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HIGH TEMPERATURE INTERACTION OF HYDROGEN WITH INTERMETALLIC COMPOUND $CaNi_5$

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ABSTRACT

The intermetallic compound $CaNi_5$ disproportionates rapidly into CaH_2 and Ni when treated with hydrogen above 350°C. The kinetics of this reaction in the initial stages follows the nucleation and growth mechanism. The pressure-composition-temperature isotherms for hydrogen interaction with $CaNi_5$ in the temperature range 640°C to 725°C have been determined and the ΔH_f for $CaNi_5$ is calculated to be 12.9 kcal/mol. Differential thermal analysis confirms the scheme proposed for the $CaNi_5$-H_2 reaction. Even a 5% disproportionation of the alloy drastically affects the kinetics of hydrogen sorption at room temperature.

INTRODUCTION

In recent years there has been increasing attention to utilize the hydrides of intermetallic compounds in thermal energy conversion systems [1]. There has also been an interest in the catalytic properties of the hydride forming intermetallic compounds [2]. In all such applications, it is essential to treat the alloy with hydrogen at elevated temperatures. It is known [3] that most of the intermetallics when cycled in hydrogen at elevated temperatures show a reduction in the hydrogen sorption rate and exhibit a loss of hydriding capacity. These observations may have specific implications for technological and practical applications of these compounds. One of the

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reasons for such a behaviour by the intermetallics is believed to be due to their intrinsic degradation when cycled in hydrogen [4]. Intrinsic degradation of the alloy usually arises from the phase separation within the intermetallic compound induced by hydrogen, because most hydriding intermetallic compounds are composed of a stable hydride forming element and a transition metal [5]. It has been proposed that this phase separation (or disproportionation of the alloy) is induced by hydrogen and is significant at elevated temperatures [6]. Further, the conditions necessary for the phase separation reaction depend on the nature of the alloy used.

There are a number of studies reported in literature which deal with the disproportionation of the alloys, especially of $LaNi_5$ [4], $LaCo_5$ [7], $CaNi_5$ [8], Mg_2Cu [9], $MmNi_5$ [10] and LnAl [11] with the formation of the hydride of the non-transition element and clusters of the transition metal (as a result of thermal cycling in hydrogen). The phase separation and surface segregation have been identified in most of the alloys by a variety of techniques, but its mechanism has not been studied extensively.

As a part of the work on intermetallic compounds reported from this laboratory [9,12], studies on $CaNi_5$ alloy have been carried out since it is one of the main candidates considered for several applications. The present communication deals with the study of the interaction of hydrogen with $CaNi_5$ at elevated temperatures.

EXPERIMENTAL

The $CaNi_5$ alloy was obtained from Ergenics Corporation, U.S.A. as HYSTOR 201. Analytical grade hydrogen gas supplied by Indian Oxygen Limited was used. The reaction kinetic and isotherm measurements were done on an all-glass static reactor. For measurements at temperatures greater than 500°C, a quartz reactor tube was used. Characterization of the samples was done using a Philips (PW 1140) X-ray diffractometer and thermal analysis was carried out on a Stanton Redcroft (STA-780 series) Thermal Analyser.

The interaction of $CaNi_5$ alloy with hydrogen in the temperature range 25°C to 800°C was studied. For hydrogen sorption studies at low temperatures, the $CaNi_5$ alloy was

activated by the procedure reported elsewhere [13]. For higher temperatures the sample was evacuated to 10^{-5} torr at the reaction temperature and the sorption measurements carried out on the evacuated sample.

RESULTS AND DISCUSSION

$CaNi_5$ alloy shows hydrogen absorption at temperatures higher than 350°C. The quantity of hydrogen consumed corresponds to $2H/CaNi_5$. The kinetics of hydrogen absorption could be measured only in a short temperature interval of 350° to 420°C. Below 350°C, the absorption kinetics is very slow and above 420°C the rate of hydrogen absorption is very fast. Ivanov *et al.* [14] have treated the initial kinetic data for the uptake of hydrogen by Ce-Mg alloy in terms of the Erofeev equation, namely

$$[-\ln(1-\alpha)]^{1/n} = kt$$

where α is the fraction of the total hydrogen consumed at time t. The applicability of this equation implies that the process follows the formation of nuclei and their growth mechanism in 2 or 3 dimensions depending on the magnitude of n. The applicability of the Erofeev equation to the kinetic data obtained in the present study is seen from the plots shown in Fig.1, where the function $-\ln(1-\alpha)^{1/3}$ is plotted against t.

