Investigation of hydrogen storage properties of magnesium based composites with addition of activated carbon derived from apricot stones

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Hydrogen absorption/desorption characteristics of the 95% Mg-5% activated carbon derived from apricot stones (ACA), 90% Mg-10% ACA and 85%-15% ACA, prepared by ball milling under argon, are studied. Hydriding process is proceeded at T = 573 K and 473 K and P = 1 MPa and dehydriding at T = 623 K and P = 0.15 MPa. The highest hydrogen absorption capacity of 6.13% is reached by the 95% Mg-5% ACA at 573 K and 1 MPa. The 90% Mg-10% ACA and 85% Mg-15% ACA reached 5.36% and 5.21% hydrogen absorption capacity, respectively. The absorption curves at T = 573 K and P = 1 MPa for the composites with 10 and 15% ACA are very similar. The threefold increase of the quantity of the activated carbon in magnesium does not affect substantially the desorption kinetics of the composites.

Key words: hydrogen storage; magnesium-based composites; ball milling; hydriding-dehydriding kinetics.

INTRODUCTION

Magnesium and magnesium-based compounds are promising candidate materials for hydrogen storage. Unfortunately magnesium requires preliminary activation, it is hard to attend its high theoretical hydrogen storage capacity (7.6%) and in addition it posses slow hydrogen sorption kinetics. A lot of investigations were performed in order to improve the hydriding-dehydriding kinetics of magnesium by preparing composites on its base applying the method of high-energy ball milling and containing different additives. Various substances have been used as additives to magnesium composites obtained by ball milling. For example, some transition metals [1–4], intermetallic compounds [5–9], oxides [10–14] and some carbon containing compounds as graphite [15–24], carbon black [15, 20], carbon nanotubes [15, 19, 20] and SiC [25]. Depending of the nature of the additive, which has been added to magnesium, their catalytic effect on hydriding and dehydriding processes may differ. In some cases, as in addition of carbon containing compounds to magnesium, the role is complex and not very well elucidated. Some authors consider that graphite protects magnesium from oxidation and acts as a process control agent during ball milling, due to its lubricant properties and the reason of improvement in hydrogen sorption kinetics of magnesium is the prevention of particles and crystallites growth.

From our previous study the composite Mg-Mg$_2$Ni-graphite reached high absorption capacity and showed very good kinetic characteristics at low temperatures [22]. The obtained results indicated that the presence of carbon-containing additive leads to improvement of hydrogen storage properties of magnesium. The aim of the present paper is to investigate the effect of activated carbon derived from apricot stones on the hydrogen sorption properties of magnesium. Moreover the role of the quantity of this additive on hydriding/dehydriding kinetics of magnesium would be also studied.

EXPERIMENTAL

Preparation of activated carbon

Activated carbons were prepared by steam pyrolysis from apricot stones. Raw material was heated up to carbonization temperature of 873 K, in a stainless-steel vertical reactor placed in a tube furnace. After cooling down to ambient temperature, the solid product was activated with water vapour at 973 K for 1 h. More detailed explanation of the preparation procedure of activated carbons can be found in [26]. The activated carbon was characterized by X-ray diffraction analyses with CuKα radiation and an Autosorb-1 instrument (model AS-IT) was used to determine the specific surface area.

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Preparation of composites based on magnesium

Mixtures of powdery Mg – 5, 10 and 15% activated carbon derived from apricot stones were ball milled in planetary monomill Fritsch Pulverisette 6 for 30 min under argon with rotation speed 200 rpm and 1:10 sample to balls weight ratio. All investigated composites were characterized by X-ray diffraction analyses with CuKα radiation and hydrogen absorption and desorption measurements were performed by Sivert's type apparatus. Hydriding was proceeded at 573 and 473 K and P = 1 MPa and dehydriding at 623 K and P = 0.15 MPa. The crystallite size was calculated according to the Scherrer formula using the Topas V3 programme [27].

