

Original Research Articles

OXYGEN AND HYDROGEN REACTION “IN SITU” WITH MAGNESIUM AND TANTALUM INTO MECHANICAL MILLING SYSTEM WHEN A SOLVENT IS USED

Abstract

The purpose of this paper is the preparation “in situ” of magnesium–tantalum phases when reacted with oxygen and hydrogen during mechanical milling process. Different phases were formed as function of milling time. High energy ball milling was utilized to prepare hydrogenated compounds programming between 5 and 20 hours and ball powder weight ratio was 10 and using methanol as control agent. SEM and XRD were used for its characterization. XRD results at 20 h of milling only hydrogenated species (Ta_2H and $TaH_{0.5}$) and $Mg(OH)_2$ were obtained.

Keywords: Tantalum hydrides, high energy ball milling, solvent dissociation, XRD, SEM.

1. INTRODUCTION

Different techniques have been used to prepare metal alloys, between them, can be mentioned conventional techniques as wet chemistry method, similarly there are various techniques from the point of view physical used for the same purpose as electrical arc, induced thermal fusion or high energy mechanical alloying process which was used in this study, where nanocrystalline, amorphous, nanocomposites, and quasicrystalline materials including intermediate phases, etc. may be prepared [1-5]. At present mechanical alloying process has been used extensively to obtain principally metal alloys, but its mechanism is not completely understood and depends of each milling system. The mechanical alloying through high energy ball milling has been used in the synthesis and modification of metal hydrides, and other inorganic solids, while organic compounds have been obtained such as transition metal complexes in the presence or absence of a suitable solvent [6]. Many materials for use in

hydrogen storage mainly metallic combinations as well as nanoporous compounds have been synthesized and studied that can contribute in hydrogen technology development [7]. So they can meet these requirements in many laboratories at international level, researches are performed to obtain new materials that can be used for practical purposes particularly in fuel cells. The aim of this technological challenge is to store the maximum amount of hydrogen in a minimum volume or mass of storage system safely (gravimetric and volumetric hydrogen density as gas and liquid systems) [8-10]. Various compounds for reversible absorption/desorption hydrogen process are considered among them Mg-base alloys [11-17]. On the other hand, the preparation of hydrogenated compounds such as hydrides or complex materials that are based in tantalum element is very limited and mainly using mechanical alloying technique which was utilized in the present investigation. Certain works related to preparation and studies of tantalum hydrides which consider monohydrides as complex compounds on basis of this metal, these works include crystallographic properties and thermodynamic aspects, high temperature reactions in Ta-H system and liberation of hydrogen achieved by hot vacuum treatment at 1000°C and pressure of 10^{-5} mm Hg have been reported, also some other physicochemical parameters as hardness, mechanical properties, electrical resistance, density, and superconductivity have been considered [18-22]. In this work chemical reactions between oxygen and hydrogen with Mg and Ta metals were carried out “in situ” during mechanical milling procedure using methanol as process control agent, resulting different phases depending of milling time. One of the goals consists in reacting Mg and Ta with hydrogen within the mechanical milling system to see if it could form the magnesium hydride in situ as in previous works tantalum hydride was obtained by dissociating the control means in its elementary components including hydrogen (23). According to our experience it has demonstrated that when some type of solvent is used during mechanical milling

experimental conditions are created inside the container to separate them on each of its elementary components.

2. MATERIALS AND METHODS

Magnesium and tantalum metal particles with a purity of 99.8% were mixed in the desired quantity to reach a nominal composition of 25wt% Mg and 75wt% Ta corresponding to the stoichiometric mole ratio 1:3. The chemical reactions were carried out by mechanical alloying technique with a high energy ball mill type spex, this system was fabricated in our Institute. Then Mg and Ta powders, three stainless steel balls of 12.7 mm in diameter and methanol as process control agent were put into a stainless steel vial for milling. The ball to particles weight ratio was 10. In a little lucite glove box under argon gas all metal samples were handled without exposure to air. The milling time is an important parameter for material preparations which a time period was defined between 5 to 20 h, in ambient conditions particularly the temperature. In order to monitor the possible phase's formation, a small amount of ball milled material was taken out from stainless steel vial at time intervals of 5, 10 and 20 h. From a series of experiments, it was found that these periods of time were most appropriate for checking the possible change in structural materials particularly hydrides formation. During milling the temperature increases and warms the vial, to keep this parameter as low as possible a ventilator placed on the container was used to avoid overheating in all milling system. 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 metal hydrides and identify their corresponding phases. The measurements were realized at a power between 20 – 25 kV, 25 mA. A diffracting beam monochromator and Cu K α radiation was used. The material was placed in a portable sampler with the scanning angular interval from 15 – 25 to 120° in 2 theta. A Scanning Electron Microscope JEOL 5900 LV equipped with an

