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The improvement of the hydrogenation properties of nickel-metal hydride battery alloy by surface modification with platinum group metals (PGMs)

D.B. Willey[a,b], I.R. Harris[a,*], A.S. Pratt[b]

[a]*School of Metallurgy and Materials, The University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK*
[b]*Johnson Matthey Technology Centre, Blounts Court, Blounts Courts Road, Sonning Common, Reading, RG4 9NH, UK*

Abstract

Because of their higher power densities, low memory effects and more environmentally friendly constituents, Nickel Metal Hydride (NiMH) batteries have become a strong competitor to NiCad batteries. The use of multicomponent alloys has been found to improve cell lifetimes, while further improvements to the cell performance are obtained by surface coating or 'microencapsulation' techniques with various metals or metal oxides. In the present work, a technique of coating hydride powders with one or more Platinum Group Metals (PGMs) has been developed, which enables the alloy to be charged/discharged rapidly with hydrogen with the additional advantage of being extremely resistant to deactivation. The hydrogenation kinetics of the uncoated and PGM doped alloys were assessed by gravimetric analysis, with periodic exposure to the atmosphere in an attempt to deactivate the powders. It was observed that, in the solid–gas studies, the Ru and Pd/Ru coated alloys were readily charged/discharged with hydrogen, even after long periods in air. Thus, the use of PGMs in this application represents a valuable advance both in the technology of NiMH batteries and of hydrogen storage. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Electrodes; Platinum group metals; Kinetics

1. Introduction

Multicomponent AB_5-type metallic hydride electrodes, particularly those based on $LaNi_5$, have been investigated extensively for over 15 years. These alloys are currently used in NiMH rechargeable batteries and this technology is now a major competitor to NiCad batteries.

Substituting both the lanthanum and nickel components with elements such as neodymium, cobalt, aluminium, manganese and titanium has been found to improve the cycle life of the cells [1–3]. However, $LaNi_5$ based alloys cast from the pure constituent elements were too expensive for commercial exploitation. Therefore, the rare earth mixture known as mischmetal was found to be an adequate alternative to refined lanthanum [4,5] and substitution with the above elements produced alloy powders with suitable hydrogen capacity and long cycle life.

Further improvements in the performance of the hydride electrodes was obtained with the development of the 'microencapsulation' technique. This involved the electrochemical coating of the hydride electrodes with up to 10 wt.% copper or nickel. This technique protected the electrode from oxygen produced at the nickel electrode during charge and discharge in addition to improving the current collection and protecting the alloys from degradation due to the electrolyte [6,7]. Other surface improvements were obtained by coating with various metals [8], metal oxide [9] or by fluorine treating the surface [10,11].

All of these techniques improved either the discharge capacities or cycle life to varying degrees, yet each technique has its disadvantages. For example, the microencapsulation technique requires a high concentration of metal that does not take part in the storage of hydrogen, thus increasing the unit weight of the electrodes, while full coatings of other metals and metal oxides add to the cost of the electrode price. There are also various safety issues associated with the use of fluorine.

The catalytic properties of PGMs in many aspects of physical sciences and engineering have long been appreciated. Palladium is a binary hydrogen storage material which meets nearly all of the ideal storage criteria [12], in addition to catalysing hydrogen dissociation in many reactions including the formation of intermetallic hydrides. Palladium electrodes were suggested 30 years ago [13], yet

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*Corresponding author.

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due to their cost did not become a commercial success. Recently, palladium has been used to modify the electrode surfaces [14] and it has been found to enhance discharge capacity. Another PGM used in metal hydride electrode technology has been ruthenium in the form of ruthenium (IV) oxide which was found to be beneficial to the discharge efficiency. Both palladium and ruthenium (IV) oxide were thought to improve either the hydrogen dissociation at the surface of the alloy, or the cleavage of water into the hydrogen and hydroxide components in the electrochemical cell.

In this paper the hydrogenation kinetics and deactivation resistance of an AB_5-type storage alloy surface modified with a discontinuous coating of PGMs [15] has been investigated. Three coatings have been examined, namely palladium, ruthenium and a combination coating of the two PGMs. The solid–gas hydrogenation characteristics were measured by gravimetric analysis.

