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Decomposition–re-formation reactions under H_2 of intermetallics based on $LaNi_5$

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Abstract

Hydrogen decomposition–re-formation processes of $LaNi_5$ -type intermetallics are known to produce activated homogeneous materials with variable microstructures (e.g. of relevance to aspects of an alternative hydrogen economy such as battery or hydrogen storage applications). An example is $LaNi_5$, $H_2 \rightarrow LaNiH_2$, $Ni \rightarrow LaNi_5$. The route and thermodynamics of these processes have been investigated on $La(NiAl)_5$ and $La(NiCo)_5$ -based materials. It was found that for intermetallics with high exothermicity (e.g. $LaNi_5$ and $La(NiAl)_5$), relatively forcing conditions have to be used in the decomposition process. Other compounds such as $La(NiCo)_5$ readily decomposed and re-formed near 500 °C.

Keywords: Hydrogen decomposition–re-formation; Hydrogen storage applications

1. Introduction

Aspects of the fundamental phenomenology of metal hydrides have been reviewed in Refs. [1–3]. Recently this subject has received a renaissance through technological applications of materials such as $LaNi_5$ for practical applications, especially in heat exchange [4] and battery systems [5]. From a technological point of view, problems concern prices of materials and limits in cycle life. The typical rechargeable H storage material is based on $(LaX)(NiM)_5$, where $x \equiv Ce$ (to reduce plateau pressure P_c and price) and M can be Co (to reduce P_c and lattice expansion on hydriding, although it increases price).

The degradation process on cycling involves surface segregations of Ni and $La(OH)_3$. This degradation is minimized by preparation methods yielding special microstructures (e.g. columnar) [6]. Modification of particle size and microstructure can be attempted through comminution of the specially prepared original material, through decrepitation in the initial hydriding process or through a decomposition–re-formation (DR) process under H_2 at elevated annealing temperature T_a above a kinetically limiting temperature range for sufficient metal diffusion ($T_k \approx 800$ – 1100 K). Such processes have been used both for permanent-magnet-type materials

[7,8] as well as for hydrogen storage materials of the $CaNi_5$ type [9]. For the latter, DR processes have been shown to lead to higher activated materials in special microstructures and are the focus of this study. In principle, the R process alone, say from LaH_2 and Ni or $LaNiH_2$ and Ni, can be successful in this direction, leading potentially to altogether new preparation methods for these materials.

It is generally known that intermetallics under H_2 can undergo various decomposition processes in the temperature range of sufficient metal diffusion. A classical example [10] is Mg_2Ni , $H_2 \leftrightarrow MgH_2$, Ni. It has been further shown that these decomposition reactions can involve different steps presentable in a van't Hoff representation. An example [9] is $LaNi_5$, $H \leftrightarrow LaNi_{13}H_2$, Ni, $LaNiH_2 \leftrightarrow LaNiH_4$, Ni $\leftrightarrow LaH_2$, Ni. In order to understand the driving force for these reactions, one has to analyze enthalpic and entropic contributions. We write $\ln P_{H_2} = \Delta H^*/RT + \Delta S^*/R$ (van't Hoff), where the asterisks denote a quantity per mol H_2 . ΔS^* can be approximated by $30 \text{ cal K}^{-1} \text{ mol}^{-1}$, since all processes involve the similar condensation of a gas into a solid. For 1 atm H_2 , then, $\Delta H^* = T_a \Delta S^*$, defining a critical annealing temperature for the transformation.

It is clear that total decomposition, say according to (1) $LaNi_5$, $H_2 \leftrightarrow LaH_2$, Ni, depends on the relative exothermicity of intermetallic (IM) vs. LaH_2 . For $LaNi_5$, $\Delta H(\text{IM}) = -30 \text{ kcal}$ and for LaH_2 $\Delta H^* = -50 \text{ kcal}$.

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Therefore the overall reaction (I) has $\Delta H^* = -20$ kcal and will proceed at $T_a < 667$ K under 1 atm H_2 . This T_a is too low to make the reaction observable within reasonable time intervals. However, the reaction can be run within minutes by moving on the ΔH^* van't Hoff line to higher temperatures and pressures. The actual reaction need not be a total cleavage reaction as (I) but can involve several disproportionation steps. The energetics among these reactions, however, are usually situated rather close together, so that (I) can exemplify the general trend which we have summarized in a rule of increased stability of the intermetallic vs. decomposition with increased exothermicity of the intermetallic itself.

