INFLUENCE OF GRAPHITE UPON THE KINETICS OF HYDROGEN SORPTION IN $Mg@Mg_{17}Al_{12}$

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Abstract

Influence of graphite addition to the ball-milling charge composed of Mg splinters and $Mg_{17}Al_{12}$ particles upon the hydrogen sorption was investigated at sorption temperature 623 K. Measurements were carried out by Sieverts method. Graphite facilitates the ball-milling: It prevents re-agglomeration of crushed particles into large secondary particles. It also suppresses sticking the milled material to the balls and walls of the milling jar. It was found that an increase of carbon concentration up to a certain limit c_L lying between 14 and 23 wt. % C, carbon increases both the absorption and the desorption rates and hydrogen storage capacity. Above c_L, carbon causes a considerable decrease in HS capacity, which spoils the application potential of $Mg@Mg_{17}Al_{12}/C$. Crystallite size of the material under study, obtained by XRD, is in the order of tens of nm.

Keywords: Hydrogen storage, Mg alloys, graphite

1. INTRODUCTION

A great effort has been devoted to the improvement of hydrogen storage (HS) parameters in Mg-based alloys [1]. These alloys are prospective for HS, due to their relatively high HS capacity, low specific gravity and moderate price. The magnesium hydride MgH_2 is the principal hydrogen storing phase in these materials (HSA). Contrary to high thermodynamic stability of MgH_2, which causes too high sorption temperatures (typically above 523 K) and lazy sorption kinetics, the Mg-based HS alloys are still in the focus of interest of many research groups [2,3]. Summarizing recent development (for reviews see, e.g. in [1,4]), it can be concluded that not too significant achievements were reached in decreasing of MgH_2 stability by alloying up to now. It is believed that this originates in too low formation enthalpy of MgH_2. Alloying elements are *expelled* from the alloy during the MgH_2 formation and lose their beneficial effect upon the sorption by forming new - from the HS point of view ineffective - crystalline phases.

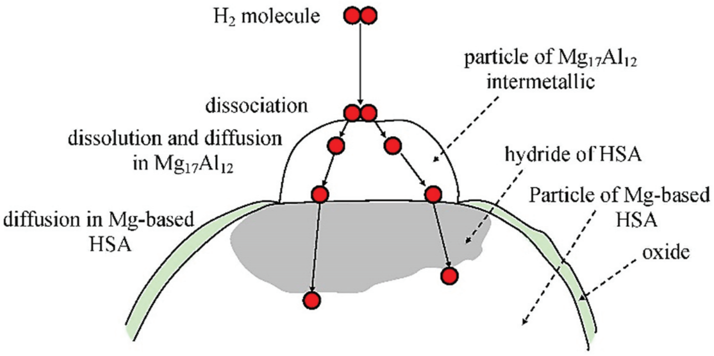


Figure 1 Catalyzing $Mg_{17}Al_{12}$ particle on the surface of HS grain - schematically

It seems that much more significant effect has been reached by nano-sizing and catalysis [5,6]. Nano-sizing led to a substantial decrease in hydrogen diffusion length and therefore, to an improvement of hydrogen sorption kinetics. Catalysis of the hydrogen sorption is a complex process and not all experimental results reported in the literature are understood in detail [7]. Hence, the character of the research in this field is *heuristic*. It was observed that it is advantageous to store hydrogen in relative large grains of Mg (or Mg-based alloy) that retain high HS capacity. It is neccessary, however, provide these grains - *storage* *tanks* - with sufficiently effective entrance/exit gates for easy hydrogen transmission. Particles of catalyzing phase located on the surface of larger grains can act as the gates for hydrogen (**Figure 1**).

