American Chemical Science Journal
11(4): 1-9, 2016, Article no.ACSJ.22845
ISSN: 2249-0205

SCIENCEDOMAIN *international*
www.sciencedomain.org

Mg_2Cu Alloy Preparation by Mechanical Alloying Process and Its Characterization Using X-ray Diffraction and Scanning Electron Microscopy

José Luis Iturbe-Garcia[1*], Beatriz Eugenia López-Muñoz[1] and Luis Zamora Rangel[2]

[1]Department of Chemistry, Instituto Nacional de Investigaciones Nucleares, Km 36.5 Carretera México-Toluca s/n, la marquesa, C.P. 52045, Ocoyoacac, Estado de México, México.
[2]Department of Materials, Instituto Nacional de Investigaciones Nucleares, Km 36.5 Carretera México-Toluca s/n, la marquesa, C.P. 52045, Ocoyoacac, Estado de México, México.

Authors' contributions

This work was carried out in collaboration between all authors. Author JLIG designed the study, performed the statistical analysis, wrote the protocol, wrote the first draft and revised the final manuscript. Authors BELM and LZR managed the analyses of the study. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/ACSJ/2016/22845
Editor(s):
(1) Georgiy B. Shul'pin, Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia.
Reviewers:
(1) Azuddin Mamat, University of Malaya, Malaysia.
(2) Gadang Priyotomo, Indonesian Institute of Sciences, Indonesia.
Complete Peer review History: http://sciencedomain.org/review-history/12561

Original Research Article

Received 30th October 2015
Accepted 12th November 2015
Published 4th December 2015

ABSTRACT

In this work the synthesis of intermetallic Mg_2Cu is presented. Elemental particles of magnesium with a purity of 99.8% and Cu 99.9% were mixed in desired quantity to reach a nominal composition of 40-60 and 80-20 wt% for magnesium and copper in each composition respectively. The synthesis of compound was carried out by mechanical alloying technique with a high energy ball mill type spex which was constructed in our Institute. Then Mg and Cu particles were put into a stainless steel vial and three stainless steel balls and methanol as milling media and process control agent respectively. The ball to particles weight ratio was 10:1. The milling time was defined only between 1 to 5 h, at room temperature. This technique was used because the conventional method of thermal fusion could not be induced to synthesize this alloy. The metal powders were

---

Corresponding author: E-mail: joseluis.iturbe@inin.gob.mx;

analyzed before and after milling by X-ray diffraction and scanning electron microscopy (SEM). The results obtained by XRD shows the formation only of Mg_2Cu phase in short milling time in both compositions. These results show that due to the high impact between milling media, material and control agent can be obtained this alloy easily and fast by mechanical alloying technique.

Keywords: Mg_2Cu alloy; mechanical alloying technique; XRD-SEM characterization.

1. INTRODUCTION

Different classes of materials for hydrogen storage have been intensively studied during the last decades [1-3]. Diverse methods exist to prepare metallic alloys and used as hydrogen retention between them the mechanical alloying technique is now widely used for this porpose [4-6]. Ball milling can often produce unique and metastable materials that cannot be prepared by conventional techniques as wet chemistry method. The ball milling process presents certain advantages e.g. smaller restrictions with respect to composition, shorter milling time and an experimental technique routinely used in the preparation of metal alloys such as nanocrystalline, amorphous, nanocomposites, crystalline and quasicrystalline intermediate phases etc. [4,7,8]. Although the technique has been used quite extensively, at present the process of mechanical alloying is not completely understood. The mechanical alloying through high energy ball milling has been used in the preparation and modification of metal hydrides, and other inorganic solids, while organic compounds have been synthesized, including transition metal complexes in the presence or absence of a suitable solvent [9]. Several compounds have recently been synthesized by this technique such as alanates [10-19], borohydrides [20-23]. In many cases this approach implies by-products formation in the preparation of these materials when metals or intermetallics are combined with chemical reagents containing hydrogenated compounds. The hydrogen storage materials fulfilling international goals should be based on light weight elements. Various compounds for reversible absorption/desorption hydrogen process are considered among them Mg-base alloys [24-26], these ones are attractive materials for hydrogen storage applications because their high gravimetric hydrogen storage densities of up to 7.6 wt.% for example the case of MgH_2 [27]. The intermetallic considered in this study is focused to obtain Mg_2Cu compound of a fast manner through mechanical alloying process and thereafter can be used as a precursor material in synthesis of magnesium hydride. This technique has the advantage to prepare some alloys which can be considered as cold fusion because the metals not reach high temperatures but rather significant pressures depending on the mill type and therefore the high impact between the milling media, sample and container walls, using less milling time unlike conventional methods and when some mixed metals having different physicochemical properties, which would be one disadvantages in their preparation by other methods.