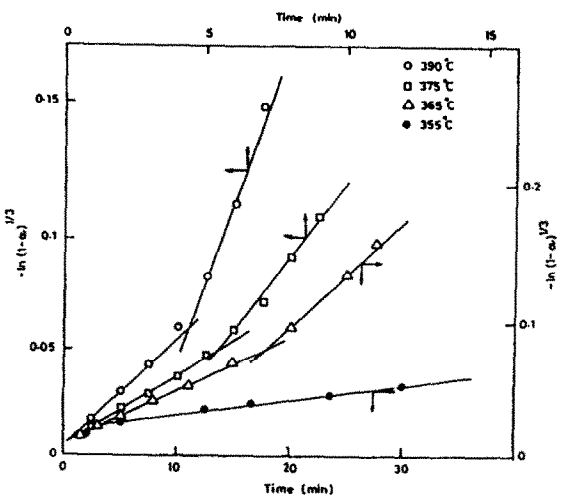

Fig.1. Kinetic plots for the hydriding of $CaNi_5$ at different temperatures.

The plots show gradient changes at a particular value of α (0.15 to 0.2) for all the temperatures studied. This indicates that the growth mechanism is different in the initial stages compared to the processes when $\alpha > 0.2$ and this arises out of the variation in the available interface and of volume for the growth mechanism at different stages.

In view of the observation that the reaction rates were very high above 420°C, the phases present as a result of hydriding at high temperatures were identified by X-ray diffractometry and the results are shown in Fig.2. It was observed that, neither the alloy nor the hydride phases ($CaNi_5H_{1.0}$ and $CaNi_5H_{4.8}$ normally obtained by room temperature hydriding were

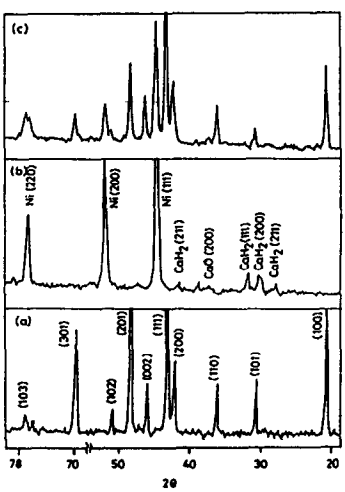

Fig.2. X-ray diffraction patterns for (a) fresh $CaNi_5$ alloy, (b) $CaNi_5$ alloy hydrided at 520°C and (c) partially regenerated alloy after hydriding at 520°C.

present (see Fig.2b). On the other hand, the XRD pattern showed the presence of CaH_2, nickel metal and traces of CaO (the latter formed by the oxygen impurities present in the hydrogen used or by subsequent handling in air for XRD measurements) phases only. However, this multiphasic system when evacuated at temperatures above 520°C, reverted back to $CaNi_5$ slowly. The reversal to the intermetallic ($CaNi_5$) phase has been confirmed by XRD (Fig.2c) and by measuring the room temperature hydrogen sorption capacity which agreed with that observed for fresh $CaNi_5$ alloy. It is to be remarked that normal impurities present in hydrogen which drastically impede the room temperature hydrogen sorption by

these alloys, do not impede to the same extent the high temperature hydrogen absorption (the alloy does not show any absorption at room temperature with hydrogen containing one per cent oxygen impurity, but still shows absorption at high temperatures though with a decreased rate).

The hydrogen absorption isotherms obtained for $CaNi_5$ in the temperature range 640° to 725°C are given in Fig.3. The

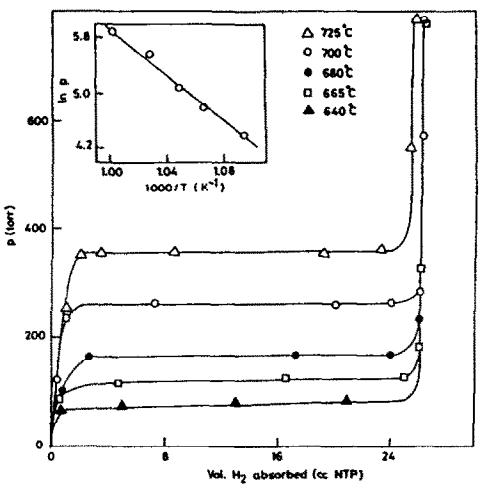

Fig.3. Hydrogen absorption isotherms for the $CaNi_5$ alloy at different temperatures. Inset shows the Van't Hoff plot for hydrogen absorption (wt. of alloy = 0.39 gms).

enthalpy of the hydrogen sorption was calculated from the Van't Hoff plot (see inset in Fig.3) drawn using the values of the plateau pressures at different temperatures. As postulated above, if the hydriding process gives rise to disproportionation of the alloy, then the observed enthalpy change, as a result of hydriding, must correspond to the following reaction:

$$CaNi_5 + H_2 \rightleftharpoons CaH_2 + 5\ Ni$$

The observed value is -31.1 kcal/mol H_2. Since the heat of formation of CaH_2 is reported to be -44.0 kcal/mole, one can obtain a value of -12.9 kcal/mole for the heat of formation of $CaNi_5$. This value corresponds reasonably well with the value of -14.4 kcal/mole calculated by the model proposed by

Miedema [15]. Thus, this procedure appears to be a promising method for the estimation of the heat of formation of intermetallics containing one easily hydride forming element.