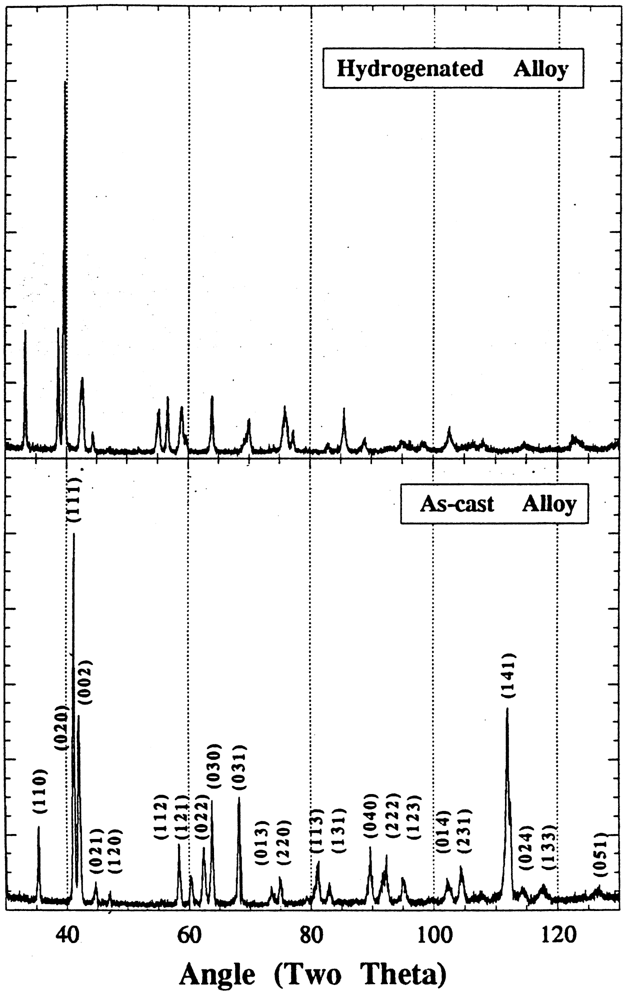


Fig. 1. X-ray diffraction traces of: (a) as-cast alloy; (b) hydrogenated alloy.

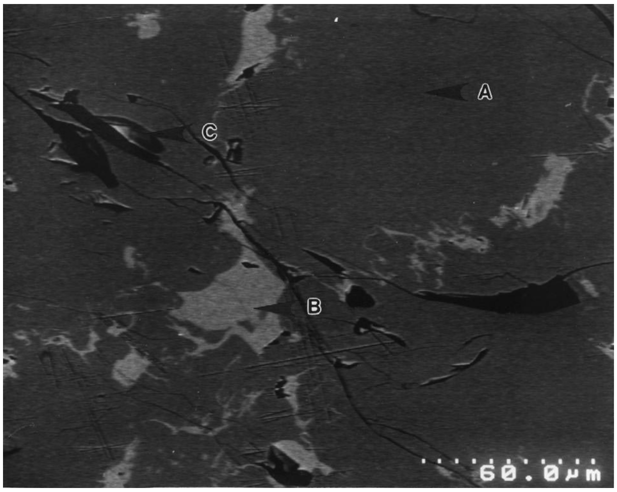


Fig. 2. Back scattered electron micrograph of as-cast MmAlCoMnNi alloy: (A) AB_5-type material; (B) A_2B_7-type material; (C) porosity.

2. Experimental

The cast AB_5-type electrode alloy was supplied by Johnson Matthey Rare Earth Products and after analysis was found to have the composition $La_{0.9}Nd_{0.05}Pr_{0.05}Al_{0.3}Mn_{0.4}Co_{0.65}Ni_{3.5}$. A Philips Xpert X-ray diffractometer was used to confirm the crystal structure. The alloy was examined on a JEOL 6300 SEM to identify the various phases present.

Prior to coating with the PGM, the alloy was exposed to five hydrogen decrepitation cycles to pulverise and activate the alloy. The particle size of the powders produced due to the decrepitation process were measured on a Coulter LS130. The morphology and sizes of the particles before and after coating were examined on a Hitachi S4000 FEG high resolution SEM (HRSEM).

