Journal of Alloys and Compounds 509S (2011) S592–S594

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Structure of Mg–C nanocomposites produced by mechano-chemical synthesis

A.D. Rud [a,*], A.M. Lakhnik [a], S.S. Mikhailova [b], O.V. Karban [b], D.V. Surnin [b], F.Z. Gilmutdinov [b]

[a] *G.V. Kurdyumov Institute for Metal Physics of NASU, 03680 Kiev, Ukraine*
[b] *Physical-Technical Institute UrB RAS, Izhevsk, Russia*

ARTICLE INFO

Article history:
Received 13 August 2010
Received in revised form 14 October 2010
Accepted 27 October 2010
Available online 4 November 2010

Keywords:
Hydrogen storage materials
High-energy ball milling
Mechano-chemical synthesis
Scanning and transmission electron microscopy
X-ray diffraction

ABSTRACT

The carbon distribution in the Mg–C composites produced by ball milling of elemental magnesium with amorphous carbon and graphite powder was studied by X-ray diffractometry (XRD), transmission electron microscopy (TEM), Auger electron spectrometry (AES) and X-ray photoelectron spectrometry (XPS). Specific surface area of the composites was characterized by BET-method. It was found that a thin carbon coating layer on the surface of individual particles is formed. This carbon layer prevents particles agglomeration and promotes the magnesium powdering. A possible structure model of the magnesium–carbon composite has been proposed.

1. Introduction

Wide set of additives and techniques are applied to improve hydrogen sorption properties in magnesium [1–4]. Last decade great efforts are focused on the investigation of hydrogen sorption properties in magnesium–carbon composites [5–13] produced with the use of the various carbon allotropes. A considerable improvement of hydrogen sorption/desorption kinetics in the magnesium–carbon composites is noted in most papers. It should be noted, there is unclear understanding about the nature of the carbon beneficial effect on the hydrogen sorption/desorption by magnesium–carbon composites. The contradictory and sometimes entirely opposite viewpoints are delivered about effect of carbon materials on the hydrogen sorption by magnesium.

In Ref. [6], the morphology of the Mg–C composites was studied by SEM with EDS mapping. It was found that the surface of the milled Mg particles is enriched by carbon that can reduce the agglomeration of particles. But the employed technique does not allow to elucidate the structure of individual particles. The aim of the present study is to investigate the structure and carbon distribution peculiarities in the Mg–C nanocomposites prepared by ball milling of magnesium with graphite and amorphous carbon powder.

2. Experimental details

The Mg–C composites were prepared from magnesium coarse grained powder, spectrally pure graphite (G) and amorphous carbon powder (AC) produced by electrical discharge technique in the organic liquids. It was revealed that amorphous carbon powder used for synthesis of Mg–C nanocomposites possesses a structure with graphite-like type of the short-range order [14].

To prepare the samples for each experiment, a weight fraction of 20% of carbon powder was added to the magnesium powder. Mechanical alloying of each mixture was carried out at room temperature using a Fritsch Pulverisette-6 ball mill. The ball-to-powder ratio was 30:1. The powder mixture weight was 16 g. The rotation speed was 400 rpm and the milling time 20 h. Before milling, the stainless steel vial (volume of 250 ml), containing a powder mixture and 15 steel balls (diameter of 20 mm), was evacuated to a pressure of 10^{-2} to 10^{-3} Pa. To prevent oxidation, the as-milled powders were handled in the glove-box under purified argon (99.998%) atmosphere and stored in the box in the argon-filled containers. Hydrogenation of the samples was performed in a Sieverts-type apparatus. The initial hydrogen pressure was 0.5 MPa. The Mg/AC and Mg/G samples (~1.5 g) were continuously heated (~3 K/min) to the temperatures of 180 °C and 225 °C, respectively, with subsequent isothermal exposure during 1 h.