It is accordingly clear that less exothermic (stable) intermetallics can be decomposed under less forcing conditions. Stabilities of intermetallics are not always known experimentally. However, predictive schemes have been given by Miedema [11] and Bouten and Miedema [12]. Based on these schemes, one expects that $La(Ni_{1-x}M_x)_5$ should result in a reduction of $\Delta H(IM)$, i.e. the enthalpy of the intermetallic, for $M \equiv Co$ and Mn but not for $M \equiv Al$. This should result in a decrease in T_a for the decomposition reaction. We shall here demonstrate that this is indeed the case. We also explore whether DR processes can lead to special microstructures involving the coating of one component on another with different DR characteristics. For the actual materials we include preparations which have technological interest in battery applications.

2. Experimental methods

Melted materials were ground into coarse particles and put into stainless steel–quartz containers at temperatures ranging from 500 to 900 °C under varying pressures of H_2 . Uptake of gas in this decomposition step was monitored. Subsequently a vacuum was applied near 500–1000 °C and a re-formation of the original or a new compound was observed through pressure monitoring. The re-formed compound was exposed near ambient to H_2 and its absorption–desorption behavior studied. X-Ray patterns were taken in the original, decomposed and re-formed states. In some cases mixtures of the as-melted materials were used for the DR process.

3. Results

3.1. Compound $LaNi_5$

The as-melted compound, after an initial activation involving a short heat treatment, takes up hydrogen with equilibrium plateau pressures of about 2 atm for

absorption and about 1.5 atm for desorption. When treated at 550 and 600 °C under 100 atm H_2 pressure, X-ray analysis and pressure monitoring do not point to any appreciable decomposition of the compound. The routine “re-formation” treatment under vacuum at 600 °C results in a compound with an unusual hydriding behavior at ambient. The compound, when exposed to H_2 in situ, shows improved hydriding kinetics but with an increased equilibrium plateau pressure of about 5 atm in the first hydriding cycle after DR. The desorption plateau pressure is slightly lower than that of the original compound. In the second cycle the H_2 absorption plateau drops to a value similar to that of the original compound. There is a slight increase in the total hydrogen uptake after DR.

3.2. Compound $La_{0.8}Nd_{0.2}Ni_{2.5}Co_{2.4}Al_{0.1}$

The compound received as melted had slow kinetics for H_2 uptake at ambient and so required a brief heat treatment at 300 °C under H_2 to improve the hydriding–dehydriding kinetics. It had a sloping plateau for H_2 uptake between 0.2 and 0.3 atm and a total uptake at 2 atm pressure of 4.1 H/f.u. (f.u., formula unit).

This compound required H_2 pressures greater than ambient at 550 °C for decomposition. The decomposition

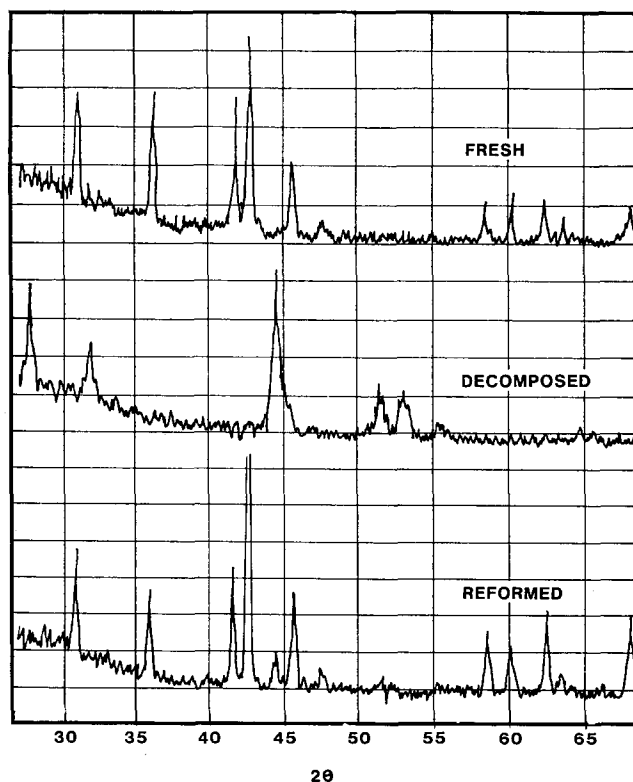


Fig. 1. X-Ray pattern of $La_{0.8}Nd_{0.2}Ni_{2.5}Co_{2.4}Al_{0.1}$ in fresh, decomposed and re-formed states as described in the text. The decomposed state corresponds to LaH_2 and Ni derived phases.

reaction was complete in a few hours at 550 °C under 60–100 atm pressure. Regeneration to the original AB_5 compound was accomplished by applying a vacuum at 600 °C for a brief period. The success in the DR sequence is documented in Fig. 1. The re-formed compound was very active for H_2 uptake under ambient, with improved sorption kinetics, lower plateau pressure (0.1–0.2 atm) and increase in total capacity (4.4 H/f.u.). These H_2 uptake results are represented in Fig. 2.

