

HYDROGEN ABSORPTION PERFORMANCES AND POISONING TOLERANCE OF AB₅-TYPE HYDROGEN STORAGE ALLOY SURFACE-MODIFIED BY ELECTROLESS DEPOSITION OF Cu AND Pd

Ren J., Williams M., Lototsky M.*

South African Institute for Advanced Materials Chemistry / University of the Western Cape
PO Box X17, Bellville / Cape Town, 7535, South Africa

*Fax: +27 (021) 9599314

E-mail: mlototsky@uwc.ac.za

Introduction

Rare earth metal-based AB₅-type hydrogen storage alloys offer a good medium for room-temperature hydrogen absorption as a result of their versatility, reasonable plateau pressures, low hysteresis, rapid activation, relatively high hydrogen selectivity, and low heat of hydride formation [1]. However, AB₅-type alloys exhibit poor cyclic stability and activation properties during hydrogen absorption in the presence of impurities (e.g. H₂S, CO, O₂, H₂O) [2]. Rapid losses in hydrogen sorption capacity and kinetics have been observed when cycling AB₅ alloys in H₂S- and CO-containing H₂ gas streams [3].

A common feature of the hydrogen storage alloys is that hydrogen absorption is impeded due to formation of oxides and hydroxides on the alloy surfaces after storage in non-inert environments.

Hydrogen storage using AB₅ alloys will not be practical unless they can be made more tolerant towards impurities. This problem can be addressed by engineering catalytic elements onto the surface of the alloys. For improved resistance of the hydrogen storage alloys towards impurities and significantly enhanced initial activation an encapsulation technique was adopted, as it is an effective and well-known method in protecting the surface from attack by electrophilic gaseous impurities in hydrogen [4].

Typically, platinum group metals (PGM's) such as Pd have been used to encapsulate hydrogen storage alloys. Previous works have demonstrated faster activation and improve cyclic lifetime in AB₅ alloys through PGM encapsulation [5]. These PGM layers are most effectively deposited using electroless plating. It was also previously found that PGM electroless plating resulted in removal of mixed rare earth metal-Ni oxides found on the surface of the alloy [6].

However, PGM deposition is a costly exercise and alternative surface "dopants" are sought for the preservation of hydrogen storage capacity and activation properties.

Deng *et al.* [7] presented a surface modification technique for AB₅ alloys based on the electroless plating of copper using CuSO₄ solutions as the metal precursor salt and HF as the catalyst. Compared with the unmodified alloy, the

modified alloys showed superior charge-discharge abilities, longer cycle lifetimes, decreased contact resistances and charge transfer resistances.

The work undertaken presents experimental results on the influence of the preparation history of Cu-coated AB₅-type hydrogen storage alloys on surface morphology and hydrogen sorption performances. A comparison was made with the core and Pd-treated sample materials.

Experimental

The multi-component AB₅ -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 DL1) was used in this work as the substrate alloy. The average particle size of the alloy powder was between 10-100 μm and its specific surface area was 0.05 m²/g.

Preparation of Cu-encapsulated AB₅ was conducted using an electroless plating technique. The amount of CuSO₄ was varied from 1.0 to 20 wt. % (2.0 ml HF, 3.0 min, 20°C), with respect to the alloy weight, and the volume of the HF catalyst was varied from 2.5 to 12.5 ml (all other parameters fixed at 5.0 wt.% CuSO₄, 3.0 min, 20°C). The alloy powder (10 g) was immersed in 50 ml of the copper plating solution. After plating the alloy powder was washed in deionized water and methanol and dried in vacuum at 60 °C.

Pd surface-modified alloys were also prepared using electroless plating and compared to Cu-coated samples. The experimental procedure was described elsewhere [6].

Samples were characterized using SEM, AAS, and volumetric measurements of hydrogen absorption (sample weight ~1.0 g; T=20 °C, P_{H₂}~5.0 bar; no vacuum heating before first hydrogenation; further hydrogenations were preceded by heating the sample in dynamic vacuum to T=200 °C for 1.0 hour).

Results and discussion

SEM analyses (Fig. 1) were conducted by comparison of images collected for the alloy surface modified with 9.0 wt. % CuSO₄, as an example, to that of the unmodified alloy. Deposition of large Cu agglomerates was observed on the surface of the AB₅-type hydrogen storage alloys after Cu electroless plating.

Spherical Cu particles as large as 1.0 ~ 5.0 μm in size were observed on the surface of the Cu-coated sample. The deposited Cu layers were generally discontinuous in nature.

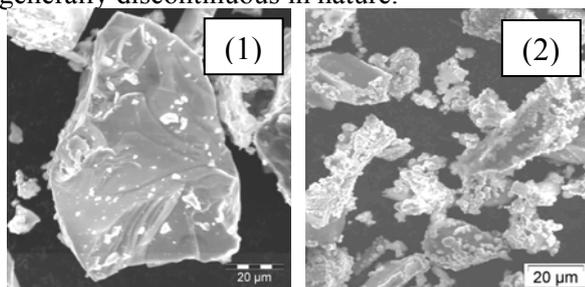


Fig. 1. SEM images of AB₅-type alloys: (1) unmodified, (2) surface-modified using Cu electroless plating (9.0 wt. % CuSO₄).

