

# MAGNESIUM SURFACE MODIFICATION BY A COMPLEX METALLIC COVERAGE

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## Introduction

The works devoted to improvement of kinetics of hydrogen absorption by magnesium and dehydrogenation  $MgH_2$  there are actual today.

In the previous work [1] it is shown, that during the plating (by Ni) of the magnesium powder by reduction of organometallic compound in a gas, the  $MgH_2$  formation and interreaction of a part of the precipitated nickel with magnesium (forming  $Mg_2Ni$ ) took place. As a result the high density  $MgO$  oxide layer has destroyed and rate of the first saturation of a material by hydrogen has increased in comparison with pure magnesium.

We have continued works on modifying of a magnesium surface by the yielded method and have carried out the deposition of 10 wt. % of copper and 10 wt. % of complex nickel-copper (5 % Ni + 5 % Cu) coverings.

## Experiment

The initial material is magnesium powder MPF-4 grade with a particle size  $\leq 100 \mu m$ .

Covering was obtained by heating of the mixture magnesium powder with copper acetylacetonate or with mixture copper and nickel acetylacetonates in the hydrogen flow at 440 °C. The obtained materials were washed out by ethanol to remove the decomposition products of organometallic compounds. The amount of plating metal was determined by chemical analysis method.

Samples of plated Mg were investigated by scanning Auger-microprobe JAMP-10S, scanning electron microscope JSM T-10 and X-ray analysis.

Hydrogen storage properties of plated magnesium [ $Mg+Cu$ ,  $Mg+(Ni-Cu)$ ] were investigated on Sieverts apparatus at hydrogen pressure 2.5 MPa and temperature range 300-500 °C.

## Results and discussion

In contrast to nickel coating depositing in the form of continuous film on separated sites of magnesium surface, the copper coating which also depositing on separated sites, has island film type. It was not possible to hold definitely the

distribution of elements on the surface in the case of nickel-copper covering.

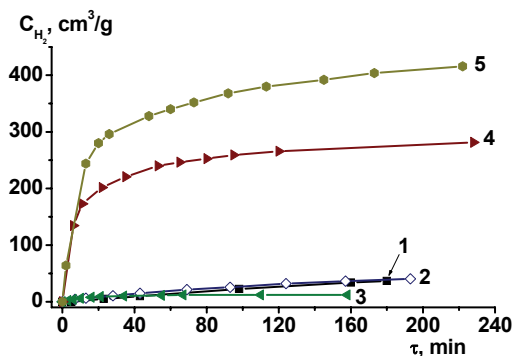
The sample  $Mg+Cu$  besides magnesium contains also copper, intermetallic compound  $Mg_2Cu$  and magnesium hydride. The magnesium with nickel-copper covering contains such phases as magnesium, intermetallic compounds  $Mg_2Ni$ ,  $MgNi_2$  and  $Mg_2Cu$ , and magnesium hydride. After hydrogenation the phase compositions of materials remain without changes, the quantity of magnesium hydride increases only.

Magnesium (MPF-4 grade) absorbs 6.53 wt. % (in 9th cycle) of hydrogen, that is 86% of maximum hydrogen capacity, at temperatures 350-380 °C and pressure 4 MPa. The total time of hydrogen saturation changes from 6 hours in the first cycle till 1.5 hours in the ninth. Dehydrogenation of  $MgH_2$  occurs at 450 °C. The rate of dehydrogenation and the completeness of decomposition are increase with increasing of hydrogenation-dehydrogenation cycles [2]. The same magnesium absorbs 5.3 wt. % of hydrogen in the third cycle at 2.5 MPa and 400 °C on our data.

