

EFFECT OF DIFFERENT CARBON ALLOTROPIES ON MAGNESIUM HYDROGEN SORPTION KINETICS UNDER REACTIVE BALL MILLING

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Introduction

To date magnesium is a most perspective material for solid-state hydrogen storage due to its high capacity (7.67 %wt.), its low cost and its abundance on the earth's crust. However for widespread utilization of magnesium it is necessary to overcome drawbacks related to poor kinetics and unacceptable sorption/desorption temperature. The reactive ball milling (RBM) of magnesium with different additives (rare-earth metals, transitional metals, oxides etc.) is widely applied to improve sorption kinetics. In the last years the magnesium-carbon composites synthesized by ball milling of magnesium with different carbon materials (CM) type of nanotubes, nanowires, etc. are considered to be perspective materials for hydrogen sorption. They have a fast hydrogen sorption kinetics and high hydrogen capacity. However, it should be noted there is no a clear understanding of nature of carbon beneficial effect on the hydrogen sorption by magnesium-carbon composites. The aim of the present work is to investigate the effect of different carbon allotropic additives on the structure and sorption properties of Mg-C composites synthesized by reactive ball milling.

Results and discussion

The samples were prepared from commercially available magnesium powder, spectrally pure graphite, amorphous carbon powder (AC) obtained by electrical discharge technique [2], ultra dispersive diamonds (UDD) and carbon nanotubes (CNT).

The reactive ball milling of the mixtures was carried out in home-made milling vial equipped by pressure transducer and valve at room temperature using a high-energy Fritsch Pulverisette-6 ball mill. Initial hydrogen pressure was about 0.5-0.6 MPa. The amount of hydrogen stored by the powder during RBM was measured from hydrogen pressure drop in the milling vial. The ball milling was continued until the hydrogen pressure in the milling vial decreases.

The sample weight, the percentage of components (80% Mg – 20% CM) in initial

mixture of powders, the milling speed, the amount of steel balls and the ball to powder ratio were the same in the all experiments. X-ray diffraction analysis was performed using DRON-3M diffractometer. The morphology of the synthesized composites was characterized using JEOL JSM 6360 and Hitachi H800 electron microscopes. To investigate the structural changes of carbon allotropies before and after RBM a DFS-24 Raman spectrometer was used.

It was found that the all carbon allotropic additives significantly (in 3-4 times) improve hydrogen sorption kinetics (Fig. 1, plots 2-5) in comparison to pure magnesium (Fig. 1, plot 1). The fastest hydrogen sorption kinetics occurs for Mg-AC sample (Fig. 1, plot 5).

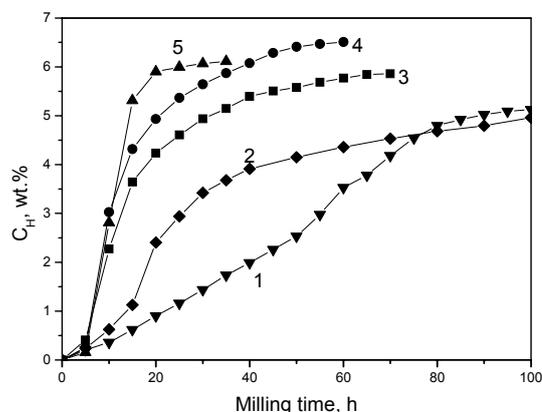


Fig. 1. Hydrogen sorption kinetics by different Mg-CM nanocomposites under RBM: 1 – Mg; 2 – Mg-C; 3 – Mg-CNT; 4 – Mg-UDD; 5 – Mg-AC.

X-ray diffraction patterns of the as-prepared samples show a presence only of magnesium hydrides and a small amount of magnesium in the powders (Fig. 2). There are no any other phases in the powders after RBM (in particular magnesium carbides). Peaks associated with magnesium hydride are very broadening due to the very fine grain size as result of RBM. The reflections coming from the initial carbon substances are not observed (Fig. 2). It indicates about drastic destruction of initial microstructure of carbon materials. TEM investigations confirmed this