Overall effect of catalyzing particles involves easy dissociation of H_2 molecule on its surface, rapid diffusion of H atoms through the particle and transfer into the HS phase (**Figure 1**). At present, it is impossible to judge the convenience of $Mg_{17}Al_{12}$ with respect to all the above mentioned demands due to lack of experimental data. Sorption behavior of $Mg_{17}Al_{12}$ itself has been studied, e.g. in [8-11]. The authors reported that $Mg_{17}Al_{12}$ in hydrogen can *reversibly* decompose according to the following scheme [8]

$$Mg_{17}Al_{12} + 9\ H_2 \leftrightarrow 9\ MgH_2 + 4\ Mg_2Al_3 \qquad (1)$$

$$Mg_2Al_3 + 2\ H_2 \leftrightarrow 2\ MgH_2 + 3\ Al. \qquad (2)$$

The present paper contributes to investigation of hydrogen sorption kinetics in $Mg@Mg_{17}Al_{12}$ at the temperature of 623 K (operation temperature of pure MgH_2). Varied grades of graphite additions are tested with respect to the morphology and sorption kinetics of $Mg@Mg_{17}Al_{12}$.

2. EXPERIMENTAL

Four alloys (**Table 1**) composed of Mg with particles of $Mg_{17}Al_{12}$ were prepared by ball-milling (BM). Mg was used in the form of splinters, spectral, pure graphite was added in the form of fine powder and small particles of $Mg_{17}Al_{12}$ were pre-prepared by induction melting of pure components and crushing in the mortar. The mixture for BM was composed of Mg: 3g, $Mg_{17}Al_{12}$: 0.38 g + C according to composition in the **Table 1**) The samples were ball-milled using *Fritsch- Pulverisette 6* (450 rpm, 10min milling / 50min cooling - 14 times repeated; mass ratio of the balls to the charge was about 240). Powder samples were taken out of the BM jar in an Ar protective atmosphere. The mass of powder samples for the sorption experiments was about 150 mg. The samples were pre-annealed at 633 K for 2 hours.

Table 1 Carbon concentration c_C in experimental alloys and mean grain size *d* after BM

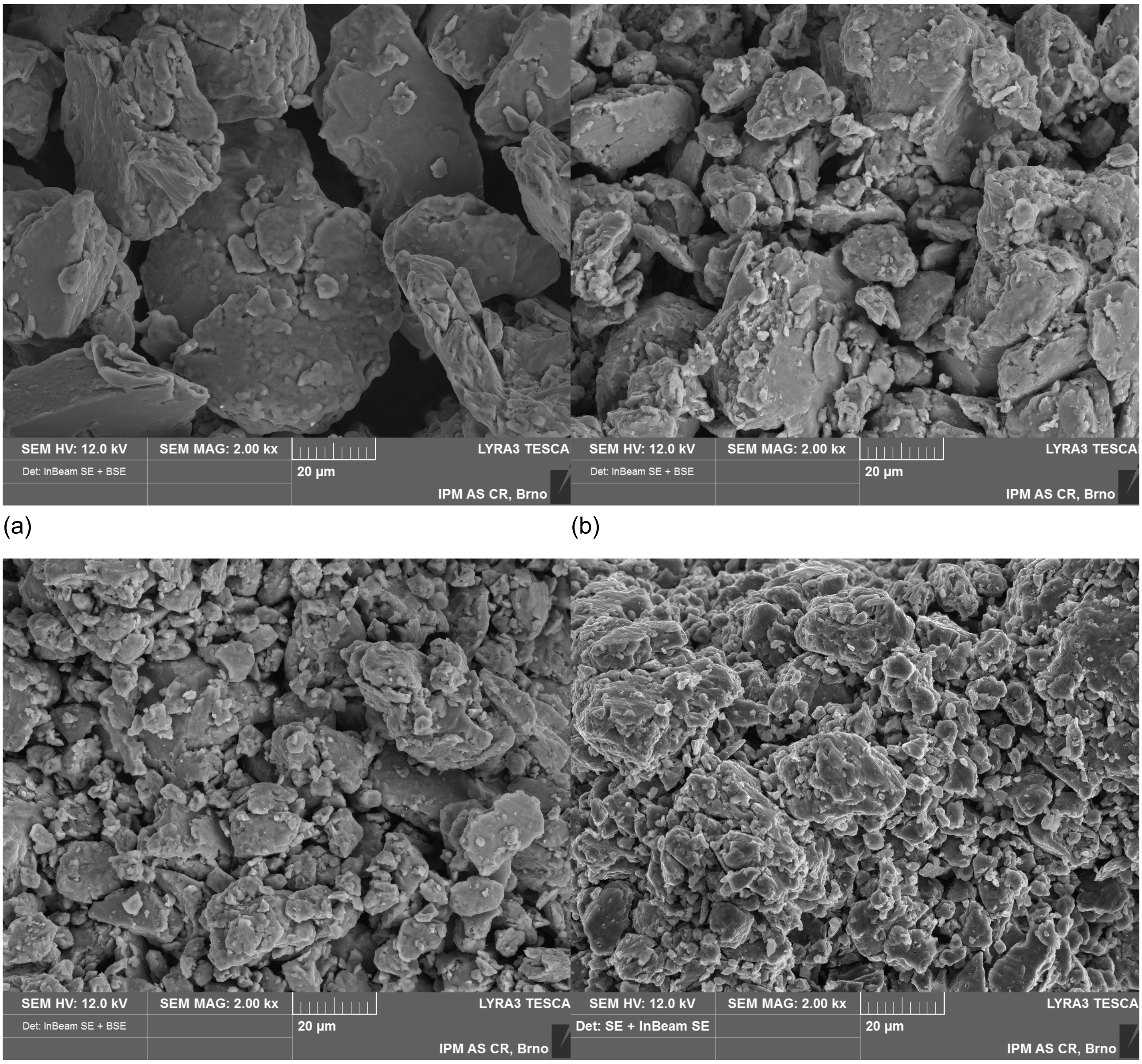
ALLOY	c_C	*d*
	wt. % C	μ*m*
A1	0	38
A2	7	20
A3	14	13
A4	23	9