A specific surface area (S_{BET}) of the powders was measured by BET-method using an automated Autosorb-1C system. X-ray diffraction (XRD) patterns were recorded with the Fe-filtered Co Kα radiation by the steps of 0.05° (2θ) from 10 to 100° with counting time of 5 s at each step. The crystallite sizes of the Mg–C composites were estimated by MAUD software [16]. Morphology of the magnesium–carbon composites was characterized by Hitachi H800 transmission electron microscope (TEM) operating at 200 kV accelerating voltage at room temperature.

Auger electron spectra (AES) were measured on the JAMP-10S Auger electron spectrometer. A base pressure during the analysis was about 10^{-7} Pa and the scanning area was about 1 μm^2. The content of each element was determined with ±5% accuracy. The average thickness of the layer under analysis was 1–3 nm. The surface of the samples was etched by argon ions with a purpose to estimate an element distribution over the thickness of a sample. The thickness of the etching layer comprises about 1.5, 7.5, and 13.5 nm for ball milled Mg/AC, and 0.5, 1.0, 1.5, and 7.5 nm for ball-milled and hydrogenated Mg/AC.

---

[*] Corresponding author. Tel.: +380 44 4243210; fax: +380 44 4242561.
E-mail address: rud@imp.kiev.ua (A.D. Rud).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.10.155

X-ray photoelectron spectra (XPS) were recorded with the ES-2401 electron spectrometer using the nonmonochromatic Mg Kα radiation at 200 W. The base pressure during the analysis was about 10^{-6} Pa. A fixed take-off angle of 45° was used. The spectrometer was calibrated using the $Au4f_{7/2}$ line at 84 eV. The spectra were recorded at the pass energy of 50 eV and step size of 0.1 eV. The spectra were charge-corrected by setting the C1s peak from the hydrocarbon contamination at the value of 285 eV.

3. Results and discussion

It was ascertained in our previous study [15] that using the amorphous carbon powder, produced by an electrical discharge technique in the organic liquids, as an additive to magnesium through ball milling enhances its hydrogen sorption kinetics. The synthesized Mg/AC composites offer essential advantages over pure magnesium and composites produced by co-milling of magnesium and graphite. The Mg–C composites prepared by co-milling Mg with AC exhibit a higher hydrogen capacity (~5 wt.%) against Mg/G composites (~1.8 wt.%). The hydrogen sorption process runs much faster in the Mg/AC powders [15]. This behavior may be caused due to the different dispersity of the composites ($S_{BET} = 136\,m^2/g$ and $35\,m^2/g$ for the Mg/AC and Mg/G, respectively). The initial S_{BET} of the carbon powders equals ~160 m^2/g and ~5 m^2/g for amorphous carbon and graphite, respectively. Based on this observation, there is a correlation between the starting specific surface areas of carbon materials and the specific surface areas of synthesized nanocomposites.

Fig. 1 shows the XRD patterns of the hydrogenated Mg/G and Mg/AC composites. It is obvious that the hydrogenation reaction in

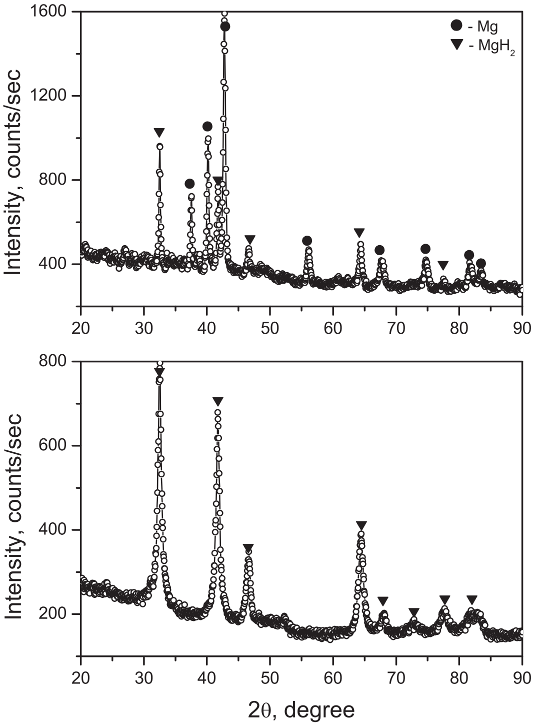

Fig. 1. XRD patterns of Mg/G (*a*), and Mg/AC (*b*) composites after ball milling and hydrogenation.