energy dispersive microanalysis by X-ray (EDAX) system was also used before and after milling to determine the morphology and elemental composition of the powders.

3. RESULTS AND DISCUSSION

The figure 1 shows a micrograph of Ta and Mg metals utilized in this investigation. The image 1A corresponds to Ta particles; Tantalum powder having particle size of 350 mesh^{nm?} according to provider (sigma-aldrich) which has appearance of sintered material with morphology heterogene possibly the structure of this powder is due to preparation method and according to image these particles are formed by agglomerates which have empty spaces type pores. The Mg particles are shown in the micrograph 1B, which were given a treatment with a lime from an ingot before mechanical milling process, the ingot was prepared in the materials department in our institution (ININ) 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 scale reported on image the particle sizes in average were higher of 1 mm. Both images were obtained at 5000 and 100 magnifications for tantalum and magnesium respectively. According to the results by EDAX for elemental composition, Ta and Au elements were only present in (fig. 1A), which shows that tantalum is a pure metal without any impurity. Gold appears because the sample surface was subjected to a coating with this element to prevent an over electric charging when microscopic analysis was realized. On the other hand, the same results of EDAX corresponding to magnesium sample (fig. 1B), only Mg and Au were identified, the presence of gold was for coating sample before microscopic analysis as mentioned. Generally, the material must be reduced in size to nanometer scale in which the probability of reacting with hydrogen increases.

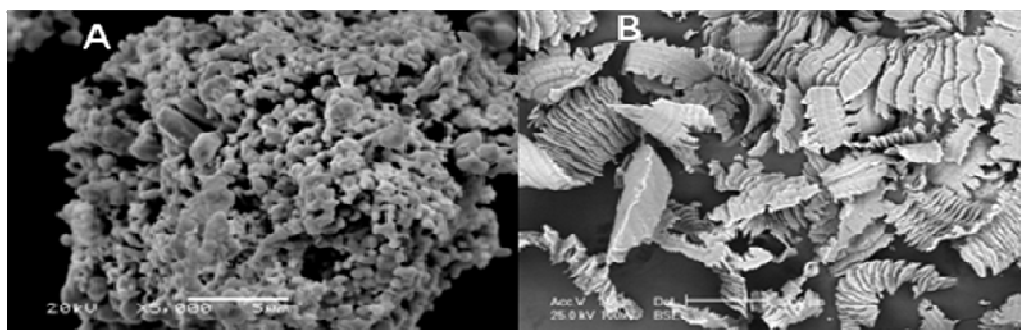


Figure 1. Micrograph of tantalum and magnesium particles before mechanical milling process.

The figure 2 shows Ta and Mg powders after 20 h of milling. According to the results of SEM, the particle size after this milling time was morphologically changed. Great difference between images exist and is noted for the particle sizes since scales smaller than a micron have been obtained and agglomerate accumulation is also observed which they are almost uniformly distributed. Nanometric sizes were obtained when powder material was diminished after this milling time. The results registered by SEM shows cumulus which at the same time are composed of very small particles, the image A represents the material in general whose morphology is not defined, on the other hand, image B was more detailed the images were observed at X5000 and X25000 respectively and according to results of diffraction, the images corresponding to the phases mainly tantalum hydride. Both physical and chemical changes of this material was experimented such as silvery to dark color, particle size from largest to smallest and metal to its corresponding oxide among others. The material after 20 h of milling analyzed by EDAX where Mg, Ta, C, O and Au elements were identified. The presence of C is mainly due to the tape where Mg – Ta powders were placed for its analysis because it is made of carbon and possibly a little 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 demonstrated elsewhere (24). The oxygen may be reacted

during milling with magnesium in small concentration such that the results of X-ray diffraction did detect the corresponding hydroxide. Most of hydrogen was reacted with Ta and after finish mechanical milling process only its hydrogenated specie was identified and carbon probably was mixed with Mg – Ta phases without combining chemically with these compounds and **du** to small concentration not was also detected. And Au is used to cover the sample surface to avoid an electrical overcharge during SEM analysis.

