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Metallic hydrides: from gas storage to batteries

Selected intermetallic compounds (IMC) can react reversibly with gaseous hydrogen to form metallic hydrides. Their remarkable thermodynamic properties make them suitable for safe energy storage in the future use of non polluting hydrogen as an energy carrier. Solid-state storage is a promising alternative to very high pressure tanks or cryogenic liquid H_2 vessels. Metallic hydrides can be formed also electrochemically from water reduction. These properties are used nowadays at an industrial level to produce rechargeable NiMH batteries. In order to optimise these compounds, fundamental as well as technical questions have still to be addressed. Neutron diffraction is the ideal tool to probe hydrogen in the crystal structure and to investigate in situ the complex mechanisms involved in the solid gas or electrochemical processes.

Solid gas reaction: Hydrogen absorption in IMC is characterised by a hydrogen capacity of about one hydrogen per metal atom. The stability of the formed hydride is determined by its hydrogen equilibrium pressure at a given temperature. Thus, thermodynamic properties of hydrides are usually described in pressure-composition isothermal (PCI) curves [1,2]. Three domains can be observed (figure 1b): at low H content, a single phase solid solution domain occurs (so-called α-phase). This region is followed by a two-phase domain, where the saturated α-phase transforms into the β-phase. It corresponds to a constant plateau pressure that extends in composition as long as the transformation reaction takes place. For higher pressure, again a solid solution single-phase domain occurs, corresponding to the β-phase. These different domains can be characterised during in situ neutron diffraction experiments. As shown in the figure 1a, the multi-substituted $LaNi_5$-type compound $Mm(Ni_{0.712}Mn_{0.076}Al_{0.058}Co_{0.15})_5$ (Mm stands for mishmetal, a cheap mixture of rare earth) is loaded under hydrogen pressure by a controlled step by step process up to tenth of bars. At each step, the sample is allowed to relax until it reaches equilibrium [3].

From the collected data, crystallographic analysis is carried out allowing phase determination and hydrogen atom localisation within the crystal structure (figure 2). Due to hydrogen absorption, the cell volume of the β-phase is much larger than that of the α-phase. Typical values up to ΔV/V=25% are commonly observed for these materials. Thus, huge constraints are created by this volume expansion leading to important decrepitation of the material. Useful information about the mechanism related to hydrogen