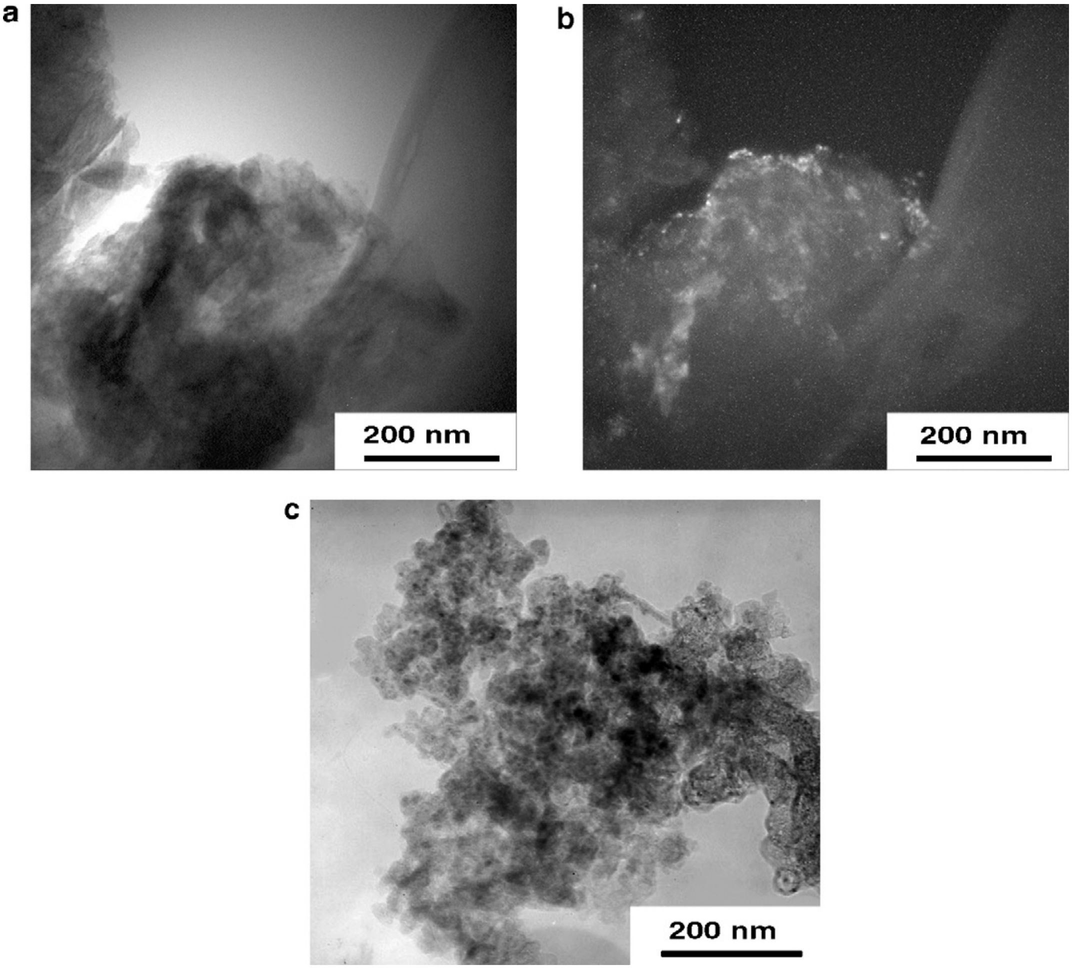

Fig. 2. TEM micrographs of the hydrogenated Mg–C composites: Mg/G (a and b) and Mg/AC (c): (a) and (c) are bright field images and (b) is a dark field image.

