

PALLADIUM MIXED-METAL SURFACE-MODIFIED AB_5 -TYPE INTERMETALLIDES ENHANCE HYDROGEN SORPTION KINETICS

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ABSTRACT

Surface engineering approaches were adopted in the preparation of advanced hydrogen sorption materials, based on 'low-temperature', AB_5 -type intermetallics. The approaches investigated included micro-encapsulation with palladium and mixed-metal mantles using electroless plating. The influence of micro-encapsulation on the surface morphology and kinetics of hydrogen charging were investigated. It was found that palladium-nickel (Pd-Ni) co-deposition by electroless plating significantly improved the kinetics of hydrogen charging of the AB_5 -type intermetallics at low hydrogen pressure and temperature, after long-term pre-exposure to air. The improvement in the kinetics of hydrogen charging was credited to a synergistic effect between the palladium and nickel atoms in the catalytic mantle and the formation of an 'interfacial bridge' for hydrogen diffusion by the nickel atoms in the deposited layer. The developed surface-modified materials may find application in highly selective hydrogen extraction, purification, and storage from impure hydrogen feeds.

INTRODUCTION

Breakthroughs in hydrogen separation, purification, and storage technologies require composite materials that meet the scientific and technological requirements of hydrogen processing, including excellent sorption stability, resistance to surface poisoning in impure hydrogen and fast reaction kinetics. It has been recognised that the key elements for substantial advancement in this field will be provided by new strategies in the preparation of novel composite materials wherein the surface composition and structure are specifically tailored for their desired application.

Technologically flexible 'low-temperature', rare earth metal AB_5 -type intermetallics are potentially attractive materials for the sorption of hydrogen, because they have good reversibility in hydrogen sorption, fast kinetics in hydrogen sorption under mild conditions, tunable plateau pressures, reasonable cycle lifetimes, and low hysteresis.^{1,2,3,4} The hydrogen charging/discharging capacities of the AB_5 -type intermetallics exhibit substantial sensitivity to the chemical state of the surface. In particular, exposure of the AB_5 -type intermetallics to air prior to hydrogen absorption results in selective surface oxidation of the rare earth metals. Surface oxidation yields friable, hydrogen-permeable rare earth oxides and simultaneous segregation of metallic nickel. Segregated clusters promote the processes of dissociative chemisorption and associative desorption of hydrogen (H_2) molecules, which improves the hydrogen sorption performance of the material.⁵

As hydrogen sorption from impure hydrogen feed streams is likely to involve exposure to chemically aggressive electrophilic gaseous components (e.g. hydrogen sulphide [H_2S], carbon monoxide [CO], oxygen [O_2] and water [H_2O]), the rationale for improving their hydrogen sorption kinetics and surface poisoning resistance, by surface modification of AB_5 -type intermetallics, emerges. AB_5 -type intermetallics tend to exhibit susceptibility to these gases, passivating the surface, and thus inhibiting hydrogen dissociation/recombination processes.

There are several methods to eliminate the negative effects of impurities on hydrogen sorption properties of intermetallics: creation of multi-phase materials,⁶ introduction of deoxidisers,⁷ fluorination,^{8,9} alkaline ion implantation,¹⁰ and micro-encapsulation.^{11,12,13} The last method is especially efficient when platinum group metals are used as a modifier, because it facilitates an increase in the resistance of intermetallics, even to strong gaseous poisons, such as CO .¹⁴ The surface coatings of platinum group metals enable rapid dissociation of hydrogen molecules, while still maintaining the charging activity of the intermetallic, even after extended exposure to contaminated hydrogen. In particular, palladium has the ability to catalyse hydrogen exchange reactions, promote easy activation, and increase poisoning tolerance.^{13,14,15,16} It is impermeable to larger molecules, and as a result palladium also exhibits an infinitely high selectivity towards hydrogen. Palladium micro-encapsulation also gives intermetallics the ability to absorb hydrogen at low temperature, without a special activation step, and enhanced kinetics of hydrogen charging. Palladium catalytic layers can typically be deposited using a wet chemical technique such as electroless plating, which is known for its ability to plate irregular surfaces and prepare metal layers of uniform thickness.