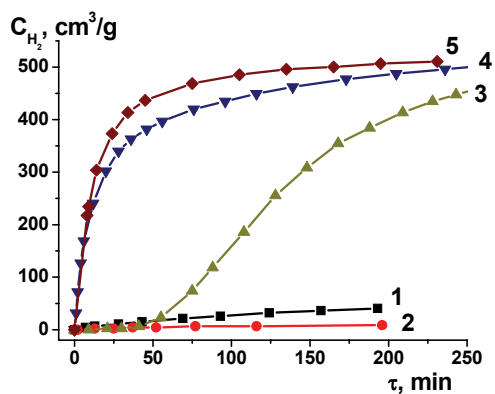
In contrast to nickel, copper does not influence on the first hydrogen absorption in comparison with the pure magnesium powder (Fig. 1). The activation of  $Mg+Cu$  material occurs at hydrogen absorption-desorption cycling with increasing the amount of absorbed hydrogen (4.8 wt. % in 4th cycle) (Fig. 2). The hydrogen absorption kinetic for this sample, as well as for magnesium, is defined probably by formation of local areas of magnesium metal surface.

The greatest influence on the first hydrogenation of magnesium among all investigated coverings has rendered the nickel-copper covering. The hydrogen absorption by such material in amount 2.8 wt. % already begins at 300°C ( $P_{H_2} = 2.5$  MPa). With increasing of the temperature to 400°C the amount of absorbed hydrogen increases to 3.7 wt. % (Fig. 1). However in the second cycle there is observed the decreasing of hydrogen capacity on one thirds value at preservation of sorption rate in initial (10-15 minutes) period, as well as at the first saturation. Thus, for this material „diffusive braking” in the second cycle comes faster, than in

the first. The gradual increasing of the amount of absorbed hydrogen occurs at the following absorption-desorption cycling.



**Fig. 1.** The kinetics of the first hydrogenation of investigated materials: **1** – Mg,  $T = 400\text{ }^{\circ}\text{C}$ ; **2** – Mg+10Cu,  $T = 400\text{ }^{\circ}\text{C}$ ; **3** – Mg+10Cu,  $T = 450\text{ }^{\circ}\text{C}$ ; **4** – Mg+5Ni+5Cu,  $T = 300\text{ }^{\circ}\text{C}$ ; **5** – Mg+5Ni+5Cu,  $T = 400\text{ }^{\circ}\text{C}$ .



**Fig. 2.** The kinetics of hydrogen absorption-desorption cycling for sample Mg+10Cu: **1** – 1st cycle,  $T = 400\text{ }^{\circ}\text{C}$ ; **2** – 2nd cycle,  $T = 400\text{ }^{\circ}\text{C}$ ; **3** – 3rd cycle,  $T = 450\text{ }^{\circ}\text{C}$ ; **4** – 4th cycle,  $T = 450\text{ }^{\circ}\text{C}$ ; **5** – 5th cycle,  $T = 450\text{ }^{\circ}\text{C}$ .

Dehydrogenation  $\text{MgH}_2$  occurs at  $500\text{ }^{\circ}\text{C}$  for 20 minutes. At lower temperatures the rate of decomposition is too small and on full dehydrogenation some hours are required. The copper covering does not render essential influence on dehydrogenation conditions of the saturated material. Nickel-copper covering reduces time of full dehydrogenation at  $400\text{ }^{\circ}\text{C}$  to 25 minutes

## Conclusions

Interaction of deposited metal and magnesium surface with formation areas of this metal, intermetallic compounds and magnesium hydride took place as a result of reduction metals acetylacetonates by hydrogen.

Copper does not render catalytic influence on process of hydrogen absorption by magnesium.

Complex nickel-copper coating causes the breaking of the oxide layer integrity. Therewith nickel has catalytic effect on hydrogenation process because its particles are the centers of dissociative chemisorption of hydrogen. These two facts are the reasons of the improvement of hydrogen absorption kinetics at the first saturation.

## References

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2. Antonova M.M., Kiselyov O.G., Horpyakov O.T. Interaction of magnesium industrial powders with hydrogen. Powder metallurgy 1990; № 6: 1-6.