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Mechanical behavior of highly reactive nanostructured MgH_2

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ABSTRACT

This study analyzes the mechanical behavior of compacted disks made of MgH_2 powders co-milled with vanadium or Ti–V–Cr alloy as an additive, through the evolution of the microstructure and mechanical properties upon hydrogen cycling. The recrystallization of MgH_2 particles results from a dynamic recrystallization phenomenon associated with the reaction of hydrogenation itself. The coalescence of the nanometric particles tends to create large agglomerates, which induces an increase in porosity, and explains the progressive swelling of the composites. A relaxation of the maximum strain is observed after 10 cycles for vanadium whereas for Ti–V–Cr the expansion increases until 200 cycles. This difference of behavior is correlated to the ability of vanadium particles to prevent the recrystallization mechanisms, then to limit the agglomeration of the MgH_2 particles. From the Vickers hardness measured on compacted powders, a hardness of 0.58 GPa was estimated for highly densified magnesium hydride. Nano-indentation tests performed on compacted pellets show an enhancement of about 20% of the Young modulus as the amount of additives raises from 4 to 8 wt. %. The Young modulus markedly improves as the number of hydrogen cycles increases up to 10. The H/E ratio calculated from these data is characteristic of an intermediate state in between elastic and plastic behavior.

Introduction

The last two decades of intensive research reveal the magnesium hydride (MgH_2) as one of the most promising materials for hydrogen storage. Highly reactive and nanostructured MgH_2 powders were achieved thanks to co-milling process e.g. with transition metal additives [1–4]. An important improvement of the thermal conductivity and thermal management was realized by uniaxial compaction of magnesium hydride powder mixed with Natural Expanded Graphite (NEG) [5–7].

The phase transformations, which occur during hydrogen absorption induce a significant increase in volume and create important stresses in the material [8–12]. Depending of the metal, the pressure amplitude can achieve several GPa. In order to quantify the mechanical stability of thin films of

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hydrides, measurements were specifically addressed to the mechanical behavior of Nb–H, Pd–H and Y–H systems [13–15]. The stresses generated during hydrogen absorption are due to the lattice expansion and the initial volume could be recovered after desorption. In the case of hydride compacted powders, the successive expansion–contraction cycles induce morphological and microstructural transformations that are responsible for an irreversible swelling reducing the life-time stability of the storage vessels.

Two types of mechanical behaviors are characteristic of metal hydrides in granular state. The first one, known as decrepitation, concerns hydrides of transition metals or alloys and intermetallic compounds, which have a high temperature of melting such as Ti, V, Ti–V–Cr, FeTi or $LaNi_5$ [16–20]. During hydrogenation, the structural transitions induce internal mechanical stresses, which exceed the ultimate tensile strength of the material and generate fractures, then reducing the particles size. The widening of the grain size range leads densifying the powder bed in the bottom of the vessel where small particles accumulate. This mechanism is responsible for the irreversible swelling of material such as transition metal alloys. The second behavior is typical for the magnesium hydride in which an important re-crystallization process occurs in the nanostructured particles upon the phase transformation. The grain growth promotes the coalescence of the particles, leading to a progressive agglomeration. Meanwhile, the rearrangement of microstructure leads to an increase of the powder bed porosity. Then a dilatometry device was previously designed to measure in-operando the expansion of compacted disks and to quantify the mechanical stresses induced on the wall of a cylindrical stainless steal tube [21]. The results reveal a 3 times lower amplitude of swelling for samples containing NEG than for NEG-free samples. Since it appeared that the irreversible expansion strongly depends on the type of additive, additional experiments were scheduled. Compacted disks made of MgH_2 ball-milled respectively with 8 wt % of V and 8 wt. % of Ti–V–Cr alloy were also tested by dilatometry measurements. Correlations were established between the irreversible swelling of the composites and microstructure changes occurring during hydriding cycles: the expansion is due to the evolution of granulometry from a dense bi-modal distribution where the small particles fill the space between the large ones to a mono-disperse powder whose porosity is higher [22]. The purpose of the present paper was to go further in the analyses of the recrystallization mechanisms and to focus on the characterization of mechanical properties such as Young modulus and nano-hardness, and to correlate their behavior and the swelling effect associated to the microstructure changes of the composites upon cycling.

