Ternary metal hydrides. Development of a microporous-matrix composite material and its use as fixed bed in a solid state hydrogen storage tank

To address the issues of poor thermal conductivity and fragmentation of metal hydride particles undergoing hydriding/dehydriding reactions, a metal hydride-based composite material was developed. The active metal phase was embedded in a silica matrix and graphite filler was incorporated by ball milling technique and characterized by a number of techniques. The resulting porous composite was able to undergo hydriding/dehydriding cycling with enhanced mechanical stability and thermal conductivity properties. The composite development process was scale-up and the material was utilised as H2 loading fixed bed into a solid-state storage tank. The performances of the hydrogen storage system were studied by using the homemade "PCTH2" Sievert's apparatus developed by ENEA. The experimental results demonstrated that the developed system is able to reversibly store hydrogen with a fast loading kinetics. When coupled with a small fuel cell, the energy stored can be used for small-sized niche applications such as Uninterruptible Power Supply (UPS) for personal systems or emergency lighting in un-urbanized places

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Idruri metallici ternari. Sviluppo di un materiale composito a matrice microporosa e suo utilizzo come letto fisso di un serbatoio per accumulo di idrogeno allo stato solido

L'utilizzo degli idruri metallici per l'accumulo di idrogeno è ostacolato da alcune problematiche tecnologiche come la frammentazione delle particelle metalliche durante i cicli di carica/scarica di idrogeno e la scarsa conducibilità termica degli idruri. In questo lavoro è stato sviluppato per via meccano-chimica un materiale composito metallo-silice-grafite. Il composito poroso risultante è in grado di subire cicli di idrogenazione/deidrogenazione con proprietà migliorate in termini di stabilità meccanica e conducibilità termica. Il processo di sviluppo del materiale è stato scalato ed il composito è stato utilizzato come letto fisso di un serbatoio per accumulo di idrogeno allo stato solido. Le prestazioni del sistema sono state studiate mediante l'apparato "PCTH2" basato sul metodo di Sievert e sviluppato da ENEA. I risultati sperimentali indicano che il sistema è in grado di accumulare idrogeno con cinetica di caricamento veloce. Accoppiando il sistema ad una cella a combustibile sono ipotizzabili alcune applicazioni pratiche di nicchia come gruppi di continuità di piccole dimensioni per uso personale o sistemi di illuminazione di emergenza in ambienti non urbanizzati

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Metal hydride (MH) alloys possess the capacity of safely storing high volumes of hydrogen in the solid state. In particular, the class of MH alloys denoted as AB5 (LaNi5 being the representative intermetallic compound), exhibits an excellent volumetric storage capacity, that makes the material particularly suitable for stationary applications. However, the use of AB5 alloy for hydrogen storage (*i.e.*, as a fixed bed in a solid state tank) requires proper management of some technological issues. Among these, the mechanical instability of metal particles grains under hydriding/dehydriding reactions produces a very fine powder [1] that can seriously affect the performance of the whole device. The main detrimental effects due to decrepitating particles consist in impediment to hydrogen diffusion, alloy loss by entrapment of tiny particles in device accessories, increase in alloy deterioration by the feed gas impurities and rapid plugging of dust filters. As a consequence, a serious deterioration of the nominal overall storage capacity of the tank will result. Encapsulation of the alloy particles within various media (copper, phenolic resins and polymers) has been proposed [2-5]. In our recent work [6] we reported on an advantageous encapsulation method consisting in a particulate composite material where a hydrogen permeable matrix fixes metal particles in stable position. The method can also be beneficially applied to solve another crucial technological issue, regarding the management of the heat involved in the H_2 absorption and desorption processes [7]. Typically, the thermal conductivity of metal hydrides is on the order of 0.1 W/(mK), and various techniques have been proposed to improve it such as insertion of aluminium foam, integration of copper wire nets, compaction of porous metallic matrix, microencapsulated metal hydride compacts and expanded natural graphite/metal hydride compacts. Taking advantage from the composite nature of the developed material, a proper dispersion of a conductive material into the silica matrix can easily enhance the material conductivity.

In this paper the development of an AB5-silica composite material with enhanced thermal conductivity is reported. After chemical-physical characterizations the composite was utilised as H_2 loading material into a solid-state storage tank. The description of the device and the hydrogen storage performances of the system as studied by Sievert's method are also reported.

