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Influence of co-milling with palladium black on hydrogen sorption performance and poisoning tolerance of surface modified AB_5-type hydrogen storage alloy

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ABSTRACT

This work is focused on the effect of Pd introduction into AB_5-type hydrogen storage alloy through ball milling, in combination with conventional electroless plating technique, on hydrogen sorption performance and poisoning tolerance of the material. The AB_5 substrate alloy was milled with small (0–5 wt%) amounts of Pd black. The effect of co-milling of the AB_5 substrate with Pd on structure/phase composition, morphology, and hydrogen storage performance of the material was investigated.

It was shown that co-milling of the AB_5-type alloy powder with $\leq$1 wt% of Pd black does not result in the improvement of the material activation performance and poisoning tolerance while increasing Pd additive content produced insignificant improvements. At the same time, ball milled samples, further subjected to a standard procedure of electroless autocatalytic deposition of Pd, exhibited similar (co-milling with <1 wt% Pd) or better (co-milling with $\geq$1 wt% Pd) hydrogen uptake kinetic performances at lower Pd surface loading as compared to the non-milled AB_5 alloy powder plated with Pd at similar conditions. The observed features were credited to the higher specific surface area of the ball milled material where Pd species introduced in the course of the ball milling played a role as nucleation centres during subsequent deposition of Pd. Conversely, the Pd-plated material obtained by co-milling of AB_5 with >2 wt% of Pd black exhibited lower maximum hydrogen sorption capacities, as compared to the non-milled surface modified reference material. The most probable reason for that is in the distortion and disproportionation of the parent structure of the AB_5 substrate during its co-milling with Pd black.

1. Introduction

The rare-earth-based AB_5-type alloys are characterised by reversible and fast hydrogen absorption and desorption at near-ambient temperatures, easy activation, as well as wide tuneability of pressure – temperature conditions of hydrogenation/dehydrogenation [1–3]. They have been widely used in a number of applications including hydrogen separation and purification [4–9]. However, deterioration of hydrogen sorption performance resulting from exposure to impurities in the feeding gas hinders the use of the AB_5-type alloys in this application.

Typical methods of the improvement of poisoning tolerance of metal hydride (MH) materials are related to their surface modification which (i) provides the increase of catalytic activity of the surface towards H_2 dissociation/recombination and/or (ii) protects catalytically-active centres on the surface from the passivation by impurity species (see Ref. [5] and references therein). The most effective way of formation of new catalytically-active centres on the MH surface is related to the introduction of Platinum Group Metals (PGM, first of all, Pd), preferably, using "wet" chemical plating technique [5,7,10–12].

Mechanical milling was shown to be another efficient method of the PGM introduction into MH substrate materials including AB_5-type alloys [13–15]. Shan et al. [16] reported that in order to improve the absorption properties of the alloy using Pd, it must be in intimate contact with the surface of the alloy - which can be achieved through ball milling. Previous studies have shown that nanostructuring of the material by ball milling offers some other benefits including ability to significantly alter composition, structure and morphology of the MH substrate resulting in the

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improvement of the hydrogen sorption performance [17–20]. Ball milling is the most widely used nano-structuring technique for the tailoring of hydrogen sorption properties of materials, because of its simplicity, relatively inexpensive equipment and applicability to most intermetallic compounds.

This work is focused on the effect of introducing Pd into AB_5-type alloy by ball milling, in combination with conventional electroless plating technique, on hydrogen sorption performance and poisoning tolerance of the MH material. The substrate alloy with the composition of [La,Ce,Pr,Nd][Ni,Co,Al,Mn]$_5$ was milled with small amounts of Pd black. The effect of amount of Pd addition to AB_5 material on structure/phase composition, morphology, and hydrogen storage performance of the ball milled material was investigated in detail. Furthermore, the autocatalytic palladium deposition similar to the one described previously [21,22], was applied to the milled AB_5/Pd composite materials.

2. Materials and methods

2.1. Sample material

The multi-component (Misch-metal) AB_5 -type (A = La, Ce, Nd, Pr; B = Ni, Co, Al, Mn) hydride-forming alloy produced by Guangzhou Research Institute of Non-Ferrous Metals, China (trade mark DH4) was used in this work. The as-delivered alloy was pulverized, by ball-milling in a sodium hypophosphite solution and sieved to 200 mesh (74 μm). The material was further allowed constant exposure to air throughout the experimental studies.

2.2. Modification by ball-milling followed by autocatalytic palladium deposition

Palladium black was prepared from 250 ml of acidic solution (2 g/L $PdCl_2$ and 4 mL/L HCl) in a beaker and drop-wise addition of N_2H_4 as reducing agent until the black particles were formed for a period of 30 min with vigorously stirring of the solution at 60 °C. The mixture was stirred for further 30 min and then Pd black precipitates were filtered, washed with ultra-pure water and dried for 3 h at 80 °C. The nanostructured AB_5/Pd composites were prepared by mixing alloy powder with 0.1–5 wt% Pd black followed by mechanical ball milling of the mixture [23,24]. The milling was carried out using a FRITSCH Pulverisette planetary mill, using a hardened steel vial and balls, at a speed of 500 rpm for 60 min milling time, with a ball-to-powder ratio of 40:1, under argon gas.