Hydrogen sorption kinetics was studied using Sieverts-type gas sorption analyzer *PCT-Pro* Setaram Instrumentation. The absorption and desorption curves were measured at temperature 623 K and under hydrogen pressure between 2.5 (absorption) and 10^{-3} (desorption) MPa. The purity of both hydrogen and helium (calibration gas) was 6N. All manipulations of the milled powder was done in the glove box in protective Ar atmosphere.

3. RESULTS AND DISCUSSION

Small fraction of powder samples before and after the sorption experiment was used for the SEM observation. It is obvious in **Figure 2** that increasing content of graphite in the milling charge caused a decrease in average grain size as it is listed in **Table 1**, where the values of *d* are listed irrespective of phase composition of particles. During the cycling experiment, the grains decay due to mechanic stress originating in repeated phase transition. It can be seen in **Figure 3** that relatively great grains in A1 start to decay at the beginning, and turn to a conglomerate of much finer particles after the cycling (typically 10 sorption cycles).

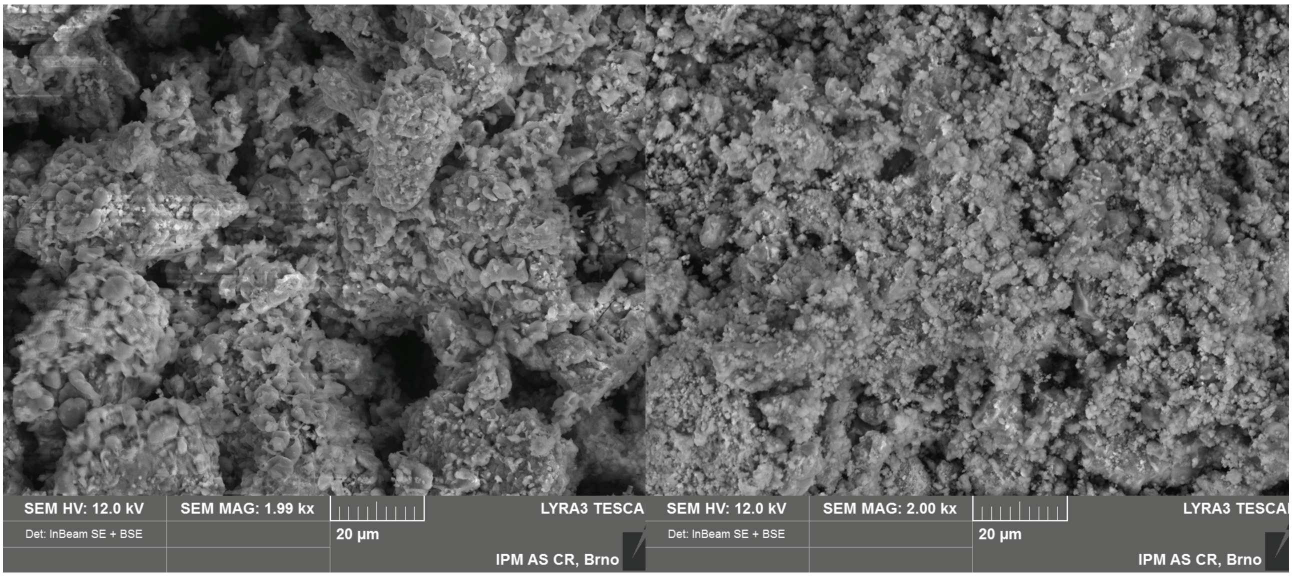
Beneficial effect of graphite (the refining of the grain size), however, cannot be substituted by cycling refinement: XRD measurements imply that certain fraction (about 1 wt. %) of Mg phase in the form of relatively great particles (in the order of units