To coat the alloys with PGMs, aqueous solutions containing the palladium and ruthenium complexes were

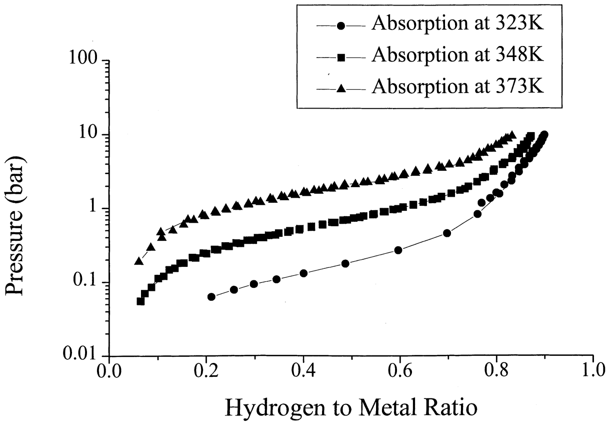


Fig. 3. PC isotherms of as-cast MmAlCoMnNi alloy.

prepared in an oxygen free environment. The hydride powders were added to the solutions while stirring vigorously and the PGMs were deposited onto the powders from the solution by the addition of strong reducing agents. For the palladium deposition the preparation was based on an electroless plating technique which induced an exchange plating type of reaction. The ruthenium deposition was a controlled reduction of the complexed metal from solutions to the hydride surface. For the combination coating, the PGMs were deposited sequentially, with ruthenium being deposited after the palladium. The surface properties of the coated powders were then examined by an XSAM 800 X-ray Photon Spectrometer (XPS).

The hydrogen absorption/desorption properties of the modified alloys were then measured by gravimetric analysis, using an Intelligent Gravimetric Analyser (IGA)