Volumetric measurements on the absorption of hydrogen at 25°C on the activated $CaNi_5$ at a pressure of 1 atm show that a hydride phase corresponding to $CaNi_5H_{4.8}$ is formed. This hydride completely decomposes to the alloy and hydrogen below a temperature of 150°C at 1 atm pressure of hydrogen [13].

From these results, one can postulate the following reaction scheme for the interaction of $CaNi_5$ with hydrogen:

$$CaNi_5 + H_2 \xrightarrow[1\ atm\ H_2]{25^\circ C} CaNi_5H_{4.8} \qquad (1)$$

$$CaNi_5H_{4.8} \xrightarrow[1\ atm\ H_2]{150^\circ C} CaNi_5 + H_2 \qquad (2)$$

$$CaNi_5 + H_2 \xrightarrow{350^\circ C} CaH_2 + 5Ni \qquad (3)$$

$$CaH_2 + 5Ni \xrightarrow[1\ atm\ H_2]{> 770^\circ C} CaNi_5 + H_2 \qquad (4)$$

The temperature required for step (4) has been confirmed experimentally and this value coincides with that derived from the Von't Hoff plot. The steps (3) and (4) do not involve any intermediates, unlike what has been reported for the $LaCo_5$-H_2 system [16], and this has been confirmed by DTA analysis of $CaNi_5$ in a flow of hydrogen which showed only one exotherm at 400°C and only one endotherm at 800°C (Fig.4).

The observed thermodynamic dissociation temperature of CaH_2 at 1 atm of hydrogen in the present investigation is 770°C while the reported value for the CaH_2 alone is around 990°C, thus showing that the presence of Ni facilitates the dissociation of CaH_2 at lower temperatures. A similar effect of Ni in the decomposition of MgH_2 has been observed by Eisenberg *et al*. [17].

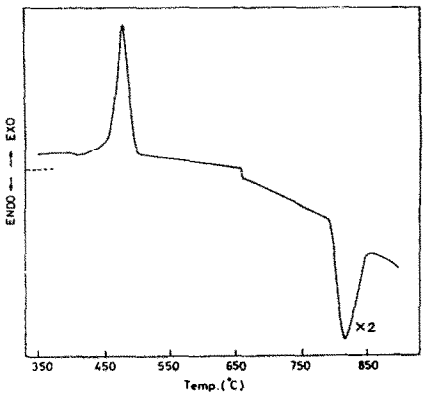

Fig. 4. Differential Thermal Analysis pattern for $CaNi_5$ alloy heated in a flow of hydrogen.

Since it has been shown that high temperature hydriding of the alloy leads to disproportionation, it was considered interesting to see how the extent of disproportionation affects the room temperature hydrogen sorption behaviour of the alloy. The kinetic plots obtained for the room temperature hydriding with various amounts of hydrogen absorbed at 500°C (proportional to the extent of disproportionation) are shown in Fig.5. It is seen that even a 5%

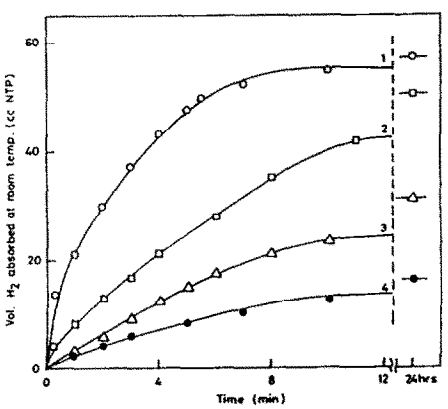

Fig.5. Kinetic plots for hydrogen absorption at 25°C for $CaNi_5$ alloy with various amounts of hydrogen absorbed at 500°C, (1) 0, (2) 1.2, (3) 6.4 and (4) 11.0 CCNTP. (wt. of alloy = 0.35 gms).

disproportionation of the alloy drastically affects the kinetic of hydrogen sorption at room temperature (Fig.5.2). These measurements are of practical utility in that they emphasise the optimum conditions for activation procedures to be developed for these alloys without allowing the disproportionation reaction to occur.

CONCLUSIONS

$CaNi_5$, at temperatures greater than 300°C, disproportionates to Ni and CaH_2 when heated with hydrogen. The disproportionation reaction is very rapid above 420°C. The kinetics of the reaction can be explained by the nucleation and growth process. The enthalpy of formation of $CaNi_5$ has been calculated from the high temperature hydrogen absorption isotherms. The disproportionation reaction affects the room temperature hydrogen absorption reaction to a great extent.

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