Materials and methods

Composite material preparation

The preparation of the AB5-silica composite material was carried on as reported in details elsewhere [6, 7]. Briefly summarizing, the following actions were carried on: i) mechanical pulverization of the AB5 hydriding alloy; ii) preparation of the silica-AB5 blends and graphite addition by intimately mixing the powders by a second milling treatment and iii) blend consolidation by cold uniaxial compression and successive thermal treatment.

All the mechanical treatments were conducted by means of a high energetic mill, SPEX 8000M miller, during the material development stage, and by the Simoloyer CM08 pilot plant for the successive composite scale-up process, see figure 1.

The selected active metal was an AB5 alloy, derived from the intermetallic compound $LaNi_5$, specifically the Hy-Stor 208 by Ergenics. The $LaNi_5$ fresh samples were mechanically treated to downsize the metal particles into powder, 10÷100 μm particles diameter.

The pyrogenic silica T30 (henceforth referred as SiO_2), supplied by the Wacker Chemie AG, was used as embedding matrix.

The metal-silica (henceforth also referred as $LaNi_5$-SiO_2) blend was obtained by mixing previously treated metal powder and pyrogenic silica in 40:60 volume ratios, corresponding to 70:30 weight ratios.

Enhancing of composite thermal conductivity was obtained by graphite (henceforth also referred as C) addition and blending in the milling apparatus. The effect of graphite insertion was tested on a set of $LaNi_5$/SiO_2/C samples at different v/v/v volume ratios namely: A) 40/20/40; B) 40/30/30; C) 40/35/25; D) 40/40/20; E) 40/45/15; F) 40/50/10.

Pellets by milled powder mixtures were obtained in different-sized cylindrical shape (10, 20 mm diameter). The powder samples were inserted in a die-set equipped with a vacuum outlet. The powder was consolidated through a step-by-step increasing in the applied pressure up to about 2.5 tons/cm^2. All the pellet

FIGURE 1 Spex 8000M mixer mill (left) and Simoloyer CM08 pilot plant (right)

samples were thermally treated at 300 °C for 2 hours in argon atmosphere to obtain consolidated samples.

Characterization methods

Composite material
chemical-physical characterization

Chemical-physical characterization was performed by different techniques. In particular, the reticulation process was followed by Thermo Gravimetric Analyses (TGA); phase purity check and micro structural analyses were performed by X-Ray Diffraction (XRD); a commercial thermal analyzer, based on the modified transient plane source technique, was used to perform thermal conductivity measurements; morphological characterization was carried on by Scanning Electron Microscopy (SEM).

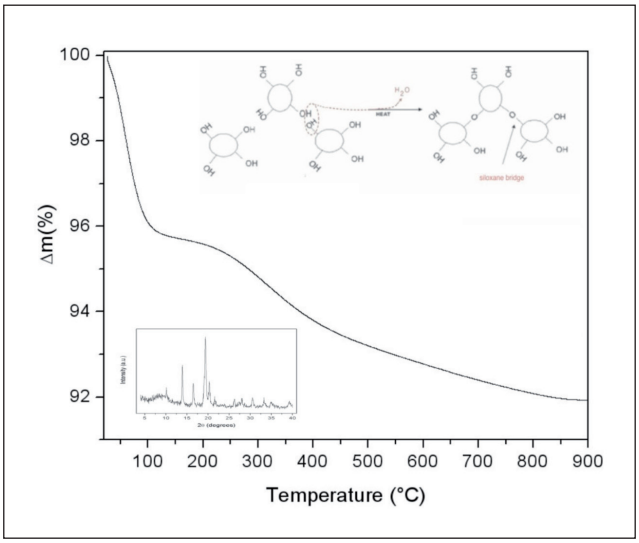

FIGURE 2 Thermo gravimetric analysis performed on pyrogenic silica in Argon atmosphere (25-900 °C, rate 5 °C/min). Insets: a simplified representation of inter-particles condensation through siloxane bridge formation (top); XRD analysis of the AB5-silica composite consolidated at 300 °C (bottom)

Hydrogen storage performance measurement

Pressure-Composition-Temperature (PCT) isotherms were measured by the homemade fully automated Sievert's apparatus PCTH2 system, developed by ENEA in collaboration with Labor srl. Instrument's main features are: temperature range 0–100 °C; pressure range 0–100 bar; low-pressure (0-3 bar) and high-pressure transducers (3-100 bar), accuracy 1%; built-in and calibrated (100 cm^3) reservoir volume.

