

HYDROGENATION OF Mg-REM-Ni ALLOYS AND COMPOSITES ON THEIR BASIS

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Introduction

Magnesium ternary eutectic alloys (having contents 70-75 wt.% Mg - 6-9 wt.% (La) Mm - 19-21 wt.% Ni) are of great interest as hydrogen storage materials. These alloys consist of Mg, Mg₂Ni and Ln₂Mg₁₇ phases and are able to absorb up to 5.4-5.8 wt.% H₂ at 520-550K and 1.0-1.5 MPa. Hydrogen releases from formed hydride phases at 610-620K and 0.15-0.20 MPa while hydrogen sorption characteristics being not changed essentially after multiple cycles hydrogenation-dehydrogenation [1,2].

The goal of the present work was to study the interaction of ternary eutectic magnesium alloys (72%Mg - 8%La - 20%Ni, 72%Mg - 8%Mm - 20%Ni) with hydrogen in details as well as to study the effect of intermetallic La_{1-x}Mm_xNi₅ additives on the kinetics of hydrogenation of the magnesium alloy.

Results and discussion

Hydrogenation was performed at hydrogen pressure of 1.5-5 MPa and temperatures 473-573 K. It was found that for the first cycle of hydrogenation was completed much more faster if the alloys were grounded down to the particle size less than 200 mkm and the alloys having less grain sizes were hydrogenated faster than the ones of coarse grains. The interaction of the alloy 72%Mg - 8%Mm(La) - 20%Ni with hydrogen produces a mixture of 3 hydride phases: MgH₂, Mm(La)H₃ and Mg₂NiH₄, with the intermetallic compound Mm(La)₂Mg₁₇ being decomposed to form MgH₂, and Mm(La)H₃.

Repetition of the cycles "sorption H₂ - desorption H₂" reduces the particle sizes of the alloy, after 5 cycles 90% of powdered sample have the particle sizes 20-100 mkm.

The desorption isotherms of the systems (Mg-La-Ni) - H₂ and (Mg-Mm-Ni) - H₂ clearly demonstrate 2 plateaus at temperatures 573-673K, which correspond to the phase transitions in the systems Mg₂Ni-H₂ and Mg-H₂ with the heat of hydride formation of -70 and -75 kJ/mol respectively.

Optical microscopy (OM), scanning electron microscopy (SEM) and X-ray diffraction

(XRD) data obtained from the surface of metallographic section of initial alloy were compared with those from the surface subjected to hydrogen impact during 1 h at 573 K and 3 MPa H₂. This comparison evidences noticeable changes in the surface structure (fig.1-2).

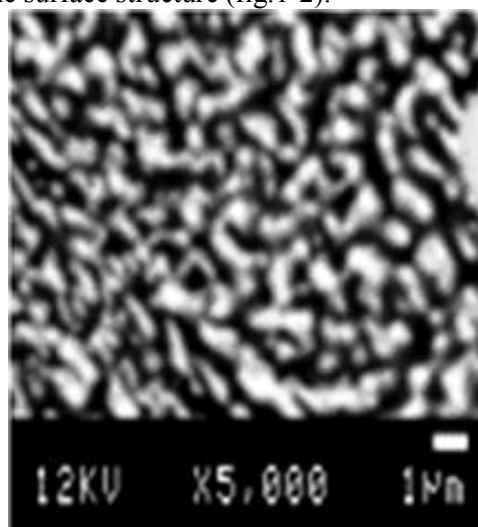


Fig. 1. SEM image (back scattered electrons) of the surface of a compact piece of the initial alloy.

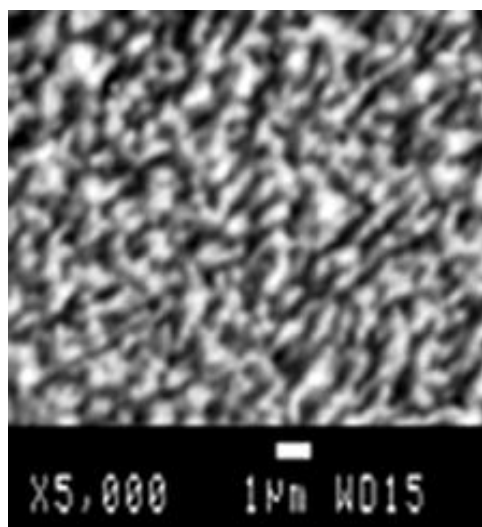


Fig. 2. SEM image of the surface of a compact piece of the alloy after hydrogenation.

