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Storage of Hydrogen in Powders with Nanosized Crystalline Domains

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Abstract

The term "nanostructured" materials is being used in the literature to denote different materials prepared by different techniques: (a) by the gas condensation of vapors in a partial vacuum and (b) by mechanical alloying, a high energy ball milling technique. We discuss the origin of this confusion and propose a differentiating nomenclature. We then discuss the use on particles with nanosized structures for the storage of hydrogen.

A comment on nomenclature

The terms "nanoparticles" and "nanostructures" are now commonly used to denote a variety of products, sometimes having quite different properties. This creates an unnecessary confusion. The term "nanoparticle" appeared in the literature around 1982 in connections with powder particles having physical dimensions of one to ten nanometers in diameter. These particles were prepared by H. Gleiter and co-workers by the gas condensation of metal vapors in a low-pressure inert atmosphere. These particles were then condensed and consolidated into a small solids, and the products were called "nanostructured" materials. The structure of such a material, as revealed by TEM, consists of nanosized crystalline domains separated by sharp grain boundaries. The grain boundary thickness is on the order of one atom diameter whereas the crystalline domains have a very low dislocation density.

In 1983, Koch and co-workers showed that binary amorphous alloy powders could be prepared by ball milling a binary mixture of elemental powders. Later, Schwarz and co-workers showed that to obtain an amorphous alloy powder, the two elemental powders must have a large negative heat of mixing in the liquid state. If the heat of mixing is positive, then the product is a crystalline powder. In both cases, the particle sizes were about 30 microns in diameter. The x-ray diffraction pattern of the heavily deformed powder had very broad diffraction peaks, indicating that the various crystalline domains that were diffracting coherently within each powder particle had very small dimensions, on the order of nanometers. Thus, the powder prepared by mechanical alloying (MA) was simply termed "nanocrystalline". This denomination does not distinguish between powders prepared by MA and by gas condensation. In the MA

powder, the crystalline domains within each particle are separated by wide amorphous-like transition regions having a very high dislocation density. These transition regions are often called grain boundaries, even though they are usually as wide as the crystalline regions. The transition regions diffract x-rays incoherently as an amorphous structure would, whereas the crystalline domains diffract coherently. Since the diffracted intensity from the amorphous-like regions is very weak, the overall shape of the x-ray diffraction pattern from a heavily deformed MA powder is quite similar to that obtained from a true nanostructured powder prepared 'a la Gleiter'. It is clear, however, that the structure of the two so-called "nanostructures" are quite different and thus the properties might also be different. It is thus advisable to denote the structures prepared by the gas condensation method as "nanostructures" (as originally used by Gleiter) and the powders obtained by MA as "heavily deformed." A post annealing treatment can be used to annihilate the high-density dislocation tangles in the mechanically alloyed powders and thus *recover* a more perfect crystalline structure. However, the annealing usually leads to grain growth.

(a) Scientific drivers and advantages of fine microstructures in the storage of hydrogen

Hydrogen presents one of the best alternatives to petroleum as an energy carrier. It is non-polluting (burning hydrogen in a fuel cell causes no CO₂ emissions) and can be easily produced from renewable energy sources. However, the development of a hydrogen-based economy is contingent on the development of safe and cost-effective hydrogen storage systems. Of the known method for hydrogen storage (cryogenic liquid, compressed gas, and metal hydrides), metal hydrides offer the best compromise of safety and cost. The metal hydride systems of current industrial interest have been classified as AB₅ (e.g., LaNi₅), AB (e.g., FeTi), A₂B (e.g., Mg₂Ni), and AB₂ (e.g., ZrV₂). The hydrogen storage capacity, the number of times the storage can be done reversibly, and the kinetics of hydrogen absorption/desorption are intimately linked to the alloy microstructure. Powder particles having nanostructured features have some definite advantages.

(b) Critical parameters in the performance of the hydrogen storage material

Of primary importance in the hydrogen storage by metal hydrides is the pressure 'plateau' at which the material reversibly absorbs/desorbs large quantities of hydrogen. For many applications, the plateau pressure should be close to ambient pressure because this allows the use of light-weight storage containers. The plateau pressure can be tailored to a specific application through alloying. For example, the plateau pressure of LaNi₅ can be lowered by the addition of a few percent tin. [1]. The next important consideration is a fast kinetics of absorption/desorption, and this can be achieved by refining the microstructure.

Magnesium is an excellent hydrogen storage medium since it can store about 7.7 wt. % hydrogen, more than any other metal or alloy. However, the absorption/desorption of hydrogen in magnesium is very slow and a catalyst is needed to accelerate the reaction. Figure 1 shows the microstructure of a Mg-11.3 at. % Ni alloy we are investigating for storing hydrogen gas. At this composition, the alloy is a two-phase mixture of pure magnesium (majority dark phase) and Mg₂Ni (small light inclusions). Most of the hydrogen is stored in the low density magnesium phase. The small Mg₂Ni inclusions

catalyze the decomposition of the molecular hydrogen, increasing significantly the hydrogen absorption/desorption kinetics. The catalyst is quite effective since it is finely divided and is in intimate contact with the pure magnesium phase.

Figure 1. Scanning electron micrograph of a Mg-11.3 at. % Ni particle used for hydrogen storage

Figure 2 shows the hydrogen absorption/desorption characteristics of this alloy. The first 'plateau' corresponds to the absorption of hydrogen into pure magnesium whereas the second 'plateau' denotes the absorption of hydrogen into the Mg_2Ni phase. The absorption/desorption on hydrogen into this alloy is very fast (comparable to that of LaNi_5) and it is clear that microstructure plays an important role in the performance of the material. Another advantage of the fine microstructure is that the alloy powder does not comminute as the result of repeated charging/discharging with hydrogen. The synthesis of the powder particles shown in Fig. 1 is accomplished by mechanically alloying a mixture of elemental Mg and Ni powders, followed by an annealing treatment. Other catalysts being studied include FeTi and LaNi_5 .

(c) Possibilities to bring the synthesis techniques to the market

Alloy powders with nanosized crystalline domains will most likely play an increasingly important role in the storage of hydrogen. The main advantages of the MA method in the synthesis of these powders are:

- MA can be used to alloy elements having vastly different melting temperatures, which cannot be easily done by conventional techniques such as arc melting.

- MA is a mature powder synthesis technique and the method can be easily scaled from the laboratory (5 to 50 gram powder batches) to industry (20-kg to 20-ton powder batches).

(d) Support for Hydrogen Storage Research

Work on hydrogen storage in magnesium-based nanostructured alloy powders is being done in the US, Canada [Dr. R. Schultz, Hydro Quebec], Europe [Prof. L. Schlapbach, Univ. of Fribourg, Switzerland], China [Prof. Qi-dong Wang, Zhejiang Univ.], and Japan [Prof. H. Fujii, Hiroshima Univ.]. In general, US funding for research on hydrogen storage has been decreasing in recent years, due in part to the prevailing low cost of imported oil. US funding for research on nickel/metal hydride batteries has also decreased in preference for funding on lithium-ion batteries.

1. M. L. Wasz, R. B. Schwarz, S. Srinivasan, and M. P. S. Kumar, "Sn-substituted LaNi_5 Alloys for Metal Hydride Electrodes", *Mater. Res. Soc. Symp. Proc.*, Vol 393, pp. 237-242 (1995).