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Effect of Mechanical Alloying of Magnesium with Inorganic Salts on Its Reactivity in Relation to Hydrogen

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Abstract

Effect of inorganic salts NaF, NaCl, MgF_2, $CrCl_3$, and $(NH_4)_2CO_3$ additives on the processes of hydrogenation and dehydrogenation of magnesium mechanical alloys has been studied. It has been demonstrated that mechanical alloying of magnesium with a series of inorganic salts not only facilitates the grinding of metal, but also modifies its surface that leads to an acceleration of hydrogenation and dehydrogenation reactions and to rather high hydrogen content of samples (up to 5.5–6 mass % with the use of NaF, NaCl, or $CrCl_3$). It has been found that salts modify differentially the metal surface that is reflected in the kinetic curves, especially, during the first hydrogenation cycle.

INTRODUCTION

As of now, the problems of hydrogen accumulation take on topic significance in connection with increasing consumption of hydrogen as a component of the modern-day industry all over the world. The last-mentioned is caused not only by its high energy content (142.7 kJ/g), but also by ecological compatibility of the processes, in which hydrogen is used as a power supply, as well as by its chemical properties.

Storage of hydrogen in the form of metal hydrides or intermetallic compounds (IMC) as compared to alternative ways shows a series of advantages: high density of the stored energy, safety of operation, high purity of hydrogen obtained upon decomposition of hydrides. To solve the applied problems, hydrogen accumulators must meet certain requirements, most important of which, as a rule, are the hydrogen capacity, operating temperature, and the rate of absorption and release of hydrogen at operating temperature.

The use of magnesium hydride as the hydrogen accumulator is attractive from the standpoint of its high hydrogen capacity (the theoretical content of hydrogen in MgH_2 comprises 7.6 mass %). However, the low rates of magnesium hydrogenation and dehydrogenation even at relatively high temperature (300–400 °C) are responsible for application of catalytic additives (usually transition elements) for improvement of kinetic characteristics of these processes. On the other hand, magnesium cannot be alloyed with very many elements of periodic system, which restricts significantly the potentials for picking a catalyst and hinders obtaining triple magnesium-containing hydrides.

The procedure of mechanical alloying (MA) helps in many respects to overcome these difficulties, the procedure being one of the most effective methods in production of the materials of a variety of compositions and microstructures including thermodynamically immiscible components. This method is now being applied to advantage for preparation of various hydrogen-accumulator materials with the enhanced sorption characteristics [1–4]. Beneficial effect of MA doped with some metals, metalloids, and oxides on kinetic characteristics of magnesium hydrogenation and dehydrogenation has been found [1–3, 5, 6]. It has been demonstrated in this work that combined mechanochemical treatment of magnesium doped with inorganic salts also exerts influence on the subsequent processes of hydrogenation and dehydrogenation of the material that has been produced in this way.

EXPERIMENTAL

The mixture of powders of metal magnesium and inorganic salt (NaCl, NaF, MgF_2, $CrCl_3$ or $(NH_4)_2CO_3$) was processed in a centrifugal planetary mill (AGO-2) in an atmosphere of argon at acceleration of 400 m/s^2. Steel barrels and steel balls of diameter 5 mm were applied. The mass ratio of balls and worked sample was 100 : 1.

Specific surface of samples was determined by the BET procedure with an accuracy of ±10 %. Iron content of samples was controlled by means of the atomic absorption analysis. X-ray diffraction analysis of samples was conducted with the use of CuK_α radiation.

Kinetics of hydrogenation and dehydrogenation was studied in a setup for high pressure made from stainless steel. The quantity of absorbed or released hydrogen was defined from the pressure change in a constant volume reactor. Hydrogen pressure was measured by means of "Sapfir-22DI" strain-gauge indicator with an accuracy of 0.2 %. Before the first hydrogenation, the reactor was evacuated and heated in dynamic vacuum about 5 Pa up to the requisite temperature. The temperature in the reactor was maintained with an accuracy of ±1 K.

RESULTS AND DISCUSSION

Mechanical alloying of magnesium with NaF, MgF_2, NaCl, $CrCl_3$, and $(NH_4)_2CO_3$ inorganic salts leads to grinding of metal particles and to an increase in specific surface of samples. The magnitude of specific surface increases with an increase in salt content of a sample and with time of mechanical treatment and depends on the nature of the salt (Fig. 1). Grinding of magnesium particles during salt-doped mechanical alloying is related supposedly to the circumstance that salts fulfil the function of surfactants, interfering with the processes of aggregation of metal particles.