Palladium surface-modified AB_5 -type intermetallics are, however, still prone to low levels of surface poisoning after long periods of exposure to air; such poisoning manifests in the gradual deterioration of hydrogen sorption capacity with repeated cycling.¹³ To address this problem, it was suggested that surface modification be conducted using mixed-metal coatings instead of pure palladium coatings. Palladium alone is also not suitable for hydrogen uptake, because of its unfavourable equilibrium pressure, high cost, and susceptibility to sulphurous gases.¹⁷ There have been few known attempts to study the influence of micro-encapsulation of palladium-based mixed-metals on the hydrogen charging performances of intermetallics.^{13,15,16,18,19} It also is known that employment of mixed-metal catalysts instead of single-metal catalysts can enhance activity and/or selectivity for a given reaction.²⁰ For these

reasons, the use of palladium mixed-metal coatings to enhance the kinetics of hydrogen charging of AB₅-type intermetallics was investigated.

Mixed-metal coatings of interest include Pd-Ni and palladium-copper (Pd-Cu). Nickel surface coatings are known to improve the overall mechanical strength and corrosion resistance of intermetallics. In addition, surface coatings of nickel are known to increase the catalytic activity of AB₅-type intermetallics towards hydrogen exchange reactions.²¹ Likewise, Pd-Cu mixed-metal coatings have the potential to enhance resistance to thermal degradation.²²

This study details approaches for the preparation of new composite materials, based on AB₅-type intermetallics that are surface-modified using Pd-Ni and Pd-Cu mixed-metal coatings deposited by electroless plating, for the separation, purification and storage of hydrogen from impure feed streams. The materials were evaluated in terms of morphological, elemental and hydrogen sorption properties. Importantly, the materials should exhibit kinetics of hydrogen charging superior to that of intermetallics that are surface-modified using palladium only.

EXPERIMENTAL METHODS

A rare earth mischmetal-nickel-based AB₅-type intermetallic La_{0.40}Ce_{0.48}(Nd,Pr)_{0.16}Ni_{3.34}Co_{0.64}Al_{0.63}Mn_{0.58} produced in collaboration with the Guangzhou Research Institute for Non-Ferrous Metals, was employed as the core material for surface modification. The intermetallic was prepared from high-purity metals by a modified arc-melting technique under an inert gas atmosphere. The melt was cast into sheets using a high-pressure roller system fitted within an oven. The sheets were further annealed at 1295 °C for 2 h under an inert atmosphere. Finally, the intermetallic was pulverised, by ball-milling, in a sodium hypophosphite (NaH₂PO₂) solution and sieved to 200 mesh (74 µm). The material was allowed constant exposure to air throughout the experimental studies. The particle size distribution was determined, using field emission scanning electron microscopy (FESEM), as 10 µm – 70 µm, with all particles possessing irregular shape.

Surface modification of the AB₅-type intermetallic was conducted using electroless plating of palladium, nickel, and copper mantles either by single-layer, mixed-bath (co-deposition), or sequential deposition, in a hypophosphite-based electroless plating bath. The intermetallic was first sensitised and activated in a palladium-tin (Pd-Sn) colloidal solution.²³ The activated intermetallics were subsequently suspended in the palladium, nickel and copper plating baths. An equivalent volume of NaH₂PO₂ solution (10 g/L) was added separately. The plating time and stirring rate were fixed at 30 min and 300 rpm, respectively. The concentrations of components in the palladium-based, nickel-based and copper-based plating solutions, as well as the volume ratio of the solutions to be mixed into the plating bath, were selected to provide a 5.0 × 10⁻⁴ mol/L to 1.5 × 10⁻³ mol/L concentration of Pd²⁺, a 1.0 × 10⁻³ mol/L to 2.5 × 10⁻³ mol/L concentration of Ni²⁺ and a 1.0 × 10⁻² mol/L to 4.0 × 10⁻² mol/L concentration of Cu²⁺ in the bath. Descriptions of the formulations for the hypophosphite-based electroless plating baths are given in Table 1.^{24,25,26}