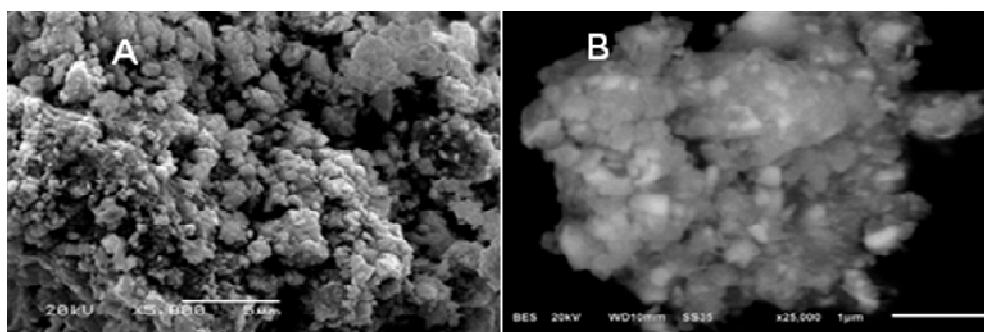


Figure 2. Micrograph of Mg-Ta powders after 20 hours of milling.

Figure 3 shown three diffraction patterns which represent to Mg, Ta elements and the phases after 5 h of milling process. With the purpose to follow the evolution in formation of different phases according to the milling time analyzes were performed on these intervals. The first spectrum at the bottom on figure corresponds to Mg sample before milling and its particles size whose image is reported in figure 1B. Only Mg phase was identified according to the JCPDS (00-035-0821) card, no other phase appeared as impurity, namely, the magnesium particles are of high purity. The deflections more intense appear at relatively small 2θ angles between 30 – 45 degrees, the majority of peaks being perfectly separated. The spectrum in middle was obtained of tantalum powder whose micrograph is indicated in figure 1A. Similarly, with 00-004-0788 JCPDS card the material was only identified as tantalum element, the line most intense at 38.463 value for 2θ angle was registered; the intensity and position of

both spectra are not interposed between them. The rest of peaks being perfectly separated at high angle values.

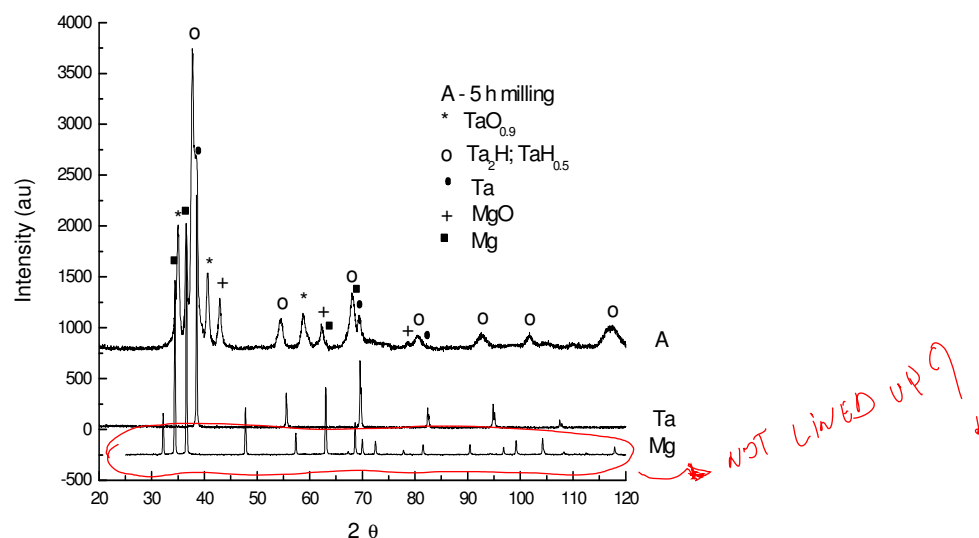
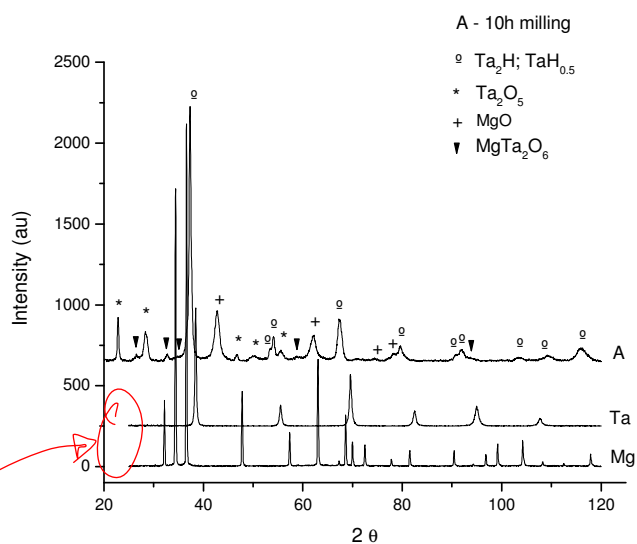


