HYDROGEN ACCUMULATING COMPOSITES BASED ON MODIFIED EUTECTIC Mg ALLOYS

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Introduction

Magnesium based multiphase alloys containing nickel and rare-earth metals, such as the binary and ternary eutectic alloys in the systems Mg-Ni and Mg-Mm(La)-Ni are known to exhibit high hydrogen sorption capacity, up to 5–6 mass. % [1]. To improve the kinetics of hydrogen sorption/desorption it is necessary to decrease the grain size of the magnesium matrix of the alloys down to sub-microns and nano-scales, as well as to increase the length of interphase boundaries [2, 3]. One of the methods to attain this goal is the preliminary modification of the alloys with the use of the intense plastic deformation, in particular, by the equal channel angular pressing (ECAP) [4].

To prepare hydrogen accumulating composites in the present work we used the following magnesium based alloys: Mg-Ni of the mass contents in the area of the binary eutectic 77 mass% Mg + 23 mass% Ni, and Mg-Mm(La)-Ni of the mass contents in the area of the ternary eutectic 72 mass.% Mg + 8 mass.% Mm(La) + 20 mass.% Ni. To further improve the interaction kinetics of the materials with hydrogen and enhance their cyclic durability we used methods of preparing composites by the planetary ball milling of mixtures of powdered hydrides of the ECAP-ed eutectic magnesium alloys and hydrides of reversibly interacted with hydrogen intermetallic compounds of the AB_5 type, such as $La(Mm)Ni_5H_6$ taken in the amount of 10 mass %. Detailed studies of the hydrogen interaction with the elaborated materials were performed.

Results and discussion

We carried out metallographic investigations of the ECAP-ed eutectic alloys Mg-Ni and Mg-Mm(La)-Ni. Conclusions were drawn on the microstructure of the alloys obtained. With the use of light microscopy, scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX) the space distribution of the constituting phases end elements was established. It was shown that the ECAP-ed alloys had mainly highly dispersed lamellae structure. Varying ECAP parameters allow one to increase the dispersion of the microstructure of the alloys (Figs. 1 and 2). X-ray diffraction analysis performed from the surface of metallographic sections of compact specimens evidenced the presence of texture in the ECAP-ed binary eutectic alloys Mg-Ni. The microstructure of the alloy had a little amount of additional third phase $MgNi_2$, along with the common Mg and Mg_2Ni phases. This third phase isn't subjected to hydrogenation under the conditions when both the phases Mg and Mg_2Ni are. The literature data point to that the phase $MgNi_2$ is absent in the eutectic alloys of the considered composition.

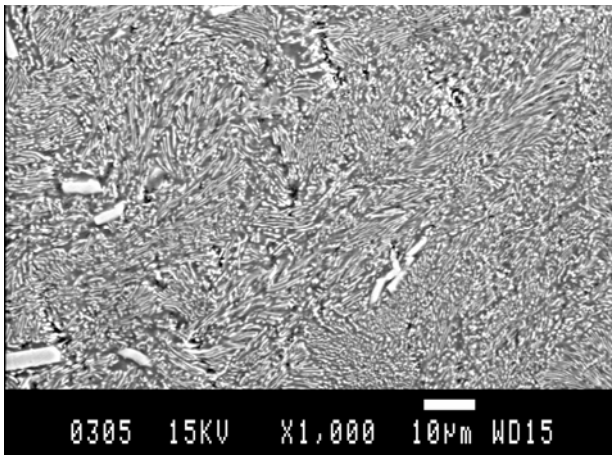

Fig. 1. SEM image (SE mode) of the binary eutectic alloy Mg-Ni, modified by ECAP at 250°C (1 pass, 10 mm/min).