X-ray diffraction (XRD) studies of the unmodified and surface-modified AB₅-type intermetallics were performed using

a Bruker Advance powder diffractometer (Madison, USA; 40 mA, 40 keV, λ_{Cu-K} = 0.15406 nm) at the Materials Research Group, iThemba Labs, in Cape Town, South Africa. Synchrotron radiation XRD (SR-XRD) studies of the unmodified and surface-modified AB₅-type intermetallics were performed using the BM01B diffractometer (λ = 0.05 nm) coupled to the Swiss-Norwegian beamline of the third-generation synchrotron radiation accelerator (6.0 GeV) at the European Synchrotron Radiation Facility in Grenoble, France. Small quantities of the samples were introduced into quartz glass capillary tubes (0.7 mm diameter), which were then sealed to the gas distribution system using carbon ferrules. The capillary tubes were connected to a goniometer head and oscillated, under vacuum, around their axes to minimise orientation effects.²⁷ The sample materials were then irradiated using X-rays from the synchrotron storage ring. After collection, the SR-XRD data were further refined by profile analysis with General Structure Analysis System software.²⁸

All prepared materials were characterised using FESEM (Zeiss Ultra 55 Limited Edition, Gottingen, Germany; 3.0 mm; 4.0 kV) for morphological studies of palladium particle size and shape on the surface of the AB₅-type intermetallics. Estimations of the intermetallic surface composition were conducted using atomic absorption spectroscopy (AAS; Philips PU9100, Eindhoven, Germany).

The influence of micro-encapsulation of the AB₅-type intermetallic on the kinetics of hydrogen charging was studied by a comparison of hydrogen absorption under mild conditions (at a temperature of about 20 °C and a hydrogen pressure of about 500 kPa), after exposure to air for approximately 2 weeks and evacuation before hydrogen charging (10⁻⁴ kPa, 20 °C). Evacuation prevented the possibility of the presence of residual oxygen on the surface of the alloy. Hydrogen charging was conducted for 24 h. The experimental results were processed by application of formal kinetic analysis, using the Avrami-Erofeev equation²⁹:

$$(H / AB_5) = (H/AB_5)_{\max} \cdot \left\{ 1 - \exp \left[- \left(\frac{t}{t_0} \right)^n \right] \right\} \quad [\text{Eqn 1}]$$

where (H/AB₅) is the actual hydrogen concentration in the intermetallic; (H/AB₅)_{max} is the maximum hydrogen concentration in the intermetallic (equal to 5, according to results of the pressure-concentration-temperature study)³⁰; t is time; t₀ is the characteristic time of hydrogen charging (reciprocal rate constant k); and the index of power, n, can be interpreted as a value indirectly connected to the reaction mechanism.