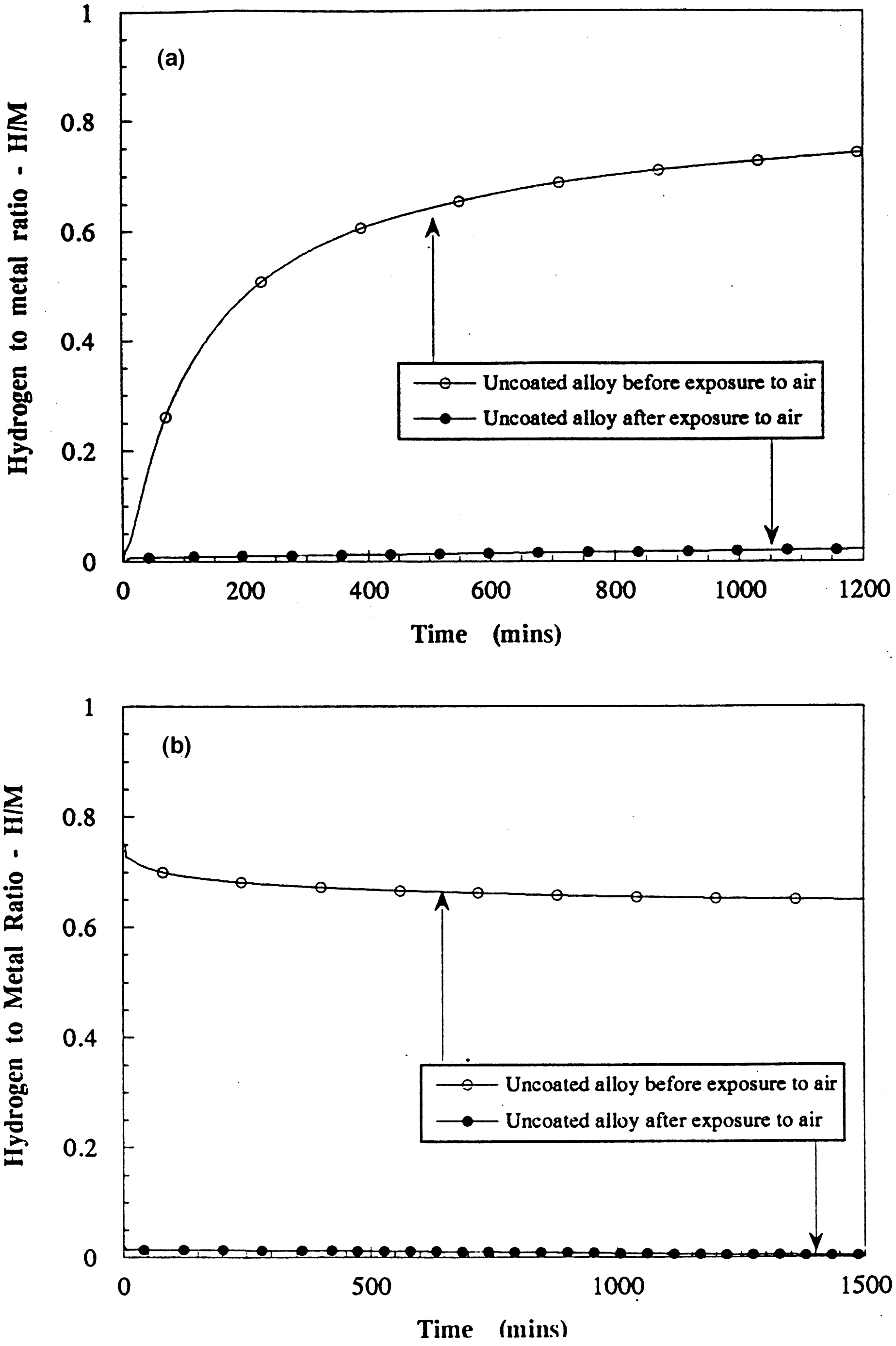


Fig. 4. (a) Absorption kinetics of as-cast MnAlCoMnNi alloy. Room temperature, 1 bar hydrogen. Comparison of kinetics before and after exposure to air for 150 min. (b) Desorption kinetics of as-cast MmAlCoMnNi alloy. Room temperature, 0.2 bar min^{-1} pump rate. Comparison of kinetics before and after exposure to air for 150 min.

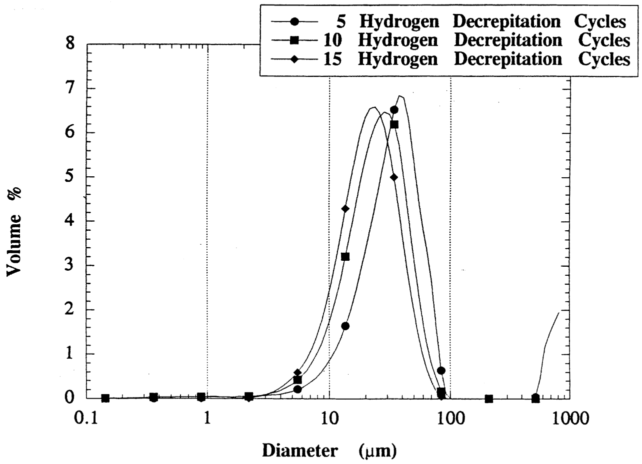
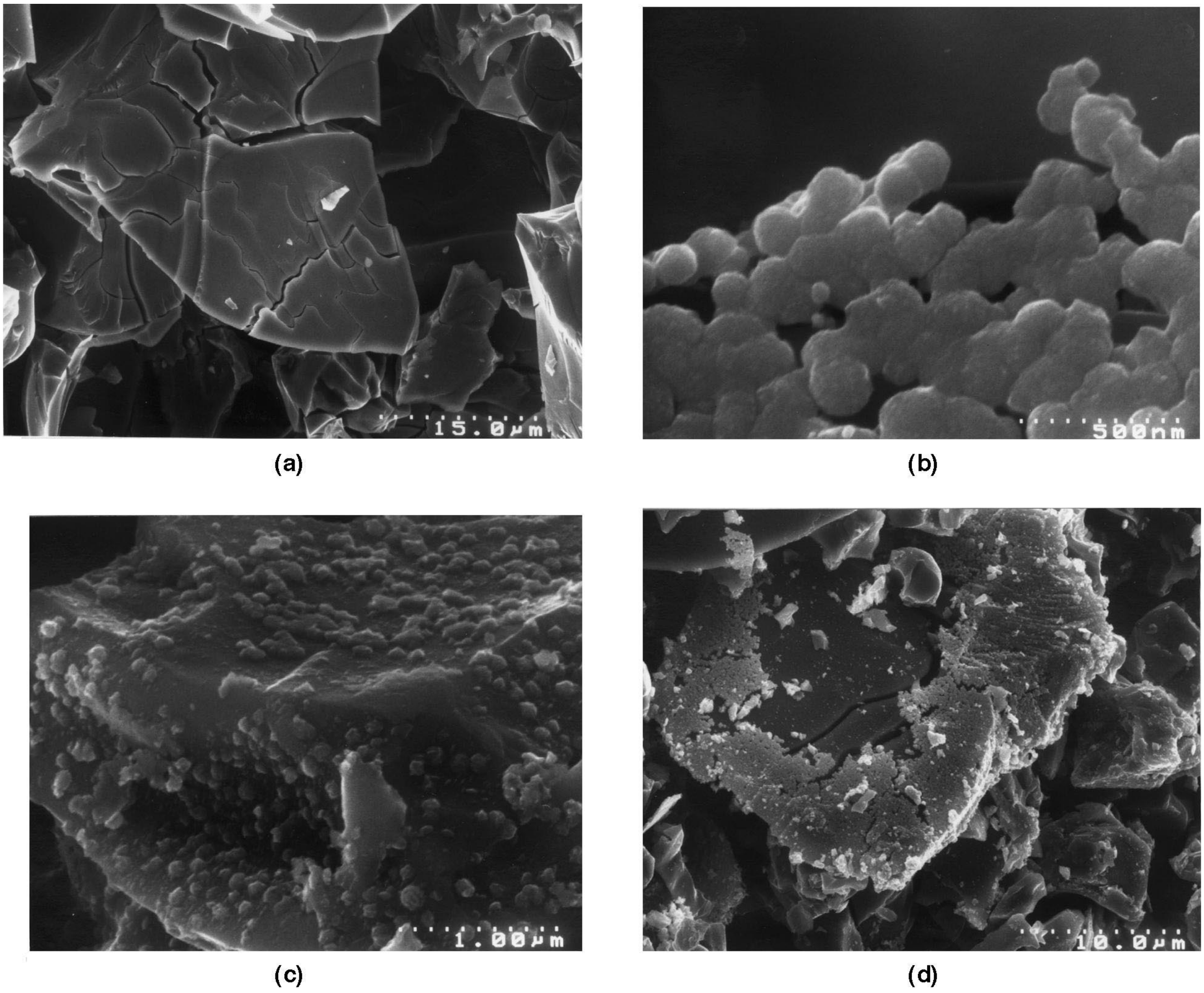


