Thermogravimetric research of hydrogen storage materials

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Abstract. During thermogravimetric research of metal hydrides we noticed mass growth of samples above 200 °C even in an argon atmosphere. Further heating is leading to the growth of weight up to 2-7 weight% till 500 °C. Second run of the same sample without taking out of DTA instrument gave only small mass changes, indicating that noticed mass increase during first run is permanent. Microscope and elemental analyses were made to determine the reason of mass growth. XRD inspection revealed the formation of new phase with bunsenite NiO structure with deformed cubic structure. The new phase is no more active to hydrogen sorption/desorption. Our results demonstrated that the usage of hydrogen storage alloys AB₅ must be taken with care – it is important not to exceed some critical temperature were irreversible structural, compositional and morphological changes will occur.

1. Introduction

Metal hydrides are specific combinations of metallic alloys that act similar to a sponge soaking up only hydrogen. Simplest and most famous one are palladium Pd, most typical are AB₅ (LaNi₅ etc.), AB (FeTi etc.), AB₂ (MgNi₂, ZrNi₂ etc.) alloys [1]. Hydrogen storage in a solid hydride is safe and does not present any of the safety problems that hydrogen stored in containers as a gas or a liquid does because hydrogen, when stored in a solid hydride form, exists in its lowest free energy state. Metal hydrides possess the unique ability to absorb hydrogen and release it later, either at room temperature or through heating of the tank. The total amount of hydrogen absorbed in metals is generally 1-2wt% (hydrogen weight from the total weight of the tank), only magnesium alloys has larger amount of stored hydrogen, around 4-6wt%, but only when heated to high temperatures or exposed to high hydrogen pressures [2]. The percentage of gas absorbed to volume of the metal is still relatively low, but hydrides are best acquired today and are commercially offered by number of companies around all the World.

Closed into the tank, metal hydrides offer the advantages of safe hydrogen delivering at a constant pressure, using temperature as promoter. The life of a metal hydride storage tank is directly related to the purity of the hydrogen it is storing. The alloys absorb not only hydrogen, but also any impurities introduced into the tank by the hydrogen, as oxygen, water vapour etc [3]. The hydrogen released from the tank is extremely pure, but the tank's lifetime and ability to store hydrogen is reduced as the impurities are left behind and fill the spaces in the metal that the hydrogen once occupied. Metals in the form of micro- and nanoparticles are inherently pyrophoric, when exposed to atmosphere

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containing oxygen. Therefore, shipment of these hydrogen storage materials becomes a safety problem, in which it has heretofore been necessary to transport such materials in an inert atmosphere.

Metal hydrides must be heated to release hydrogen for utilization, sometimes at temperatures above 200 °C. The high temperatures and heat of desorption cannot be easy provided by most hydrogen-use applications. Even internal combustion engines may not be able to provide sufficient heat to desorb the hydrogen at the required rates. The rate of hydrogen absorption and desorption, as well as the heat transfer characteristics of the material, are altered when during sorption/desorption cycling the powder results in the continued breakdown into finer particles [3]. Heating and breaking processes may be sensitive to the surface conditions of fine particles, and small amount of oxygen in surrounding atmosphere can change alloy properties dramatically.

We observed unexpected composition changes in AB₅ alloy during TG-DTA measurements in an argon atmosphere, when temperature increased above 200 °C.

2. Experimental

Commercial powdered AB₅ compounds LaNi₅ from Treibacher Industrie AG (Austria) and MmB₅ (trademark “7-10” from Metal Rear Earth Ltd (China), Mm= La, Ce, Pr, Nd and B= Ni, Co, Mn, Al, Cr) and Ni powder from Stanchem Ltd (Poland) were used as samples. Hydrogenation was made in self-built volumetric sorption reactor at pressures 5-10 bar. Before hydrogenation alloys were activated with some heating-cooling cycles in the presence of vacuum and hydrogen.

Thermogravimetric (TG) and differential thermal analysis (DTA) were performed with SHIMADZU DTG-60 instrument in Ar atmosphere (Ar 5.0 from AGA Ltd.) with flow 50 ml/min in temperature range from room temperature (RT) till 500 °C with heating rate 10 deg/min. During thermogravimetric research of metal hydrides we noticed mass growth of samples above 150-200 °C even in an argon atmosphere. Structural and morphological analyses were made to determine the reason of mass growth. Alloy samples after TG-DTA measurements were analyzed with X-Ray diffraction (XRD) equipments DRON-3 and Brucker D8, Scanning Electron Microscope EVO 50 XVP (Carl Zeiss), visual inspection was done on Optical microscope ECLIPSE L150 equipped with Color Matrix CCD.

3. Results and discussions

During thermogravimetric research of AB₅ alloys before and after hydrogenation, as well as the Ni powder, we noticed mass growth of samples above 200 °C, even in an argon atmosphere (Figure 1). Differential thermal analysis showed that mass growth process is exothermic of all three samples.