RESULTS AND DISCUSSION

X-ray diffraction patterns of activated carbon derived from apricot stones are presented in Fig. 1. Some traces of MgO and $CaCO_3$ are detected. The nitrogen surface area of activated carbon is 960 m^2/g and was calculated by using the BET equation.
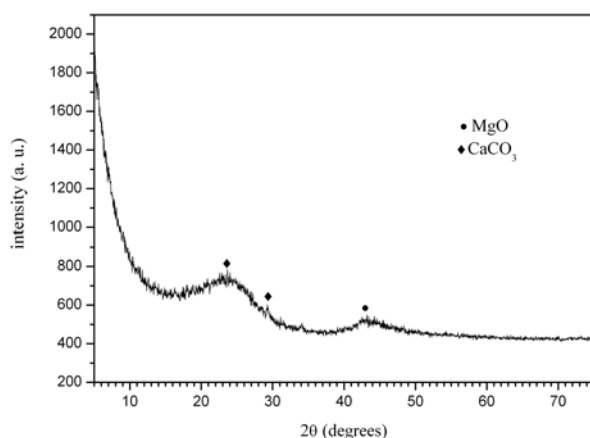

Fig. 1. X-ray diffraction patterns of the activated carbon derived from apricot stones.

X-ray diffraction patterns for the ball milled 30 min under argon composites are presented in Fig. 2. The detected phases are magnesium which is the main one and some small quantity of $Mg(OH)_2$. There is no substantial difference between the X-ray diffraction patterns of the composites with 5, 10 and 15% activated carbon derived from apricot stones.

The kinetic curves of hydriding for all composites and pure magnesium at temperature 573 K and pressure of 1 MPa are presented in Fig. 3. The addition of activated carbon derived from apricot stones has lead to improvement of hydrogen absorption kinetics and higher absorption capacity after 60 min of hydriding. The composite 95%Mg-5% ACA has reached the highest hydrogen absorption capacity. At the beginning of the process e.g. the

first 5 min all composites have practically the same rate of hydriding reaction. With advancement of the reaction the composite containing the lowest quantity of activated carbon has showed better kinetics and the highest hydrogen absorption capacity than the composites 90%Mg-10% ACA and 85% Mg-15% ACA. The theoretical hydrogen storage capacity of pure magnesium is 7.6%. The use of higher quantity of additives leads to diminution of its theoretical hydrogen storage capacity. For that reason, on the one hand, when additives are used, they reflect favourably on the hydrogen sorption characteristics of magnesium, but on the other hand, the composition has to be chosen carefully.
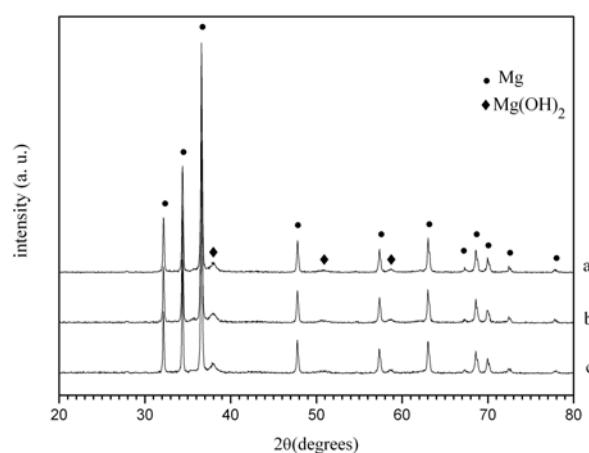

