Fast sorption kinetics for Mg-Ni /graphite composites coated by Pd using the polyol process

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Mg-based alloys are well-known for their high hydrogen storage capacities (up to 7.6 % in weight for pure Mg), unfortunately, their sorption kinetics remain slow at low temperature (below 250°C). In order to improve these kinetics, we have investigated several ways to modify the surface of alloys previously synthesized by ball-milling.

MgNi alloy is prepared from Mg and Ni powders by mechanical milling under argon atmosphere for 48 hours. The alloy appears poorly crystalline by XRD and presents a particle size in the 1-5 µm range (BET surface in the order of 1 m^2/g). TEM observations reveal that, whatever the milling time, the alloy is constituted of crystallites with a 10-15 nm size. The hydrogen storage performances of the ball-milled alloys are investigated by gravimetric measurements (Hiden IGA 001). Figure 1 shows that the reversible sorption of the as-prepared MgNi alloy remains limited at low temperature (around 1.0 % in weight at 150°C).

In order to improve the performances, both from capacity and kinetic aspects, various surface treatments are performed on the ball-milled alloy. The first approach consists of preparing a composite by adding 10 w% graphite (MCMB 25-28) to the ball-milled MgNi alloy and, then, grinding this mixture for 2 hours. Longer milling times lead to a carbide formation ($MgNi_3C_{0.75}$), which is harmful to the hydrogen storage properties. The 2 hours ball-milled powder exhibits a specific surface area of 2.5 m^2/g and a desorption of 1.4 % in weight at 150°C. The capacity increase is directly connected to the surface modification with graphite suggesting the existence of a chemical interaction between the alloy and graphite. Moreover, the carbon addition favors the reduction of NiO, initially present at the alloy surface (as detected by electronic diffraction), in very reactive and highly divided Ni particles that may act as a catalyst.

In the light of our previous results and with the aim of promoting hydrogen sorption, the MgNi /graphite composite is coated with Pd using the polyol process. This process is based on reduction of a metallic salt in an organic solvent allowing the deposition of metallic nanoparticles on the surface of MgNi alloy. A 5 w% Pd with 50 nm average particle size are deposited on the previously synthesized MgNi/graphite composite. The desorption capacity of the resulting powder is high : 1.7 % at 150°C versus 1.0 % for the starting ball-milled MgNi alloy. The corresponding desorption kinetics are presented in figure 2. The Pd effect is remarkable : 1.3 % in weight is released in 30 minutes.

From these very promising results, we decided to apply the same surface treatments to other materials, especially alloys with higher Mg contents. In this work, we will present modified alloys with an hydrogen release as high as 2.5 % in weight (at 150°C).

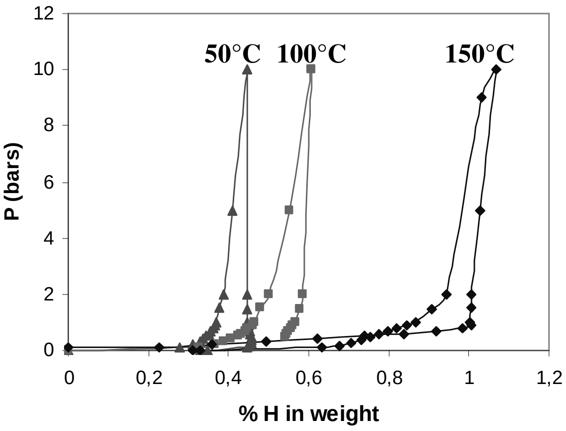

Figure 1 : Sorption isotherms of a 48 hours ball-milled MgNi alloy

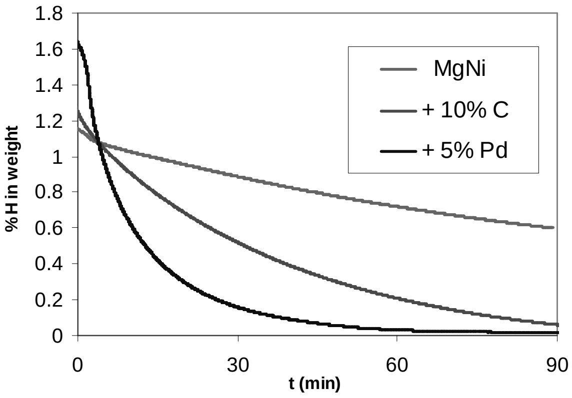

Figure 2 : Improvement of the desorption kinetics at 150°C of a ball-milled MgNi alloy