Figure 3. X ray diffraction pattern of Mg and Ta elements before and different phases spectrum (A) after 5 h of milling.

Spectrum A shows the material milled 5 h, which some peaks indicate partial formation of tantalum hydrides. At this time, tantalum hydrides (Ta_2H and $\text{TaH}_{0.5}$), magnesium and tantalum oxides (MgO , $\text{TaO}_{0.9}$) phases were formed and identified with JCPDS cards (01-089-4074, 10-089-7746 and 03-065-7449) respectively. Tantalum element appears equally which has not reacted completely after this milling time. It is assumed that hydrides formation and oxides takes place simultaneously, because when experimental conditions inside the vial are created, the methanol can be dissociated and at the same time the particles size are reduced therefore the corresponding reactions are realized partially or completely depending of elements and milling time. According to the results of diffraction, it is important to note that magnesium was firstly reacted partially with oxygen causing the formation of the

corresponding oxide (MgO), similarly the elemental magnesium was identified with their respective card which was unreacted after 5 h of milling. To explain the formation of hydrides “in situ” may be due to high impact energy generated between stainless steel balls, sample (Mg and Ta) and methanol; in such circumstances the milling reaches also high temperatures at atomic level creating the experimental conditions which causes solvent dissociation into its elementary components or at the same time, when the pressure generated in the solid, trapped between two colliding balls, can rise to an extremely high level of several GPa and facilitate genuine ultra-high pressure activated processes as has been reported in literature [6, 24]. It is interesting the sequence formation of tantalum hydrides phases during milling process which initiates a short time (5 h) and two oxides one of magnesium and another one of tantalum at same time magnesium and tantalum metals unreacted were identified, possibly due also to the temperature inside the system at short times of milling was not high enough to dissociate the methanol completely. In these milling conditions, magnesium first reacts with oxygen before doing so with tantalum to form the MgTa alloy in such a way that diffraction analysis did detect the corresponding oxide (MgO).



correct it

Figure 4. XRD pattern of Mg, Ta and (A) determined before and after 10 h of milling respectively.

Figure 4 shows the diffraction pattern 10 h after milling. At this milling time different phases among them: hydrides and oxides (spectrum A) were formed. At this time magnesium and tantalum elements were not detected and hydride phases (Ta_2H , $\text{TaH}_{0.5}$) appear with greater intensity on the diffractogram. The tantalum oxide (Ta_2O_5) according to the JCPDS cards 00-005-01315 was identified in contrast to that obtained at 5 h ($\text{TaO}_{0.9}$), magnesium oxide (MgO) and mixed magnesium-tantalum oxide (MgTa_2O_6) were also registered and identified with JCPDS cards 01-084-1679. The main deflection of hydrides phases, tantalum and magnesium are at low values of 2θ angles and all intensities of different compounds without any interference were observed. It is assumed that 10 h of milling magnesium and tantalum have been completely reacted to form their corresponding phases. According to the diffractogram some exchange reactions were carried out by increasing the milling time for example $\text{TaO}_{0.9}$ to Ta_2O_5 , phases and the combination of Mg, Ta and O to form the corresponding mixed oxide.

