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Effect of Mo additive on hydrogen absorption of rare-earth based hydrogen storage alloy

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Abstract

The aim of this study is to reveal the role of substitution of the host element in RE-based AB_5 -type alloy by Mo. For this purpose on the base of Mo-free alloy a number of VAR-melted composites were prepared. The influence of Mo additive was studied by comparison of their P - C - I characteristics with the data obtained from XRD analysis. Predicted earlier the positive influence of substitution of the host element in AB_5 -type alloys by metal with increased atomic number Z on their hydrogen absorption capacity in the main was confirmed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: RE-based hydrogen storage alloy; Substitution by Mo; P - C isotherms

1. Introduction

At present the investigations on partial substitution of the host element in the RE-based hydrogen storage alloys (HSA) are of great interest. The partial replacement of nickel by vanadium was very effective in improving the absorption capacity of AB_2 -type alloy [1] as well as the partial substitution of nickel by cobalt was a successful way in advancing cycling life for the AB_5 -type alloys [2].

In commercial $Mm(NiM)_5$ -type alloys the presence of 10 wt.% of Co has indeed improved the cycling life of Ni/MH batteries. However, it influences negatively the discharge capacity as well as initial activation [3] and it constitutes about 40% of the material cost.

Much effort has been devoted to search for a more cost-effective substitute element with high reliability to meet the requirements of applications of electric vehicles. Besides Fe [4] and Cu [5], it is believed that Mo is one of the best candidates for cobalt substitution. The reason is that the increase of hydrogen absorption capacity seems related to the increase of atomic number Z of the substituted element [6].

The aim of this study is to evaluate the influence of Mo additive in $Lm(Ni, Mn, Co, Al)_{5-x}Mo_x$ (where Lm denotes La-rich mischmetal and $0 < x < 0.15$) on P - C characteristics, phase composition and structure peculiarities.

2. Experimental details

AB_5 -type alloys were produced by vacuum melting in the Research Center of HYTEC Co. Ltd. Each composition was prepared from pure (99.9%) elements and was re-melted six times.

Equilibrium pressure-concentration isotherms were obtained using computer controlled automatic “ PCI Monitoring System” (GFE, Germany) with an accuracy of 1%.

The actual chemical composition of the obtained alloys, as well as their phase composition and structural peculiarities, were studied using chemical analysis, XRD-analysis (MAC Science MO3X XRD), SEM and EDS methods, respectively.

3. Results and discussion

To reveal the Mo additive on hydrogen absorption properties of AB_5 -type alloys on the base of Mo-free alloy 1 (see Table 1) two stoichiometric composites were prepared. In the first trial Ni was partially replaced by Mo (alloy 2). In the second trial Co was similarly substituted by Mo (alloy 3). The third (nonstoichiometric) composite was prepared with excess Mo content.

From the XRD analysis, it was found that in the above substitutions, the *hcp* structure of the basic alloy remains unchanged. However, according to the lattice data obtained for stoichiometric alloys 2 and 3, listed in Table 1, the parameters a and c as well as the ratio c/a and unit cell

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Table 1

Lattice parameters and hydrogen absorption capacity of various alloys obtained by arc-melting

N	Composition (at. ratio Lm/M)	Lattice parameters			V (Å ³)	H ₂ -abs. capacity (wt.%)
		a (Å)	c (Å)	c/a		
1	LmNi _{3.55} Al _{0.3} Mn _{0.4} Co _{0.75}	5.0287	4.0387	0.8031	88.48	1.29
2	LmNi _{3.50} Al _{0.3} Mn _{0.4} Co _{0.75} Mo _{0.05}	5.0351	4.0466	0.8037	88.85	1.49
3	LmNi _{3.55} Al _{0.3} Mn _{0.4} Co _{0.6} Mo _{0.15}	5.0317	4.0442	0.8037	88.67	1.40
4	LmNi _{3.55} Al _{0.3} Mn _{0.4} Co _{0.75} Mo _{0.05}	5.0378	4.0361	0.8012	88.71	1.49

volume increased after the substitutions. It was seen also that the changes are more significant when Ni is replaced by Mo. Hence, due to the modification of alloy 1 the unit cell volume as well as the vacancies for hydrogen interstitial seems to be changed positively as a function of Mo additive.

To confirm this assumption the *P-C-I* characteristics of the alloys were studied (Fig. 1). Comparing curve 1 with 2 it was indicated that the equilibrium plateau pressure remained almost the same until 0.9 wt.%, afterward alloy 2 continued to exhibit absorption properties until concentration at 1.1 wt.%. Hence, results indicated that Mo additive delayed the formation of AB₅-hydride (β -phase) and, in accordance with increased hydrogen absorption capacity, the electrical C/D capacity of the battery on its base would be increased.