Some contamination of samples by the material of milling bodies occurs during MA and iron content of samples increases (Fig. 2). However, the last-mentioned has only a weak dependence both on the salt nature and on its concentration in the sample. Upon 5 min of MA, the content of iron in the samples varied within the limits of 0.17–0.25 mass % (except for the $(NH_4)_2CO_3$ admixture) and differed a little from that in magnesium, which was subject to the same procedure, but without salt additives (0.2 % Fe). This testifies that the halides studied do not make for an additional pollution of magnesium during mechanochemical treatment, whereas ammonium carbonate somewhat raises iron mass fraction in a sample (0.38 %) supposedly due to an interaction with the ball surface and the surface of barrel walls.

The decrease in magnesium particle sizes, certainly, has an influence on the

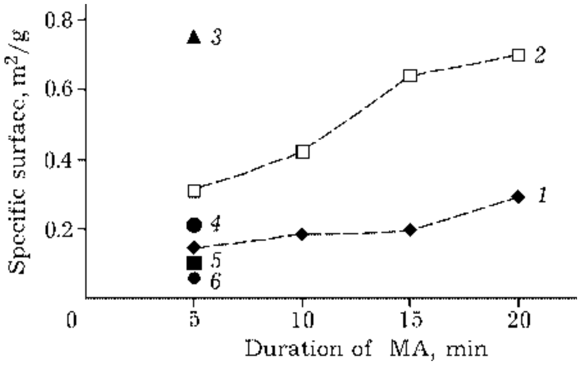

Fig. 1. Dependence of specific surface of samples on time of MA for magnesium mechanical alloys with inorganic salts: *1* – Mg–5 % NaF, *2* – Mg–10 % NaF, *3* – Mg–5 % NaCl, *4* – Mg–5 % $CrCl_3$, *5* – Mg–5 % $(NH_4)_2CO_3$, *6* – Mg–5 % MgF_2.

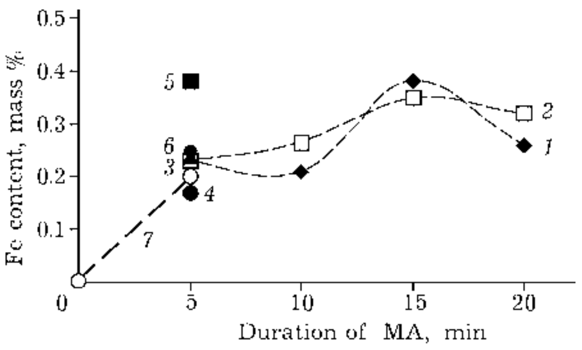

Fig. 2. Dependence of iron mass fraction on time of MA in the samples of magnesium mechanical alloys with inorganic salts: *1* – Mg–5 % NaF, *2* – Mg–10 % NaF, *3* – Mg–5 % NaCl, *4* – Mg–5 % $CrCl_3$, *5* – Mg–5 % $(NH_4)_2CO_3$, *6* – Mg–5 % MgF_2, *7* – Mg without salt additives.