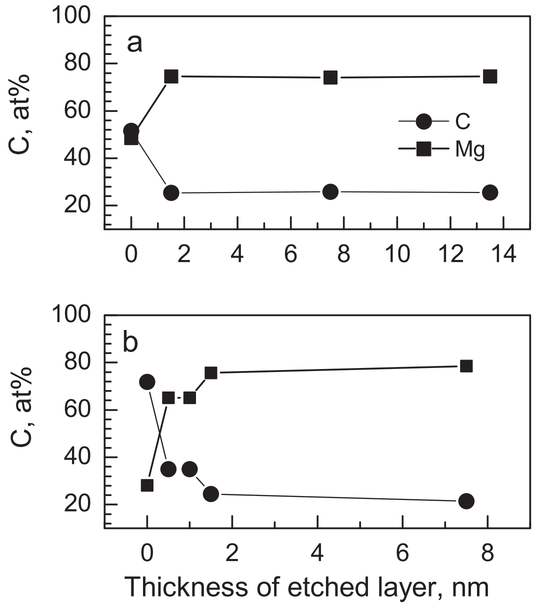

Fig. 3. The relative element content in the surface layers of the Mg/AC composite from AES data: (a) after ball milling and (b) after ball milling and subsequent hydrogenation.

the Mg/G powder is incomplete. In contrast to this sample, there are only MgH_2 peaks for the Mg/AC powder. It should be emphasized, that there are no peaks coming from the magnesium carbides in the XRD patterns and the C1s spectra in the XPS data. This implies the lack of the interaction between magnesium and carbon atoms. It follows from the XRD data that the amorphous carbon additive promotes the formation of very fine magnesium powder with crystallite size of ∼24 nm. A higher crystallite size (∼60 nm) is observed for the Mg/G powder after ball milling.

Fig. 2 demonstrates the TEM images of hydrogenated Mg/G and Mg/AC composites. It shows that milling significantly reduces particle sizes in the composites. The size of particles does not exceed 60 nm for Mg/G composites (Fig. 2a and b) and 30 nm for the Mg/AC composites (Fig. 2c). The particles are agglomerated.

The surface of the Mg/AC composites at the initial state and after the hydrogen sorption experiment was studied by AES and XPS. The obtained results demonstrate that only Mg, O and C are present at the surface layers of the samples. The appearance of oxygen is a result of a sample contact with environment before AES and XPS measurements due to the high reactivity of nanocomposites obtained after ball milling. It follows from the AES and XPS results that the surface layers of both samples are enriched by carbon (Fig. 3), what is in agreement with previously published data [6]. The etching of surface layer of the order of 1.5 nm leads to the approximately twofold decrease of relative carbon content for the ball-milled composite. Further etching does not essentially change the relative element content. For Mg/AC composites, the carbon content more than twice reduces after etching of 0.5 nm after hydrogen sorption. The following etching causes progressive reduction of carbon content. According to the XPS data, the surface layers in Mg/AC composites at initial and hydrogenation states are enriched by carbon in graphite-like form.

Taking into account the absence of the carbon peaks on XRD pattern, it may assume that carbon spread over the powder surface with the layer thickness of approximately 3–5 nm. The formation of the carbon layer on the surface of the composites protects them against oxidation, particles agglomeration and mechanical fusion during the ball milling.

It follows from the TEM, XPS and AES data that the nature of the carbon material influences on the surface structure of Mg-based composites. High dispersive amorphous carbon powder provides the formation more fine magnesium composites in the contrast to coarse grained graphite powder. As follows from XRD, XPS and AES data, there is no interaction between magnesium and carbon atoms with the formation of magnesium carbide. Thus, the synthesized composites can be described as aggregates of magnesium (or magnesium hydride) particles either immersed into a carbon medium or coated by thin carbon layers.