of μm) survives in originally carbon-free alloy even after cycling. Two XRD patterns shown in **Figure 4** document the much more effective refining effect of graphite in comparison with refining by cycling of coarse-grained alloy A1 (the greater width of diffraction lines indicate small particles). Rietveld analysis revealed that the size of Mg particles that took part in repeated hydrogen charging in alloy A1 (diffraction domains) was about 73 nm and average size of domains in $Mg_{17}Al_{12}$ particles was about 28 nm. Moreover, in the A1 remained about 1 wt. % of Mg particles, which size was about 3.2 μm. In alloy A4, however, the average size of Mg and $Mg_{17}Al_{12}$ particles was 17 nm and 7 nm, respectively already before the cycling.



(a) (b)

(c) (d)

Figure 2 Alloys 1 - 4 (a - d, respectively) after the BM



(a) (b)

Figure 3 ALLOY I after 4 sorption cycles (a) and after 10 cycles (b) 0/25/350C

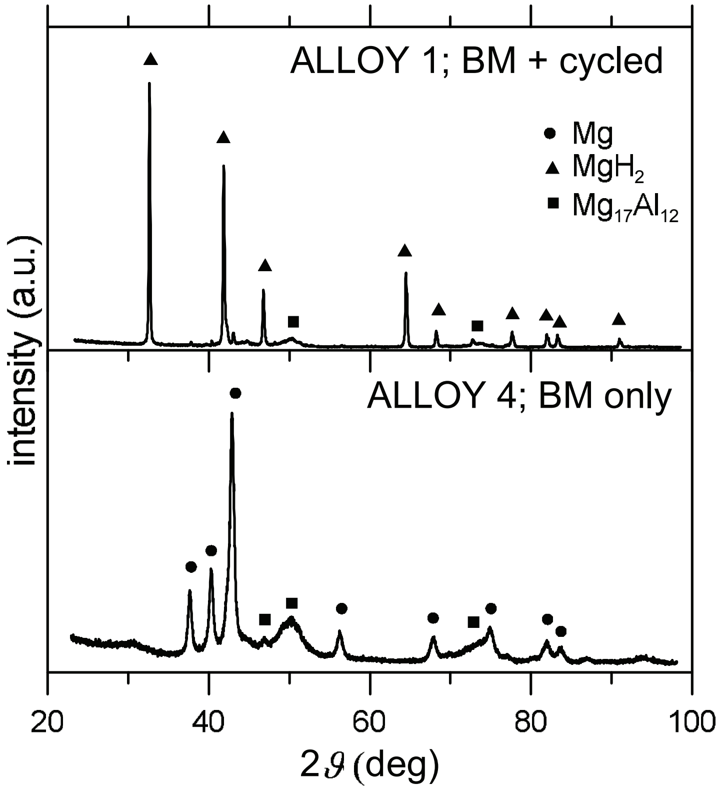


Figure 4 Example of XRD pattern obtained with the use of *X'Pert Pro MPD* device using CoK_{α} radiation

Distribution of carbon over the surface of particles was almost uniform over each of the both phases; the $Mg_{17}Al_{12}$ phase seems to be covered slightly more intensively than the Mg phase. This can be seen in concentration maps in **Figure 5**, that - at the same time - support the presumed morphology depicted schematically in **Figure 1**.