2. MATERIALS AND METHODS

Elemental particles of magnesium with purity of 99.8% and Cu 99.9% were mixed in desired quantity to reach a nominal composition of 40 – 80 wt% for Mg and 60 – 20 wt% of Cu corresponding to the stoichiometric mole ratio of 2:1. The synthesis of Mg_2Cu alloy was carried out by mechanical alloying technique with a high energy ball mill type spex which was fabricated in our Institute details about its construction are reported elsewhere [28]. Then the Mg and Cu particles were put into a stainless steel vial and three stainless steel balls of 12.7 mm in diameter for milling and methanol as process control agent was also used. The ball to particles weight ratio was 10. The milling time was defined only between 1 to 5 h, at room temperature in an inert atmosphere. All metal samples were handled without exposure to air in a little lucite glove box under argon gas. In order to monitor the possible phase's formation, a small amount of ball milled material was intermittently taken out from stainless steel container at interval times of 1, 3 and 5 h. From a series of experiments, it was found that these times were most appropriate for checking the possible alloy formation. To avoid overheating of milling system a ventilator was placed on container and electric motor. The structural evolution during milling was determined by X-ray diffraction analysis in a Siemens D5000 diffractometer adapted to an X-ray tube to explain the possible chemical processes that occur during milling in the formation of intermetallic compound and identify their corresponding phases. The measurements were taken at a power of 40 kV, 45 mA. A diffracting beam monocromator and Cu Kα radiation was used. The material was placed in portable samples with the scanning angular intervals from 10-25 to 70-80° in 2θ. A Scanning Electron Microscope JEOL 5900 LV equipped with an energy dispersive microanalysis by X-ray (EDAX) system was also used to determine the morphology and chemical composition of powders.

3. RESULTS AND DISCUSSION

The Fig. 1 shows a micrograph of Cu and Mg elements utilized in the alloy preparation. The image A corresponds to Cu particles and these ones of Mg are shown in micrograph B. The Cu powder having particle size of 350 mesh according to provider (Sigma-Aldrich) which has appearance of a sintered material with morphology heterogene type stalagmites this ones may be due to preparation method. The particles of Mg which were given a treatment with one lime from an ingot before mechanical milling process, this ingot was prepared in the department of materials in our Institute, these particles have elongated shapes and toothed at the sides because, firstly that the relatively soft metal and the way that surface has to be roughened lime. According to the scale reported on image the particle sizes in average were higher of 1 mm. The images were obtained at 5000 and 100 magnifications for copper and magnesium respectively. Based to the results of EDAX, Cu and Au elements were only present, which shows that copper is a pure state without any kind of impurity. Gold appears because the sample surface was subjected to a coating with this metal to prevent an over electric charging when microscopic analysis is realized. On the other hand, in X-ray spectrum of magnesium sample (not presented), only Kα lines of Mg and Au were identified, the presence of gold was for coating sample before microscopic analysis as mentioned above.

Fig. 2 shows the Mg and Cu powders milled 5 hours, in this image cumulus and small particles are observed with morphology totally different to elemental particles shown in Fig. 1. This image was obtained at 5000 increases and according to scale reported on image, the particle sizes are less than five microns. According to the results of X ray diffraction (Fig. 5) after 5 hours of milling only Mg_2Cu alloy was formed.

