# \_PROCEEDINGS OF THE CONFERENCE "PHYSICAL CHEMISTRY IN RUSSIA AND\_\_ BEYOND: FROM QUANTUM CHEMISTRY TO EXPERIMENT" (CHERNOGOLOVKA)

# Features of the Hydrogenation of Magnesium with a Ni-Graphene Coating

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Received July 22, 2019; revised July 22, 2019; accepted September 17, 2019

**Abstract**—The kinetics of the hydrogenation of magnesium composites with graphene-like material (GLM) on which nickel particles are deposited (Ni/GLM) and dehydrogenation of  $MgH_2+Ni/GLM$  composites is studied. The mechanism of the reactions is revealed using the obtained results and the mathematical processing of curves with the Avrami–Erofeev equation. It is found that Ni/GLM considerably accelerates the hydrogenation of Mg and the decomposition of MgH<sub>2</sub> in the composite. The hydrogen-accumulating Mg+Ni/GLM composite is shown to have cyclic stability with rapid and virtually complete reversible hydrogenation.

*Keywords:* hydrogen, magnesium, carbon, magnesium hydride, hydrogen-accumulating composite, Avrami–Erofeev equation

DOI: 10.1134/S0036024420050222

## INTRODUCTION

Magnesium hydride is a promising material for hydrogen storage, due to its high reversible weight  $(7.6 \text{ wt } \% \text{ H}_2)$  and volumetric (110 g H/L) hydrogen capacity [1-3]. We have patented ways of obtaining a nickel-graphene catalyst for hydrogenation [4] and hydrogen-accumulating materials based on magnesium [5]. The originality of our way of forming magnesium systems is the mechanochemical treatment of magnesium with a Ni-graphene composite in hydrogen. This approach eliminates the main disadvantages of magnesium as a hydrogen-accumulating material: (1) the bad kinetics of hydrogenation because of the formation of a continuous hydride layer through which hydrogen atoms diffuse poorly; (2) the high temperature of hydrogenation and dehydrogenation: (3) the sintering of small magnesium particles during the thermal decomposition of hydride; (4) and the weak heat capacity of magnesium hydride, which hinders the creation of a metal hydride accumulator [1, 2, 6]. A composite consisting of submicronic magnesium particles with a Ni-graphene coating has good kinetics of hydrogenation, due to the presence of catalytic Ni particles and small Mg/MgH<sub>2</sub> particles on the surface, and the high heat capacity resulting from the

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graphene-like structure of the carbon material. Composite particles also do not sinter during  $MgH_2$  dehydrogenation, due to the carbon coating.

Studying the kinetics and mechanism of solidphase chemical reactions in metal—hydrogen systems is of special interest, since it yields results allowing targeted searches for materials with improved hydrogensorption characteristics. The aim of this work was to investigate the kinetics of the reversible hydrogenation of magnesium particles with a Ni-graphene coating in order to identify the limiting stages and the mechanism behind the process.

## **EXPERIMENTAL**

To prepare our composites, we used magnesium powder with particle sizes of 0.5-1 mm and a nickelgraphene catalyst obtained by combined reduction of Ni(II) and graphite oxide according to the procedure described in [6, 7]. This was a graphene-like material (GLM) with a specific surface area of  $600-650 \text{ m}^2/\text{g}$ , on which Ni nanoparticles (25 wt %) were deposited uniformly. The MgH<sub>2</sub> composites with 10 wt % of the Ni-graphene catalyst (MgH<sub>2</sub>+Ni/GLM) were made via high-energy grinding in a Pulverisette-6 ball mill at an initial hydrogen pressure of 25 atm. Hydrogen (99.9999% purity) from a laboratory metal hydride



**Fig. 1.** (Color online) (a) SEM micrograph and (b) XRD patterns of the composite obtained in the (1) first and (2) after ten cycles of hydrogen desorption—sorption.

accumulator was used. The volume of the steel grinding bowl was 80 mL; the ratio of the weight of steel balls to the weight of the material being ground was 40/1; the mill rotation speed was 500 rpm; and the grinding time was 10 h.

The phase composition of the resulting composites were analyzed via powder X-ray diffraction (XRD) using DRON-UM2 X-ray diffractometer (Cu $K_{\alpha}$  radiation). The microstructure of the samples was studied using Zeiss LEO SUPRA 25 scanning electron microscope.