Fig. 5. Particle size distribution of the MmAlCoMnNi alloy over 15 hydrogen decrepitation cycles.

system, produced by Hiden Analytical Ltd. The alloy was assessed within a temperature range of 50–100°C for the PC isotherms and under constant pressure conditions of 1 bar hydrogen at room temperature for the other studies.

3. Results

The X-ray diffraction studies show the primary phase in the cast alloy to be the AB_5 (hexagonal) Haucke phase (Fig. 1) with lattice parameters $a=5.053$ Å (±0.004 Å), and $c=4.037$ Å (±0.004 Å). The alloy was also hydrogenated and then stabilised at room temperature with CO_2. The lattice parameter of the hydrogenated alloy was found to be $a=5.40$ Å (±0.02 Å) and $c=4.13$ Å (±0.03 Å) (Fig. 1) corresponding to a volume expansion due to hydrogenation of 17%.



(a) (b)

(c) (d)

Fig. 6. (a) Untreated alloy powder after five hydrogen decrepitation cycles. (b) Palladium coated powders. (c) Ruthenium coated powders. (d) Combination coated powders.

Fig. 2 shows a back scattered electron image of the as-cast alloy. The alloy has a two phase microstructure with some porosity. The majority phase corresponds to the AB_5-type, while the second phase is the rare earth-rich A_2B_7 compound and is less than 10 wt.% of the total.

The hydrogenation properties of the cast alloy were assessed by measuring the PC isotherms in addition to a room temperature hydrogenation under 1 bar hydrogen. At 50°C, the cast alloy absorbs >0.8H/M (Fig. 3).

Fig. 4a and b displays the absorption and desorption kinetics of the base alloy powder at room temperature. The slow absorption time could be attributed to the gradual poisoning of the powder in the low vacuum atmosphere (2×10^{-5} bar). After exposing the alloy to air for 150 min at room temperature, the absorption process is virtually halted. The desorption times are also very slow, indicating that the base alloy is severely affected by exposure to air.