The consolidated composite material within the tank was degassed through a membrane vacuum pump (down to 10^{-2} bar) and activated (under static pressure $p(H_2)$=30 bar, at 90 °C, for 2 days). PCT isotherms cycle-life absorption/desorption curves were recorded after the activation. The absorption/desorption measurements were performed by charging/discharging the manifold with subsequent aliquots of H_2 (fixed ΔP method) until the thermodynamic equilibrium content was reached. The absorption kinetics of the tank was obtained by charging the device through gas doses addiction. The calibration of the empty volume in the sample holder (empty volume in the reactor and in the connecting lines up to the manifold) was performed in the same measurement condition before each analysis.

Results and discussion

Material development and characterization

TGA analysis reported in Figure 2 permitted to follow the thermal behaviour of the silica powder. The first mass loss immediately starts with the heating process. It can be assigned to surface bonded water desorption. Starting from about 150 °C, a second water loss process appears with a maximum rate around 300 °C. This process is due to interparticular siloxane bridge formation. Pyrogenic silica nanoparticles are arranged

in aggregates sized 200-500 nm [8]. The starting of water loss is due to the formation of new siloxane bridges between nanoparticles, as sketched in the inset (top) of Figure 2. The interparticles condensation through siloxane bridge formation continues within the range 500-800 °C with an almost constant rate.

The composite pellet samples set containing graphite powder was studied in terms of their thermal conductivity properties. The experimental results are reported in Figure 3 as a function of the graphite fraction. The set of composite samples A, B, C, D, E, F exhibited thermal conductivity values ranging from 3.2 W/mK for sample A (graphite, 40%) up to 1.7 W/mK for sample F (graphite, 10%). Thus, even small volumes of graphite filler added to the silica metal composite were able to produce significant enhancements in thermal conductivity of the samples and the trend was almost linear with the filler content. For comparison, data for a $LaNi_5/SiO_2$ pellet at 40/60-volume ratio (G) were also reported. The measured value of 1.3 W/mK resulted significantly higher than the thermal conductivity of a literature $LaNi_5$ powder samples (0.2 W/mK), indicating that by simply forcing the contact between metal particles, the uni-axial powder consolidation process is able to promote a thermal conductivity enhancement of the compact with respect to the starting powder. However, in order to enhance the material thermal conductivity to values compatible with practical application, the addition of third elements, such as graphite, is advantageous.

On the consolidated material, accelerated charge/discharge tests by High Pressure Differential Scanning Calorimetry (HP-DSC) were previously carried on to evaluate the matrix ability to retain the particles [7]. After testing, no evidence of free particles was found. Figure 4 shows the SEM image of a fractured metal particles embedded in the matrix after hydrogen cycling.

Solid-state hydrogen storage tank development and characterization

The tank was developed by ENEA in collaboration with Labor Srl. The whole process of designing and developing the final prototype is going to be published elsewhere. Here we limit to describe the main characte-

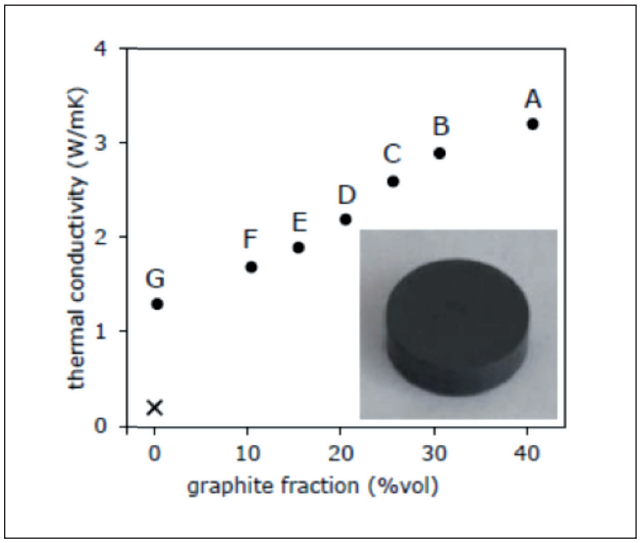

FIGURE 3 Thermal conductivity as a function of the graphite fraction measured for $LaNi_5/SiO_2/C$ pellet samples (inset) at different v/v/v volume ratios: A) 40/20/40; B) 40/30/30; C) 40/35/25; D) 40/40/20; E) 40/45/15; F) 40/50/10. As a reference, data for a $LaNi_5/SiO_2$ pellet at 40/60-volume ratio (G) and for a literature $LaNi_5$ powder samples (×) are also reported