![Figure 1. Weight growth observed of 3 different samples in Ar atmosphere (before hydrogenation).](image-url)
Visual inspection of samples shows that after annealing at temperatures above 200 °C, AB5 alloys and nickel powder changed colour to darker tones (Figure 2).

![Figure 2. Optical inspection of powdered alloys and nickel before and after annealing.](image)

Heating of AB5 alloys above 200 °C leads to mass growth from 3-7 wt% (Figure 1), while nickel powder increases in weight only on 0.7 wt%. Grain dimensions of all 3 samples before annealing were similar – 1-5 microns, while after heating alloys turned to agglomerated compound with spongy flake-like structure (Figure 3).

![Figure 3. Electron scanning microscope photos of fine powdered LaNi5 before (left) and after (right) annealing above 200 °C.](image)

Second heating run of the same sample in the same circumstances is giving only small weight changes above 300 °C, indicating that noticed weight increase during first drive is permanent. Hydrogenated alloys in TG analysis from RT to 200 °C firstly indicated weight loss during hydrogen release (accordingly 1.31wt% for LaNi5 ; 1.02wt% for alloy 7-10 and 0.06wt% for Ni powder), and next weight growth above 200 °C, but different as before hydrogenation (Table 1). Nickel powder absorbs hydrogen only in small quantities and no markedly differences were noticed in weight growth before and after hydrogenation – same 0.77wt%.

The oxidation behaviour of the AB5 type intermetallic compounds CaNi5 and LaNi5 has been studied at different temperatures ranging from 100 to 800 °C by Christopher et all [4]. Their found that the element A (Ca, La) is first oxidized rapidly followed by slower oxidation of nickel and that CaNi5 is more resistant to oxidation and decomposition than the LaNi5 alloy. Previous researches of behaviour of AB5 alloy in oxidizing atmosphere (see [4]) confirms the first oxidation of element A, and formation of lanthanum oxides as well as mixed lanthanum nickel oxides. XRD inspection of our
samples revealed that after heating of alloys AB₅ above 200 °C, the new phase of black nickel oxide (similar to bunsenite structure) appeared (Figure 4).

Table 1. Summarized results from TG and DTA analysis of AB₅ alloys and powdered nickel.

| Sample       | Before hydrogenation | After hydrogenation |
|--------------|----------------------|---------------------|
|              | Weight growth, %wt   | Position of exothermic peak, °C | Reaction heat, Joules | Weight growth, %wt | Position of exothermic peak, °C | Reaction heat, Joules |
| LaNi₅        | 3.14                 | 289                 | 3570                 | 7.43             | 342                 | 6400                 |
| Alloy 7-10   | 6.44                 | 261                 | 4220                 | 4.08             | 289                 | 1660                 |
| Ni powder    | 0.74                 | 420                 | 291                  | 0.77             | 420                 | 231                  |

Before annealing above 200 °C an alloy 7-10 has deformed LaNi₅-type hexagonal structure P6/mmm with lattice parameters a=5.0358 Å and c=3.9929 Å (ideal LaNi₅ structure has a=5.002 Å, b=5.002 Å, c=4.058 Å) and volume of elementary cell V=87.65 Å³. After annealing structure changes radically to cubic bunsenite (NiO) type structure Fm-3m with lattice parameter a=4.1769 Å. No presence of oxides from element A (La, Pr, Ce, Nd) was found in remarkable quantities. Nevertheless the formation of amorphous phase was noticed – see broad maximum in XRD spectra of annealed sample at 30 degrees (instead of first reflex with index 101 in LaNi₅ structure of initial material). We didn’t found similar results in published research papers.

Next investigations will be performed with same materials to test the change of their structure in different environments (air, oxygen). Our results demonstrated then the usage of hydrogen storage alloys AB₅ (at least alloy with trademark “7-10” and LaNi₅ without any stabilizing elements must be taken with care – it is important not to exceed some critical temperature were irreversible structure, compositional and morphological changes will occur.

EDAX analysis of elemental composition of samples before and after oxidation shows the increase of oxygen content from 1.07wt% in fresh alloy LaNi₅ sample to 4.44wt% in annealed sample.
4. Summary
Heating of AB₅ alloys above 200 °C leads to mass growth from 3-7 wt%, indicating that noticed mass increase during first run is permanent. Microscope and XRD inspection revealed the formation of new phase with bunsenite NiO structure with deformed cubic structure (a=4.17 Å). The new phase is no more active to hydrogen sorption/desorption. From the above observations it can be expected that due to hydrogenation/dehydrogenation reactions on AB₅ intermetallics, when oxygen-containing reactants are used, alloy will decompose.

Our results demonstrated that the usage of hydrogen storage alloys AB₅ (at least alloy with trademark “7-10” and LaNi₅ without any stabilizing elements must be taken with care – it is important not to exceed some critical temperature were irreversible structure, compositional and morphological changes will occur.

5. References
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