Fig. 2. X-ray diffraction patterns of the composites obtained after ball milling 30 min under argon:
a) 95% Mg-5% ACA; b) 90% Mg-10% ACA;
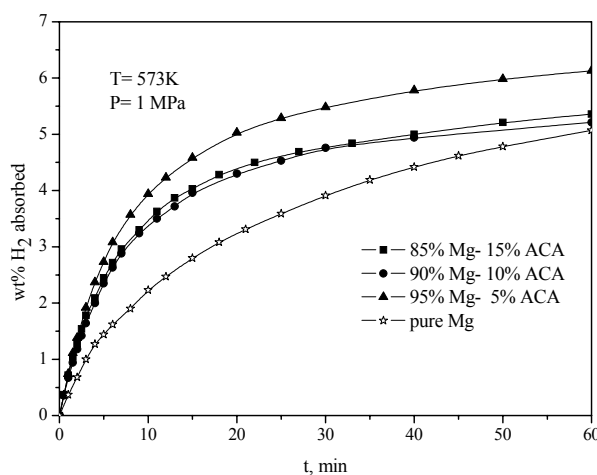c) 85% Mg-15% ACA.

Fig. 3. Kinetic curves of hydriding of the composites 95% Mg-5% ACA, 90% Mg-10% ACA, 85% Mg-15% ACA and pure magnesium.

At 473K and 1 MPa all composites under consideration after 60 min of hydriding reached hydrogen absorption capacity about 1%.

The kinetic curves of dehydriding for all compo-

sites and pure magnesium at 623 K and 0.15 MPa are presented in Fig. 4, here the rate of the hydrogen desorption reaction is very similar for all composites. The quantity of activated carbon does not affect hydrogen desorption kinetics. Pure magnesium has showed slower desorption kinetics, but finally it reached 6.5% desorption capacity. The difference in the desorption capacity is associated with different amount of magnesium in the composites.
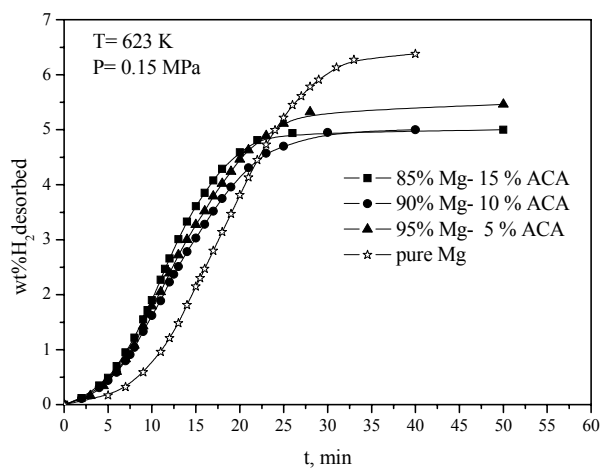

Fig. 4. Kinetic curves of dehydriding of the composites 95% Mg-5% ACA, 90% Mg-10% ACA, 85% Mg-15% ACA and pure magnesium.

The positive effect of carbon addition to magnesium based materials on the hydrogen sorption characteristics is not only associated with augmenttation of specific surface area during ball milling, but also with the antisticking effect of carbon and its ability to prevent the restoration of the oxide layer on the surface. In this way carbon eliminates the unfavourable effect of this layer on the dissociative chemisorption of hydrogen. The large amount of carbon containing additive could block the hydrogen diffusion pats and to overtake its positive effect as antistacking agent. Obviously, 15% of activated carbon, derived from apricot stones, is not enough quantity to observe this blocking effect.

The average crystallites size is presented on Table 1. After ball milling of the composites some small diminution of crystallites size by increasing the quantity of activated carbon is observed. The facilitation of the hydrogen diffusion in materials with smaller crystallites should be associated with an increase in absorption capacity. In this connection, due to the fact that the crystallite size of the composites under consideration shows no substantial difference, their hydrogen absorption capacities values should also be similar. The maximum hydrogen absorption capacity for the sample with 5% activated carbon is almost 1% higher than this reached by the other two composites. In the litera-

ture it is usually assumed that the hydrogen sorption characteristics of magnesium based systems strongly affect by crystallites size [3]. From our results it is obviously that even 5% of activated carbon derived from apricot stones has positive effect on the hydrogen absorption/desorption properties of magnesium. Further increase of the quantity of activated carbon e.g. 10% and 15% leads to diminution of the hydrogen absorption rate and capacity. Addition of this type of activated carbon makes also the activation of the composites easier, as could be seen at Table 2. The composite with 15% of activated carbon reached almost 1.49% H_2 at first cycle after 60 min of hydriding and pure magnesium only 0.26% H_2.

