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SYNTHESIS OF NANOSCALED MAGNESIUM POWDERS IN THE HIGH-FREQUENCY ARC DISCHARGE AND STUDY OF THEIR HYDROGEN SORPTION CHARACTERISTICS

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Currently the problem of effective hydrogen storage is a very significant obstacle to the widespread application of hydrogen energetics. Hydrogen storage in the bound state as a metal hydride systems is the most promising due to the high volumetric hydrogen density [1]. According to theoretical estimates the amount of the hydrogen absorbed in magnesium hydride is more than 7.6 wt.% what makes it particularly interesting to use for the purpose.

We have synthesized nanoscaled magnesium powders in the high-frequency arc discharge and studied their hydrogen sorption characteristics under pressure. Fig. 1 shows a plasma-chemical plant to synthesize nanoscaled powders. In the water-cooled sealed chamber (1) there were located two electrodes : the water-cooled hollow nickel rod (2) and the graphite crucible (3). Magnesium was placed in a graphite crucible and was maintained in a molten condition (5) by the inductor (4). The AC arc discharge (66 KHz, 12 A) (6) was carried out between the nickel electrode and the molten magnesium. The sample 1 was obtained in a hydrogen atmosphere, the sample 2 - in an atmosphere of hydrogen and helium. Argon as a plasma forming gas was also in the chamber during the synthesis. Gas was supplied with the rate: H_2 - 5 l/min, Ar - 5 l/min, He - 3 l/min. The vaporized magnesium coagulated with nanoparticles formation and settled on the walls of the chamber 1.

The study of the sorption parameters of synthesized samples was carried out on the developed plant [2]. Before dehydrogenation the samples were purified of adsorbed gases by maintaining in vacuum at a temperature 100°C for 10 minutes. For the sorption cycle 3MPa-pressed hydrogen was applied into the sample-filled cell at 400°C for 10 minutes. After cooling, the cell was placed into the inductor and heated to 600°C at 10°C/min. The desorbed hydrogen got accumulated in the special measuring chamber of known volume, wherein the pressure was determined. The amount of the released hydrogen was resulted from the pressure difference before and during the heating.

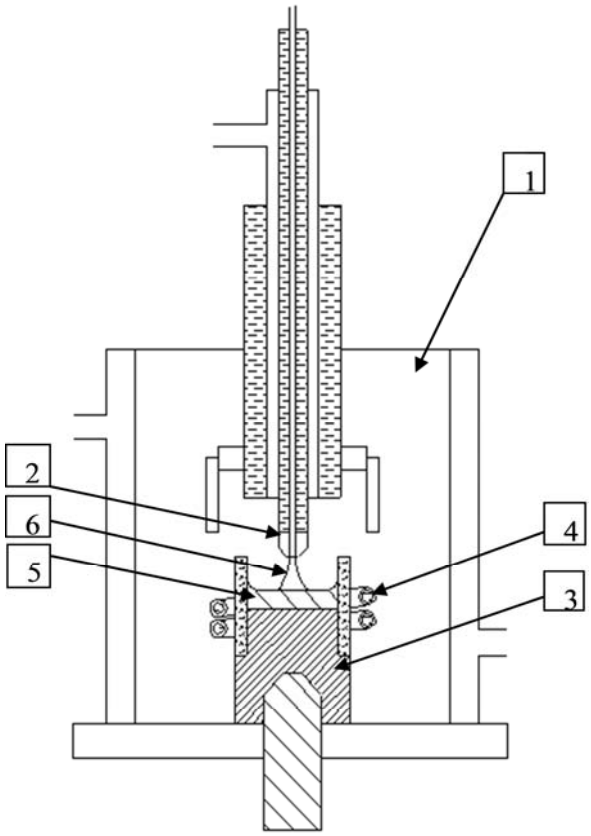

Fig.1. Plasma-chemical plant for the nanoparticles synthesis

Using scanning electron microscopy of the high resolution microscope SEM Hitachi S-5500 the images of synthesized nanoparticles were obtained (Fig. 2). Particles size varies 50 - 500 nm. Moreover, there were well-crystallized particles and the particles of spherical shape, what could result from their melting during the synthesis.