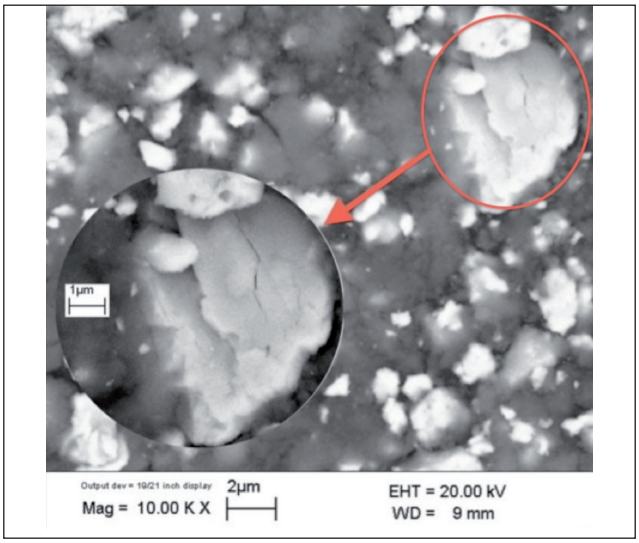

FIGURE 4 SEM image of porous composite sample after absorption/desorption cycling test. The picture evidences the metal particles fragmentation due to the large volume mismatch associated with hydrogen loading/unloading processes

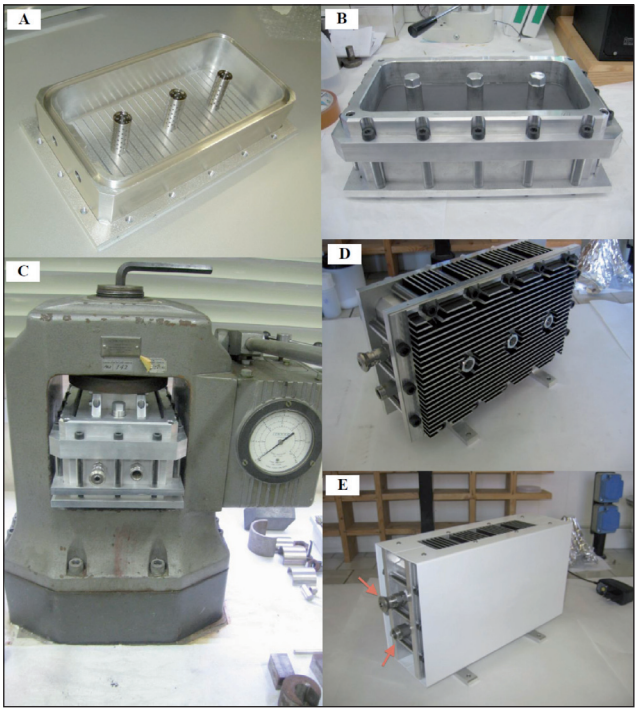

FIGURE 5 A) The alloy aluminium case, a view of the internal design; B) the moulding case filled with the composite powder; C) the material consolidation step by pressing within the moulding system; D) the assembled tank, a view of the external heat exchange system design; E) the final tank configuration with the external carter, the arrows indicate the H_2 inlet quick coupling connector (top) and the security valve (bottom), respectively

ristics of the device, which was tested as tank for the metal hydride-based composite developed by ENEA. All the components were aluminium-made by using the alloy Al 6061-T6, with excellent characteristics such as high strength, good workability, and high resistance to corrosion. Unconventional parallelepiped geometry was chosen and a particular internal design was optimized to favour the hydrogen diffusion within the fixed bed, see Figure 5A. The three inner cylindrical elements possess double functionality both structural and for gas diffusion within the material bed. A separate twin case was properly designed with inner flat surfaces and used to mould the powder in the form of parallelepiped bed, see Figure 5B. The moulding case was filled with the composite powder material and closed by an end plate. The material was consolidated by pressing the system at 30 bar and by successive heat treatment under vacuum condition, see Figure 5C. After the consolidation phase, the composite material brick was carefully transferred within the case of Figure 5A, and the final tank assembled with a proper top plate (having the same design and structural characteristics of the bottom face). The external carter was equipped with a number of fins and two additional fan coolers for the thermal exchange by forced ventilation. On the short side a quick coupling connector for the H_2 inlet (figure 5D), and a security safe valve (set @31 bar) were mounted. The final system of Figure 5D

