal cell with a 17% volume increase upon hydriding to CaNi_5H_5 .

With the exception of the above work, there has been little other fundamental work on CaNi_5 , at least relative to the large amount of research on the prototypical AB_5 , LaNi_5 . It was clear to us that the behavior of CaNi_5 , forming more than one hydride phase, was more complex than LaNi_5 . In addition, the $\text{CaNi}_5\text{-H}_2$ isotherms of reference 5 showed an unexplained large "low-pressure-offset", i.e., the lower plateau (0.5 atm) began at the relatively high hydrogen content of $x \approx 1$ in CaNi_5H_x . This implied either: [a] the α $\text{CaNi}_5\text{-H}$ solid solution could be quite high in H-content; or, [b] there was yet another hydride phase at low x (<1) and low pressure (<0.1 atm at 25°C). The low pressure, dilute hydrogen region of the $\text{CaNi}_5\text{-H}$ system has now been explored independently at our two laboratories with identical results to be jointly presented herein along with some further pressure-composition-temperature (p-c-T) data on the established hydride phases. In addition, we have developed a p-c isotherm for the $\text{CaNi}_5\text{-D}_2$ system up to CaNi_5D_6 showing some interesting isotopic effects. Finally, a few comments will be made on the reported tendency for CaNi_5 to disproportionate when hydrided.

Experimental

Both samples and p-c-T measurements were made independently in the two laboratories contributing to this report: Inco Research & Development Center, Inc. (IRDC) and the National Research Council Canada (NRCC). The IRDC samples were made by air induction melting of commercial purity Ca ingot (99+%) and Ni pellet (99.98+%) in batches of about 12 kg. This procedure, designed to simulate likely commercial practice, is discussed in more detail elsewhere (1,5). The NRCC samples were prepared by the diffusion reaction of 99.99% purity Ca and Ni followed by annealing in degassed, argon-backfilled, welded stainless steel containers at temperatures up to 950°C . In both cases, the CaNi_5 samples produced were characterized by various techniques including powder x-ray diffraction, chemical analysis, spark source mass spectrometry, and optical metallography. All samples used for the data herein were virtually single phase CaNi_5 after preparation, with overall purities of 99-99.9%. Purity variation within this range did not substantially affect the p-c-T results.

P-c-T measurements were made using volume-calibrated stainless steel manifolds equipped with capacitance or strain-gage type pressure transducers and bourdon-tube pressure gages. Isotherms were determined in either absorption or desorption modes using the usual static (stepwise) gas titration techniques with appropriate corrections for the nonideality of H_2 . The H_2 used was 99.999+% pure and the D_2 used was 99.5+% pure. Sample temperatures were maintained within $\pm 0.1^\circ\text{C}$ during a given run. Prior to obtaining data, samples were activated and hydride/dehydride cycled about three times. All samples activated easily at room temperature and pressures of <20 atm (2 MPa). It should be noted that freshly prepared and crushed CaNi_5 will often activate at only 1 atm (0.1 MPa) H_2 pressure.

The $\text{CaNi}_5\text{-H}_2$ System

Figure 1 shows a complete 25°C H_2 absorption/desorption hysteresis loop for CaNi_5 prepared by the IRDC method. Three plateaus are evident. The intermediate (~ 0.5 atm) and upper (~ 25 atm) plateaus are those observed earlier (1,5). A small plateau is also evident at low pressure (0.03 $\sim$ 0.04 atm) in the dilute hydrogen region, reported here for the first time. The hysteresis for the lowest plateau is measurable, although almost negligibly small. The intermediate and upper plateaus show moderate degrees of hysteresis as is more common for AB_5 hydrides. The intermediate absorption plateau shows a very small onset overpressure (usually difficult to see in static isotherms).

FIG. 1

Static H₂ absorption/desorption hysteresis loop for CaNi₅ at 25°C.