The Fig. 3 shows the X ray spectrum of MgCu intermetallic analyzed by EDAX where C, O, Mg, Cu and Au elements were identified. The presence of C is mainly due to the tape where Mg_2Cu powders were placed for its analysis because it is made of this material and possibly from methanol used as control agent process. The presence of oxygen may be also due to methanol where the conditions were created into container during milling and solvent dissociation was realized in their components oxygen, carbon and hydrogen which was demostrated elsewere [29]. The oxygen may be reacted with magnesium in a too much small concentration such that the results of X-ray diffraction did not detect the corresponding oxide because the equipment sensitivity is less than 1%. The hydrogen perhaps escape when the container was opened after finish mechanical milling process and carbon probably is mixed with Mg – Cu alloy without combining chemically with this compound and du to small concentration not was also detected. And Au is used to cover the sample surface to avoid an electrical overcharge during scanning electron microscopy analysis, the C and Au picks are not indicated on spectrum. On the other hand, it is very difficult to measure the local microscopic temperature during milling because dynamic nature of this process. In our system, external temperature measurement was performed on the top cap vial by a digital thermocouple; the results of monitoring of this parameter during different milling times give knowledge of a gradual increase in temperature. In these working conditions, the initial temperature was 16±3℃ (ambient) and after one hour of milling increased to 30±2℃, when the milling process is prolonged, heat generated also increases registering a temperature of 45±5℃ for 5 h of continuous milling. Another series of experiments was carried out by controlling the temperature during milling and an air flow over external surface vial was provided by a ventilator to maintain the temperature as low as possible, the recorded value during milling time was 28±2.5℃ throughout milling time from start until 5 h continuously; it is probably that this temperature is not generated throughout the powder only at the site where the impact between milling media and material is performed therefore we suppose that in this particular case, the local temperature does not influence the process of compounds preparation because the same results were obtained in both cases from nominal compositions.

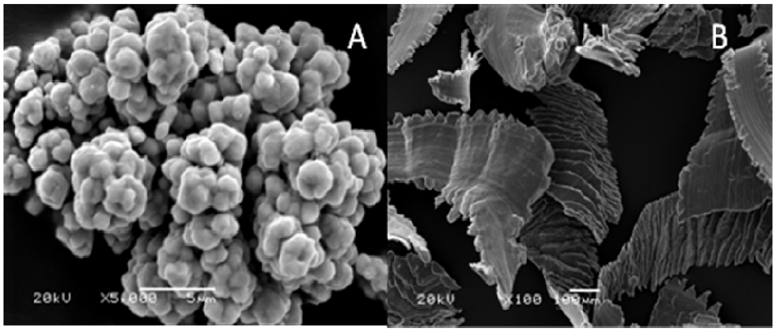

Fig. 1. Micrographs of Cu and Mg particles before mechanical milling process A and B respectively

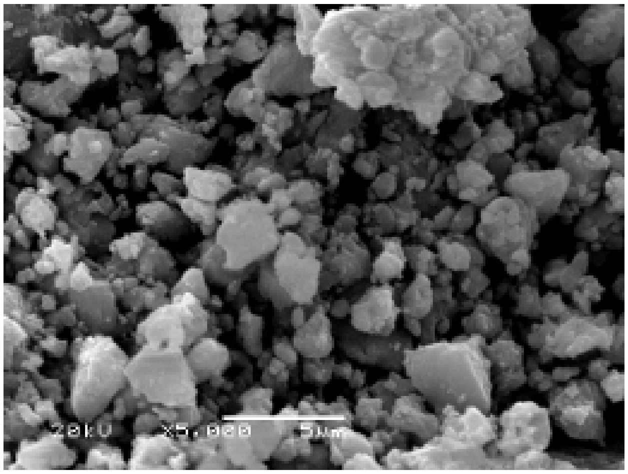

Fig. 2. Micrograph of magnesium-copper powders after 5 h of mechanical alloying process under X5000 magnifications