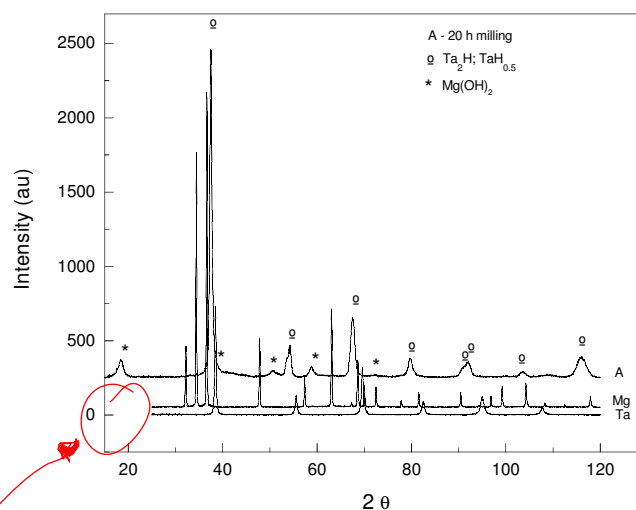


Figure 5. XRD pattern of Mg, Ta elements before milling and different phases formed after 20 h of milling, spectrum (A) where only tantalum hydrides and magnesium hydroxide phases were observed.

Figure 5 shows diffraction pattern of hydride phases with 20 h of milling process, where only tantalum hydride and magnesium hydroxide phases were identified this last in little lines intensity (spectrum A). All deflections on the spectrum correspond to Ta_2H , $TaH_{0.5}$ and $Mg(OH)_2$ phases; during this stage any Mg and Ta oxide compounds were detected. It shows clearly that the main tantalum hydrides intensities in 2θ angle not interfere with magnesium or tantalum elements whose lines values are 37.762, 36.624 and 38.463 respectively. Others results of X ray diffraction at milling time of 30 h were realized. The importance of these results is that the same phase of magnesium hydroxide and only tantalum hydrides were conserved by long period of milling time (30 h) spectrum no reported. Finally at 20 h of milling or less only tantalum hydrides and magnesium hydroxide phases were obtained. On the other hand, in this research due to difference in physicochemical properties between these two elements especially their melting points (3017 and 923° C for Ta and Mg respectively), and in these conditions it was difficult to obtain MgTa alloy by mechanical alloying. During the mechanical milling process, high energy is generated by the great impact between the container walls, milling media and material, this energy is probably high at atomic level creating the conditions to break chemical bonds of methanol which is used as control agent and dissociates in hydrogen, carbon and oxygen. Then the elemental states of hydrogen and oxygen were reacted with Mg and Ta elements during milling. Each binding energy between the various atoms of methanol have different values. From the four hydrogen atoms contained in the methanol, three are bonded to carbon whose bonding energy is 415 kJ/mol. Other bond located in the solvent is carbon – oxygen which has value of 352 kJ/mol and fourth hydrogen

atom bonded to oxygen has a binding energy of 460 kJ/mol. Possibly during high-energy mechanical milling they are created the physicochemical conditions originated by different types of events taking place within the container of milling system for solvent dissociation into its elemental components. It should be mentioned, that these values are an average energies because the energy of a given bond depends slightly on the other atoms bonded in a given compound. When the solvent dissociates into its components within the milling system to obtain the elements oxygen, hydrogen and carbon; probably oxygen and hydrogen remain as negative ions which reacts quickly with magnesium and tantalum. The carbon rest in elemental form and mixed with the other compounds without reacting with Ta, Mg or its oxides and the concentration is too low, that the analytical methods used did not detect it. In these experimental conditions, a possibility for hydrides formation may be that some of elements Mg, Ta and subsequently their intermediate compounds formed during milling act as catalysts improving the reaction conditions causing dissociation of the control agent in its components, H, O and C. Another possibility in the formation of different phases of magnesium and tantalum may be too the particle size reduction as function of milling time. Which being smaller probably facilitates the formation of tantalum hydrides as shown on diffractograms. Or it could be a combination of different events occurring within the milling process for methanol dissociation. It is interesting to note that the tantalum hydrides phases were synthesized “in situ” during the short milling time. We can say that by varying the milling time different phases of tantalum (oxides and hydrides) were formed and at 20 h or less of milling process changed the oxides to hydrides and magnesium hydroxide phase was identified. With these results we can to have another alternative method for preparing “in situ” some metal hydrides at low temperature and practically normal pressure and simultaneously to have a source of hydrogen by conversion of methanol or any other solvent during mechanical milling process. In these experimental conditions such as the different milling times used in