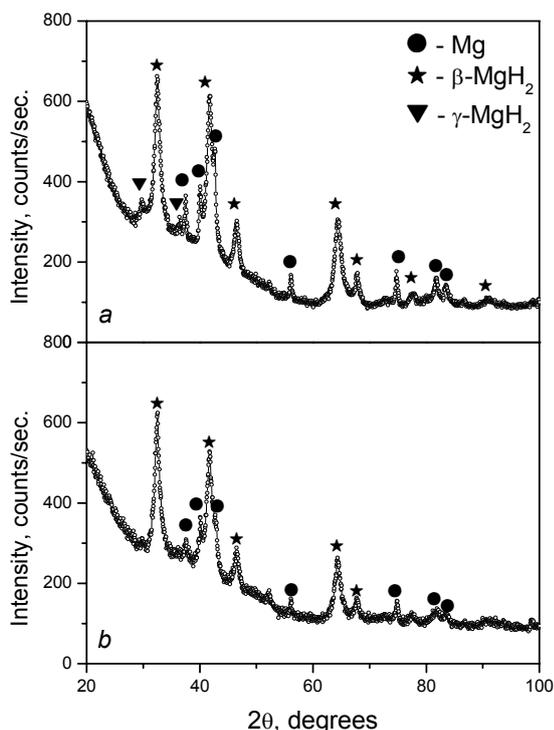


Fig. 2. XRD patterns of the as-prepared powders: Mg (a) and Mg-AC (b).

inference (Fig. 3). The as-milled magnesium powder contains particles with average sizes ranging from 80 to 120 nm (Fig. 3a). In contrast, the particles of magnesium-carbon powders are much finer. For example, the average diameters of magnesium hydride particles are predominantly less than 20 nm. There are only single particles with sizes about ~50-80 nm (Fig. 3b).

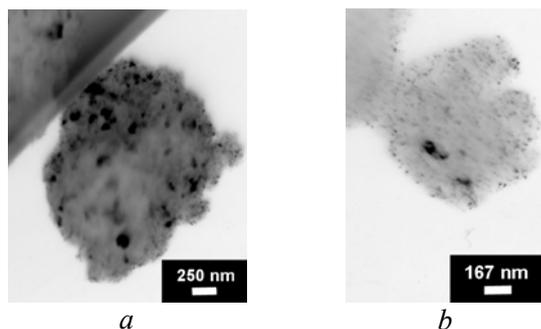


Fig. 3. TEM images of as-milled samples of Mg (a) and Mg-AC (b).

To elucidate microstructure evolution of carbon substances during ball milling the Raman spectra of carbon in the as-milled powders were recorded (Fig. 4). After ball milling, the relative intensity ratio of the D to the G band on the Raman spectra changed, what indicates that the percentage of disordered carbon and the defects density became much higher as a result of RBM. The

locations of the D and G bands are still the same as for non-milled carbon. It means that carbon remains in the free state after RBM: there is no chemical bond between carbon and magnesium in the powders. This is in agreement with the XRD investigations. The average crystalline size of carbon materials along their basal planes estimated from the Raman spectra is ~6 nm.

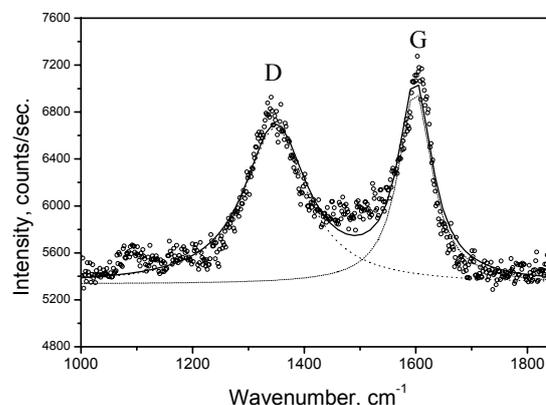


Fig. 4. Raman spectra of Mg-AC sample after RBM.

Conclusions

It was found, that addition of all kinds of carbon materials to magnesium leads to reduction in 3-4 times the hydrogenation duration in comparison with undoped magnesium. The significant grain size reduction of magnesium hydride due to formation of carbon coating layer between single particles during reactive ball milling has been established. The carbon coating layer prevents particles agglomeration, oxidation of fresh cracked surface and thus activates the surface. This results in simultaneous involving a much greater amount of magnesium into chemical interaction with hydrogen. Thus hydrogenation process proceeds considerably faster. Among the additives, amorphous carbon promotes more fine powdering of magnesium under ball milling in comparison with other carbon allotropies. Perhaps, it is caused by features of its structure.

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References

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