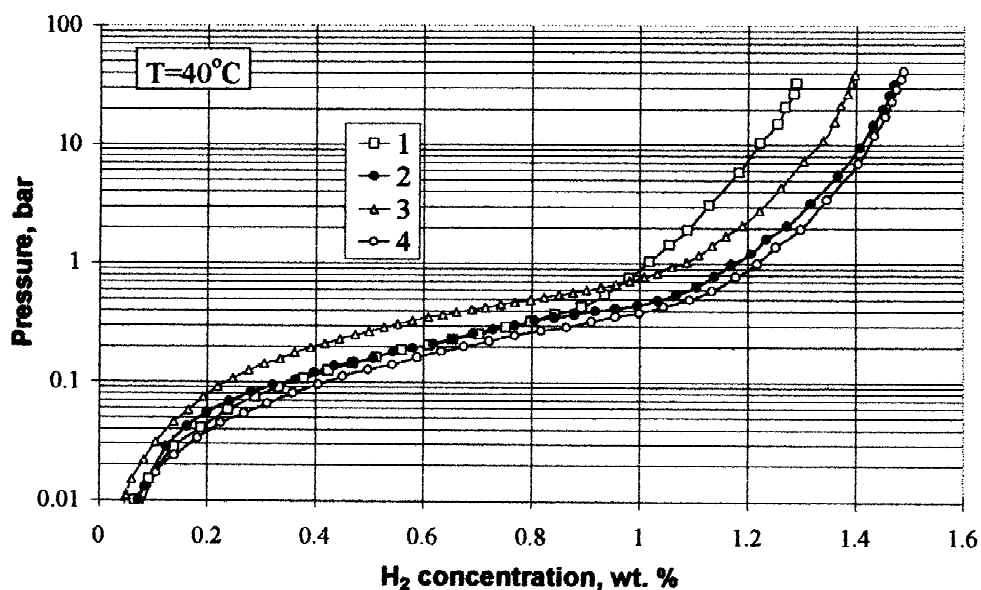
Comparison of the *P-C* isotherms of alloys 1 and 3 indicated that at substitution of Co by Mo both the hydrogen absorption capacity and the equilibrium plateau pressure are increased. However, in this case the capacity was increased less than that for alloy 2, which is in

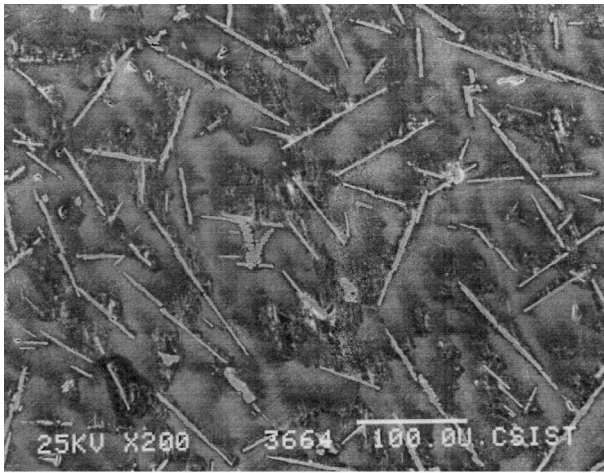
conformity with the less significant changes in the lattice parameters of alloy 3.

From the increasing tendency of the unit cell volume of alloys 2 and 3 it must be expected that the cycle life of a Ni/MH battery would be reduced in comparison with those of un-modified Co-containing HSA.

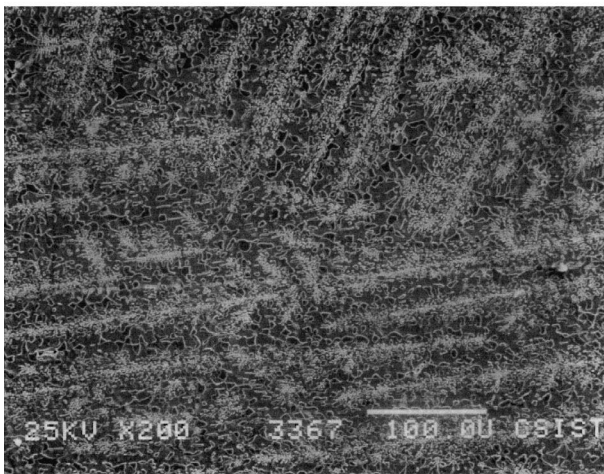
Finally, comparing curve 4 with 1 we can conclude that the effect of delaying formation of (MmB₅)-hydride is more pronounced for nonstoichiometric alloys. Based on the fact that Mo never forms solid solution with rare-earth element La [7], the increase of hydrogen absorption capacity seems consistent with the prediction [6] that the increase of the capacity could be related to the increase of atomic number *Z* of the substituted Mo.

However, it must be noted that the changes in the unit cell volume and, especially, in the plateau pressure of alloy 3 cannot be explained only by increasing atomic number *Z* of the substituted Mo (i.e., by the difference in the atomic sizes for pairs Ni–Mo and Co–Mo). According to the results obtained by SEM (Fig. 2) the surfaces of alloys 2 and 3 seems to be refined as a function of Mo addition.

Fig. 1. *P-C* absorption isotherms of alloys obtained by arc-melting, $T=40^{\circ}\text{C}$.



(a)



(b)

Fig. 2. SEM photographs of the alloys: (a) alloy 2; (b) alloy 3.

Otherwise, due to the increase in the Mo content in the alloy, the influence of new phase tracks, which formed with participation of Mo and Co, cannot be excluded.

4. Conclusions

Substitution of the host elements in the RE-based AB₅-type alloys by metal with increasing atomic number Z can indeed improve the hydrogen absorption capacity of the unmodified basic alloy. However, the influence of the tracks of formed new phases with the participation of Co and Mo cannot be excluded completely.

References

- [1] T. Shibao, Y. Moriwaki, N. Yanagi, T. Iwagi, National Technical Rep. 29 (1983) 78.
- [2] H. Ogawa, M. Ikama, H. Kawano, I. Matsumoto, J. Power Sources 12 (1998) 393.
- [3] P.H. Notton, P. Hokkelling, J. Electrochem. Soc. 138 (1991) 1877.
- [4] K. Yasuda, J. Alloys Comp. 253 (1997) 621.
- [5] F. Lichtenberg, U. Kohler, A. Fohzer, N.G.E. Adkins, A. Zuhttel, J. Alloys Comp. 253 (1997) 570.
- [6] M. Bououdina, P.D. Rango, D. Fruchart, J.L. Soubeyroux, J. Alloys Comp. 253 (1997) 221.
- [7] K.H.J. Buschow, H.H. Van Mal, Hydrogen-containing materials, in: Intercalation Chemistry, Academic Press, 1982, p. 409, Chapter 13.