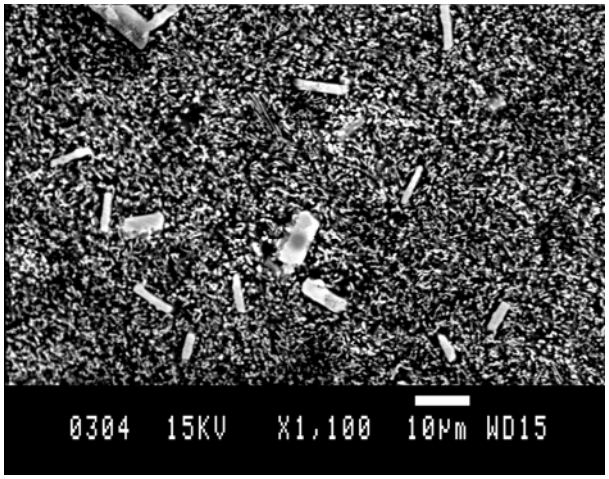

Fig. 2. SEM image (SE mode) of the binary eutectic alloy Mg-Ni, modified by ECAP at 300°C (4 passes, 15 mm/min).

The hydrogen sorption properties of the ECAP-ed magnesium alloys were investigated. With the use of a Sieverts-type experimental installation curves of hydrogen uptake and release were plotted. It was found that the ECAP-ed eutectic magnesium alloys Mg-Ni and Mg-Mm(La)-Ni, exhibited improved kinetics of interaction with hydrogen as compared to the initial non-modified alloys (Fig. 3). This data confirmed that these modified alloys are perspective for elaboration on their basis materials with enhanced hydrogen sorption characteristics.

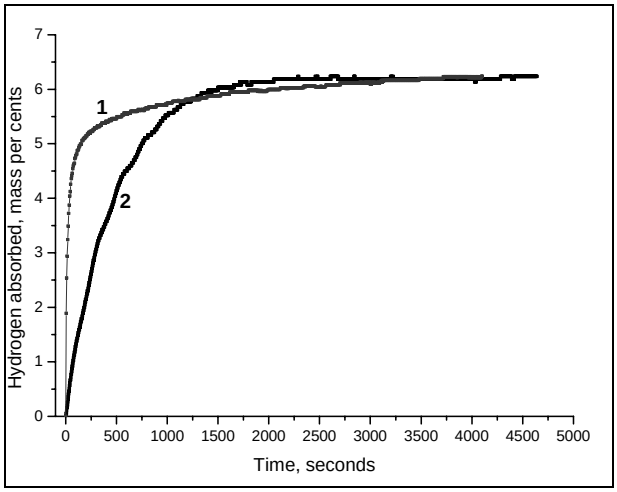

Fig. 3. Hydrogen absorption curves at 350ºC by the binary eutectic alloy Mg-Ni: modified by ECAP (1) at 250°C (1 pass, 10 mm/min) and the initial (2).

The cyclic durability of the elaborated hydrogen accumulating composite materials was studied in the processes of hydrogen sorption-desorption. In contrast to the procedure of high-energy ball milling in an inert atmosphere the proposed in the present work method of mechanochemical activation in the hydrogen vial atmosphere substantially increases the cyclic durability of both the powdered hydrides based on the ECAP modified ternary eutectic alloys Mg-La(Mm)-Ni and the composites based on the alloy Mg-Mm-Ni added with 10 mass % of the hydride of internmetallic compound $La(Mm)Ni_5H_6$.

Conclusions

The elaborated hydrogen accumulating composite materials may be used for compact and safe hydrogen storage, for feeding middle- and high-temperature hydrogen-air fuel cells, and as a hydrogen source for preparative chemistry and catalyst.

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References

1. Tarasov BP., Lototskii MV., Yartys VA. Problem of Hydrogen Storage and Prospective Uses of Hydrides for Hydrogen Accumulation. Russ. Chem. Journal 2007; 77(4): 694–711.

2. Løken S, Solberg JK, Mæhlen JP, Denys RV, Lototsky MV, Tarasov BP, Yartys VA. Nanostructured Mg-Mm-Ni hydrogen storage alloy: Structure–properties relationship. J. Alloys and Compounds 2007; 446–447:114–120.

3. Tarasov BP, Fursikov PV, Borisov DN, Lototsky MV, Yartys VA, Pedersen AS. Metallography and Hydrogenation Behavior of The Alloy Mg-72 mass%-Ni-20 mass%-La-8 mass%. J. Alloys and Compounds 2007; 446–447:183–187.

4. Skripnyuk V, Rabkin E, Estrin Y, Lapovok R. The Effect of Ball Milling and Equal Channel Angular Pressing on the Hydrogen Absorption. Acta Materialia 2004; 52: 405–414.