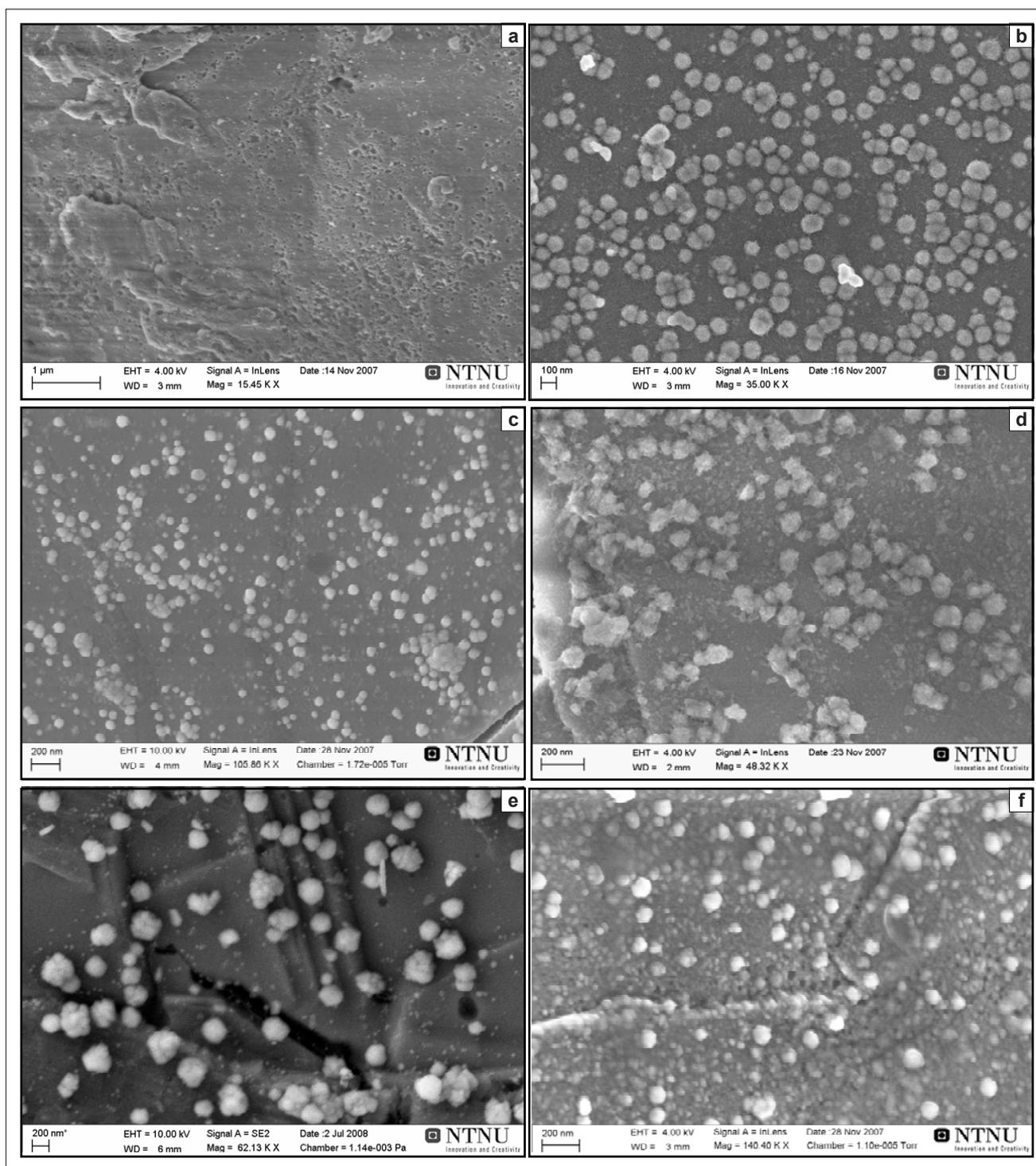
RESULTS AND DISCUSSION

The surface morphologies of the unmodified and surface-modified AB₅-type intermetallics are shown in Figure 1. The unmodified intermetallic was composed of particles which, generally, exhibited irregular shape and relatively smooth surfaces, and which were free of porous structure (Figure 1a).

The palladium coatings on the AB₅-type intermetallics were found to be discontinuous in nature (Figure 1b). The observation of discontinuous palladium coatings on the surface of AB₅-type intermetallics was shared by Willey et al.¹³, Doyle et al.¹⁶, Pratt et al.¹⁸ and Harris et al.¹⁹ The deposited palladium particles were somewhat spherical in appearance and exhibited an average particle size of 135 nm. They also exhibited a coarse, granular appearance that may be credited to their amorphous nature after impregnation of phosphorus into the palladium layer.

TABLE 1
Chemical constitution of hypophosphite-based palladium, nickel and copper electroless plating baths

Palladium-based plating solution		Nickel-based plating solution		Copper-based plating solution	
PdCl ₂	2 g/L	NiCl ₂	0.8 g/L	CuSO ₄	10 g/L
HCl	4 mL	NiSO ₄	1 g/L	NiSO ₄	2 g/L
NH ₂ OH	160 mL	Na ₂ (EDTA)	8 g/L	H ₃ BO ₃	35 g/L
NH ₄ Cl	27 g/L	Na ₂ [(OOCCH ₂) ₂ C(OH)COO]	1 g/L	Na ₂ [(OOCCH ₂) ₂ C(OH)COO]	25 g/L
pH	9	pH	9	pH	10
Plating temperature	50 °C	Plating temperature	50 °C	Plating temperature	70 °C



Working distance = 3 mm; current = 80 μ A; accelerating voltage = 4.0 kV

FIGURE 1

Field emission scanning electron micrographs of (a) unmodified AB₅-type intermetallics and those modified by (b) palladium deposition, (c) Pd-Ni sequential deposition, (d) Pd-Ni co-deposition, (e) Pd-Cu sequential deposition and (f) Pd-Cu co-deposition

Agglomeration of the palladium particles was not observed on the intermetallic surface.