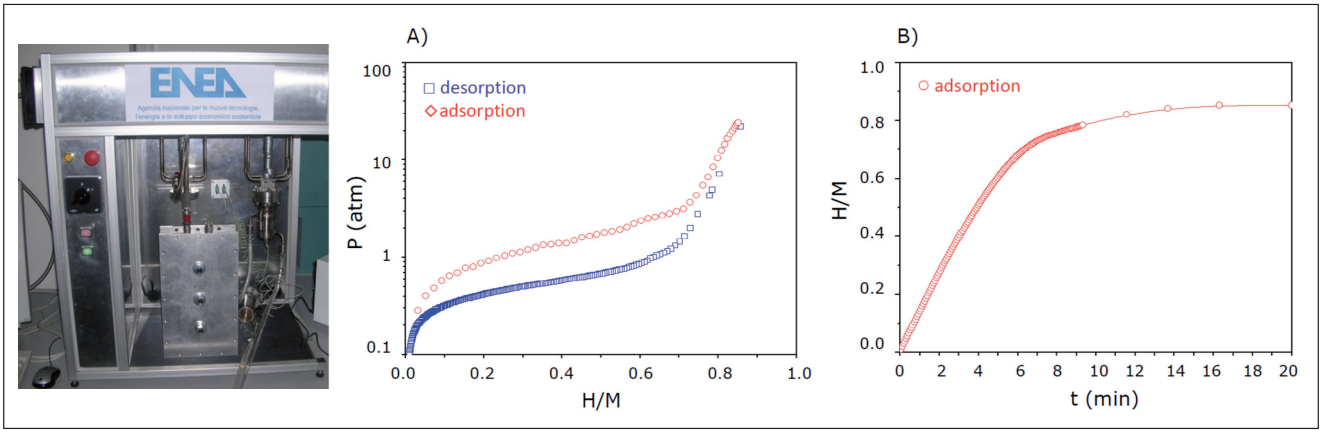

FIGURE 6 Left: $PCTH_2$ homemade Sievert's apparatus, the experimental set-up. Right: tank characterization by Sievert's apparatus: A) absorption/desorption hydrogen cycle; B) hydrogen absorption kinetic

had nominal volume of 1730 cm^3, external dimension of 180x330x110 mm and weight 4.4 kg, excluding the fixed bed.

The hydrogen storage tank assembled with the consolidated material was characterized by using the homemade PCTH2 Sievert's apparatus shown in Figure 6.

Preliminary calibration measurements were performed at 27 °C to measure the volumes of the empty tank, the flexible pipe and the connector, that resulted to be 1734 cm^3, 20 cm^3 and 12 cm^3, respectively. Following the degas and activation processes, the tank was characterized by performing around 10 hydrogen absorption/desorption cycles at $p(H_2)$=10 bar, T=27 °C. The cycles were reproducible within the experimental error with any significant variation of the maximum hydrogen storage capacity. An exemplificative curve is reported in Figure 6A. The fixed bed has a maximum hydrogen storage capacity of 0.82 at 10 bar, corresponding to 1.16% weight (considering the active metal phase within the composite). This value can be traduced in 23.4 grams of hydrogen. An evaluation of the hydrogen absorption kinetics of the tank was also obtained as reported in Figure 6B. By operating at 30 bar the tank approaches the 95% of its maximum storage capacity (measured at 10 bar) in about 9 minutes.

Conclusions

In this paper we presented the development of an innovative experimental device for solid-state hydrogen storage. The composite material design, processing and functional characterization derive from the latest years activities performed in the Materials Chemistry and Technology lab of ENEA.

The positive synergy with Labor srl brought us to ideating, designing and realizing the storage system in the described form. Applicative activities based on the above-presented technologies are being carried on towards new developments and project proposals as well.

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