this work magnesium hydride was not synthesized, it appears that the mechanical milling has been selective only to obtain the tantalum hydride. On the other hand, it is very difficult to measure the local microscopic temperature during milling because of its dynamic nature of the milling 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 the different milling times give knowledge of a gradual increase in temperature. In these working conditions, the initial temperature was 18° C (ambient) and after one hour of milling increased to 31° C, as the milling time also increases the temperature at 5 h later was 45° C. Another series of experiments was carried out by controlling the temperature and during milling an air flow over the external surface of vial was provided to maintain the temperature as low as possible by a ventilator, the recorded value during the milling time was 27° C throughout the milling time from the start till 5 h of continuous milling; it is probable that this temperature is not generated throughout the powder only at the site where the impact between the milling media and the material is performed therefore we suppose that in this particular case, the local temperature does not influence the compounds preparation process because the same results were obtained in all milling times programmed, and dissociation phenomena of control agent in its elemental components and the chemical reactions take place with Ta and Mg metals giving rise to their corresponding phases. Even though the exact mechanism of the phenomena that occur within the container should be considered case by case, it seems that mechanical milling processes in solid materials are mainly due to structural changes. In effect, ball mill of high energy produces a wide variety of defects due to the collision of the balls resulting in continuous fragmentation, coalescence, vacancies, dislocations, and other events at the collision sites and high pressure generated in the compound during milling process. It has been reported that prolonged milling can also destroy the crystallinity of the material that leads to its complete or partial amorphization [24]. On the other hand, when the milling includes a

solvent, may occur dissociation in each of its components which react with the mixture of metals inside sealed vial giving rise to the formation of chemical compounds including hydrides that depending on the type of solvent and ball mill used. During the last two decades a number of promising new materials have been developed and studied. However, still no materials satisfying each of the main targets with respect to storage capacities, thermodynamics and kinetics aspects have been found, and further research in this field is required. Hydrogen storage in solid materials having high volumetric and gravimetric densities is the long term goal in hydrogen economy. These efforts will involve combinations of theory and experiments, development and improvement of novel methods for synthesis and last, but not least “in situ” methods and development of strategies and combination of different techniques in hydrides preparation. Many research efforts are currently under way to develop new technologies to prepare new materials for use in hydrogen storage. Metal hydrides are attractive candidates for a safe way of storing hydrogen for a broad range of practical purpose such as portable, mobile or static application. However, more research is needed in order to develop metal hydrides preparation with alternative methods that meet all the technological requirements.

4. CONCLUSION

Mg, Ta powders and methanol as control agent were mixed and mechanical milling process was used to prepare “in situ” hydrogenated phases. Due to high impact energy between components into container of mechanical milling system the experimental conditions were created for methanol dissociate in their elemental atomic components (C, O and H). The oxygen and hydrogen gases were reacted with Ta and Mg metals “in situ” into container. Several intermediate phases during milling process as a function of time mainly oxides of these two elements (Mg and Ta) were formed and subsequently transformed. Hydroxide and

hydride phases as final products after 20 hours of milling were obtained for Mg and Ta respectively. The tantalum hydride was readily formed. The mechanical ball milling can be used as an alternative method to prepare some hydrides, possibly with an appropriate catalyst can improve the hydride preparations using a variety of metals.

