INFLUENCE OF CARBON CONTAINING ADDITIVES TO HYDROGEN SORPTION PROPERTIES OF "PSEUDOALLOYS" Mg-REM-Ni

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Introduction

The hydrogen sorption capacity of ternary eutectic alloys of magnesium with nickel and lanthanum (mish metal) meet the modern requirements of metal hydride hydrogen storage systems – more than 5 mass.% [1]. However, high temperature of hydrogen sorption/desorption, poor kinetics of hydrogen transfer and sintering susceptibility hinder the practical use of such materials for hydrogen accumulating. Therefore actual is an elaboration of modification methods of such alloys in order to decrease the temperature and raise the hydrogen sorption/desorption rate. To reach this goal we propose here to form magnesium "pseudoalloys" – polymetallic materials – by sintering highly dispersed metal hydrides and composites on their basis with carbonaceous additives, such as graphite and carbon nanofibers.

Thus the aim of the present work is to study hydrogen interaction with "pseudoalloys" of the composition 72 mass.% Mg – 8 mass.% Mm(La) – 20 mass.% Ni (further on – Mg-Mm(La)-Ni), to find the optimal conditions of synthesis of the composite, as well as investigation of the influence of carbonaceous additives and ball mill parameters (milling rate, vial media) to the hydrogen sorption properties of the prepared materials.

Results and discussion

Electrolytic graphite was premilled in a planetary ball mill at 200 min^{-1} for 60 min. Nanofibers used in the work were synthesized by A.A. Volodin according to a procedure described elsewhere [2].

"Pseudoalloys" were prepared by sintering a mixture of the hydrides MgH_2, $Mm(La)H_3$ и Mg_2NiH_4 at 350°C. The ratio of the hydrides in the mixture corresponded to the one of the components of hydrogenated ternary eutectic alloy Mg-Mm(La)-Ni.

Thermal analysis of preliminarily dehydrided pseudoalloys at 250–300°C shows the presence of endoeffect on the DSC curve. The minimum of the peak lies at around 500ºC, that corresponds to the melting temperature of the "pseudoalloy" and is in agreement with the melting point of the ternary eutectic alloy Mg-Mm(La)-Ni prepared by the common method.

Composites of the "pseudoalloy" with 10 mass. % of graphite or the nanofibers were synthesized by treatment in a planetary ball mill at the milling rate of 500 min^{-1} in the argon vial media. The ball mill duration varied from 30 min to several hours. The Table 1 shows data on the influence of the ball mill duration on hydrogen sorption properties of the composites. The data allow one to draw a conclusion that the composites prepared during 90 min of the ball milling are the most readily hydrogenated.

Hydrogenation of all prepared materials was performed at the temperature of 300°C under the hydrogen pressure 20 bar. X-ray diffraction pattern of the product of the first hydrogenation reveals both the peaks of the hydrides and the peak of non-hydrogenated magnesium. Incompleteness of the hydrogenation was confirmed by the hydrogen absorption curves. At the carbonaceous additions however the hydrogenation was completed by 90% already in the first cycle. Thus, the X-ray diffraction pattern of the hydrogenated composite with the graphite addition (after the first hydrogenation) one can see the peaks corresponding to three hydride phases: LaH_3, Mg_2NiH_4, and MgH_2 (Fig. 1).

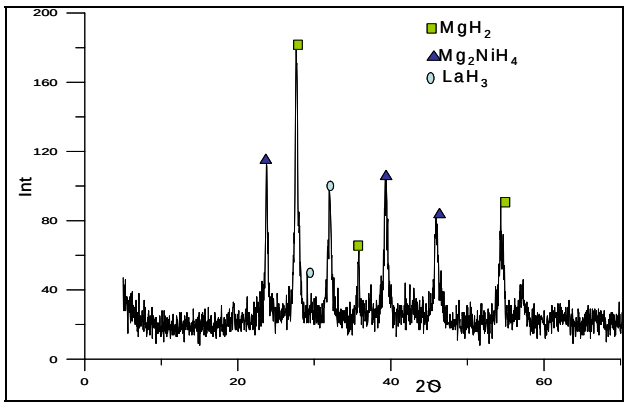

Fig. 1. X-ray diffraction pattern (CuK_α) of the hydrogenated composite of the "pseudoalloy" with 10 mass% of graphite.