a b

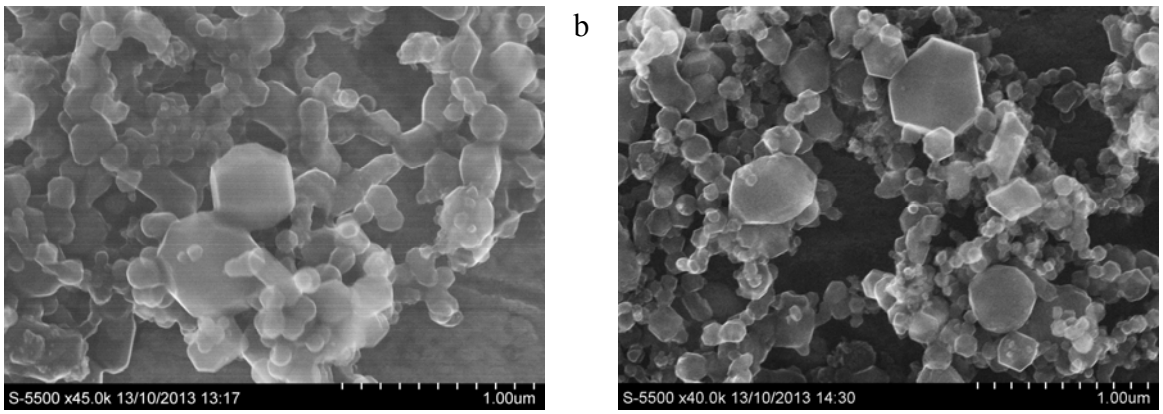

Fig.2. Electron microscopic images of magnesium nanoparticles:
a) sample 1, b) sample 2

According to XRD, MgH_2 phase formation occured after hydrogenation under pressure in both obtained samples. XRD diagrams also contained reflections corresponding to Mg, MgO, Mg_2Si and Ni phases. Mg_2Si and Ni phases formation could be associated with the impurities presence in vaporized magnesium.