Experimental

Nanostructured MgH_2 powders were made by co-milling with respectively 4 and 8 wt. % of pure vanadium (samples A and B), or with 4 and 8 wt. % of $Ti_{0.5}V_{1.9}Cr_{0.6}$ alloy (samples C and D). A pure MgH_2 powder was also ball-milled as reference (sample E). All the powders were prepared in the same experimental conditions (milling time, ball to powder ratio, etc …). Moreover for the present study we have not added any NEG, in order to better enlight the impact of different metal additives on the microstructure and the mechanical behaviors of compacts. Hydrogenation/dehydrogenation cycles were applied using a volumetric Sievert device (HERA). Absorption was performed under 1 MPa H_2-gas pressure and desorption under 15 kPa, both at 310 °C. The thermodynamic parameters were chosen far from equilibrium in order to boost the reaction kinetics of our materials.

A laser granulometer Malvern Mastersizer 2000 was used to characterize the particles size distribution. The samples were dispersed in ethanol and ultrasounds were applied for 5 min in order to eliminate particles agglomerates. The obtained suspension was then measured in the Malvern Mastersizer 2000 with a speed of the fluid circulation pump of 1950 rpm and an obscuration percentage of the laser beam of about 18%. The evolution of the microstructure and the morphology of the MgH_2 particles was studied by Scanning Electron Microscope (SEM Zeiss Ultra +).

The experimental in-situ dilatometry device was previously described in Ref. [21]. It is composed of a SS316L cylindrical sample holder and 2 Linear Variable Differential Transformers (LVDT) as displacement transducers. Contrarily to the previous study [22], the sample holders we used here are thin wall tubes with 20.1 mm internal diameter and 0.5 mm thick. The use of thin-walled sample holders permits a better mechanical sensitivity upon increasing the deformation amplitude and can reveal more accurately the different stages of materials behavior. The ball-milled powders were compacted uniaxially as pellets of 2 cm diameter and 1 cm height. The maximal number of hydrogenation–dehydrogenation cycles for each material depends on their swelling stabilization.

Micro-hardness measurements were carried out on compacted magnesium hydride powder using a BRUCK device. Pellets with 2 cm diameter were obtained submitting 3.14 g of powder to pressures ranging from 40 to 100 MPa, the height depending on the applied pressure. In order to visualize more accurately the mark of indentation on the sample surface a very thin gold film of 15 nm was deposited. The loading time of the experiment was set at 10 s under an applied load of 3 N. The Vickers micro-hardness μH was calculated from the applied load P and the diagonal lengths of the mark d_1 and d_2 according to the relation (1), the angle of 136° being defined by the geometry of the pyramidal tip [23]:

$$\mu H = \frac{2\sin\left(\frac{136^\circ}{2}\right)P}{d_1 d_2} \quad (1)$$

Depth-sensing nano-indentation tests were carried out using a Nano Indenter (Nano Test 600, Micro Materials, Wrexham, UK). This system can produce indentation loadings with very large ranges of applied forces (0–500 mN) and resulting displacements between 0 and 50 μm. The force and displacement resolutions are as small as 3 nN and 10 nm. For each test, a batch of hundred imprints, ordered in 10 × 10 array, were introduced using a Berkovich tip diamond indenter on the sample surface with 80 μm mesh to avoid the interaction between the marks. The maximum applied force was set at 100 mN. The samples A, B, C and D were compacted uniaxialy into pellets of 8 mm diameter and 3 mm height with a pressure of 100 MPa. For each of the compositions, a pellet