Kinetic hydrogen desorption and sorption curves were measured on a Siverts-type laboratory apparatus in the temperature range of  $300-350^{\circ}$ C and the pressure range of 1.2-5.5 atm. The hydrogen pressure was 1.2 and  $\leq 1.3$  atm at the beginning and end of dehydrogenation, respectively, so the conditions of the process were close to isobaric. The experimental data were mathematically processed using the Avrami–Erofeev kinetics equation in the form

$$\alpha = A(1 - \exp[-(kt)^n]), \qquad (1)$$

where  $\alpha$  is the fraction of the reacted phase at moment in time *t*; *A* is the asymptotic  $\alpha$  value when  $t \rightarrow \infty$ ; *k* is the rate constant (its reciprocal is the characteristic reaction time), and *n* is the Avrami factor.

The samples of  $MgH_2$  and  $MgH_2 + 10$  wt % GLM ( $MgH_2+GLM$ ) prepared similarly to the  $MgH_2+Ni/GLM$  composites were used as reference objects.

## **RESULTS AND DISCUSSION**

According to the XRD data, the composites obtained in synthesis contained two crystalline phases

of magnesium hydride:  $\alpha$ -MgH<sub>2</sub> with a rutile-type structure and  $\gamma$ -MgH<sub>2</sub> with an orthorhombic structure. Figure 1 presents micrograph and the XRD pattern of the composite. The positions of diffraction peaks (Fig. 1b) correspond to the Bragg reflections of  $\alpha$ -MgH<sub>2</sub> and  $\gamma$ -MgH<sub>2</sub> phases with unit cell parameters a = 0.4515 nm, c = 0.3019 nm and a = 0.4526 nm, b =0.5448 nm, c = 0.4936 nm, respectively [8]. The  $\gamma$ -MgH<sub>2</sub> phase is known to be metastable under the conditions of hydrogen sorption-desorption cycles, and as we showed in [8, 9], disappears after the first step of dehydrogenation. It follows from the scanning electron microscopy (SEM) data (Fig. 1a) that the particle size of magnesium hydride in the synthesized  $MgH_2+GLM$  and  $MgH_2+Ni/GLM$  composites ranged from 500 nm to several µm and did not change sappreciably during cycles of hydrogen desorption and sorption [8, 9], while the size of coherent scattering domains (CSDs) grew for the  $\alpha$ -MgH<sub>2</sub> phase. After the tenth cycle of hydrogen sorption, the size of the CSD in the 110 direction is thus 30-40 nm (initial value, 7–10 nm; Fig. 1b). In the MgH<sub>2</sub> reference sample without additives, the particle size grows abruptly during cycling, which indicates their sintering. We may assume that introducing the GLM into the composites prevents the sintering of submicronic magnesium particles under the conditions of the thermal decomposition of hydride.

The Avrami–Erofeev equation that we used to study the mechanism of hydrogen sorption and desorption by the composites has been actively used in the kinetic modeling of the reactions of the hydrogenation and dehydrogenation of hydrogen-accumulating materials based on magnesium [10–16]. Phase transformation reactions in metal–hydrogen systems are known [14] to be controlled by mechanisms of



**Fig. 2.** (Color online) (a) Hydrogen desorption curves at 350°C and 1 atm for samples of (1) MgH<sub>2</sub>, (2) MgH<sub>2</sub>+GLM, and (3) MgH<sub>2</sub>+Ni/GLM; (b) hydrogen sorption curves at 5.5 atm and 300°C for samples of (1–3) Mg and (4–6) MgH<sub>2</sub>+Ni/GLM in the (1, 4) first, (2, 5) fifth, and (3, 6) tenth hydrogenation cycles; (c) (1) curve 5 from panel (b) and its approximation by the Avrami–Erofeev equation with (2) one and (3) two summands in the right side; (d) dehydrogenation curves for the MgH<sub>2</sub>+Ni/GLM composite at temperatures of (1) 320, (2) 330, (3) 340, and (4) 350°C.

both nucleation and growth (N-G) and diffusion (DF). The contribution from these complementary mechanisms is determined by numerical value *n* of the Avrami factor: if  $0.5 \le n < 1.0$ , the reaction is controlled only by diffusion; if  $2.5 \le n \le 4.0$ , the reaction proceeds exclusively by the N-G mechanism; and if *n* ranges from 1.0 to 2.5, both mechanisms work in parallel. For instance, when n = 1 there is both diffusion

determined by geometry and nucleation occurring at grain boundaries [15].