REFERENCES

1. 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 Comp.* 2005; 404–406: 413-416.
2. Yoonyoung K, Eung-Kyu L, Jae-Hyeok, S, Young WC, Kyung BY. Mechanochemical Synthesis and Thermal Descomposition of $\text{Mg}(\text{AlH}_4)_2$. *J Alloys Comp.* 2006; 422: 283-287.
3. Suryanarayana C. Mechanical Alloying and Milling. *Prog Mat Sci.* 2001; 46: 1-184.
4. 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; 5: 259-270.
5. Fecht HJ, Hellstern E, Fu Z, Johnson WL. Nanocrystalline Metals Prepared by High-Energy Ball Milling. *Metall Trans A.* 1990; 21: 2333-2337.
6. 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.
7. David E. An overview of advanced materials for hydrogen storage. *J Mat Processing Technology.* 2005; 162-163: 169-177.
8. Chapelle D, Perreux D. Optimal design of a Type 3 hydrogen vessel: Part I-Analytic modelling of the cylindrical section. *Int J Hydrogen Energy.* 2006; 31: 627-638.

9. Peschka W. Operating characteristics of a LH₂-fuelled automotive vehicle and of a semi-automatic LH₂-refuelling station. *Int J Hydrogen Energy*. 1982; 7: 661-669.
10. Schlapbach L, Züttel A. Hydrogen-storage materials for mobile applications. *Nature*. 2001; 414: 353-358.
11. Selvam P, Viswanathan B, Swamy CS, Srinivasan V. Studies on the thermal characteristics of hydrides of Mg, Mg₂Ni, Mg₂Cu and MgZn_{1-x}m_x (m =Fe, Co, Cu or Zn; 0 < x < 1) alloys. *Int J Hydrogen Energy*. 1988; 13: 87-94.
12. 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.
13. Iturbe-García JL, García-Núñez RM, López-Muñoz BE. Synthesis of the Mg₂Ni Alloy Prepared by Mechanical Alloying Using a High Energy Ball Mill. *J Mexican Chem Soc*. 2010; 54(1): 46-50.
14. Jain IP, Lal C, Jain A. Hydrogen storage in Mg: a most promising material. *Int J Hydrogen Energy*. 2010; 35: 5133-5144.
15. Zaluski L, Zaluska A, Tessier P, Strom-Olsen JO, Schulz R. Catalytic effect of Pd on hydrogen absorption in mechanically alloyed Mg₂Ni, LaNi₅ and FeTi. *J Alloys Comp*. 1995; 217: 295-300.
16. Liang G, Huot J, Boily S, Van Neste A, Schulz R. Catalytic effect of transition metals on hydrogen sorption in nanocrystalline ball milled MgH₂-Tm (Tm = Ti, V, Mn, Fe and Ni) systems. *J Alloys Comp*. 1999; 292: 247-252.
17. Aguey-Zinsou KF, Ares Fernandez JR, Klassen T, Bormann R. Effect of Nb₂O₅ on MgH₂ properties during mechanical milling. *Int J Hydrogen Energy*. 2007; 32: 2400-2407.
18. Park KY, Kim HJ, Suh YJ. Preparation of Tantalum Nanopowders through Hydrogen Reduction of TaCl₅ Vapor. *Powder Technology*. 2007; 172: 144-148.

19. Rothernberger KS, Howard BH, Killmeyer RP, Enick RM, Bustamante F, Ciocco MV, Morreale BD, Buxbaum E. Evaluation of Tantalum-Based Materials for Hydrogen Separation at Elevated Temperatures and Pressures. *J Membrane Sci.* 2003; 128: 19-37.
20. Porschke E, Shaltiel D, Klatt KH, Wenzl H. Hydrogen Desorption from Tantalum with Segregated Oxide Surface Layers. *J Phys Chem So.* 1986; 47: 1003-1011.
21. Esayed AY, Northwood DO. Metal Hydrides: A Review of Group V Transition Metals—Niobium, Vanadium and Tantalum. *Int J Hydrogen Energy.* 1992; 17: 41-52.
22. Miller GL. Corrosion by chemicals, gases and liquids metals, vol. 6, Finniston HM., Ed., Butterworths Scientific Publications, London. 1959; 431-543.
23. 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.
24. Lohstroh W, Roth A, Hahn H, Fichtner M. Thermodynamic Effects in Nanoscale NaAlH₄. *Chem Phys Chem.* 2010; 11(4): 789-792.