Figure 2 shows the p-c-T behavior of the CaNi₅-H₂ system in desorption using a sample prepared by the NRCC method. The order of the measurements was 80, 25, 40, 60, and 10°C. The results agree with the IRDC results given in Figure 1. Only the 10°C isotherm shows the third and highest plateau since pressure measurements were limited to 15 atm. As evidenced by the full hydriding to $x \approx 6.2$ observed in the last isotherm (10°C), no significant disproportionation of the CaNi₅ hydrides occurred during this measurement sequence. The invariance of the main plateau pressure with x is evidence that the sample of the intermetallic CaNi₅ was homogeneous. All the isotherms, except that at 10°C clearly exhibit the entry into the additional low x plateau. It was not observed at 10°C because the low pressure cutoff for these measurements was 0.01 atm (1 kPa), above the plateau pressure at that temperature (see Figure 3). Since hysteresis of this lowest plateau was virtually zero and since error analysis indicated that measurements in the absorption sense would yield more accurate determination of low x values, particularly for regions where pressure < 0.1 atm, the detailed isotherm measurements in the region $0 < x < 1.0$ shown in Figure 3 were made via absorption. A nearly pressure-invariant region, hence a two-phase region, for x approximately 0.2 to 0.8 is evident at all the measurement temperatures.

Based upon these isotherms, it is clear that the pseudo-binary system CaNi₅ - H₂ contains 4 phases, an α solution of H in CaNi₅ and three compound hydrides of average compositions approximately CaNi₅H, CaNi₅H₅ and CaNi₅H₆, designated as the β , γ and δ phases respectively. The α solution extends to about $x \approx 0.2$ but this probably includes both the chemisorption and trapping regions which have been observed in related systems (9,10). The β and γ phases appear to exhibit substantial regions of hydrogen solubility; for example, at 25°C the β phase exists for approximately CaNi₅H_{0.75-1.2} and the γ phase exists for about CaNi₅H_{4.5-5.5}. Up to a pressure limit of 65 atm (6.5 MPa), the δ phase exists for CaNi₅H_{6.2+}. Preliminary results of a detailed calorimetric study (11) have confirmed the existence of the β phase and its relatively wide solubility range.

FIG. 2

Static H₂ desorption isotherms for CaNi₅.

FIG. 3

Static H₂ absorption isotherms for CaNi₅ in the dilute hydrogen region.

Using plateau pressures for $x = 0.5$ and $x = 3.0$, obtained from the data illustrated in Figures 2 and 3, the Van't Hoff plots for the $\alpha + \text{H}_2 \rightarrow \beta$ and $\gamma \rightarrow \beta' + \text{H}_2$ transitions respectively, shown in Figure 4, were obtained. For the second transition, the β phase is designated as β' to indicate that it differs slightly in composition from the β phase material formed by the first transition. Insufficient data exist to permit a similar analysis for the $\gamma + \text{H}_2 \rightarrow \delta$ transition. From these results the standard enthalpies of the first two transitions are -43.0 and $-33.5 \text{ kJ (mol H}_2\text{)}^{-1}$ respectively. The latter value is directly comparable to the Van't Hoff based enthalpy reported earlier, $-31.8 \text{ kJ (mol H}_2\text{)}^{-1}$ (5). The accuracy of these enthalpies is uncertain considering the apparent relatively rapid variation in the phase boundaries with temperature.

FIG. 4

Van't Hoff plots for the $\alpha \rightarrow \beta$ and $\gamma \rightarrow \beta'$ plateaus of FIGS. 2 and 3.

The formation of four distinct phases (one metal solid solution and three hydrides up to AB_5H_6) under easily obtainable conditions [H_2 pressure $< 100 \text{ atm}$ (10 MPa)] is a unique phenomenon among known $\text{AB}_5\text{-H}_2$ systems. LaCo_5 shows four plateaus (five phases) up to LaCo_5H_9 , but the two highest plateaus are achievable only at very high pressures [$\sim 1000 \text{ atm}$ (100 MPa)] at room temperature (12). The distinct plateaus can be discussed in terms of interstitial site occupancies, although we are aware of no neutron diffraction data for the CaNi_5 hydrides to allow us to be specific. Lakner et al (12), taking into account the Switendick limit of 0.21 nm for H-H closest approach in a crystal (13), have convincingly shown that there is a maximum filling of nine interstitial positions theoretically possible for hydrogen atoms in an AB_5 structure: six tetrahedral and three octahedral. In the case of LaNi_5 , with one plateau up to LaNi_5H_6 , the free energy changes involved in the filling of the first six sites are identical. In the case of CaNi_5 , with three distinct plateaus up to CaNi_5H_6 , it is evident that the filling of various sites represents greatly differing free energy changes.