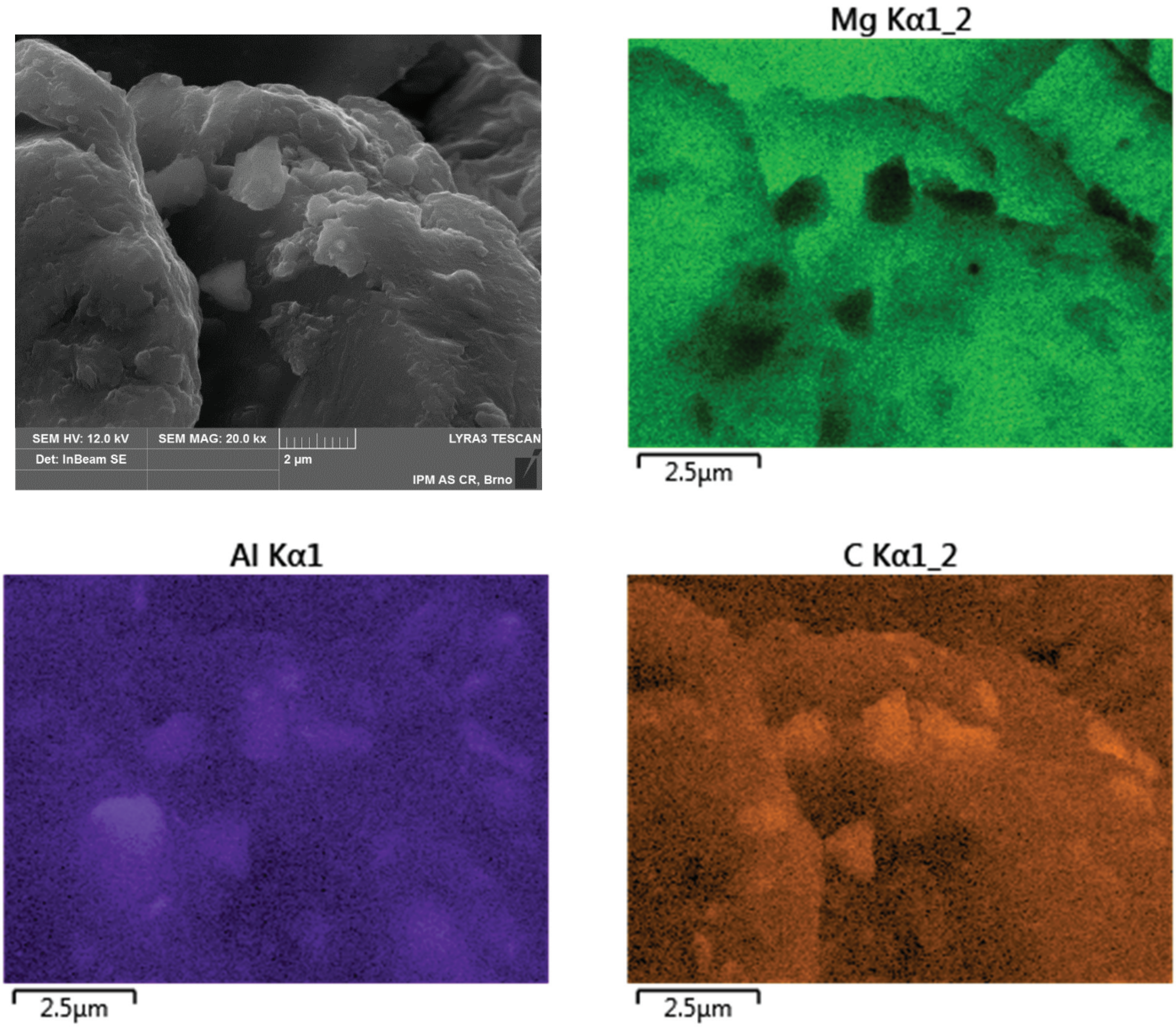


Figure 5 Concentration maps - Alloy A4

Experimental alloys were subjected to hydrogen charging/de-charging cycles. An example of cyclic curve is plotted in **Figure 6**.