Table 1. Average crystallite size values (in nm) of the composites after ball milling and hydrided at 573 K and 1 MPa.

composite	ball milled	hydrided
95% Mg-5% ACA	80	131
90% Mg-10% ACA	70	122
85% Mg-15% ACA	73	130

Table 2. Hydrogen absorption capacity of the composites after 60 min of hydriding at I cycle at T = 623 K and P = 1 MPa.

composite	absorption capacity, % H_2
pure Mg	0.26
95% Mg-5% ACA	0.86
90% Mg-10% ACA	0.99
85% Mg-15% ACA	1.48

CONCLUSIONS

The results obtained on the absorption-desorption characteristics of the composites: 95% Mg-5% activated carbon derived from apricot stones (ACA), 90% Mg-10% ACA and 85% Mg-15% ACA demonstrate the positive effect of the additive on the hydrogen absorption properties of magnesium. The investigated composites posses easier activation, increased absorption capacity at temperature 573 K and improved hydriding-dehydriding kinetics, compared to pure magnesium. Due to the fact that the duration of mechanical activation doesn't lead to significant change in the crystallinites size, the dehydriding kinetics shows no substantial change. Contrariwise, the hydriding kinetics shows some difference. The best hydrogen absorption kinetics and the highest hydrogen absorption capacity is reached by the composite 95% Mg-5% activated carbon derived from apricot stones.