Fig. 5 shows the particle size data of the as-cast alloy after 5, 10 and 15 hydrogen decrepitation cycles. By the 5th hydrogen cycle, there is a mean particle diameter of ~40 μm which does not change dramatically on further cycles. As a standard treatment, the alloy was exposed to five hydrogen cycles prior to the coating procedure.

Fig. 6a–d show electron micrographs of the untreated,

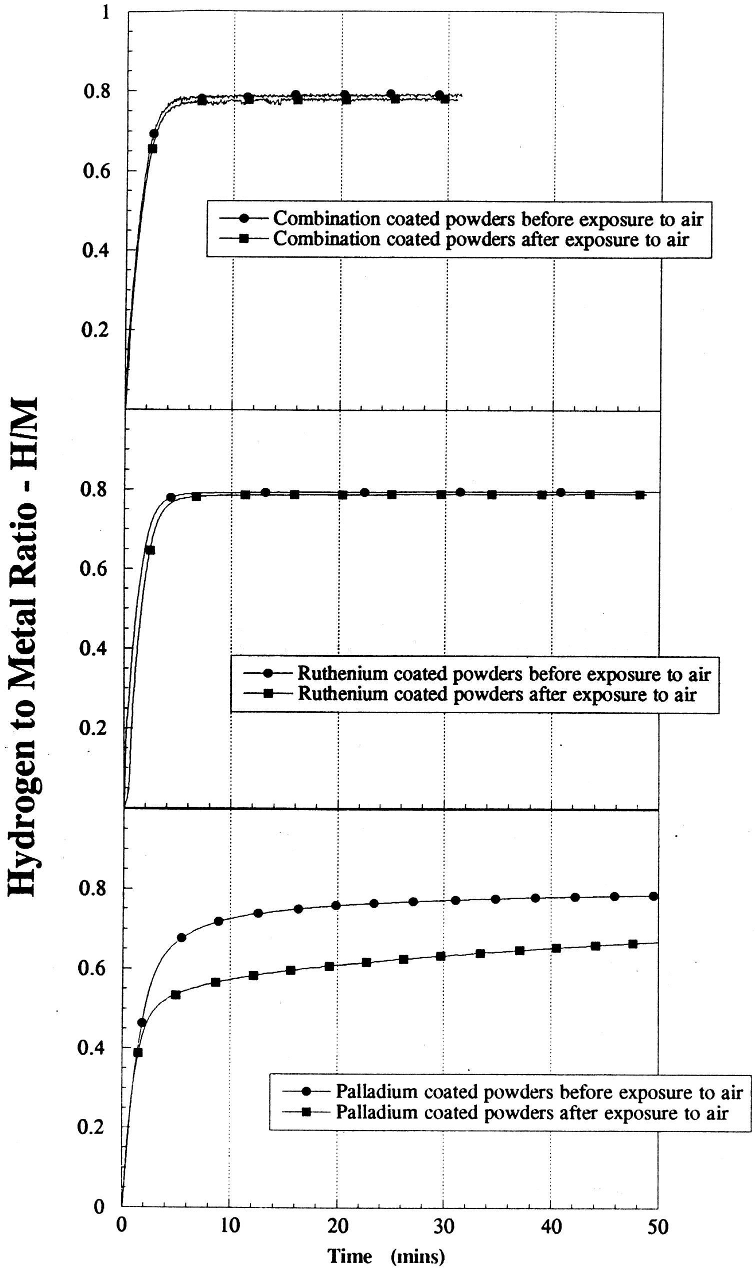


Fig. 7. (a) Absorption dated of PGM coated MnAlCoMnNi alloy, before and after exposing to air for 150 min. (b) Desorption data of PGM coated MnAlCoMnNi alloy, before and after exposing to air for 150 min.

palladium, ruthenium and Pd/Ru combination coated powders. After five hydrogen cycles the powder of the base alloy (Fig. 6a) has clean facetted surfaces, (showing the brittle nature of the hydrogen decrepitation process) and an average particle size of approximately 40 μm (in good agreement with the data shown in Fig. 5).

The coatings on the treated powders are discontinuous, with the morphology of the palladium coating consisting of smooth plate-like particles of 150 nm diameter (Fig. 6b), while the morphology of the ruthenium coating (Fig. 6c) is more nodular in nature, having a slightly finer particle size of 100 nm. The combination coating (Fig. 6d) also shows the discontinuous nature of the deposition process and is similar in nature to that of the ruthenium coating, which is to be expected, as this coating was applied after the palladium.

