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Stress effect on the swelling/shrinking behavior of an AB2 alloy during hydrogenation cycles

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ABSTRACT

The stress influence on a $Ti_{0.85}Zr_{0.15}Mn_{1.33}V_{0.3}$ alloy during hydrogenation cycles has been studied in a special design test cell for mechanical studies during hydrogenation. The alloy was synthesized in an induction melting furnace with an inert Ar atmosphere. The full basic characterization of the material is presented, from a structural and morphological point of view by X-ray powder diffraction (XRPD), Scanning Electron Microscopy (SEM), Energy Dispersion X-ray spectroscopy (EDX) and laser grain size analysis, and, from a thermodynamic point of view by the measure of the Pressure composition Isotherms (P-c-I) at 23 and 80 °C. Besides, in order to measure the mechanical properties of the material, volume variations measurements during hydrogenation cycles were performed. The samples were milled up to sizes beneath 1.25 mm, and afterwards placed into a cylindrical die under three different levels of axial stress, 0.0325 MPa, 0.12 MPa and 0.84 MPa, for more than 100 cycles. For higher stress levels the powder bed shrinks as cycles continue, while for lower stresses the powder bed swells. A natural tendency for the powder to decrepitate and agglomerate was observed, as the size distribution of the particles reduces and the shape become uneven, generating an increase of the porosity and volume in the case of the lower stress sample. As the stress increases, the grains rearrange easily and a polydisperse distribution of particles facilitates the accommodation of smaller grains between bigger ones, producing a reduction in the porosity and volume of the hydride bed after several cycles.

Introduction

Metal hydride hydrogen compression (MHHC) offers significant advantages in comparison to other technologies. The main advantages include simplicity in design and operation, absence of moving parts, compactness, safety and reliability, the possibility to consume waste heat instead of electricity, and low energy cost [1,2]. Furthermore, two key features in the design of MHHC are the shape-optimization of the vessel to improve its heat exchange, and, the quantity of hydride that can be introduce in order to have a greater amount of

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hydrogen to compress [1,3]. However, stresses have a larger impact on the integrity of the system, specially, when a container is filled with a large quantity of hydride, and/or, the hydride powder bed have a slender geometry that could increase its stress at the bottom of the container vessel (like a vertical cylinder) [4–6]. As a result, it becomes extremely important to know beforehand the mechanical behavior of the hydride in order to design the optimal geometry and quantity of mass that can be inside of an hydride container without causing any structural damage [1,7,8].

In previous investigations, the effect of the stresses generated by the hydride during hydrogenation cycles has been measured. Nasako et al. [5] measured the amount of stress generated on the vessel surface by the alloy swelling with the objective of increasing the life time of the reaction vessel in heat systems that employ two AB5 alloys ($LaNi_{4.55}Al_{0.45}$ and $La_{0.8}Y_{0.2}Ni_{4.8}Mn_{0.2}$), from which several effects were found, such as generation of stresses at the bottom of the vessel depending on the amount of hydrogen ab-/desorption cycles and the initial packing fraction. Furthermore, a two-step mechanism for stress accumulation consisting of an initial agglomeration between the particles and a consecutive filling of void space by smaller decrepitated particles was proposed. Charlas et al. [8] studied the cyclic swelling of a combination of two hydrides (Ti–Cr–V + Zr–Ni) in one granular bed, from which some phenomena were analyzed. First, it was observed a general decrease in the porosity of the powder bed during hydrogenation stages, while simultaneously, the porosity was rising at absorption and diminishing at desorption through each cycle. Also, it was observed that the gradual settlement of the packed bed decreases the general porosity and the volume of the powder due to a segregation and rearrangement of the particles after decrepitation. Lin et al. [9] analyzed the deformation on the walls of a high temperature reaction vertical vessel system with 1 mm of thickness. Their results indicated that the larger strain was found at the bottom of the cylinder due to a pulverization-densification mechanism. In addition, the effect of increasing the packing fraction was analyzed, specifically, it was found that a bigger initial particle size induce a larger circumferential strain on the walls, mainly at the bottom of the tank. On the other hand, in the field of hydride vessel design, authors like Na Ranong et al. [10] took into account some basic features about heat transfer and the effect of mechanical behavior, specially, the volume expansion of the powder, in order to generate a basic guide to design a hydride pressure vessel. Furthermore, to lesser the volume expansion effect on the hydride container, these authors recommended to use a variation in the positioning of the vessel (i.e. horizontally/vertically), a wall enforcement of the container, the use of a compensating element, and/or, the use of a wall that can deform plastically.