REFERENCES

1. I. G. Konstanchuk, E. Yu. Ivanov, M. Pezat, B. Darriet, V. V. Boldyrev, P. Hagenmuller, *J. Less-Common Met.* **131,** 181, (1987).
2. J.-L. Bobet, E. Akiba, B. Darriet, *Int. J. Hydrogen Energy,* **26,** 493, (2001).
3. A. Zaluska, L. Zaluski, J. O. Strom-Olsen, *Appl. Phys. A, Mater. Sci. Proc.,* **72,** 157, (2001).
4. L. E. A. Berlouis, E. Cabrera, E. Hall-Barientos, P. J. Hall, S. B. Dodd, S. Morris, M. A. Imam, *J. Mater. Res.,* **16,** 45, (2001.)
5. G. Liang, J. Huot, S. Boily, A. Van Neste, R. Schulz, *J. Alloys Comp.,* **297,** 261, (2000).
6. M. Zhu, Y. Gao, X. Z. Che, Y. Q. Yang, C. Y. Chung, *J. Alloys Comp.,* **330–332,** 708, (2002)
7. M. Khrussanova, J.-L. Bobet, M. Terzieva, B. Chevalier, D. Radev, P. Peshev, B. Darriet, *J. Alloys Comp.,* **307,** 283 (2000).
8. P. Wang, H. F. Zhang, B. Z. Ding, Z. Q. Hu, *Acta Mater.,* **49,** 921, (2001).
9. R. Vijay, R. Sundaresan, M. P. Maiya, S. Srinivasa Murthy*, Int. J. Hydrogen Energy,* **32,** 2390, (2007).
10. M. Khrussanova, M. Terzieva, P. Peshev, I. Konstanchuk, E. Yu. Ivanov, *Z. Phys. Chem. (N.F.),* **164,** 1261, (1989).
11. W. Oelerich, T. Klassen, R. Bormann, *J. Alloys Comp.,* **315,** 237, (2001).
12. J.-L. Bobet , B. Chevalier , M. Y. Song, B. Darriet, *J. Alloys Comp.,* **356–357,** 570, (2003).
13. K. S. Jung, E. Y. Lee, K. S. Lee, *J. Alloys Comp.,* **421,** 179, (2006).
14. F. Tonus, V. Fuster, G. Urretavizcaya, F. J. Castro, J.-L. Bobet, *Int. J. Hydrogen Energy,* **34,** 3404, (2009).
15. C. Z. Wu, P. Wang, X. Yao, C. Liu, D. M. Chen, G. Q. Lu, H. M. Cheng, *J. Alloys Compd.,* **414,** 259, (2006).
16. S. Bouaricha, J.-P. Dodelet, D. Guay, J. Huot, R. Schulz, *J. Mater. Res.,* **16,** 2893, (2001).
17. C. X. Shang, Z. X. Guo, *J. Power Sources,* **129,** 73, (2004).
18. M. Güvendiren, E. Baybörü, T. Öztürk, *Int. J. Hydrogen Energy,* **29,** 491, (2004).
19. M. A. Lillo-Ródenas, Z. X. Guo, K. F. Aguey-Zinsou, D. Cazorla-Amorós, *Carbon,* **46,** 126, (2008).
20. Z. G. Huang, Z. P. Guo, A. Calka, D. Wexler, H. K. Liu, *Mater. Lett.,* **61,** 3163, (2007).
21. H. Imamura, Y. Takesue, T. Akimoto, S. Tabata, *J. Alloys Compd.,* **293–295,** 564, (1999).
22. J.-L. Bobet, E. Grigorova, M. Khrussanova, M. Khristov, P. Stefanov, P. Peshev, D. Radev, *J. Alloys Compd.* **366,** 298, (2004).
23. S. Dal Toè, S. Lo Russo, A. Maddalena, G. Principi, A. Saber, S. Sartori, T. Spataru, *Mater. Sci. Eng. B,* **108,** 24, (2004).
24. H. Imamura, I. Kitazawa, Y. Tanabe, Y. Sakata, *Int. J. Hydrogen Energy,* **32,** 2408, (2007).
25. A. Ranjbara, Z. P. Guoa, X. B. Yu, D. Wexler, A. Calka, C. J. Kim, H. K. Liu, *Mater. Chem. Phys.*, **114,** 168, (2009).
26. K. Gergova, N. Petrov, S. Eser, *Carbon*, **32,** 693, (1994).
27. Topas V3, General profile and structure analysis software for powder diffraction data, Brucker AXS, Karlsruhe, Germany, 2006.

ИЗСЛЕДВАНЕ НА СОРБЦИОННИТЕ ХАРАКТЕРИСТИКИ ПО ОТНОШЕНИЕ НА ВОДОРОДА НА КОМПОЗИТИ НА БАЗАТА НА МАГНЕЗИЙ С ДОБАВКА ОТ АКТИВЕН ВЪГЛЕН ПОЛУЧЕН ОТ КАЙСИЕВИ КОСТИЛКИ

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(Резюме)

Изследвани са абсорбционно-десорбционните характеристики по отношение на водород на композити със състав 95% Mg-5% активен въглен получен от кайсиеви костилки (АСА), 90% Mg-10% АСА и 85%-15% АСА, механоактивирани в инертна среда. Процесът на хидриране протича при Т = 573 K и 473 K и P = 1 MPa, а на дехидриране при Т = 623 K и P = 0.15 MPa. Композитът 95% Mg-5% АСА достига най-висок абсорбционен капацитет от 6.13% при 573 K и 1 MPa. Композитите 90% Mg-10% АСА и 85%-15% АСА достигат абсорбционен капацитет 5.36% и 5.21% съответно. Ходът на абсорбционните криви при Т = 573 K и P = 1 MPa за композитите съдържащи 10 и 15% АСА е доста сходен. Трикратното увеличаване на количеството на добавката от активен въглен към магнезия не се отразява на кинетиката на десорбция на изследваните композити.