The autocatalytic Pd deposition on the ball milled materials was carried out using NaH_2PO_2 as a reducing agent; 100 g AB_5 per 1 L of Pd-containing plating solution ("normal" load), plating time 30 min. Further details are presented in Ref. [5].

2.3. Characterisations

Studies of the hydrogenation absorption performance were conducted using in-house built volumetric Sieverts'-type installations at the University of the Western Cape (UWC) [5]. The materials were further characterised using scanning electron microscopes (SEM) at UWC and University of Cape Town, South Africa. High-resolution SEM studies were carried out at Norwegian University of Science and Technology (NTNU, Trondheim). Energy-dispersive spectroscopy (EDS, Edax Genesis, 100 live seconds) was used for the determination of the Pd surface loading as a function of the preparation history of the sample materials as well as their elemental composition. X-ray diffraction (XRD) studies of the unmodified and surface-modified AB_5-type intermetallides were performed using facilities at iThemba Labs, South Africa. Surface area analysis was carried out using Brunauer-Emmett-Teller (BET) technique.

Measurements of the hydrogen absorption performance of the studied samples using Sievert-type volumetric installation were undertaken after their exposure to air (≥24 h at the room temperature), without activation by vacuum heating.

Kinetics of hydrogen absorption by the samples from pure H_2 and gas mixtures in a running flow mode, was studied using procedure similar to the one reported earlier [5,7,25]. Hydrogen absorption rates, *r*, in the running-flow mode were estimated using simplified thermal calculations. After each absorption (20–30 min long), the sample was dehydrogenated by the heating of the reactor (20–200 °C, ramp rate 5 °C/min) connected to a pre-evacuated closed volume of volumetric Sievert setup that allowed to determine the amount of hydrogen absorbed in the sample.

Further details of the characterisation are provided in the Supporting Information; Section S1.

3. Results and discussion

Fig. 1 shows kinetics of hydrogen uptake by the non-activated samples (#1–10). The summary of the preparation conditions and properties of the materials (Pd loading, specific surface area, kinetic parameters of hydrogen absorption) is presented in Table 1. Fig. 1 and Table 1 also contain the reference data on the sample prepared by the surface modification of the as-delivered alloy powder after autocatalytic Pd deposition at the same plating conditions [5,22].

It can be seen from Fig. 1 that the samples ball milled with 0–1 wt % of Pd black (curves 2–4) did not show improvements as compared to the as-delivered parent material (curve 1): less than 0.02 wt% of hydrogen was absorbed during 24 h. This was due to severe surface oxidation of both initial and ball milled alloy powders, where the oxide layer on the surface of the AB_5 alloy behaves as a barrier which inhibited hydrogen dissociation and penetration of H atoms into the bulk material.

The increase of the content of Pd black (curves 5 and 6 for 2 and 5 wt% Pd, respectively) resulted in modest improvements of hydrogen sorption performance, but the hydrogenation remained very slow. This observation confirmed that the co-milling of the AB_5

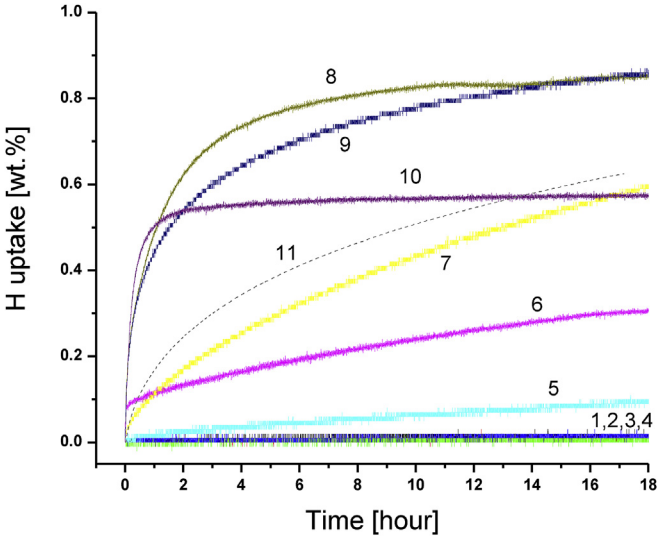

Fig. 1. Dynamics of hydrogen absorption (T = 20 °C, P_{H2} = 5 bar) by ball milled AB_5/Pd composites with and without autocatalytic Pd deposition after pre-exposure to air and no preliminary activation (vacuum heating). Curve numbers correspond to the number of sample (Table 1). Curve (11) corresponds to the non-milled AB_5 powder (200 mesh/74 μm) coated by Pd at the same conditions [5] as for the samples 7–10.