Good dispersion of the particles was observed after sequential and co-deposition of Pd-Ni, similar to that observed after pure palladium deposition (Figures 1c and 1d). The Pd-Ni coatings were also found to be discontinuous in nature, while very little agglomeration of the particles was observed on the intermetallic surface. Surface particles were fairly spherical in shape after Pd-Ni sequential deposition, while Pd-Ni co-deposition resulted in particles with a very rough appearance. Average particle sizes of

92 nm and 105 nm were determined after Pd-Ni sequential and co-deposition, respectively.

Similarly, Pd-Cu sequential-deposited and co-deposited coatings were found to be discontinuous in nature and well dispersed (Figures 1e and 1f). In both cases, the surface particles were observed to have fairly rough shapes, with particles exhibiting a nodular appearance. Average particle sizes of 291 nm and 109 nm were determined for the intermetallics that were surface-modified using Pd-Cu sequential- and co-deposition, respectively. The larger particle size of the sequentially

deposited Pd-Cu layer, compared to the co-deposited layer, may be credited to the dominant surface presence of the copper particles, as confirmed by the reddish-brown appearance of the surface-modified intermetallide particles.

XRD studies of the unmodified AB₅-type intermetallide (Figure 2) have shown that the material contains a major CaCu₅-type intermetallic phase (95 net wt. %) with lattice parameters $a = 0.5003$ nm, $c = 0.4052$ nm and a minor AB₅-type intermetallic phase (4.7 net wt. %) with similar lattice parameters $a = 0.5023$ nm, $c = 0.4079$ nm. The lattice parameters corresponded well with those reported previously ($a = 0.495$ nm – 0.505 nm, $c = 0.402$ nm – 0.405 nm) for a similar intermetallide La_{0.8(1-x)}Ce_{0.8x}(PrNd)_{0.2}B₅, where B₅ is Ni_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}, $x = 0 - 1$.³¹ It was most likely that the presence of the second AB₅-type intermetallide phase was a direct result of inhomogeneity in the B-component of the parent AB₅-type intermetallide. Similarly, Willey et al.¹³ detected the presence of 10 net wt. % of a second phase, ascribed as A₂B₇. Trace quantities (0.7 net wt. %) of a mixed rare-earth-nickel oxide (RE₂NiO₃) perovskite-type oxide phase, having K₂NiF₄-type structure,³² $a = 0.38572$ nm; $c = 1.2660$ nm, were detected and most probably originated from the surface oxidation of the material. This phase is present in unmodified sample only and disappears after surface treatment of the alloy.

The SR-XRD diffractogram of the AB₅-type intermetallide, surface-modified by palladium coatings derived from NaH₂PO₂-based electroless plating baths, showed that the material contained relatively unchanged lattice constants in terms of the major and minor AB₅-type intermetallic phases (Figure 3). A palladium phase was detected (± 1.0 net wt. %) at $2\theta = 12.8^\circ$. The measured XRD patterns did not show the presence of crystalline palladium, which allows for the deduction of the amorphous nature of the palladium coating, and is due to the inclusion of phosphorus into the metal coating.

The SR-XRD diffractogram of the AB₅-type intermetallide that was surface-modified by Pd-Ni co-deposition is shown in Figure 4. No clear peaks from either of the deposited nickel and palladium particles were observed. This observation may be due to the amorphous state of the particles or the lack of detectable quantities for SR-XRD analysis. Similarly to palladium-deposition, the material also contained relatively unchanged lattice constants in terms of the major and minor AB₅-type intermetallic phases. Identical observations were made for the intermetallide that was surface-modified using Pd-Cu co-deposition. In addition, the absence of peaks corresponding to the deposited nickel and palladium particles may be a result of the relatively low surface loadings of these two metals on the surface of the AB₅-type intermetallides.