At low degree of hydrogenation of the alloy the XRD images show the absence of the lines corresponding to the phase La₂Mg₁₇ as well as the presence of the ones of lanthanum hydride

phase. However the lines of the phases MgH_2 and Mg_2NiH_4 are not observed (fig.3). One may assume that at the initial stage of hydrogenation the hydrogenolysis of the phase $\text{La}_2\text{Mg}_{17}$ takes place, the reaction proceeding to a considerable depth from the surface of a compact piece. It seems to be due to the hydrogen diffusion rate through grains and interphase boundaries is much higher than that through grains their selves.

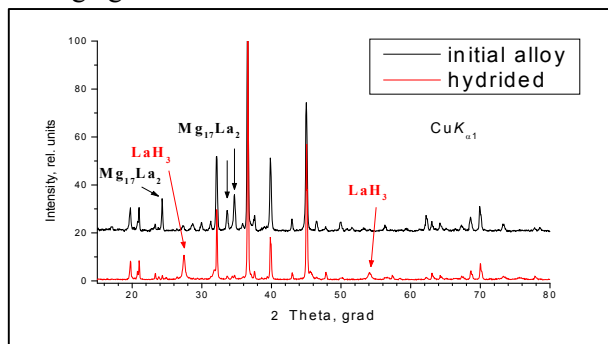


Fig.3. X-ray diffraction data of the surface of a compact piece of the alloy before and after hydrogenation.

The comparison of optical microscopy (fig. 4) and SEM (fig. 1, 2) images for both surfaces evidence a decrease in grain sizes after the hydrogenation, which may confirm decomposition of one of the phases during the initial hydrogenation stage.

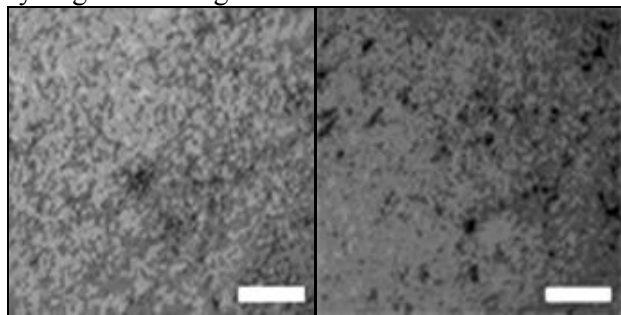


Fig.4. Images of the initial (left) and hydrogenated surface of the alloy (scale bar is 10 mkm).

The mixtures of hydrogenated alloys Mg-Mm(La)-Ni and La(Mm)Ni_5 were mechanochemically treated to prepare hydrogen storage composites with various content ratios. The performed investigations demonstrate the homogeneity of the composites, the absence of new phases and the composites having particle sizes 10-80 mkm.

The hydrogenation and dehydrogenation processes of the obtained composites were studied. These composites were found to interact with hydrogen much faster than initial mixtures of the powders. The desorption isotherms (Fig.5)

obtained at temperatures 523 - 573K demonstrate 2 plateaus, which are correspond to the phase transitions in the systems $\text{Mg}_2\text{Ni-H}_2$ and Mg-H_2 (isotherms for the systems $\text{La(Mm)Ni}_5\text{-H}_2$ and La(Mm)-H_2 are not revealed because of their small quantity).

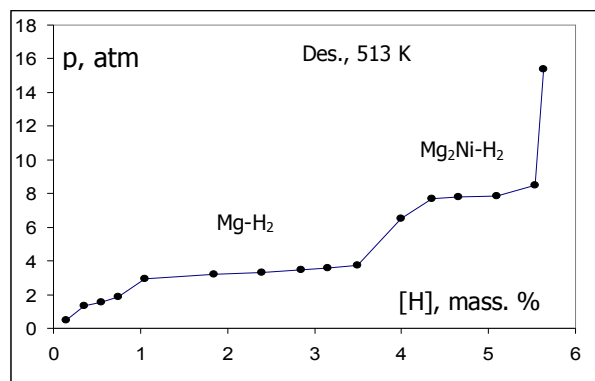


Fig.5. Desorption isotherms in the system $\text{Mg-Mm(La)Ni}+2\% \text{La(Mm)Ni}_5\text{-H}_2$.

It was found that the hydrogenation rate of the composites was determined by the heat transfer rate, the hydrogen sorption capacity was about 5 mass. %. The capacity is stable after multiple cycles "sorption - desorption H_2 ".

Conclusions

The alloys with low grain sizes were determined to have the best hydrogenation kinetics. The additives of intermetallide La(Mm)Ni_5 were found to enhance the rate of hydrogen uptake and to decrease the temperature of dehydrogenation.

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References

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