3.3. Compound $LaNi_{4.5}Al_{0.5}$

This compound did not decompose under H_2 in the temperature range 500–800 °C at pressures up to 100 atm as shown by pressure monitoring as well as X-ray patterns.

3.4. Compound $LaNi_{4.2}Mn_{0.8}$

X-Ray patterns of the as-melted state of this compound, though of the AB_5 structure, had very broad and ill-defined peaks. The kinetics of H_2 uptake were rather slow and an activation treatment was required. The compound decomposed readily under H_2 at 550 °C and less than 20 atm pressure to LaH_3 and Ni (and Mn) as shown. Re-formation to the original AB_5 compound was achieved by applying a vacuum (10^{-3} atm) at 600 °C. The re-formed compound showed an increase in H_2 uptake kinetics and total hydriding capacity.

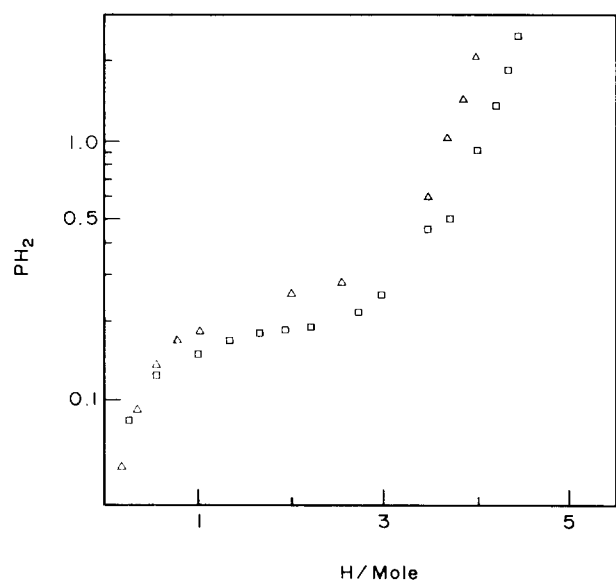


Fig. 2. Pressure-composition (PC) curves for $La_{0.8}Nd_{0.2}Ni_{2.5}Co_{2.4}Al_{0.1}$ at 298 K after DR.

3.5. Mixture of $LaNi_{4.5}Al_{0.5}$ (I) and $La_{0.8}Nd_{0.2}Ni_{2.5}Co_{2.4}Al_{0.1}$ (II)

A mixture of I (60 wt.%) and II (40 wt.%) in the as-melted condition showed a rather sloping plateau for H_2 uptake with a continuous change in the plateau pressure from 0.1 to 0.6 atm. The mixture was subjected overnight to decomposition under a hydrogen pressure of 80–100 atm at 550 °C. Pressure monitoring suggested that only $La_{0.8}Nd_{0.2}Ni_{2.5}Co_{2.4}Al_{0.1}$ underwent decomposition-re-formation involving annealing under vacuum at 600 °C, which resulted in an active H_2 absorber with lowered plateau pressure (continuously changing

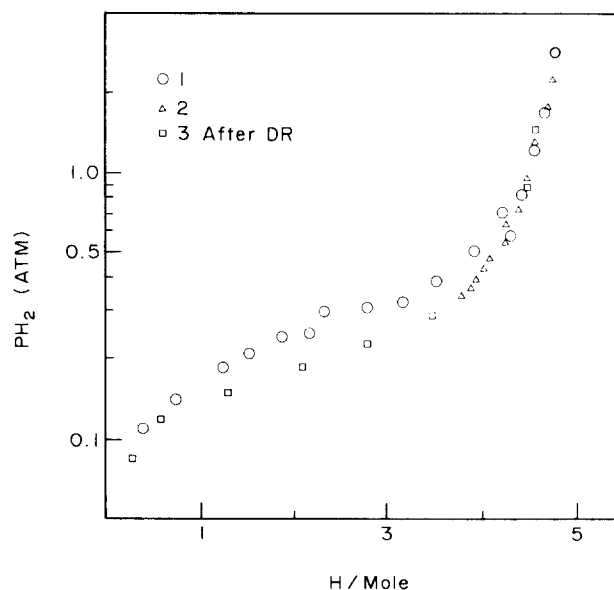


Fig. 3. PC curves for mixture of $LaNi_{4.5}Al_{0.5}$ (I) and $La_{0.8}Nd_{0.2}Ni_{2.5}Co_{2.4}Al_{0.1}$ (II) after comminution and DR.