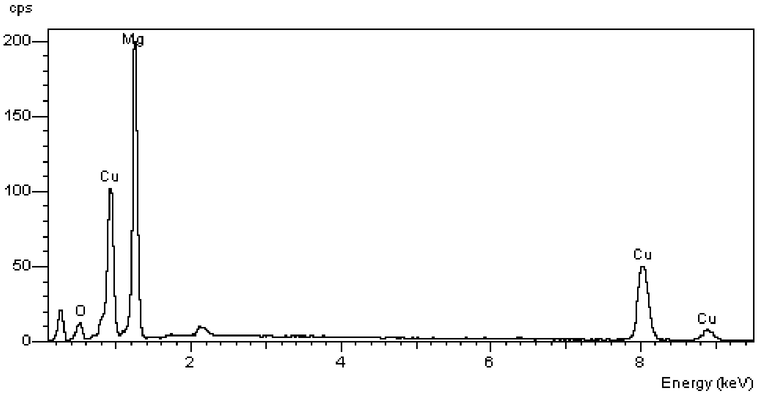

Fig. 3. X ray spectrum of elements identified by EDAX from MgCu powders after 5 h of mechanical milling

Fig. 4 shows a X-ray diffraction patterns of three samples that correspond to Cu, Mg and Mg_2Cu materials. The spectrum at bottom corresponds to copper metal; the magnesium spectrum is located in middle and the located on the top appertain to the compound obtained after 5 h of milling which was identified as Mg_2Cu alloy. The two spectra of original metals (Mg and Cu) shown a single phase, normally no impurity from pure materials were observed. With 00 – 001 –

1141 and 00 – 004 – 0836 JCPDS cards both metals were identified. Finally, the spectrum obtained after 5 h of milling corresponds to Mg_2Cu phase according to 03 – 065 – 1116 JCPDS card. This spectrum has five principal peaks in the interval of 20 to 45 degrees in 2 theta scale. The spectra are compared with the purpose to know if after 5 h of milling the original metals had fully reacted and if another phase was formed. We can see in these results that spectra of any of both lines as Cu and Mg interfere with Mg_2Cu intermetallic peaks. In these experimental conditions and with high energy mechanical alloying used only Mg_2Cu phase was formed.

Fig. 5 shows three X ray diffraction patterns of Mg – Cu compounds which were milled during one, three and five hours. Analyses were performed to evaluate and follow up on formation of Mg_2Cu alloy during the milling time considered. The spectrum in the lower part corresponds to the sample that was milled one hour. In these circumstances begins to form the Mg-Cu alloy as indicated by the deflections that appear on 2θ angles signaled with asterisks, it is surprising to see the rapid formation of intermetallic Mg_2Cu in only one hour of milling, may be due in part to physicochemical properties of each metal and to the milling size media (12.7 mm in diameter) which causes a great impact between these milling media, sample and container walls. On the other hand, values of deflection angles corresponding to the original elements of Mg and Cu that have not reacted to form the intermetallic at this time were also identified. The spectrum in half was obtained after three hours of milling, it can be seen the reduction intensities of Mg and Cu peaks indicating that have not yet been completely combined and an increase in signal of Mg_2Cu peaks that correspond to alloy formation. At this milling time, it could not identify two significant lines which values appear at angles of 21.5 and 44.5 in 2 theta, possibly due to the formation of an intermediate phase which unfortunately is not in our XRD system library cards and with more milling time (5 h) this interphase was tranformed and only Mg_2Cu phase was identified. Finally, after 5 h of mechanical milling the spectrum which is at top of figure was obtained, can be seen all characteristics lines corresponding only to Mg_2Cu phase which were identified by other JCPDS card (00 – 013 – 0504). The most intense peaks at 2 theta angles are located at 39.492 and 44.600 degrees, two less intense deflections located between the angles 19.280 and 20.027 are overlapped. In the spectrum does not identify any other phase, that is to say, during 5 hours of milling only Mg_2Cu alloy was formed therefore Mg and Cu were completely combined. It should be mentioned that the spectra were obtained by considering the metals in a nominal ratio of 40:60 wt% for magnesium and copper respectively.