XPS analysis of the surfaces of the uncoated and coated alloys was performed. High levels of oxygen were observed for all the samples and the former can be attributed to the rare earth oxides that form readily on the surfaces of intermetallic hydrides, as reported by Schlapbach [16]. The PGMs are all found to be in the metallic state, with a decreased concentration of palladium in the combination coating, in accordance with the nucleation of ruthenium on the palladium coating during subsequent deposition.

The hydrogen absorption and desorption behaviour of

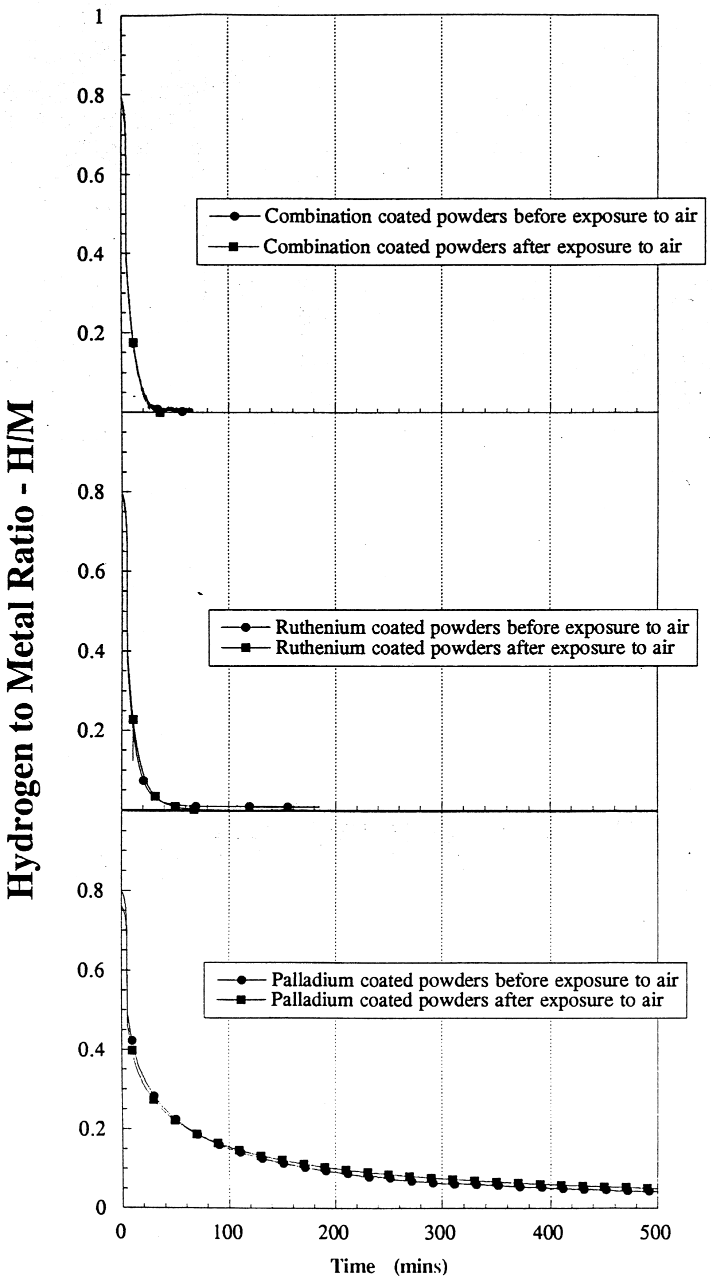


Fig. 7. (*continued*)

the coated alloys was assessed in the same way as that of the base alloy. Fig. 7a and b show the absorption and desorption reactions at room temperature, 1 bar hydrogen. It is observed that the ruthenium containing alloys absorb and desorb hydrogen faster than the alloy with the palladium single coating – and much more rapidly than the uncoated alloy under the same conditions.

In addition to the rapid sorption kinetics before exposure to air, Fig. 7a and b show the sorption kinetics after exposing to air for $2\frac{1}{2}$ h. The palladium coated alloy is adversely affected by exposure to air, while the ruthenium coated alloy exhibits the same rapid sorption times as those of the unexposed material.