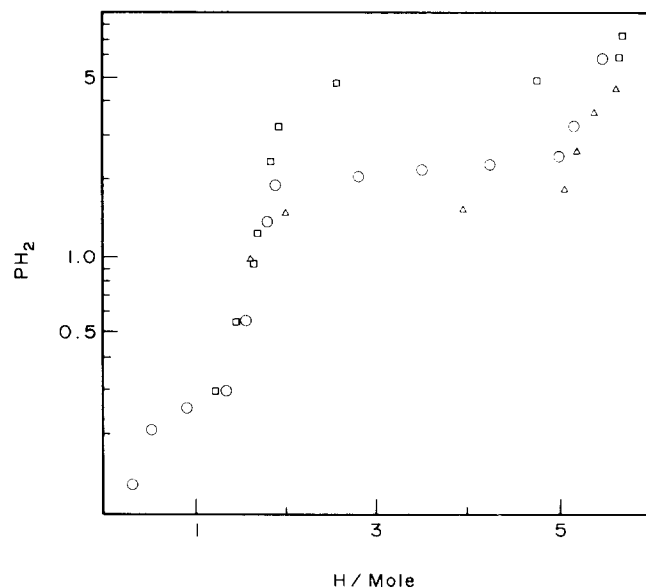


Fig. 4. PC curves for mixture of $LaNi_5$ (I) and $La_{0.8}Nd_{0.2}Ni_{2.5}Co_{2.4}Al_{0.1}$ (II) at 298 K after comminution and DR.

between 0.1 and 0.4 atm) and a very small increase in total H₂ content (Fig. 3).

3.6. Mixture of LaNi₅ (I) and La_{0.8}Nd_{0.2}Ni_{2.5}Co_{2.4}Al_{0.1} (II)

The reaction was performed with a similar sequence (with a similar proportion of I and II) as in the previous case. In the present case there are two distinctly different plateau pressures for the two compounds, with a sloping, ill-defined plateau at about 0.2 atm for compound II and a well-defined one at about 2 atm for compound I. After the DR process there is an overall increase in hydriding kinetics and an increase in the H₂ content from 5.5 to 5.7 H/f.u. (under similar conditions). There still are two different plateaux (indicating again very little or no evidence for a coating of compound I by II as discussed below). Pressure–composition isotherms are presented in Fig. 4.

4. Discussion

We show that the decomposition–re-formation process can be successfully applied to a range of AB₅-type alloys. It is evident that the ease with which decomposition of the intermetallic could occur (relatively low T_a) is inversely related to its stability as given by its heat of formation in Miedema's scheme. In addition to the improved hydriding characteristics as a result of the DR process (as pointed out at various instances in Section 3), the study also provides information on the effect of the alloying elements on the stability of the intermetallic itself.

LaNi₅, though a stable compound, has been shown to decompose under H₂ at elevated temperatures and pressures [9]. Substitution of Al in place of Ni increases the stability of the compound, necessitating more severe conditions for its decomposition. Co and Mn substitutions have the reverse effect on LaNi₅, making it more susceptible to decomposition under milder conditions, i.e. under an H₂ pressure less than 100 atm at 550 °C. This is in line with the prediction for lower exothermicity of LaM₅ with M ≡ Co and Mn compared with M ≡ Ni. The effects on DR extend into the “pseudobinary” and are strong. They allow a calculation of the actual heat of formation of the intermetallic.

The DR process appears to have had a unusual effect on the room temperature hydriding behavior of pure LaNi₅, with an increase in the first hydriding plateau pressure after DR and a return to lower values thereafter. We explain this in the following way. It has been shown that the surface of the LaNi₅ particles is composed of La₂O₃ and Ni with the adjacent LaNi₅ bulk. Because La₂O₃ will not re-form under the conditions of the present study, the outermost layer will become slightly Ni enriched under these conditions. This epitaxial Ni-rich surface then results in an increase in the equilibrium hydriding pressure as observed in the first cycle after DR. On complete uptake of H₂ there is a considerable increase in the cell volume, creating strain which results in the break-up of the Ni-rich surface layers and exposure to the lower Ni concentration bulk. This phenomenon explains the drop in P_{H_2} in the first desorption cycle and the subsequent rehydriding.

Concerning the mixtures involving one non-decomposing component I (under the present conditions), no coating interactions were observed. In the case of coating, two possibilities are expected. Either the higher P_c component coats on the lower P_c component or vice versa. In both cases asymmetric hysteresis curves should be obtained. No signs of this are observed. This indicates that so far no “macroscopic” transactions were involved. Changes in experimental conditions could perhaps lead to this technologically interesting phenomenon.

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