Lakner et al (12) have shown that several AB_5 compounds exhibit additional plateaus at very high H_2 pressures, often reaching or approaching the theoretical maximum composition of AB_5H_9 . High pressure isotherms have not been developed for CaNi_5 . It seems likely that CaNi_5 would exhibit even more plateaus at pressures above those used in this study [$\sim 65 \text{ atm}$ (6.5 MPa)].

The $\text{CaNi}_5\text{-D}_2$ System

Studies of the $\text{CaNi}_5\text{-D}_2$ system have yielded unusual results that add to the list of interesting CaNi_5 properties. A 25°C D_2 desorption isotherm is shown in Figure 5 and compared to a 25°C H_2 desorption isotherm obtained on the same sample (prepared by the IRDC method). First of all, it can be seen that the deuterides of CaNi_5 also exhibit three plateaus for virtually the same compositions as the hydrides. This, of course, is not unusual. What is somewhat unusual is that the isotopic pressure effects are different for each plateau. The normal isotope effect is that the deuteride tends to exhibit slightly higher dissociation pressure than the corresponding hydride (14). For CaNi_5 (Figure 5), the $\beta \rightarrow \alpha$ plateau indeed shows a higher pressure for the β -deuteride, consistent with the normal isotope effect. The intermediate $\gamma \rightarrow \beta$ plateau shows no detectable isotope effect. Finally, the upper $\delta \rightarrow \gamma$ plateaus shows a pronounced inverse isotope effect, the δ -deuteride exhibiting only about 1/3 the plateau pressure of the δ -hydride.

FIG. 5

Comparison of the H_2 and D_2 static desorption isotherms of CaNi_5 at 25°C .

Isotope effects in hydrides are usually discussed in terms of hydrogen/deuterium entropy effects (14). These effects are clearly site dependent in CaNi_5 , resulting in quite different qualitative effects for each phase. This suggests that isotopic studies such as these should aid in the understanding of the specific local H-site energetics. Finally, because the deuterides of CaNi_5 are virtually identical in composition to the hydrides, neutron diffraction studies on deuterides should give structures that are in close correspondence to the hydrides.

Stability of CaNi₅ Hydrides

Those interested in using CaNi₅ either for fundamental studies or engineering applications should be aware of its apparent tendency to disproportionate in hydrogen environments. Indeed most, if not all, AB₅ hydrides have the thermodynamic tendency to disproportionate. In the case of CaNi₅, one would ultimately expect the reaction

to dominate, although intermediate stages of decomposition (e.g., Ca₂Ni₇H_x) are possible. Because disproportionation of AB₅ hydrides involves diffusion of A and/or B atoms, it should be highly temperature dependent. LaNi₅H₆ disproportionates very slowly at room temperature, but can degrade rapidly at temperatures on the order of 300°C (15).

The experimental evidence for CaNi₅ disproportionation is mixed but seems to strongly suggest a greater tendency for disproportionation than LaNi₅. Sheft et al (16) reported a loss of about half the CaNi₅ hydrogen capacity during "several years" storage at room temperature in hydrided form. Sirovich and Ginsburgh (17) reported a substantial loss of capacity, along with isotherm distortion, after using CaNi₅ hydrides for a week in the 49-100°C range. It should be noted that Sirovich and Ginsburgh were able to regenerate the alloy by annealing for 24 hours at 461°C under vacuum. Goodell (18) observed a significant loss of CaNi₅ capacity during about 250 hydride/dehydride pressure cycles at about 85°C. Oesterreicher et al (19) noted significant disproportionation of CaNi₅H_{5.5} during one year storage. More encouraging than the above results are those of Bawa and Ziem (20), who found good stability of CaNi₅H_{3.4} during storage for more than a year and also good cyclic stability to more than 5000 absorption/desorption temperature cycles (up to 60°C). Bawa and Ziem feel that CaNi₅ can be used if the temperature is kept below 60°C. It is clear from the general trend of observations cited above that care must be used with CaNi₅ to avoid the disproportionation problem.

Concluding Remarks

We feel that the CaNi₅-H₂ system represents a unique example in the field of AB₅ intermetallic compound hydrides and is comparable in research potential to LaNi₅. Its easily achieved, multi-plateau characteristics and its unusual isotope effects offer fertile ground for fundamental studies. Its relatively low cost offers important possibilities in the applications field. Even its main drawback, susceptibility to disproportionation, offers some interesting research challenges.

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