Elemental analysis was conducted using AAS to ascertain the quantities of palladium, nickel, and copper deposited on the surface of the encapsulated intermetallide materials. A comparative table (Table 2) presents the surface elemental properties of the sample materials. Deposited nickel could not be resolved from the nickel surface matrix of the AB₅-type intermetallide. The AAS analyses showed that fairly low palladium and copper loadings were deposited onto the surface of the AB₅-type intermetallide after electroless plating.

Measurements of the influence of Pd-Ni and Pd-Cu mixed-metal coatings on the kinetics of hydrogen charging of surface-modified AB₅-type intermetallides were undertaken after exposure to air, and without thermal activation (Figure 5). Results of the fit of the experimental data by the Avrami-Erofeev equation are presented in Table 3; the sequence corresponded to the increase in the calculated rate constant (k).

Sample materials could be divided into two groups, in terms of their hydrogen absorption behaviour. The first group included the unmodified intermetallide, the intermetallide modified by sequential deposition of palladium and nickel (or copper), as well as the intermetallide modified by co-deposition of palladium,

nickel and copper. These materials were characterised by slow hydrogen absorption, reaching an estimated characteristic time of hydrogen absorption, $t_{0.9}$, of between 74 h and 340 h and a hydrogen sorption capacity corresponding to $H/AB_5 = 0.35 - 1.35$. The poor kinetic performances of the surface-modified intermetallides belonging to this group may have originated from the formation of dense nickel (or copper) layers on the surface, which acted as inhibitors to the transport of hydrogen, and limited the catalytic ability of the palladium component of the deposited layer.

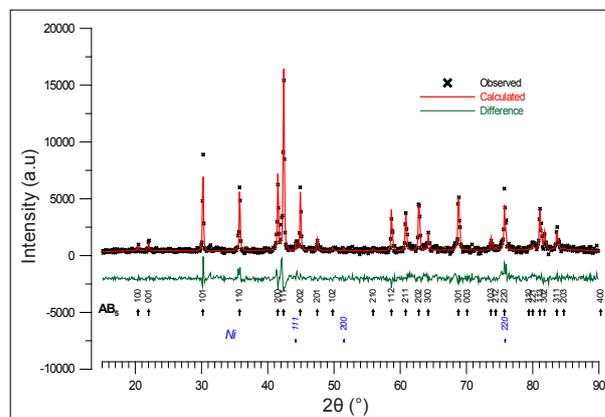


FIGURE 2
A fitted X-ray diffractogram of the unmodified AB₅-type intermetallide

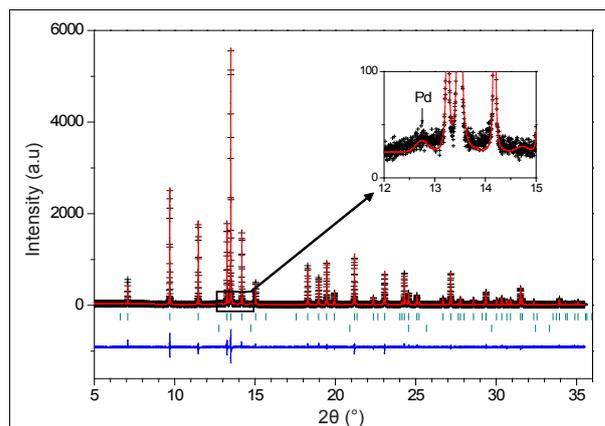


FIGURE 3
A fitted synchrotron radiation X-ray diffractogram ($\lambda = 5.0$ nm) of the AB₅-type intermetallide that was surface-modified using palladium electroless plating