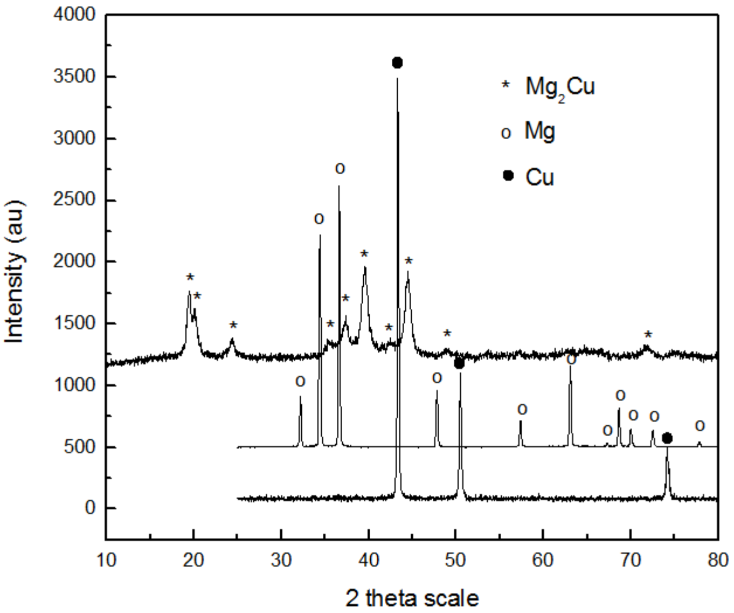

Fig. 4. X-ray diffraction patterns of elemental Cu, Mg and Mg_2Cu alloy

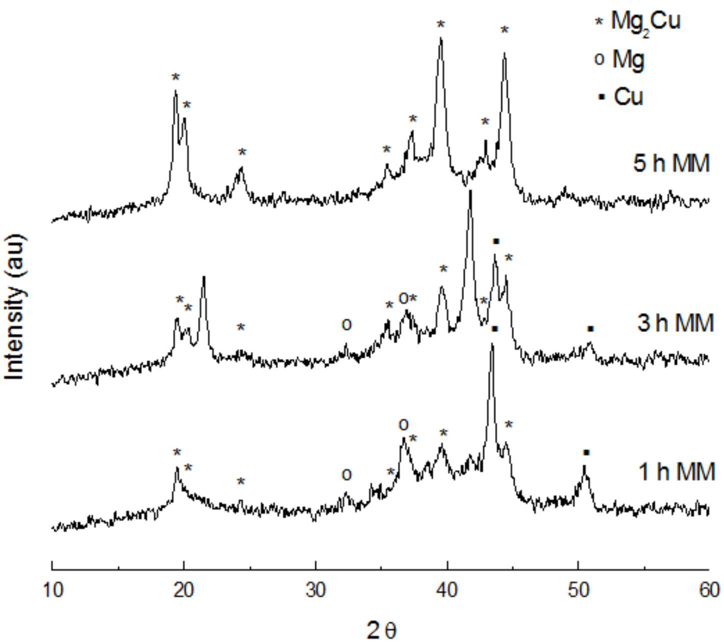

Fig. 5. X ray diffraction patterns of Mg and Cu milled 1, 3 and 5 hours using high energy ball milling system for Mg_2Cu preparation

Fig. 6 shows the X ray diffraction pattern of Mg_2Cu alloy after 5 hours of mechanical alloying with nominal composition of 80-20 wt% as well as the metallic magnesium spectrum. In the first spectrum all intensities corresponding to Mg_2Cu phase were observed which these same intensities were also obtained with nominal ratio of 40-60wt% using the same milling time. The spectrum of Mg is placed together with the Mg_2Cu compound to compare and see if this element had not reacted and if some of their peaks correspond to angle 2theta values of the alloy, it should be mentioned that the deflections with greater intensity were cuted on axis "y" due to the value of the scale. In these experiments the percentage used for the intermetallic was 40% higher for Mg and 40% lower for Cu, we can see that any peak of magnesium corresponds to Mg_2Cu phase and the corresponding deflections at 2 theta angles whose values are 37.281 and 39.492 have different intensities to those obtained in Fig. 4, that is, as if the intensities depend on the percentages of each element, the most intense that appears angle of 37.281 and the second peak (39.492) has less intensity. It may be that when analyzing the samples, the radiation interacted on preferential planes of the crystal lattice of Mg_2Cu compound. All diffractograms obtained after 5 h of milling have the characteristic peaks of Mg_2Cu phase whose Miller indices are 040, 111, 131, 331, 080 (100) 440 (100), these intensities are the most important and located at 2 theta angles with values sitthe between 19.280 and 44.600 degrees. According to both JCPDS cards considered in its identification has an orthorhombic crystal lattice.