As a result, the objective of this study is to investigate experimentally the mechanical properties of an AB2 hydride at three different levels of stress. Specifically, in order to perform an analysis of the mechanical behavior of the hydride, an evolution of the relative swelling of the grains and of the powder bed should be developed. Hence, at each level of stress, several absorption–desorption hydrogenation cycles were applied to the hydride until it reaches stabilization in the change of the hydride volume. The variation in the volume will determine how the deformation modes are in the powder and how the powder grains in the stack rearranged.

Materials and methods

The alloy $Ti_{0.85}Zr_{0.15}Mn_{1.33}V_{0.3}$ was synthesized from raw elements (with a purity of Ti = 99.99%, Zr = 99.5%, Mn = 99.9%, V = 99.7%) by an induction melting process under an argon atmosphere of 1 bar. A 5% weight excess of Mn was used for the synthesis. The fusion of the materials was performed by turning the obtained ingots several times in order to homogenize their composition. The microstructure and elemental chemical composition were investigated by scanning electron microscopy (SEM, Hitachi S-3000N OK) and energy dispersive X-ray spectroscopy (EDX), respectively. Moreover, X-ray powder diffraction (XRPD, PANALYTICAL X'pert PRO θ-2θ) analysis was achieved by using CuKα radiation in a θ-2θ configuration and a further Rietveld refinement was performed to determine the phases and lattice constants of each material before and after hydrogenation cycles. Furthermore, Pressure-composition Isotherms (P-c-I) for each material were experimentally determined in a Sieverts-type volumetric reactor. With this aim, the experiments were carried out inside a constant-temperature room at 23 (1) °C. Along this paper, numbers in parenthesis stand for the error on the last digit. Pressure measurements were obtained with a MKS Baratron capacitance manometer with a 1% of reading accuracy and temperature sensitivity of 0.04% of full scale/°C up to 200 bar. The experimental system volume for the sample was 30 (1) cm^3 (5.8 (2) cm^3 of hydrogenation cell volume, including the powder bed. Previous to the P-c-I measurements, the samples were milled during 5 min in a Spex 8000 shaker mill and then sieved under 45 μm in an Ar atmosphere. Then the powder (1.01 (1) g) was introduced in the Sieverts reactor, where the activation was made at room temperature (23 (1) °C) and at a pressure of 25 bar. The P-c-I isotherms were obtained at 23 and 80 °C for absorption and desorption, after 3 cycles of activation. These P-c-I temperatures were established in order to study the thermodynamic behavior of the material in the operation range of a first stage metal hydride compressor that has been designed.

Furthermore, the test bench for the mechanical properties measurements is described in Ref. [8]. In the system, a Linear Variable differential transformer (LVDT) sensor is employed to measure the vertical displacement generated by the volume expansion in the test cell while a control flux of hydrogen is getting in and out of the cell. Moreover, for the temperature measurement a thermocouple is set in direct contact with the sample. For the experiments, the inner layout of the test cell was changed in order to admit lower quantities of material and also apply three levels of stress through springs with different stiffness. Hence, from the same ingot melted, three samples were taken to measure, in each one, a different level of stress at hydrogenation and dehydrogenation stages. The samples were crushed and sieved below 1.25 mm, then they were placed in the cylindrical test cell with a diameter of 25 mm and a height of 25 (1) mm, where the three springs were placed over a moving piston in order to simulate the effect