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Hydrogen storage behaviour of Pd-polymer composites

P. Mengucci¹, G. Barucca², G. Carotenuto³, R. Checchetto², A. Di Cristoforo¹, A. Miotello², E. Santeccchia¹

¹Dipartimento SIMAU, Università Politecnica delle Marche, Ancona, Italy

²Dipartimento di Fisica, Università di Trento, Trento, Italy

³Institute of Composite and Biomedical Materials, National Research Council, Napoli, Italy.

p.mengucci@univpm.it

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Solid state hydrogen storage based on metal hydrides represents a viable way to obtain storage systems that are safe and efficient at the same time even though their practical implementation is mainly limited by the decrepitation phenomenon and the slow hydrogen sorption kinetics.

Composite materials constituted of a metal forming hydride dispersed into a porous matrix can be used to overcome those limitations. In particular, the confinement of nanometric particles (nanoconfinement) has been proved to enhance the thermodynamic and kinetic properties of the composite materials [1, 2]. The synthesis of nanoconfined composites can be performed by chemical and electrochemical methods as well as by laser ablation techniques, generally requiring considerable experience and expensive equipment [3]. In order to overcome those drawbacks we produced a metal-polymer composite material from commercially available components by using a simple polymerization procedure not requiring specific equipment. The metal-polymer system studied in this work is formed of Pd metal particles embedded in a polysilossane polymeric matrix. Polysilossane exhibits high hydrogen permeability while Pd forms the interstitial PdH_{0.67} metal hydride.

Aim of this work is to study the hydrogenation properties of the obtained composites and to investigate the microstructural changes induced by the hydrogen absorption/desorption cycles.

The Pd particles (Sigma-Aldrich, Pd 99.9%, nominal surface area between 40 and 60 m²/g) were manually dispersed into a self-curing acetic silicon polysilossane formulation (Saratoga). Three different compositions were prepared with a nominal Pd content (in wt%) of 5% (sample A), 15% (sample B) and 50% (sample C). The hydrogen sorption measurements were performed in a Sievert's type apparatus at three different temperatures: 60°C, 80°C and 100°C. For each temperature, the hydrogenation properties of the samples were evaluated at three different pressure values: 0.2 atm (low pressure), 1 atm (intermediate pressure) and 2 atm (high pressure).

The structural characterization was performed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive microanalysis (EDS).

The pure Pd powder is formed of spherical particles with a diameter ranging from 200 nm to 400 nm. In the composite samples the Pd particles tend to form clusters whose mean size increases with the Pd content reaching a maximum value for sample C (Pd 50%), as shown in Figure 1.

After repeated hydrogen sorption cycles the structure of the samples is almost unchanged and even the crystalline state of the Pd particles remains unaltered suggesting the complete reversibility of the Pd \leftrightarrow PdH_{0.67} reaction. Since the polymeric matrix always evidenced a negligible contribution to the hydrogen stored, the amount of hydrogen desorbed during the dehydrogenation process for the different samples was attributed only to the formation of the PdH_{0.67} hydride.

The total amount of hydrogen desorbed by each sample, expressed as the H/Pd atomic ratio, is plotted in Figure 2. as a function of the desorption time. In Figure 2. the slope of the initial increase of each curve depends on the desorption kinetics, that ends at the beginning of the plateau, while the height of the plateau measures the total hydrogen absorbed amount. It is evident that the pure Pd powder always exhibits the fastest kinetics independently on the pressure and temperature values. However, in spite of the slowness of its reaction kinetics, sample A (Pd 5%) always stores the highest amount of hydrogen of all the other composites (Figure 2.). This behaviour is much more pronounced at high temperature and pressure values (Figure 2.b) where sample A stores a hydrogen amount even higher than the pure Pd powder, close to the stoichiometric limit of H/Pd=0.67. On the contrary, regardless of the temperature and pressure values sample C (Pd 50%) always shows the worst performance in terms of hydrogen stored amount (Figure 2.).