After different milling times used in Mg_2Cu alloy preparation, and according to XRD patterns under these experimental conditions any other phase particularly hydrides were observed, the hydrogen generated during milling into container does not react with magnesium or copper and perhaps is released when the system was opened. The preparation of Mg_2Cu alloy was attempt carry out by melting of metals in an electric furnace, but the results were not satisfactory, that is, the alloy was not obtained by this method in any weight ratio from both Mg (40-80) and Cu (60-20). It is very difficult to dissolve metals by means of heat perhaps because they have certain physicochemical properties very different especially their melting points. We suppose that Mg_2Cu alloy preparation using mechanical milling is influenced by some general properties of copper and magnesium metals, for example, its melting point (1084.62°C), electronegativity (1.9) etc. To explain the possible mechanism in which Mg and Cu forms the Mg_2Cu alloy is assumed that during mechanical alloying process, two types of events are realized; these are events of welding and fracture. In the process, the powders can be catched either between a pair of balls in motion by high impact or between a ball and the wall of the vial. The mixture of magnesium and copper undergo an intense plastic deformation, originating particles in form of flakes. These features suggest the beginning of diffusion of copper into magnesium and viceversa which leads to alloy formation. The Cu and Mg metal atoms are few electrons in its valence shell, usually 1 and 2 respectively. These atoms easily lose these electrons (valence electrons) during milling process become positive ions and they are arranged in space forming upon impact the metal lattice. The electron configuration $[Ar]3d^{10}4s^1$ of copper has one s-orbital electron on top of a filled d-electron shell and are characterized by high ductility and electrical conductivity. The filled d-shells in this element do not contribute much to the interatomic interactions, which are dominated by the s-electron through metallic bonds. Unlike in metals with incomplete d-shells, metallic bonds in copper are lacking a covalent character and are relatively weak. This explains the low hardness and high ductility of single crystals of copper. Numerous copper alloys exist, many with important uses. On the other hand, magnesium is a chemical element with electron configuration $[Ne]\ 3s^2$, melting point only of 650℃, electronegativity 1.32 (Pauling scale). Its common oxidation number is +2. These basic characteristics mean that these two metals by high-impact process are mixed and the alloy is now obtained thorough mechanical alloying so that it requires short time for its preparation increasing the number of applications. With the experimental conditions used in this work it can obtain Mg_2Cu alloy by mechanical alloying in different percentages of Mg and Cu elements, this alloy can be used as precursor for preparing the magnesium hydride one of the materials that is actually under study to be used in hydrogen technology due to its high gravimetric hydrogen capacity and it can be used in fuel cells. In mechanical milling procedure, the milling size media have an important influence in intermetallic preparation, for example, when the balls used are larger in diameter stronger is the impact inside milling system including the container walls and sample in these conditions the disolution process between metals occurs rapidly, it is clear that the alloy preparations by this technique depends of some physicochemical properties of each metal to be considered.