Elemental analysis of the Cu content on the surface of the alloy was conducted using AAS to ascertain the influence of CuSO₄ concentration on Cu loading on the alloy. Results were collected and are presented as Fig. 2. Trace quantities of Cu were detectable and the Cu content was found to increase with an increase in the CuSO₄ concentration in the electroless plating solution.

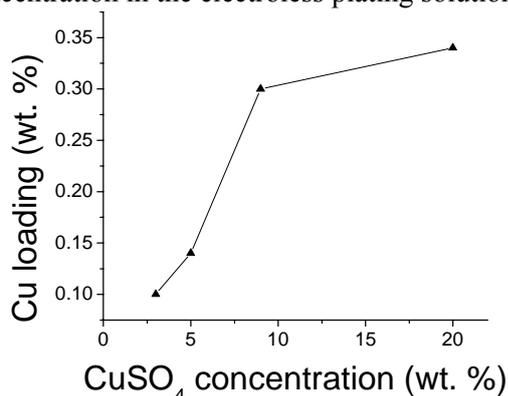


Fig. 2. Influence of CuSO₄ concentration on Cu loading on AB₅-type alloy surface-modified by the electroless deposition.

For the Pd-modified sample, slow H absorption ($H/AB_5=3.6$ in 20 hours) was observed even on the first hydrogenation cycle carried out without activation. No H absorption was observed at the same conditions for the core alloy and the material surface-modified by Cu deposition. After activation by vacuum heating, all the samples exhibit similar, very fast, hydrogen absorption kinetics: the H absorption is completed in ~10 minutes, and the maximum H capacity gradually decreases with increase of Cu amount in the sample (Fig. 3A). It was found (Fig 3B) that Cu and Pd deposition reduces the effect of surface poisoning after 2.0 hour exposure of the freshly-prepared hydride to air. However, for the material surface-modified with Cu, H absorption kinetics is slowed down in a great extent. In contrast, the sample surface modified with similar amount of Pd (total loading ~0.6 wt.%) does not exhibit

essential deterioration of its H absorption kinetics after the air exposure (curve 6).

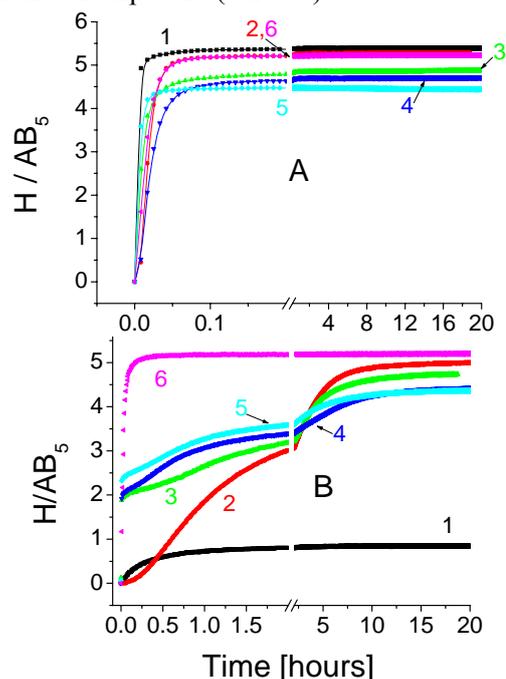


Fig. 3. Dynamics of hydrogen absorption by the activated AB₅-type before (A) and after (B) 2.0 hour exposure to air: (1) unmodified, (2) 3.0 wt. % CuSO₄, (3) 5.0 wt. % CuSO₄, (4) 9.0 wt. % CuSO₄, (5) 20 wt. % CuSO₄, (6) Pd (NaH₂PO₂, 30min).

In **conclusion**, surface modification of the AB₅ alloy by electroless deposition of copper increases its poisoning tolerance, but does not improve the activation performances and results in a gradual decrease of H absorption capacity. The material surface modified with similar amounts of palladium, known as an effective H₂ dissociation catalyst, exhibits far superior poisoning tolerance, together with the facilitation of the activation.

Acknowledgements

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References

1. Mungole MN, Balasubramaniam R. *Int. J. Hydrogen Energy*. 2000; 25: 55-60.
2. Sandrock G, Goodell PD. *J. Less-Common Metals*. 1984; 104: 159-173.
3. Dantzer P. *Mat. Sci. Eng.* 2002; A329-331: 313-320.
4. Uchida H., *Int. J. Hydrogen Energy*. 1999; 24: 861-869.
5. Rivera MA, et al. *J. Power Sources*. 2006; 155: 470-474.
6. Williams M, et al. *Mat. Chem. and Phys.* 2009; 115: 136-141.
7. Deng C, Shi P, Zhang S, *Mat. Chem. and Phys.* 2006; 98: 514-518.