It can be seen that there is a certain scatter in kinetics and ultimate carbon content in subsequent cycles due to non-homogeneity of small samples (hundreds of milligrams). It is illustrated that the first absorption to the ultimate carbon concentration takes more time than the following ones. The comparison of this initial (formation) kinetics for all experimental alloys is shown in **Figure 7a**. It is clear that the higher content of graphite (and smaller average grain size) the shorter time is needed to hydride formation. This rules also for following cycles (**Figures 7b. c**), but the kinetics is much faster.

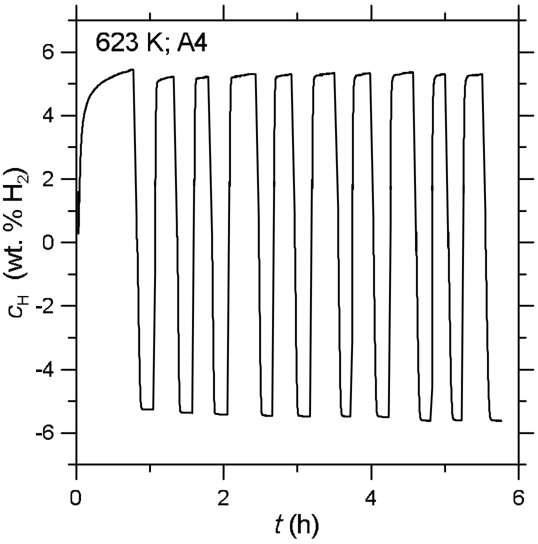


Figure 6 Cycling of alloy A4

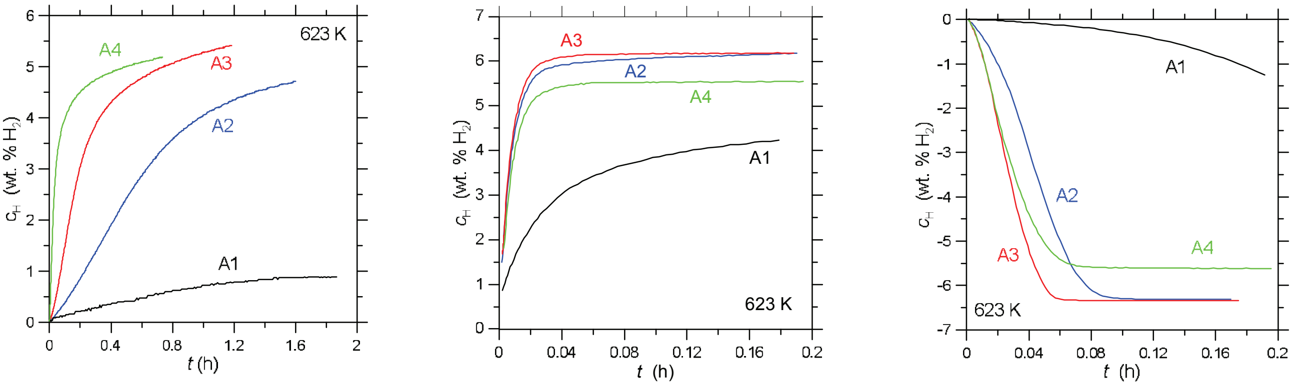


Figure 7 Kinetics of initiation (the first kinetic cycle) - (a) and kinetics of H_2 absorption - (b) and desorption - (c) in alloys A1 - A4 after cycling

It is also obvious in **Figure 7a-c** that carbon concentration exceeding 14 wt. % led to a decrease in HS capacity. This may originate in too much carbon that starts to restrict relative fraction of the phase that can storage hydrogen (Mg).

4. CONCLUSION

Graphite added to BM charge refines the mean grain size of milled alloys Mg@$Mg_{17}Al_{12}$ and improves the hydrogen sorption kinetics. The carbon content above 14 wt. %, however, decreases the HS capacity. Disproportionation according to **Equations 1, 2** was not observed at the experimental temperature of 623 K.

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