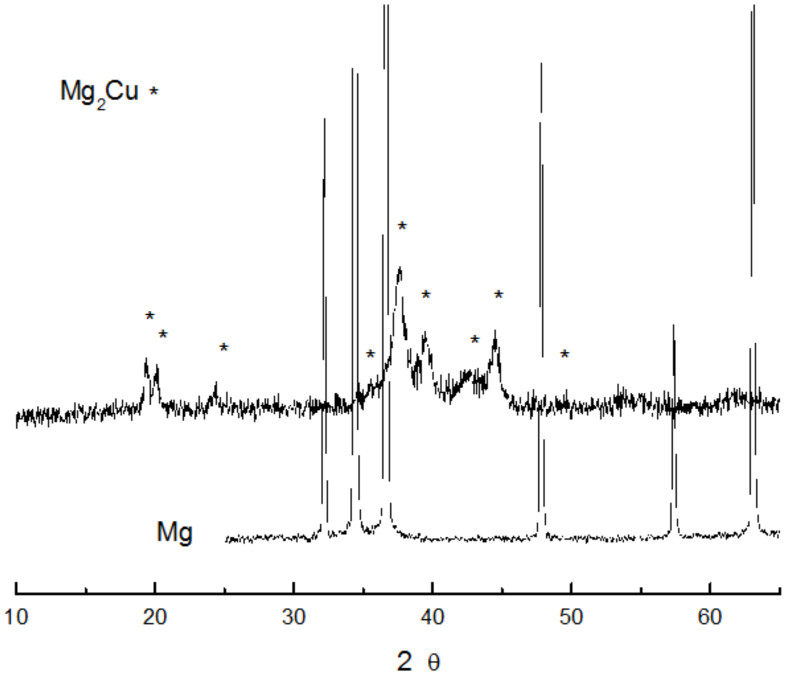

Fig. 6. X ray diffraction patterns of Mg_2Cu with a ratio 80:20w% after 5 h of milling and Mg element

4. CONCLUSIONS

Mg_2Cu alloy was obtained by mechanical alloying process using short milling times, the DRX technique was utilized to identify the Mg_2Cu phase, according to SEM analysis particle sizes of nanometer order could be observed. The mechanical alloying method has certain advantages in preparation of this alloy (Mg_2Cu) with respect to melting metals method which could not synthesize this material. The MgCu alloy with nominal composition of 40-60 and 80-20 wt% were considered in this work and only Mg_2Cu phase was obtained. The Mg_2Cu alloy can be used as a precursor for magnesium hydride preparation. Due to the high impact energy, the alloy begins to form from the first hour of ball milling. Mg_2Cu phase was obtained programming only 5 h of mechanical milling.

ACKNOWLEDGEMENTS

We would like to thank to the ININ for the financial support of the project CB303 and the personnel of the scanning electron microscope and X-ray diffraction machine for their valuable support.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Sakintuna B, Lamari-Darkrim F, Hirscher M. Metal hydride materials for solid hydrogen storage: a review. Int J Hydrogen Energy. 2007;32:1121–1140.
2. Fichtner M. Nanotechnological aspects in materials for hydrogen storage. Adv Eng Mater. 2005;7:443–455.
3. Zaluski L, Zaluska A, Strom-Olsen JO. Nanocrystalline metal hydrides. J Alloys Comp. 1997;253-254,70–79.
4. Gutfleisch O, Dal Toè S, Herrich M, Handstein A, Pratt A. Hydrogen sorption properties of Mg–1 wt.% Ni–0.2 wt.% Pd prepared by reactive milling. J Alloys Compd. 2005;404–406,413–416.
5. Yoonyoung K, Eung-Kyu L, Jae-Hyeok S, Young WC, Kyung BY. Mechanochemical synthesis and thermal descomposition of $Mg(AlH_4)_2$. J Alloys Comp. 2006;422:283-287.
6. Suryanarayana C. Mechanical alloying and milling. Progress in Materials Science. 2001;46:1-184.
7. Gross KJ, Chartouni D, Leroy E, Zuttel A, Schlapbach L. Mechanically milled Mg composites for hydrogen storage: the relationship between morphology and kinetics. J Alloys Comp. 1998;259-270.
8. Fecht HJ, Hellstern E, Fu Z, Johnson WL. Nanocrystalline metals prepared by high-energy ball milling. Metall Trans A. 1990; 21:2333-2337.
9. Balema VP, Wiench JW, Pruski M, Pecharsky VK. Mechanically induced solid-state generation of phosphorus ylides and the solvent-free wittig reaction. J Am Chem Soc. 2002;124:6244-6245.
10. Mamatha M, Weidenthaler C, Pommerin A, Felderhoff M, Schüth F. Comparative studies of the decomposition of alanates followed by in situ XRD and DSC methods. J Alloys Comp. 2006;416:303-314.
11. Mamatha M, Bogdanović B, Felderhoff M, Pommerin A, Schmidt W, Schüth F, et al. Mechanochemical preparation and investigation of properties of magnesium, calcium and lithium–magnesium alanates. J Alloys Comp. 2006;407:78-86.
12. Lohstroh W, Roth A, Hahn H, Fichtner M. Thermodynamic effects in nanoscale $NaAlH_{4.}$ Chem Phys Chem. 2010;11(4): 789-792.
13. Balema VP, Balema L. Missing pieces of the puzzle or about some unresolved issues in solid state chemistry of alkali metal aluminohydrides. Phys Chem Chem Phys. 2005;7:1310–1314.
14. Chaudhuri S, Graetz J, Ignatov A, Reilly JJ, Muckerman JT. Understanding the role of Ti in reversible hydrogen storage as sodium alanate: A combined experimental and density functional theoretical approach. J. AM. CHEM. SOC. 2006;128: 11404-11415.
15. Bellosta von Colbe JM, Felderhoff M, Bogdanovič B, Schüth F, Weidenthaler C. One-step direct synthesis of a Ti-doped sodium alanate hydrogen storage material. Chem Commun. 2005;4732–4734.
16. Huot J, Boily S, Güther V, Schulz R. Synthesis of Na AlH and Na LiAlH by mechanical alloying. Journal of Alloys and Compounds. 1999;383:304–306.
17. Kojima Y, Kawai Y, Hagab T, Matsumoto M, Koiwai A. Direct formation of $LiAlH_4$ by a mechanochemical reaction. Journal of