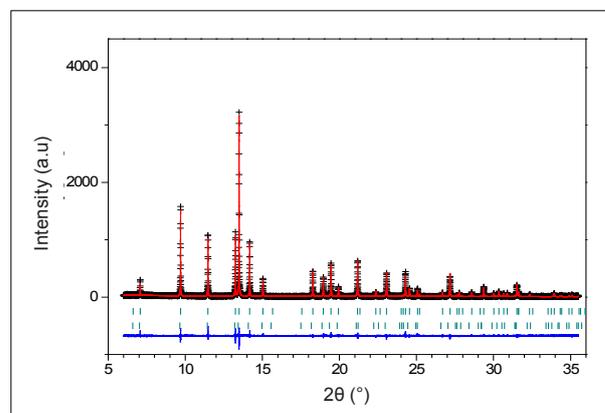
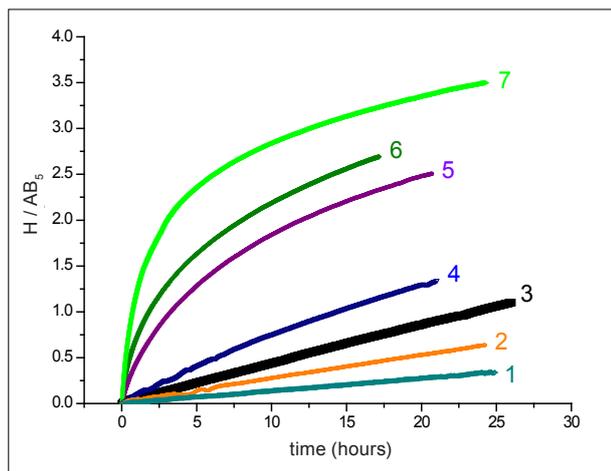


FIGURE 4
A fitted synchrotron radiation X-ray diffractogram ($\lambda = 5.0$ nm) of the AB₅-type intermetallide that was surface-modified using Pd-Ni co-deposition by electroless plating



Hydrogen absorption occurred at a temperature of 20 °C and a hydrogen pressure of 500 kPa.

FIGURE 5

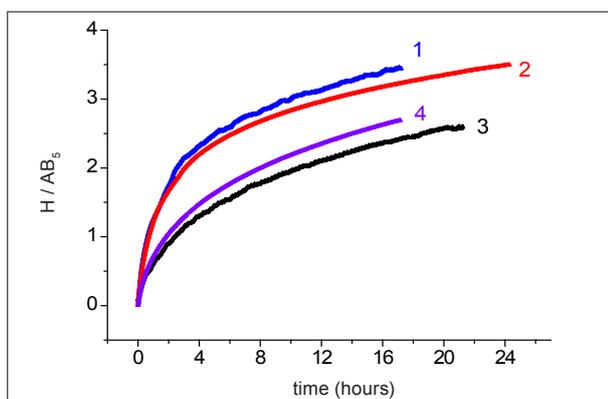
Dynamics of hydrogen absorption for AB₅-type intermetallics after: (1) Pd-Cu sequential-deposition, (2) Pd-Ni sequential-deposition, (3) no deposition (unmodified), (4) Pd-Ni-Cu co-deposition, (5) Pd-Cu co-deposition, (6) palladium deposition and (7) Pd-Ni co-deposition

TABLE 2

Elemental analysis of palladium and copper loading on AB₅-type intermetallics after sequential-deposition and co-deposition in palladium mixed-metal electroless plating baths

Sample	Palladium loading (wt. %)	Copper loading (wt. %)
Unmodified	-	-
Pd-Ni seq-dep	0.38	-
Pd-Ni co-dep	0.24	-
Pd-Cu seq-dep	0.49	0.05
Pd-Cu co-dep	0.34	0.04
Pd-Ni-Cu co-dep	0.03	0.02

Electroless plating was performed in a bath containing NaH₂PO₂ at a temperature of 50 °C for 30 min.



Hydrogen absorption occurred at a temperature of 20 °C and a hydrogen pressure of 500 kPa. Electroless plating was performed in a bath containing NaH₂PO₂ at a temperature of 50 °C for 30 min.