In conclusion, by limiting the hydrogen diffusivity during the sorption processes the polymeric matrix slows down the hydrogen kinetics of the composite samples. On the other side, the worsening of the

hydrogen storage capacity at the increase of the metallic content can be related to the formation of the Pd clusters that reduce the surface area exposed to H_2 . In this respect, sample C (Pd 50%) still shows a “polymer-like” behaviour due to the fact that the metallic domains of its structure are not well interconnected so that hydrogen cannot migrate freely through them. In this way, the beneficial effect of the bulk-like system given by sample C is prevented.

Further work is in progress to deeper investigate the role of the polymeric matrix as well as the influence of the cluster size on the hydrogenation behaviour of the Pd-polymer composites.

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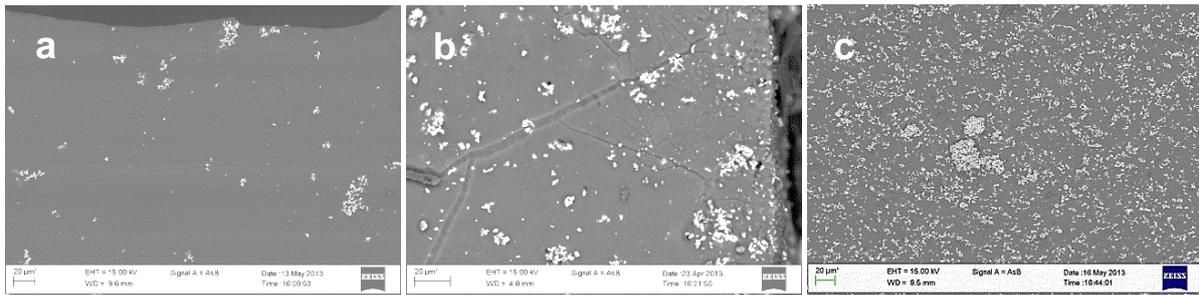


Figure 1. SEM images of the composite samples in the as-produced condition (in wt%): a) Pd 5%, b) Pd 15% and c) Pd 50%.

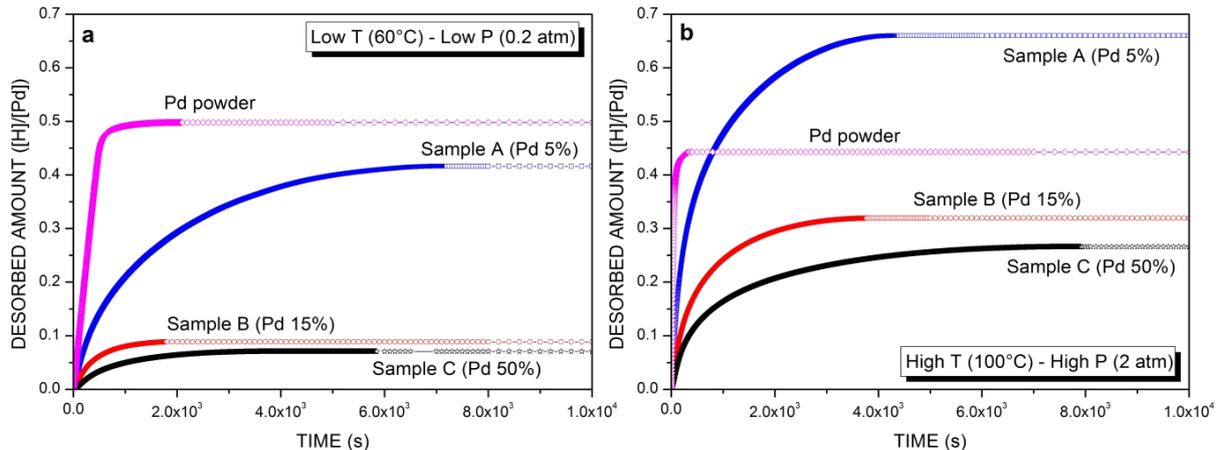


Figure 2. Hydrogen sorption kinetics of the composite samples: a) low temperature and low pressure values and b) high temperature and high pressure values. The Pd powder curves are reported as a reference.