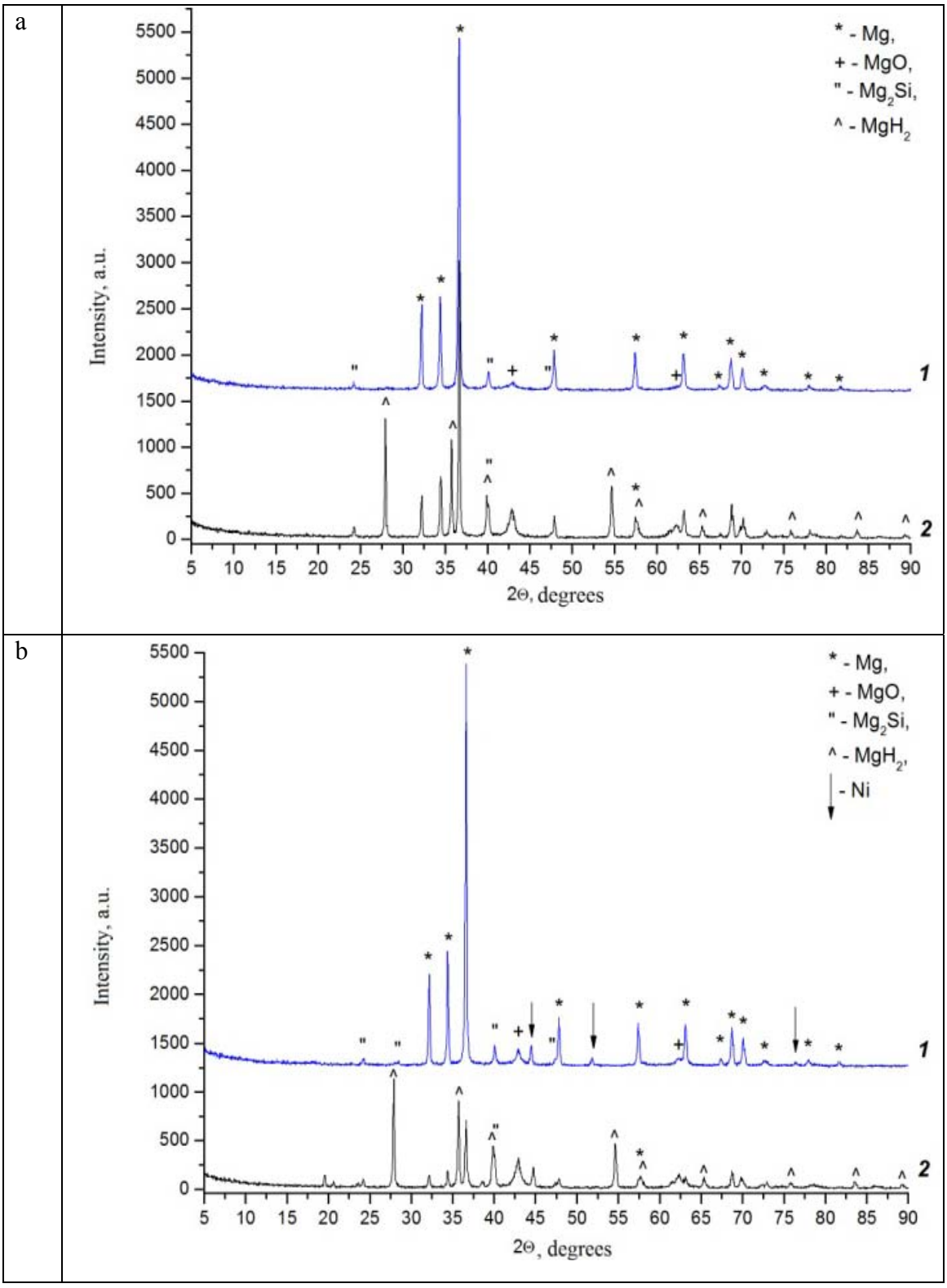

Fig.3. X-ray diffraction diagrams of the samples before (1) and after hydrogenation under pressure (2): a) - sample 1, b) - sample 2;

The desorbed hydrogen mass–temperature dependence curves are presented in Fig.4. Sample 1 desorbed 3,58 wt.% and 3,25 wt.% at the first and second cycles, respectively. The hydrogen evolution took place in the temperature range 300-500°C. Being heated sample 2

emitted only 0,3 wt.% of absorbed gases, and its desorbed gas–temperature dependence was close to linear. Such a difference between readings is specified by various synthesis parameters.

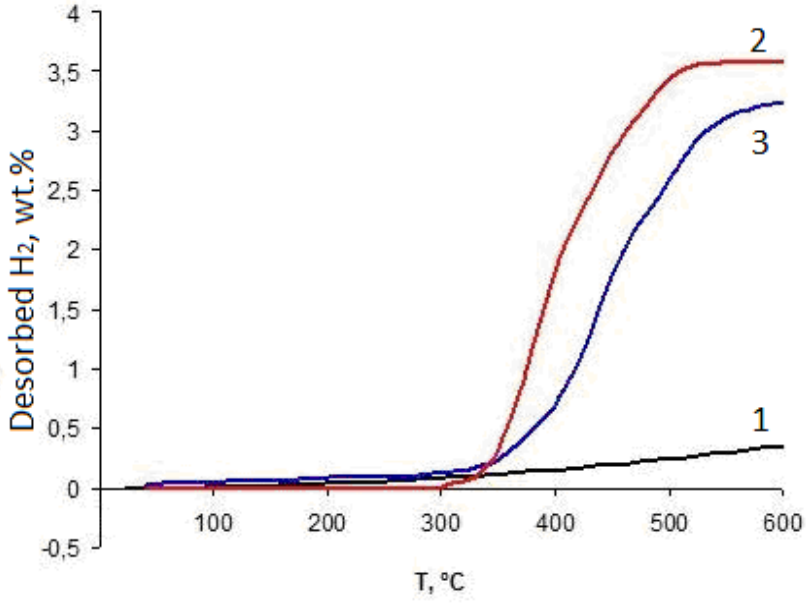

Fig.4. Temperature dependence of the amount of desorbed hydrogen:
1 – first desorption cycle (sample 2); 2 (3) – first (fifth) desorption cycle (sample 1)

These results can be explained in accordance with the Sieverts's law. The solubility of hydrogen in the metal S_{H_2} is proportional to the partial pressure of hydrogen in the gas mixture P_{H_2}: $S_{H_2} \sim k \cdot \sqrt{P_{H_2}}$, wherein k – Siverts's constant [3]. Since the sample 1 was synthesized in the hydrogen atmosphere, and the sample 2 - in the hydrogen-helium mixture, the partial pressure while the sample 1 formation was much higher than that (P_{H_2}) of the sample 2.

Thus, nanoscaled magnesium-based powders, obtained in a high-frequency arc discharge in the hydrogen atmosphere, can be considered as promising hydrogen sorbents. Subsequently it is planned to modify the plant and provide the hydrogen partial pressure close to 100 % during the synthesis.

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