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The optimization of $MmNi_{5-x}Al_x$ hydrogen storage alloy for sea or lagoon navigation and transportation

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ABSTRACT

Among hydrogen storage materials, the $MmNi_5$ (Mm = mischmetal, a mixture of rare earth elements) family of alloys has good properties for transportation technologies due to their ability to react reversibly with hydrogen at moderate pressures and temperatures. It is also known that different composition of Mm or partial substitution of Ni by other elements modifies the hydride stability and induces a wide range of plateau pressures, giving them an excellent versatility.

This work investigates a set of $MmNi_{5-x}Al_x$ materials exploring different kinds of Mm and Al content (x = 0.15,0.20,0.25), in order to determine which composition best satisfies specific working conditions for possible employment in transportation by sea or lagoon where the water of the lagoon is used as a coolant. In the specific case of a public transportation ship (the classical "vaporetto") on the Venice Lagoon, hard restrictions are required for these conditions since hydrogen sorption pressures are a key factor when considering the lagoon average temperature variations between winter and summer seasons.

Experimental results of the present study led to a map of Vant'Hoff that let select the best material according to the required conditions.

Introduction

Development of technologies for transportation based on the use of hydrogen requires improved methods for gas storage. Storing hydrogen at the solid state with suitable materials could be the best compromise among the other methods for small volume systems. In this case materials with high hydrogen gravimetric and volumetric capacity are required, but also materials with suitable properties for the specific application.

AB_5 alloys demonstrated to be suitable materials for hydrogen storage applications. In fact these materials showed peculiar properties as they could be easily activated and they have quite good tolerance to the impurities of hydrogen used for absorption [1].

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For the soft sorption conditions required for the hydriding and dehydriding reaction, $LaNi_5$ is a noteworthy absorber of hydrogen reacting reversibly with hydrogen at moderate pressure and temperature [2,3]. Due to these features, the intermetallic compound $LaNi_5$ and its derivatives are one of the most widely studied materials for the hydrogen storage at solid state [4].

It is also known that the partial substitution of La or Ni modifies the stability and induces a large change in both the stability and the capacity of the related hydrides, conferring them an excellent versatility. For instance, the La site (A-site) partial substitution, i.e. by Ce, destabilises the hydride, shifting the equilibrium plateau to higher pressure. Even Pr, Nd and Sm demonstrated to sort similar effects of Ce on hydride destabilization. In order to maintain the plateau pressure to suitable levels, the content of La should not be low. Moreover an improvement in terms of corrosion resistance could be obtained by the presence of Nd or Ce [5–8]. The partial replacing of Ni (B-site) with Al, Fe, Mn, Cr, Sn decreases the plateau pressure of hydride. The presence of these elements modifies the structure of $LaNi_5$ destabilizing the hydride [8–12].

For a commercial use, Mischmetal (Mm), in substitution of lanthanum, is a suitable solution in order to reduce the cost of the alloy and to confer a longer cycle lifetime to the material. The composition of Mm, which always depends on the batch, influences the equilibrium pressure of hydrogen in the $MmNi_5$-based hydride [13]. Therefore alloys prepared using Mm from different batches can show different equilibrium pressure of hydrogen [14].

This work investigates materials of the type $MmNi_{5-x}Al_x$ with different rare earths and Al concentrations.

The aim is to select the hydride powder whose characteristics best fit with its employment in sea or lagoon transportation.

In particular, parameters were selected for navigation in the Venice Lagoon. A prototype of hydrogen boat, designed by Venezia Tecnologie S.p.A., has been already tested with compressed hydrogen gas storage system in order to feed a fuel cell. The boat navigated, under a special regulation, on the “Canal Grande”. The boat has a displacing hull and has been equipped with two PEM fuel cells (5 kW each), two buffer battery packs (48 V each), two electric motors (20 kW each) and a system for monitoring, acquiring and recording of the most important parameters (hydrogen consumption, tension, current, torque at the propeller). This boat has the right characteristics to test a hydride storage system.

In this work it has been taken into consideration the possibility of installing, instead of compressed gas storage, a tank on the boat with metal hydrides for hydrogen supply.

Considering the possibility to install such a system on it, environmental condition and hydride's specifics, have to be taken into account. The hydride has to absorb and desorb hydrogen in the range of temperature 0–30 °C because the water average temperature in the lagoon in winter is about 5 °C and 25 °C during summer season.

The pressure values have to allow an efficient hydrogen supply to the fuel cell PEM (>3.0 bar) and the storage system has to be recharged in safety conditions (<30 bar).

Experimental

Alloys preparation

Two kinds of Mischmetal (named in the following tests as Mm(I) and Mm(II)) purchased by Treibacher Industrie AG were used for the alloys preparation. They differ in the elemental composition as reported in Table 1.

The $MmNi_{x-5}Al_x$ samples were produced in arc furnace consisting in a water-cooled copper crucible with a non-consumable tungsten electrode, under 99.999% purity argon atmosphere. The alloys were melted starting from Mm (I or II), with the addition of Ni and Al in order to obtain the following compounds: $Mm(I)Ni_{4.85}Al_{0.15}$; $Mm(II)Ni_{4.85}Al_{0.15}$; $Mm(II)Ni_{4.80}Al_{0.20}$ and $Mm(II)Ni_{4.75}Al_{0.25}$.

The single components of the alloy (Mm, Ni and Al) were cut in ingots, whose weights were calculated in order to obtain the required stoichiometric amount. Slight excess in weight has been considered for Mm because of its native oxide. Fusion was carried out in Ar atmosphere at about 500 mbar. The alloy buttons were remelted at 940 °C for 24 h to ensure homogeneity in the microstructure.

Characterization

The microstructure and morphology were analyzed by X-Ray Diffraction (XRD) and Scanning Electron Microscope.

XRD spectra were recorded using Philips powder diffractometer with CuK_α radiation with Bragg-Brentano geometry equipped with a graphite monochromator positioned in the diffracted beam.

ZEISS EVO MA15 (LaB_6 source), operating at 20 kV, was equipped with EDS INCA microanalysis and backscattered electron (BSE) detectors.

Hydrogen sorption cycles and pressure–composition isotherm (PCI) curves were performed in Sievert's volumetric apparatus (Hydrogen Sorption Analyzer by Cantil srl). The sample has been inserted in the sample chamber which is connected to a vacuum and a gas supply line. Before measurements, the chamber is evacuated. Successively the temperature is controlled and set to the desired value. Then pressure in the chamber is increased, in the case of absorption, or reduced in the case of desorption at the desired values. The pressure is monitored during the hydrogen sorption measurement in order to ascertain the entity of gas absorbed or desorbed by the material and the measurement is repeated for 180 cycles. Pressure-Composition-Isotherms have been obtained by setting a temperature value and increasing or reducing slowly hydrogen pressure. During absorption the pressure raises rapidly till plateau pressure. The sample starts

Table 1 – Composition of Mm(I) and Mm(II).

Element	Mm(I) [wt %]	Mm(II) [wt %]
La	22	33
Ce	50	49
Pr	6	4
Nd	18	13
Other	4	1