4. Conclusions

The Mg–C composites are synthesized by ball milling of elemental magnesium with amorphous carbon powder and graphite. The size of magnesium particles after milling depends on the nature of initial carbon powder. Graphite and amorphous carbon are accumulated on the surface of magnesium particles and promote magnesium dispersion. The thickness of the carbon protective layer is between 3 and 5 nm. The structure of the composite is aggregates of magnesium nanosized particles either immersed into carbon medium or coated by thin carbon layers.

Acknowledgements

The work was partially supported by the joint Project of NAS of Ukraine (# 36-08-10) and RFBR (# 10-08-90419), by the joint Project of NAS of Ukraine and STCU (# 4951) and by the Project of NAS of Ukraine (# 40-10).

References

[1] R.A. Varin, T. Czujko, Z.S. Wronski, Nanomaterials for Solid State Hydrogen Storage, Springer Science + Business Media, New York, NY, 2009.
[2] V.M. Skripnyuk, E. Rabkin, Y. Estrin, R. Lapovok, Int. J. Hydrogen Energy 34 (2009) 6320–6324.
[3] J.-L. Bobet, F.J. Castro, B. Chevalier, Scr. Mater. 376 (2004) 33–37.
[4] R.V. Denys, A.B. Riabov, J.P. Maehlen, M.V. Lototsky, J.K. Solberg, V.A. Yartys, Acta Mater. 57 (2009) 3989–4000.
[5] H. Imamura, N. Sakasai, T.J. Fujinaga, J. Alloys Compd. 253–254 (1997) 34–37.
[6] Z.G. Huang, Z.P. Guo, A. Calka, D. Wexler, H.K. Liu, J. Alloys Compd. 427 (2007) 94–100.
[7] C.Z. Wu, P. Wang, X. Yao, C. Liu, D.M. Chen, G.Q. Lu, H.M. Cheng, J. Alloys Compd. 414 (2006) 259–264.
[8] D. Chen, L. Chen, S. Liu, C.X. Ma, D.M. Chen, L.B. Wang, J. Alloys Compd. 372 (2004) 231–237.
[9] C.X. Shang, Z.X. Guo, J. Power Sources 129 (2004) 73–80.
[10] S.N. Klyamkin, B.P. Tarasov, E.L. Straz, R.V. Lukashev, I.E. Gabis, E.A. Evard, A.P. Voyt, Int. Sci. J. Altern. Energy Ecol. 1 (2005) 27–29.
[11] M.A. Lillo-Ródenas, Z.X. Guo, K.F. Aguey-Zinsou, D. Cazorla-Amorós, A. Linares-Solano, Carbon 46 (2008) 126–137.
[12] V. Fuster, G. Urretavizcaya, F.J. Castro, J. Alloys Compd. 481 (2009) 673–680.
[13] A. Chaise, P. de Rango, Ph. Marty, D. Fruchart, S. Miraglia, R. Olivès, S. Garrier, Int. J. Hydrogen Energy 34 (2009) 8589–8596.
[14] A.D. Rud, N.I. Kuskova, L.I. Ivaschuk, D. Fruchart, A.E. Perekos, L.Z. Boguslavskii, V.I. Oreshkin, in: V. Fortov (Ed.), Physics of Extreme States of Matter 2009, Institute of Problems of Chemical Physics of RAS, Chernogolovka, 2009, pp. 248–251.
[15] A.D. Rud, A.M. Lakhnik, V.G. Ivanchenko, V.N. Uvarov, A.A. Shkola, V.A. Dekhtyarenko, L.I. Ivaschuk, N.I. Kuskova, Int. J. Hydrogen Energy 33 (2008) 1310–1316.
[16] L. Lutterotti, S. Matthies, H.-R. Wenk, IUCr: Newsletter of the CPD 21 (1999) 14–15.