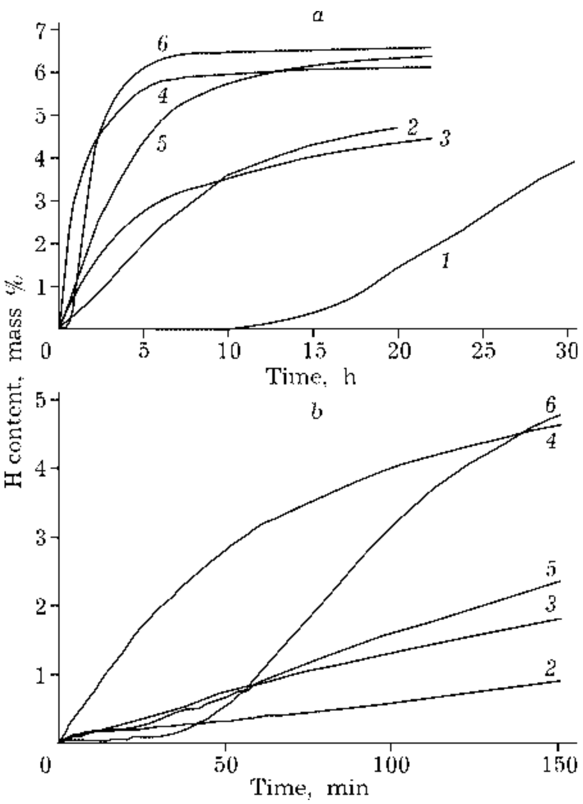

Fig. 3. Kinetics of hydrogenation in the first cycle: *a* – long-term experiment; *b* – the beginning of hydrogenation. Magnesium was produced by cathode sputtering [7], close-cut fraction of 20 mm *(1)*; the mechanical alloys were produced during 5 min of MA *(2–6)*: Mg–5 % $(NH_4)_2CO_3$ (*2*), Mg–5 % MgF_2 (*3*), Mg–5 % $CrCl_3$ (*4*), Mg–5 % NaF (*5*), Mg–5 % NaCl (*6*). Conditions: $T = 623$ K, $P_{H_2} = 1.5$ MPa.

hydrogenation process, but still it cannot be responsible for so significant acceleration of the reaction, especially in the first cycle (Fig. 3), as compared to ordinary magnesium samples that are characterized by sigmoid kind of kinetic curves and by the long induction period during the first hydrogenation. No any correlation is observed also between the iron content of samples and their hydrogenation rate.

The salts $(NH_4)_2CO_3$ and MgF_2 turned out to be the least effective from all the salts that have been studied. Seemingly, MgF_2 action is limited to a mechanical disruption of integrity of a superficial oxide layer on magnesium and, together with iron impurity, this results in that hydrogenation starts with the maximum rate. However, such samples absorb a small amount of hydrogen owing to the relatively large size of magnesium particles.

In the case of $(NH_4)_2CO_3$, the starting rate of the first hydrogenation, despite a relatively higher content of iron in the sample (0.38 mass %), is even lower than is that for MA of Mg–MgF_2. Most likely, it is related to the adsorption of gas molecules on the surface of mechanical alloy particles, these molecules being formed as a result of ammonium carbonate decomposition. This hinders the dissociative adsorption of hydrogen and decreases the hydrogenation rate.

The greatest hydrogenation rate was observed on samples with $CrCl_3$ added. This case suggests not only the destruction of oxide layer on the magnesium surface, but also a catalytic action of $CrCl_3$ itself. However, the reduction of $CrCl_3$ by magnesium to form Cr clusters during the MA process is more likely, these clusters being capable to act as additional centres of hydrogen chemisorption.

Catalytic activity in reactions with hydrogen is not typical for the salts like NaF and NaCl, but they also modify the state of magnesium particle surface and affect thereby hydrogenation kinetics.

From evidence of X-ray diffraction analysis, NaCl reflexes are broadened as a result of MA and then are kept invariable upon the hydrogenation. Apparently, NaCl mechanically disturbs the oxide layer on the magnesium surface, but does not break it completely. As with pure magnesium [7], the kinetics of the first hydrogenation of Mg–NaCl mechanical alloy is controlled by the processes of formation of local sites of magnesium metallic surface and magnesium hydride nucleation on them. Nucleation proceeds more readily with partially disrupted oxide layer and the induction period is missing.

In the case of Mg–NaF MA, the broadened reflexes of NaF, which are present in the diffractograms upon MA, die out upon hydrogenation and the new ones arise instead of them that correspond to $NaMgF_3$ phase (Fig. 4). Formation of $NaMgF_3$ occurs supposedly because of NaF interaction with MgO or $Mg(OH)_2$. Integrity of the oxide layer is broken and the magnesium surface becomes exposed to hydrogen that is responsible for an acceleration of hydrogenation reaction during the first cycle. In addition, the possibility for

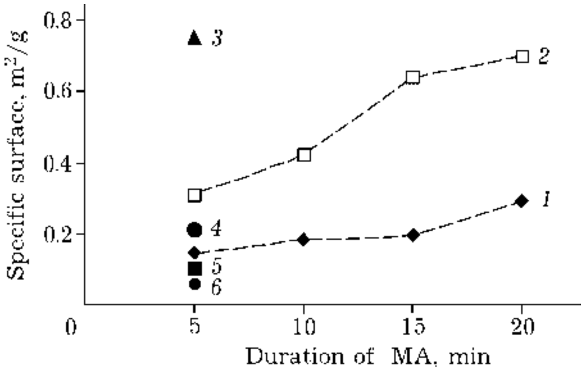

Fig. 4. Roentgenograms of Mg + 5 % NaF sample after 5 min of MA *(1)* and after hydrogenation *(2)*. Hydrogenation conditions: T = 623 K, P_{H_2} = 1.5 MPa, hydrogen content up to 0.69 %. **x** NaF; **o** NaMgF$_3$; the other peaks correspond to Mg or MgH$_2$ phases.