Figure 2 shows the kinetic hydrogen desorption and sorption curves for composites with Ni/GLM additives and the reference samples. It is seen that all desorption curves and the sorption curves for the Mg sample without additives is well approximated by Eq. (1). The situation is more complicated for the

Table 1. Results from approximating the kinetic dehydrogenation curves of the composites (Fig. 2a)

Curve	Sample	A	$k, \min^{-1}$	п	$R^2$
1	MgH <sub>2</sub>	0.8836(2)	5.817(2)	2.520(3)	0.99983
2	MgH <sub>2</sub> +10% GLM	0.8820(4)	4.22(1)	1.241(3)	0.99887
3	MgH <sub>2</sub> +10% Ni/GLM	0.8847(6)	2.507(9)	0.962(5)	0.99355

**Table 2.** Results from approximating the kinetic hydrogenation curves of Mg without additives (Fig. 2b, curves 1-3)

Curve	Cycle	A	k, min <sup>-1</sup>	п	$R^2$
1	1	0.805(1)	9.40(2)	1.161(2)	0.99964
2	5	0.777(2)	13.74(5)	1.384(3)	0.99969
3	10	0.741(2)	15.98(5)	1.428(2)	0.99984

curves of hydrogen sorption by Mg+GLM and Mg+Ni/GLM composites, and good approximation was achieved with Eq. (1) whose right side consists of at least two summands with different sets of parameters:  $A_1$ ,  $k_1$ ,  $n_1$  and  $A_2$ ,  $k_2$ ,  $n_2$ . Results from that approximation are listed in Tables 1–3.

The curves in Fig. 2a and the data in Table 1 show that introducing such additives as GLM or Ni/GLM alter the dehydrogenation reaction mechanism in comparison to MgH<sub>2</sub> without additives. The Avrami parameters are remarkably different. In addition, composites with additives (Fig. 2a, curves 2 and 3) exhibit substantially higher rates of transformation at the beginning of dehydrogenation. When n = 2.5, dehydrogenation of the MgH<sub>2</sub> sample without additives proceeds according to the N-G mechanism. For the composite with GLM additives, Avrami factor n =1.25 means that the nucleation reaction is of zero order; for the composite with Ni/GLM additives (n = 1) there is nucleation at grain boundaries. For the last two processes, it is very likely the contribution from diffusion is the factor limiting the total rate of the processes, as was assumed in [17]. The characteristic reaction time becomes very short (less than 6 min for MgH<sub>2</sub>). Introducing GLM additives slows it by approximately 30%, and introducing Ni/GLM slows it by approximately another 170%.

In the dehydrogenation of MgH<sub>2</sub> without additives, the particles of the forming magnesium phase sinter during the formation of agglomerates, deteriorating the kinetics of hydrogen absorption in the subsequent hydrogenation cycles appreciably (Fig. 2b, curves I-3). As is seen from Table 2, limiting  $\alpha$  value for the transformation of Mg into MgH<sub>2</sub> falls from >0.8 to 0.75 as a result of the cycling (this is a typical value of Mg hydrogenation at lower temperatures when MgH<sub>2</sub> is not subjected to ball milling [18]) after ten dehydrogenation—hydrogenation cycles. The characteristic reaction time and the Avrami factor grow from 9 to >15 min and from 1.2 to 1.4, respectively.

As we showed in [6], GLM layers cover the magnesium hydride particles during mechanochemical treatment, preventing their agglomeration and sintering during dehydrogenation. As a result of this and the catalytic effect of Ni nanoparticles, the rate of hydrogen absorption by composites with Ni/GLM additives is high in both the first and subsequent cycles of repeated hydrogenation (Fig. 2b, curves 4-6). The limiting  $\alpha$  value grows to 0.92–0.95 (equaling the sum  $A_1 + A_2$  in Table 3), and 80% Mg hydrogenation is reached in just 2–4 min. The considerable difference between hydrogenation reaction rate constants  $k_1 \ge k_2$ for the two summands in the right side of the Avrami-Erofeev equation, which describes the time dependence of  $\alpha$ , indicates that hydrogenation consists of two stages: rapid and slow.

Note that the observed character of changes in the kinetic parameters of repeated hydrogenation for the investigated samples is similar to those for MgH<sub>2</sub>– TiH<sub>2</sub> nanocomposites obtained as a result of the ball milling of Mg + Ti in hydrogen [12]. Performing ten desorption—sorption cycles gradually reduces the contribution from the slow stage  $A_2/(A_1 + A_2)$  with a simultaneous drop in the characteristic reaction time for the rapid stage (from 36 to 24 s) and an increase in the characteristic reaction time (from 5 to 15 min) for the slow one. Avrami factors for the rapid stage do not change appreciably during the cycling (n = 1.3), while the slow stage exhibits an increase in n, from 0.5 (diffusion-controlled process) to 1.2 (mixed type: N-G and DF).