FIGURE 6

Dynamic activation curves for non-activated, surface-modified AB₅-type intermetallics after Pd-Ni co-deposition after exposure to air for (1) 3 months and (2) 11 months; and after Pd deposition after exposure to air for (3) 3 months and (4) 11 months

The second group included the sample surface-modified by palladium and co-deposited palladium and nickel (or copper). These materials were characterised by significantly faster kinetics of hydrogen charging and absorbed more than one-half of the maximum quantity of hydrogen within 24 h ($H/AB_5 = 2.5 - 3.5$), with a characteristic time of hydrogen charging 3-fold to 7-fold lower than that of the unmodified intermetallic. Fitted n values were close to 0.5, which allowed for the assumption that hydrogen charging of these materials had a mechanism different from that of the sample materials in the first group ($n = \pm 1.0$).

TABLE 3

Fit of the experimental data for hydrogen absorption by non-activated intermetallics using the Avrami-Erofeev equation

Group	Sample	Time of hydrogen charging (h)	Rate constant, k (h ⁻¹)	Index of power
1st	Pd-Sn sensitised/activated	2.3×10^3	4.3×10^{-4}	0.95
2nd	Pd-Cu seq-dep	342	2.9×10^{-3}	1.01
	Pd-Ni seq-dep	190	5.3×10^{-3}	0.97
	Unmodified	103	9.7×10^{-3}	1.02
	Pd-Ni-Cu co-dep	74	1.4×10^{-2}	0.92
3rd	Pd-Cu co-dep	35	2.9×10^{-2}	0.65
	Palladium deposition	27	3.7×10^{-2}	0.56
	Pd-Ni co-dep	15	6.6×10^{-2}	0.45

Hydrogen absorption occurred at a temperature of 20 °C and a hydrogen pressure of 500 kPa for 24 h.

Electroless plating was performed in a bath containing NaH₂PO₂ for 30 min.

The best kinetics of hydrogen charging were observed for the AB₅-type intermetallic, surface modified by co-deposition of palladium and nickel. It was deduced that nickel particles in Pd-Ni co-deposition facilitated the creation of an interfacial 'bridge' between nickel surface clusters of the intermetallic and deposited an amorphous palladium layer. This interface may have increased the rate of transport of the hydrogen atoms, after dissociation of the hydrogen molecules on the palladium particles, towards the bulk material. Similarly, the reverse process of passing the hydrogen atoms from the bulk to the modified surface, followed by the associative hydrogen molecules desorption, can also be promoted. The improvement in the kinetics of hydrogen charging could also be credited to a synergistic effect between the palladium and nickel atoms in the catalytic mantle, which promoted the absorption and transport of hydrogen atoms.

An attempt was made to study the long-term sorption stability of the surface-modified intermetallics. Measurements of the kinetics of hydrogen charging by the sample materials were undertaken after ± 3 months and ± 11 months exposure of the samples to air, and without thermal activation. The results with respect to the absorption of hydrogen were collected and are presented in Figure 6.

Rate constants for both the samples did not deteriorate very much, illustrating the long-term sorption stability of the materials, compared to the unmodified intermetallic. In addition, the sample prepared by co-deposition of Pd-Ni retained its superior kinetics of hydrogen charging, compared to that prepared by deposition of palladium only. This observation further illustrates that the addition of nickel to the palladium-based surface layer further enhanced the sorption stability of the intermetallic material, compared to that prepared by deposition of palladium only. We have thus confirmed our hypothesis that mixed-metal surface layers on AB₅-type intermetallics offer enhanced sorption stabilities.

CONCLUSION

It was proposed that the use of mixed-metal coatings for the surface micro-encapsulation of AB₅-type intermetallics, instead of with pure palladium only, had the potential to further improve the hydrogen absorption properties and sorption stability of the intermetallic materials. Pd-Ni co-deposited coatings, prepared by electroless plating, were found to promote faster hydrogen charging performances of the air-exposed, non-activated intermetallic materials, compared to those coated with palladium only. Improvements in the kinetics of hydrogen charging were credited to a synergistic effect between the palladium and nickel atoms in the catalytic mantle and to the formation of an 'interfacial bridge' for hydrogen diffusion by the nickel atoms in the deposited layer.

The developed composite materials may find application in rapid hydrogen separation, purification and storage from contaminated hydrogen feed streams.

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