An analogous pattern is typical for the product of the first hydrogenation of the composite with carbon nanofibers, but the first hydrogenation rate and the amount of hydrogen absorbed being noticeably higher (Fig. 2).

Table 1. Influence of the ball mill duration on properties of the composites.

	Ball mill duration, min	30	60	90	300	480
"Pseudoalloy"	Surface area, m^2/g	0.5	0.9	1.2	0.9	1.2
	H (1 cycle of hydrogenation), mass.%	3.2	3.5	5.0	4.3	3.8
	Temperature of hydrogen evolution, ^oC	320	300	290	300	300
"Pseudoalloy" +10% of graphite	Surface area, m^2/g	7.5	9.0	19.4	18.5	15.0
	H (1 cycle of hydrogenation), mass.%	4.2	4.2	5.1	4.8	3.8
	Temperature of hydrogen evolution, ^oC	300	290	300	300	300
"Pseudoalloy" +10% of nanofibers	Surface area, m^2/g	7.0	10.5	18.0	17.4	16.4
	H (1 cycle of hydrogenation), mass.%	3.6	4.1	5.3	4.3	3.2
	Temperature of hydrogen evolution, ^oC	315	300	285	300	305

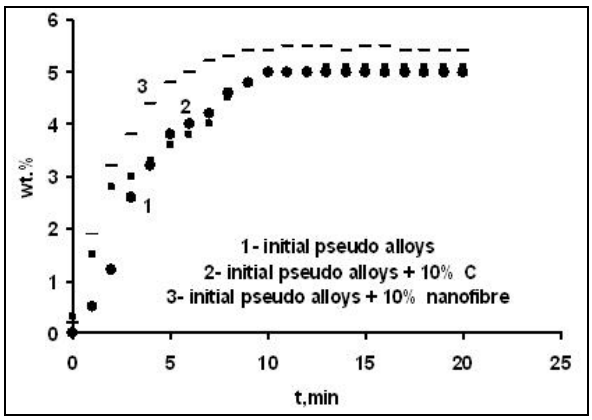

Fig. 2. Curves of hydrogen sorption by "pseudoalloy" (*1*) and "pseudoalloys" added with graphite (*2*) and nanofibers (*3*).

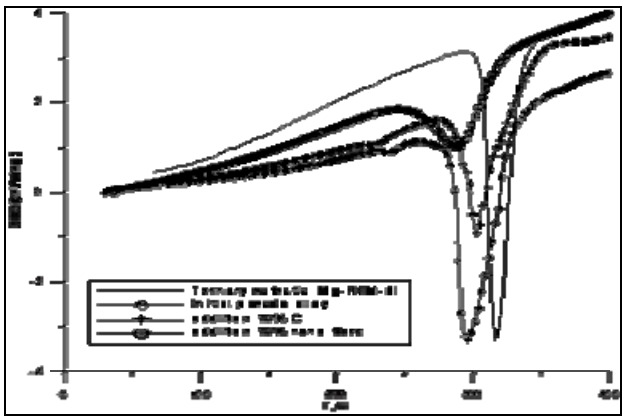

Fig. 3. Temperature of hydrogen evolution from hydrogenated alloy Mg-Mm(La)-Ni and composites on its basis.

Fig. 3 shows that the influence of the carbonaceous additives to the decrease in dehydrogenation temperature of the alloys was unessential. At this, however the composite has lower sintering susceptibility at temperatures more than 300^{o}C. At 320^{o}C the powder transformed to a spongy material and didn't lose its working characteristics during further hydrogenation–dehydrogenation cycles.

Conclusions

The elaborated approach toward the synthesis of composite materials based on "pseudoalloys" of the ternary eutectic Mg-Mm(La)-Ni with carbonaceous materials (graphite, nanofibers) leads to increase in the surface area and the hydrogenation rate, decreases sintering susceptibility of the powders. These materials have the improved hydrogen sorption characteristics.

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References

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2. Volodin A.A., Fursikov P.V., Kasumov Yu.A., Khodos I.I., Tarasov B.P. Synthesis of carbon nanofibers by catalytic pyrolysis of ethylene and methane on hydrides of intermetallic compounds of lanthanum with nickel. Russ. Chem. Bull. 2005;(10):2281–2285.