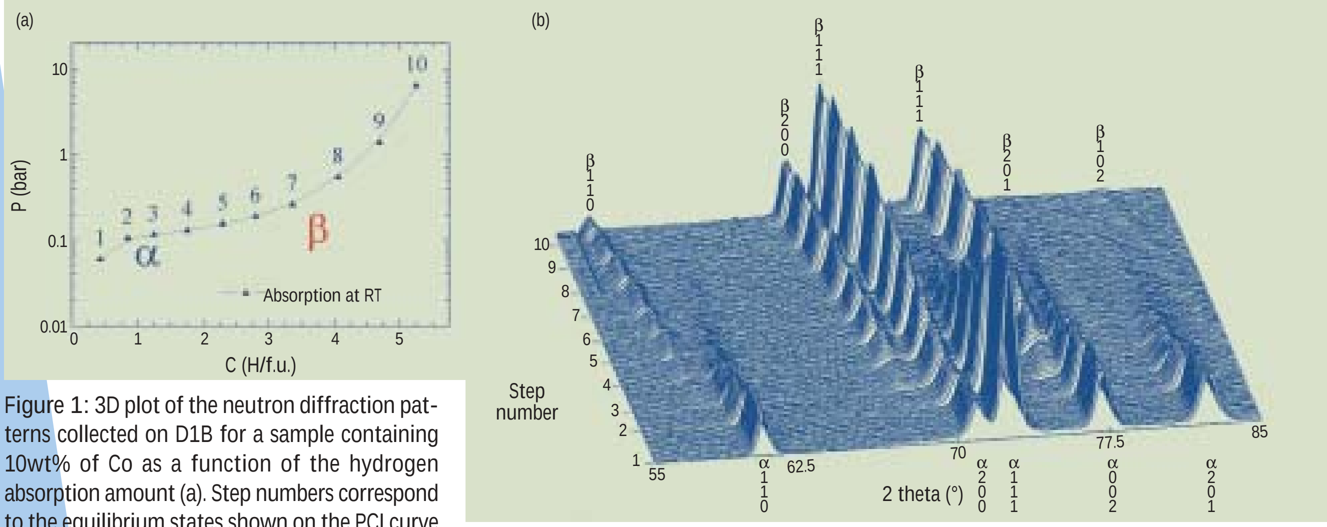

Figure 1: 3D plot of the neutron diffraction patterns collected on D1B for a sample containing 10wt% of Co as a function of the hydrogen absorption amount (a). Step numbers correspond to the equilibrium states shown on the PCI curve (b). Absorption occurs in three different sequences: i) alpha solid solution branch from steps 1 to 3, ii) alpha-beta two-phase domain (on plateau pressure) from steps 3 to 7, iii) beta solid solution branch from steps 7 to 10.

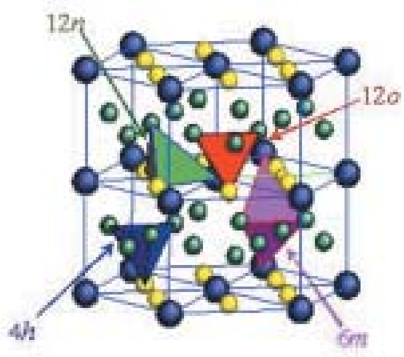

Figure 2: Crystal structure of 10wt% Co metallic hydride adopting the four-site structural model in hexagonal *P/6mmm* space group. Hydrogen sites are shown as tetrahedrons. The cell has been doubled along the c-axis for sake of clarity.

decrepitation during cycling is obtained from the analysis of the line broadening. This allows better understanding of the ageing properties of the materials by the identification of defects generated during the charge/discharge process.

Electrochemical reaction:

Extensive studies have been carried out on the rare-earth intermetallic hydrides, which are used as negative electrodes in Nickel-Metal Hydride (NiMH) secondary batteries. These hydrogen storage materials allow both, to replace highly polluting Cadmium and to increase the reversible capacity by about 20% compared to a classical NiCd battery. However, some problems remain with the use of metal hydrides in batteries. An important one is related to corrosion in highly alkaline electrolyte, which reduces the cycle life. This can be overcome by substituting cobalt on the nickel site of the intermetallic compound. The benefit brought by this element is connected to the mentioned formation of an intermediate γ-hydride [4]. It is believed that in the pure lanthanum three-substituted alloy $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$, this intermediate γ-hydride disappears to the profit of a wider β branch. However, cobalt remains very costly, and 10% in weight in the alloy represents about 40% in cost. Therefore, a lot of work has been devoted to decrease the amount of Co in the electrode material [5-7]. In situ studies using powder neutron diffraction have been performed on working negative electrode materials. This technique is very powerful since it allows a bulk analysis of the electrode in geometry very close to real batteries. Using real time experiments, different possible negative electrode materials with various weight ratios of Co have been investigated on D1B. For Co-rich alloys containing mishmetal, we have shown the existence of the intermediate γ-phase [7,8]. This phase, with an intermediate cell volume and capacity between the α-phase and the β one, plays a very important role in the strain distribution within the grain. It is believed that this phase is metastable and it exists only at the interface between the α and the β-phase (figure 3).

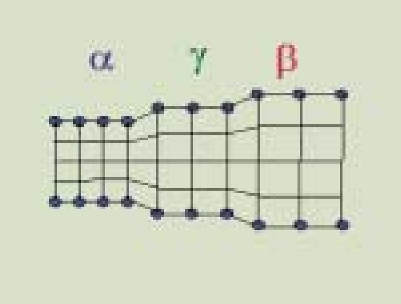

Figure 3: Schematic view of the interface α→ γ→β allowing a reduction of the strains created during the metal hydride formation.

The interesting feature is related to volume expansion. Indeed, an intermediate hydride implies a two-step process in the discrete volume expansion (α→γ, γ→β) allowing the system to reduce the strains generated at the α-β interface and, therefore, limiting the decrepitation process and minimising the subsequent corrosion processes.

Hydrogen is believed to be the energy carrier of the future and solid-state storage will be the safer way to handle this highly reactive gas. However, many steps are still to be carried out to obtain improved materials with large capacities, long cycle lifes and fast kinetics. As shown here, neutron diffraction is the perfect tool for a deep investigation of the metallic hydrides. This challenging research will allow to develop clean and competitive Electric Vehicles or Hybrid Electric Vehicles to reduce significantly greenhouse gas emission responsible for global warming.

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