The performances of the combination coated alloy, after long term exposure to air were assessed at periodic intervals and Fig. 8a and b shows the hydrogen sorption kinetics of the alloys up to a maximum time in air of 42 days. Over this period of prolonged exposure, the alloys do not undergo a significant loss, either in capacity or in absorption/desorption rate, and hence exhibit excellent stability in air.

4. Conclusion

The presence of PMGs on the surface of hydrogen storage alloys enhances both the absorption and desorption of hydrogen. The ruthenium containing coatings enable extremely rapid charging and discharging times to be obtained, as well as a high resistance in deactivation even after long exposures in air.

Separate studies [17] have also shown that these surface

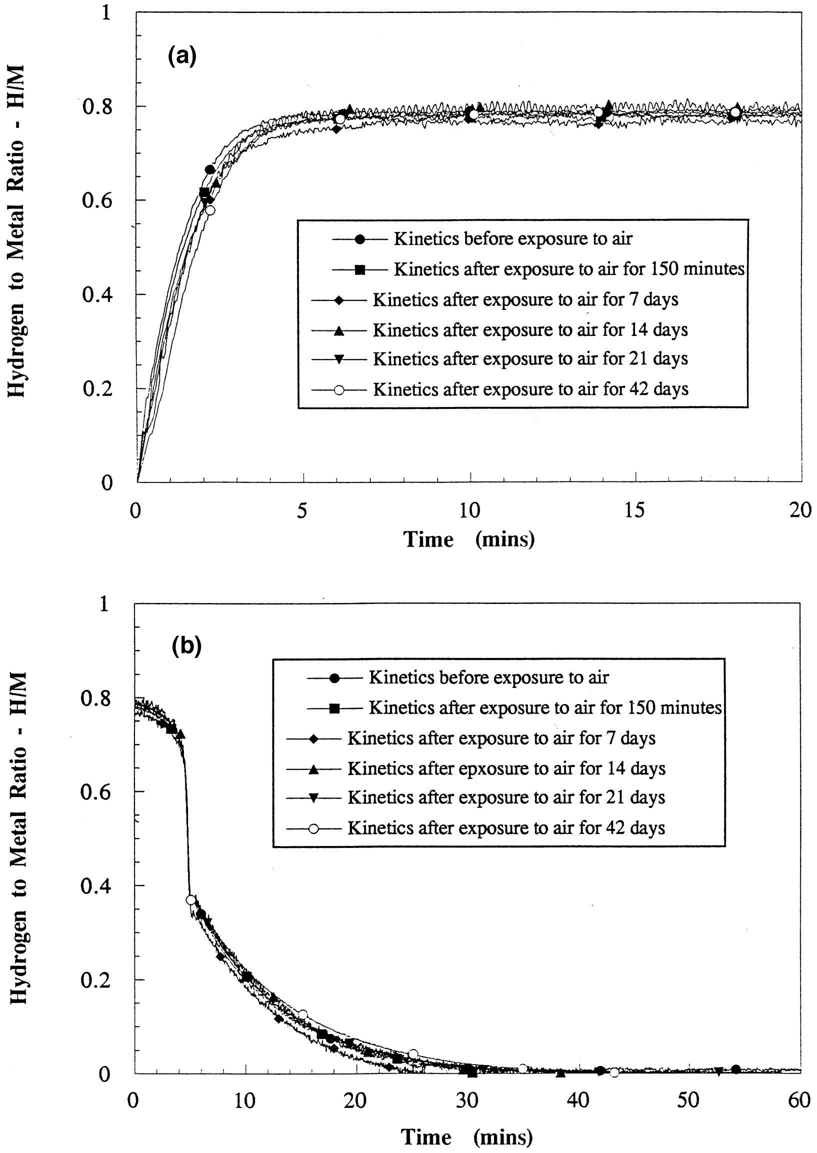


Fig. 8. (a) Absorption kinetic data of Pd and Ru coated MnAlCoMnNi alloy during long exposure (42 days) in air. (b) Desorption kinetic date of Pd and Ru coated MnAlCoMnNi alloy during long exposure (42 days) in air.

treatments also improve the electrolytic charging and discharging characteristics of the AB_5 metal hydride electrode components in NiMH rechargeable batteries. So the use of PGM surface coatings represent a valuable advance in the technology of NiMH batteries and of hydrogen storage.

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