Cox of the University of Georgia for running the carbon-13 spectra.

Registry No. $C_{11}H_{10}Cr(CO)_3$, 51731-31-8; bcht, 264-08-4; $Cr(CO)_6$, 13007-92-6.

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Hydrogen Solubility in 1:5 Compounds between Yttrium or Thorium and Nickel or Cobalt

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There is great interest in the hydrogen absorption by metals since hydrogen is a possible candidate for use as a future fuel[1] and since the nature of hydrogen in metals is not well understood.[2] Recently it was found that a number of intermetallic compounds of a rare earth metal and a transition metal absorb large quantities of hydrogen gas at the ambient temperature under moderate pressures (~1-~100 atm) with substantial change in their physical properties.[3,4] Among those intermetallic compounds, $LaNi_5$ is an attractive material for hydrogen storage because of its large hydrogen-holding capacity, its favorable equilibrium pressure, and the rapidity with which it absorbs and releases hydrogen.

Yttrium and the rare earths form similar intermetallic compounds with transition metals. It therefore seemed likely that the yttrium compounds would behave like their rare earth counterparts in respect to hydrogen sorptive power. Because of the lower atomic weight of Y, the yttrium compounds have lower density; this is of significance if the intermetallic is to be used for hydrogen storage in mobile vehicles since weight considerations are then important. In this note we report pressure-composition isotherms for the YCo_5-H system. For purposes of comparison YNi_5, $ThCo_5$, and $ThNi_5$ were also examined as possible solvents for hydrogen.

Intermetallic compounds used were prepared by induction melting in a water-cooled copper boat under an atmosphere of purified argon gas and were homogenized under vacuum at 1000° for 2 weeks to obtain single-phase compounds. Powder X-ray diffraction patterns were obtained to confirm formation of the compounds and to establish the absence of extraneous phases. The lattice constants thus obtained were in good agreement with literature values.

Samples were powdered to fine particles (~75 μ) with a mortar and a pestle in air, then introduced into a brass container, and connected to the hydriding system. Before introducing hydrogen gas (99.999% pure), the whole system was pumped out with a mechanical pump (~10^{-3} mm). Then hydrogen gas was introduced into the system at ~150 atm and pressure was measured with an Ashcroft test gauge. The system was left for some days until the pressure became constant and then evacuated by the mechanical pump. This process was repeated several times before the actual desorption measurements were done.

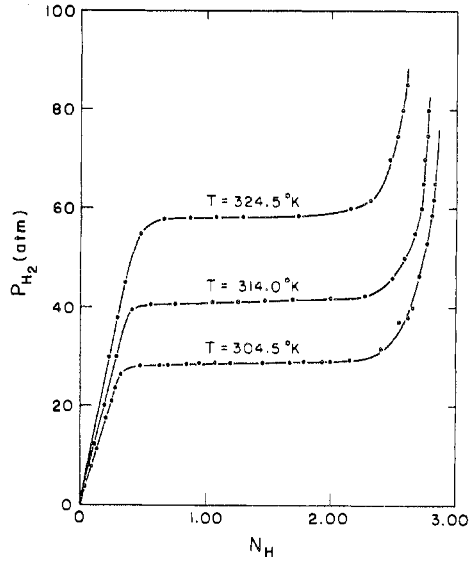

Figure 1. Pressure *vs.* composition for the YCo_5-H system at several temperatures. Composition (N_H) is expressed as the gram-atoms of H per gram formula weight of YCo_5.

YCo_5 and $ThCo_5$ absorb hydrogen gas reversibly giving the limiting composition ratio of hydrogen atom to compound of $N_H \approx 3.0$ in both cases. Pressure-composition isotherms for desorption of the YCo_5-H system at three temperatures are given in Figure 1. These show plateau pressures indicating a two-phase region, *i.e.*, a solid solution and a hydride. The $ThCo_5$-H system has a plateau pressure of 45 atm at 23°. Since this is a rather high pressure for our equipment (maximum pressure is 100 atm for precision measurement), isotherms at higher temperatures were not obtained for the $ThCo_5$-H system. YNi_5 and $ThNi_5$, on the other hand, do not absorb hydrogen gas under the applied pressure of up to 150 atm. This may be due to their high plateau pressure.[3]

After the desorption experiments X-ray powder diffraction patterns of YCo_5 and $ThCo_5$ were taken. The patterns were identical with those obtained before hydriding in each case, indicating no decomposition in either YCo_5 or $ThCo_5$. We had hoped to obtain a crystal structure of the hydride phase, but it was not possible to perform X-ray diffraction measurements on the hydride phase because of the high equilibrium pressure at room temperature.

In Figure 2, log *P*(atm) *vs.* $1/T$ is plotted for the YCo_5-H system. A linear relation is obtained corresponding to the expression

$$\log P(\text{atm}) = 5.96 - 1679/T$$

From this equation, the heat of reaction to form the hydride is obtained as $\Delta H_f = -7.7$ kcal/mol of H_2,[5] which is very close to that observed in the RCo_5 or RNi_5 systems (R = a rare earth element). For example, $LaNi_5$ and $SmCo_5$ hydrides have heats of reaction of −7.2 kcal/mol of H_2 and −7.4 kcal/mol of H_2, respectively.[3] As stated earlier, the limiting composition N_H is 3 for YCo_5 and $ThCo_5$. This is also the case for most of the RCo_5 or RNi_5 hydrides, *i.e.*, the most stable hydride has the limiting composition $N_H = 3$, although they are known to form several hydride phases.[3]. These findings seem to indicate that the crystal structure is an important factor in the hydrogen absorption by this type of compound. This is also substantiated by the fact that YCo_5, $ThCo_5$, and