hydride fluoride of composition NaMgH$_2$F to form cannot be ruled out under these experimental conditions [8, 9], this compound being isostructural to NaMgF$_3$. These two compounds show very close parameters of unit cells [9, 10] and practically cannot be distinguished in the roentgenograms. H and F atoms in NaMgH$_2$F exhibit uniform distribution over the same crystallographic sites [9] that may bear witness to a facilitated diffusion of hydrogen within this phase and consequently to the facilitated delivery of hydrogen to magnesium surface through this phase.

Rather high hydrogenation and dehydrogenation rates were evidenced for all the studied Mg–salt mechanical alloys during the second and subsequent cycles (Fig. 5); the content of hydrogen was 5.5–6 mass % (except for Mg–MgF$_2$ and Mg–(NH$_4$)$_2$CO$_3$ mechanical alloys).

Comparison of hydrogenation activation energy E_a of pure magnesium (89–96 kJ/mol [11, 12]) with experimentally obtained E_a values for hydrogenation of the activated samples of mechanical alloys confirms the assumption of catalytic activity of CrCl$_3$. Hydrogenation activation energy of Mg–5 % CrCl$_3$ mechanical alloy was equal to (70 ± 2) kJ/mol and it turned out to be higher for Mg–5 % NaF, ((79 ± 2) kJ/mol). The value E_a of hydrogenation for Mg–5 % MgF$_2$ mechanical alloy that is virtually identical as compared to pure magnesium ((90 ± 4) kJ/mol) testifies that MgF$_2$ exhibits no catalytic activity in magnesium hydrogenation.

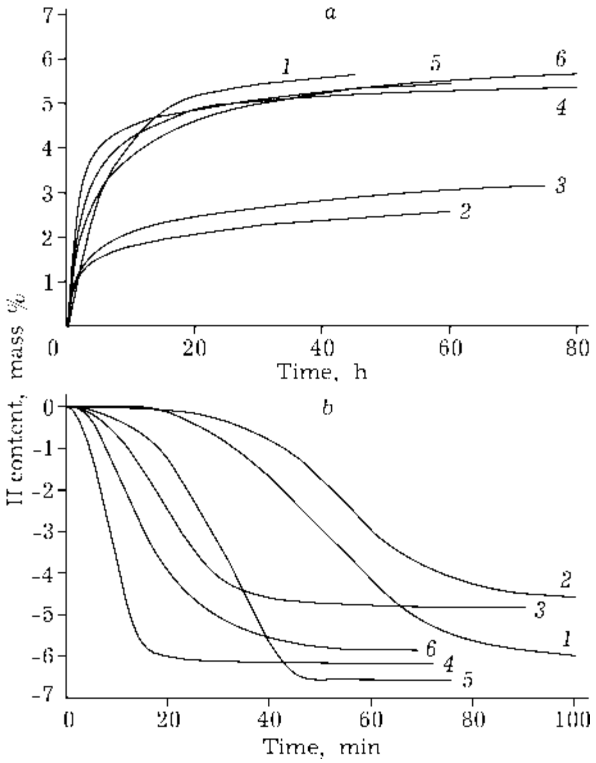

Fig. 5. Kinetics of hydrogenation (at T = 623 K, P_{H_2} = 1.5 MPa) (*a*) and dehydrogenation (at T = 623 K and P_{H_2} = 0.1 MPa) (*b*) for the mechanical alloys activated by cycling: Mg (*1*), Mg–5 % (NH$_4$)$_2$CO$_3$ (*2*), Mg–5 % MgF$_2$ (*3*), Mg–5 % CrCl$_3$ (*4*), Mg–5 % NaF (*5*), Mg–5 % NaCl (*6*).

Creating mechanical alloys that are more complex, for example, those including salt and catalytic metal, brings about further enhancement of their properties as regards the processes of hydrogen accumulation.

CONCLUSIONS

Thus, mechanical alloying of magnesium with admixtures of inorganic salts leads to grinding of metal and simultaneous modification of its surface that enhances kinetic characteristics of hydrogenation processes. It was found that the effect of various salts is different and depends on their nature. Development of optimum formulations for mechanical alloys doped with salts may cause significant improvement of kinetic characteristics for hydrogenation of magnesium-based alloys and, probably, the alloys of other hydride-generating metals as well.

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