Alloys and Compounds. 2007;441:189–191.

18. Balema VP, Pecharsky VK, Dennis KW. Solid state phase transformations in $LiAlH_4$ during high-energy ball-milling. Journal of Alloys and Compounds. 2000;313:69–74.
19. Mamatha M, Bogdanović B, Felderhoff M, Pommerin A, Schmidt W, Schüth F, et al. Mechanochemical preparation and investigation of properties of magnesium, calcium and lithium–magnesium alanates. Journal of Alloys and Compounds. 2006; 407:78–86.
20. Vajo JJ, Olson GL. Hydrogen storage in destabilized chemical systems. Scripta Materialia. 2007;56:829–834.
21. Yao Z, Wan-Shen Z, Ai-Qin W, Li-Xian S, Mei-Qiang F, Hai-Liang C, et al. $LiBH_4$ nanoparticles supported by disordered mesoporous carbon: Hydrogen storage performances and destabilization mechanisms. Int J Hydrogen Energy. 2007;32(16):3976–3980.
22. Fichtner M, Zhao-Karger Z, Hu JJ, Roth A, Weidler P. The kinetic properties of $Mg(BH_4)_2$ infiltrated in activated carbon. Nanotechnology. 2009;20:204029.
23. Liu BH, Li ZP. A review: Hydrogen generation from borohydride hydrolysis reaction, J of Power Sources. 2009;187(2): 527–534.
24. Selvam P, Viswanathan B, Swamy CS, Srinivasan V. Studies on the thermal characteristics of hydrides of Mg, Mg_2Ni, Mg_2Cu and MgZnil-xmx (m =Fe, Co, Cu or Zn; $0 < x < 1$) alloys. Int J Hydrogen Energy. 1988;13(2):87-94.
25. Palma-Sampayo A, Iturbe-García JL, López-Muñoz BE, Sandoval-Jiménez A. MgAl alloy synthesis, characterization and its use in hydrogen storage. Int J Hydrogen Energy. 2010;35:12120–12124.
26. Iturbe-García JL, García-Nuñez MR, López-Muñoz BE. Synthesis of the Mg_2Ni alloy prepared by mechanical alloying using a high energy ball mill. J Mexican Chem Soc. 2010;54(1):46-50.
27. Jain IP, Lal C, Jain A. Hydrogen storage in Mg: A most promising material. Int J Hydrogen Energy. 2010;35:5133–5144.
28. Bonifacio Martínez J, Iturbe García JL, Castañeda Jiménez G. Diseño y fabricación de un sistema de aleado mecánico para preparar compuestos intermetálicos, nanocristalinos, amorfos y cuasicristalinos. Inf Téc ININ. 2002; CB – 022 – 2002.
29. Iturbe-García JL, López-Muñoz BE. Synthesis of tantalum hydride using mechanical milling and its characterization by XRD, SEM, and TGA. Advances in Nanoparticles. 2014;3:159-166.

Peer-review history:
The peer review history for this paper can be accessed here:
http://sciencedomain.org/review-history/12561