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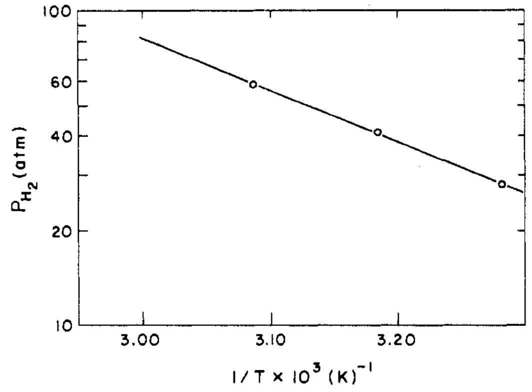

Figure 2. Semilogarithmic plot of P_{H_2} *vs.* reciprocal of the temperature in °K.

GdCo$_5$ have plateau pressures of the same order at room temperature,[3] and the lattice dimensions of the Y, Th, and Gd compounds are very close to each other. Lighter rare earth compounds have lower equilibrium pressure, and their lattice parameters are larger than those of GdCo$_5$, YCo$_5$, and ThCo$_5$.

Although these observations indicate that the stability of the hydride in a series (as, for example, the RCo$_5$-H series) is mainly controlled by the lattice dimensions, it is perhaps unwarranted to conclude that the mere size of the interstitial site available to hydrogen is the determining parameter. This undoubtedly would be the case were hydrogen anionic, but it seems unlikely that this is the situation since these intermetallics are primarily d transition metals. Hydrogen in these systems is probably not unlike that in the pure transition metals—*i.e.*, metallic.[6] The proton helps supply the field in which the delocalized electrons move. If so, the varying stability of the hydride in a series must be ascribed to the varying band structure of the parent intermetallic.

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Registry No. YCo$_5$, 12017-71-9; ThCo$_5$, 12017-70-8; H$_2$, 1333-74-0.

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Solubility of Hydrogen in RCo$_3$ Compounds

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As pointed out in the preceding note, the RT$_5$ compounds (R is a rare earth metal and T is a d-transition metal Co or Ni) are prolific absorbers of hydrogen.[1] LaNi$_5$ is an example. It absorbs hydrogen at moderate pressure up to the composition represented by the formula LaNi$_5$H$_7$.[2] Buschow and van Mal have established[3] that LaNi$_5$ has a considerable range of compositional stability and, moreover, have shown that the equilibrium pressure of hydrogen diminishes as the composition of the phase deviates from ideal stoichiometry in the nickel-poor direction. This observation aroused our interest in RT$_3$ systems in regard to their capability as hydrogen host lattices and their potential for hydrogen storage.

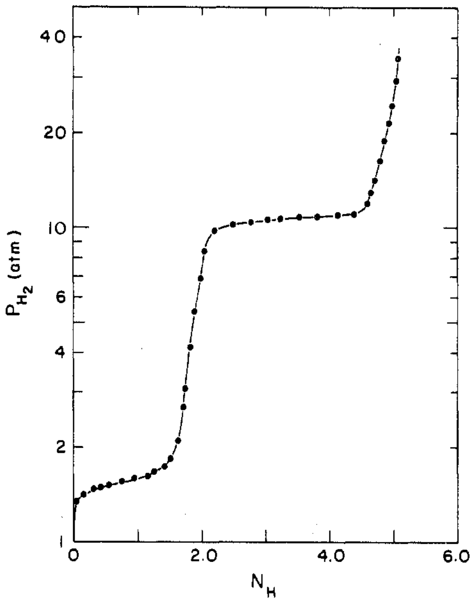

Figure 1. Pressure *vs.* composition for the ErCo$_3$-H system at 101°. Composition (N_H) is expressed as the gram-atoms of H per gram formula weight of ErCo$_3$.

From a structural point of view the RT$_3$ compounds, which are rhombohedral, can be regarded as being derived from the hexagonal RT$_5$ by an ordered replacement of T with R, *viz.*, $2RT_5 - T + R = 3RT_3$. The structural details are set forth in a number of places, for example in a publication by Lemaire and Paccard.[4] Thus, the RT$_3$ phases could be regarded as T-deficient RT$_5$ phases, and, hence, on the basis of the observations of Buschow and van Mal, one might expect the RCo$_3$ phases to be more receptive to hydrogen than their RCo$_5$ counterparts. The present work was undertaken to verify this point, to provide information as to the maximum solubility of H$_2$ in the RCo$_3$ phases and to obtain pressure-composition-temperature data for RCo$_3$-H$_2$ systems. To date, the study has been limited to the systems with R = Dy, Ho, and Er. TmCo$_3$ and YbCo$_3$ have not been included because the volatility of these rare earth metals and the difficulty in preparing the RCo$_3$ compound as a single-phase material. The lighter rare earths were not used because of the low equilibrium pressures expected for them. Attention has instead been focused on systems with hydrogen vapor pressures exceeding 1 atm since these would be the only ones of use for hydrogen storage.

The procedure used in preparing the intermetallic compounds was identical with that used in the earlier study.[5] The hydrogenation procedure was also identical. The hydrogen absorbed or evolved was measured by standard gasometric means,[2] *i.e.*, measuring the pressure of the gas in a known volume and at a fixed temperature. Results obtained for the ErCo$_3$-H$_2$ system (Figure 1) are typical. The shape of the curve suggests the existence of two hydride phases in addition to the terminal solid solution phase based upon

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