Figure 2d shows the kinetic dehydrogenation curves for the MgH<sub>2</sub> composite with Ni/GLM additives at four different temperatures in the range 320– 340°C, and rate constants k are given in Table 4. The linear approximation of the lnk dependence on 1/Tyields the energy of activation for dehydrogenation:  $E_a = 76 \pm 3$  kJ (mol H<sub>2</sub>)<sup>-1</sup>, which is notably less than the reported energies of activation for the dehydrogenation of magnesium-based materials. However, it is worth noting that to calculate  $E_a$  correctly, the k values

Curve	Cycle	Rapid stage		Slow stage			4 + 4	$A_2$	D)	
		$A_1$	$k_1, \min^{-1}$	$n_1$	$A_2$	$k_2, \min^{-1}$	<i>n</i> <sub>2</sub>	$A_1 + A_2$	$\overline{A_1 + A_2}$	<i>K</i> <sup>2</sup>
4	1	0.647(7)	0.566(1)	1.215(8)	0.270(8)	5.4(1)	0.68(2)	0.92	0.29	0.99968
5	5	0.764(3)	0.474(1)	1.33(1)	0.188(7)	14.3(9)	0.50(2)	0.95	0.20	0.99972
6	10	0.7860(8)	0.422(1)	1.261(3)	0.148(4)	14.8(4)	1.24(3)	0.93	0.16	0.99937

**Table 3.** Results from approximating the kinetic hydrogenation curves of Mg+Ni/GLM composites (Fig. 2b, curves 4-6)

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**Table 4.** Dehydrogenation rate constants for  $MgH_2+Ni/GLM$ composites at different temperatures

Curve	T, ℃	k, min <sup>-1</sup>	$P_0$ , atm	$p(T)/p(T = 350^{\circ}C)$	$k_{\rm cor},$ min <sup>-1</sup>
1	320	0.3359	3.10	0.62	0.2089
2	330	0.4196	3.98	0.76	0.3196
3	340	0.5342	5.07	0.89	0.4739
4	350	0.7054	6.41	1.00	0.7054

*k* values were obtained by approximating the kinetic curves in Fig. 2d;  $k_{cor}$ , after multiplying by the correction factor.  $P_0$  is the equilibrium pressure;  $p(T)/p(T = 350^{\circ}\text{C})$  denotes coefficients of correction. The real pressure for all curves is P = 1.25 atm.

obtained from a series of isobaric experiments must be multiplied by a temperature-independent correction coefficient in the form of the ratio  $p(T)/p(T=350^{\circ}\text{C})$ , which accounts for thermodynamic characteristics of the considered composite-hydrogen system: the temperature-dependent value of the equilibrium hydrogen pressure  $P_0$  in the system. For diffusion-controlled dehydrogenation with the investigated material (Fig. 2a, curve 3), it was proposed in [17] that the following expression be used for p(T): p = T(1 - T) $(P/P_0)^{1/2}$ ). Introducing this correction for our k values yields  $E_a = 124 \pm 1 \text{ kJ} \text{ (mol H}_2)^{-1}$ , which is consistent with the data of other works (e.g., [19-22]) where similar systems were examined: the energy of dehydrogenation activation is 121.3 kJ (mol  $H_2$ )<sup>-1</sup> for MgH<sub>2</sub> + 10% NiCl<sub>2</sub> (compared to 160 kJ (mol H<sub>2</sub>)<sup>-1</sup> for the dehydrogenation of pure MgH<sub>2</sub> [18]).

#### CONCLUSIONS

Adding GLM, and especially Ni/GLM, greatly increases the rates of hydrogen sorption and desorption in magnesium composites. The dehydrogenation reaction rate constant grows by 1.4 and 2.3 times for Mg + GLM and Mg + Ni/GLM, respectively, compared to that of Mg without additives. The hydrogenation rate constant for composites with Ni/GLM additives is 15-37 times higher than the one for the sample without additives. For all processes, the effect of additives is also expressed as a substantial reduction in the Avrami factor, testifying to the geometric constraint on the regions of nucleation (with the rate of this process growing) and the contribution from H atom diffusion becoming the limiting step. Adding Ni/GLM improves the cyclic stability as well. It provides rapid and almost complete repeated hydrogenation for at least ten cycles. During cycling, the contribution from the slow process to the kinetics of hydrogen sorption diminishes without reducing the hydrogen capacity of the composite.

#### ACKNOWLEDGMENTS

Our physicochemical studies of the materials were performed using the facilities at the Institute of Problems of Chemical Physics and scientific organizations of the South Africa and Norway.

#### FUNDING

M.V. Lototskyy is grateful to the Department of Science and Technology (DST, project KP6–S01/HySA) and the National Research Foundation of South Africa (NRF, grant 109092). V.A. Yartys would like to thank the Research Council of Norway (RCN; project 285146).

This work is supported by BRICS STI Framework Programme (project 064-RICS-MH). Russian co-authors are grateful to the Ministry of Science and Higher Education for the financial support (agreement no. 14.613.21.0087, unique identifier RFMEFI61318X0087).

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Translated by L. Chernikova