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**Synthesis of Tantalum Hydride Using Mechanical Milling and its Characterization by XRD, SEM, AND TGA**

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**ABSTRACT**

In this paper, we report the results obtained from the different phases of metal hydrides. The synthesis and characterization of tantalum hydrides and their possible use in hydrogen storage is presented which were obtained “in situ” during mechanical milling. Elemental Ta with purity of 99.8% was used in this investigation to obtain the hydrides. A high-energy milling technique was utilized to prepare hydrogenated phases. Ta hydrides and oxides were formed as function of milling process. Milling times of 5, 10 and 20 hours were used, and the ball-to-powder weight ratio was 10:1. The material was first characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The material was analyzed with TGA both before and after hydrogenation process. X-ray diffraction analysis demonstrated that only tantalum hydrides ( $Ta_2H$  and  $TaH_{0.5}$ ) were obtained during milling. We will discuss the effect of the ball-milling process about formation “in situ” of tantalum hydrides with methanol as a hydrogen source.

## **1. Introduction**

Hydrogen would be ideal as a synthetic fuel because it is lightweight and highly abundant in water and because the product of its oxidation is water. However, hydrogen storage remains a problem. Over the years, several countries have identified uses for hydrogen storage because of the rising demand for traditional fuel and the related problem of global warming caused by CO<sub>2</sub> emissions and other greenhouse gas effects. Hydrogen has come into the world's spotlight as a potential clean and high capacity energy source. Hydrogen storage is an important issue for the development of a hydrogen economy. The aim of this technological challenge is to store the maximum amount of gas in the minimum volume or mass of a storage system safely. Currently, the most popular storage method uses compressed hydrogen gas. High-pressure storage gas is contained in Type III or Type IV tanks [1]. Metal hydrides have a number of potential uses and offer a series of interesting technical applications. The major challenges related to materials for hydrogen storage can be summarized by the gravimetric hydrogen density. Because very few hydrogen storage materials reach a metal/hydrogen ratio higher than 2, hydrogen storage materials that fulfill international goals should be based on lightweight elements. Thermodynamics: The release of hydrogen should take place at conditions (temperature and pressure) matching the working conditions, such as those within fuel cells. Reversibility: Important for onboard storage, but for offboard hydrogen regenerative of hydrogen storage materials, hydrogen uptake should be a cheap and simple process. Kinetics: The use of catalysts is often important, but the use of nano-scale materials will also improve kinetics. In addition, several other factors are important, such as the availability of elements and compounds, cost and safety [2]. Different classes of materials for hydrogen storage have been intensively studied over the past few decades. Diverse methods exist to prepare metallic alloys; among them is a mechanical alloying technique. This process provides certain advantages, e.g., smaller restrictions with respect to composition; thus, nanocrystalline, amorphous, and quasicrystalline phases can be obtained. The intermetallics can be prepared as powders at low temperatures [3]. Although this technique has been used quite extensively, at present, the process of mechanical alloying is not completely understood. It has been suggested that the alloy generated due to the collision of the balls results in continuous fragmentation; coalescence events of the alloy at collision sites are steps in the process of mechanical alloying. Research and development of hydrogen storage materials have shown that, instead of AB<sub>5</sub>-type alloys such as LaNi<sub>5</sub> or CaNi<sub>5</sub>, more powerful and light A<sub>2</sub>B-type alloys play an important role [4-6]. Various metal-hydrogen systems for the reversible hydriding-dehydriding of magnesium are considered to be possible storage options, of which Mg-base alloys are attractive materials for hydrogen storage applications because of their high gravimetric hydrogen storage densities of up to 7.6 wt.% for MgH<sub>2</sub> in certain applications [7 – 18]. However, the major problem with magnesium as a reversible hydrogen storage material is the slow reaction kinetics of its adsorption/desorption process; the kinetics have been improved by adding an appropriate catalyst to the system as well as by ball milling, which introduces defects to improve surface properties. Other compounds of the most promising hydrogen storage alloys and their corresponding hydrides (such as LiBH<sub>4</sub>, Mg(BH<sub>4</sub>)<sub>2</sub>, NaAlH<sub>4</sub>,

and  $\text{Mg}(\text{AlH}_4)_2$ ) have been reported in microporous and mesoporous scaffolds [19-28]. There is limited information about the reaction of tantalum with hydrogen. This metal has the ability to react with hydrogen under certain temperatures and pressures. The maximum solubility of hydrogen in tantalum is determined by these two parameters. Degassing hydrogen from tantalum, the stability of a Ta-H system, and the liberation of hydrogen by hot vacuum treatment at  $1000^\circ\text{C}$  and a pressure of  $10^{-5}$  mm Hg have been examined in the literature. Additional physicochemical properties of Ta-H, such as hardness, mechanical properties, electrical resistance, density, and superconductivity, have also been examined [29]. In the present paper, the synthesis and characterization of Ta hydrides and their possible use in hydrogen storage are presented. During the milling process, Ta hydrides were formed “in situ” using a spex-type high-energy ball mill system.

## **2. Experimental**

Elemental particles of tantalum with purity of 99.9% were used in this investigation. The synthesis of Ta hydrides was carried out by mechanical milling with a spex-type high-energy ball mill, which was constructed in our institute. The Ta powder material was then put into a stainless steel vial. Three stainless steel balls of 12.7 mm in diameter were used for milling, and methanol was used as control media to avoid powder adhesion to the walls of the container and to the milling media. The ball-to-powder weight ratio was 10:1. The material was ball milled for 5 to 20 h, at room temperature in an inert atmosphere. All samples were handled without exposure to air in a small lucite glove box under argon gas. To monitor possible alloy formation, a small amount of the ball-milled material was intermittently removed from the stainless steel vial at time intervals of 5, 10 and 20 h. From a series of experiments, it was found that these time periods were the most appropriate for examining the possible hydrides formation. The structural evolution during milling was detected by X-ray diffraction analysis in a diffractometer (D8 ADVANCE Bruker AXS) that was adapted to an X-ray tube with a copper anode to identify the phases formed. The measurements were taken at a power of 40 kV, 45 mA. A diffracting beam monochromator and Cu  $K\alpha$  radiation was used in the same system. The material was placed on portable samples with an angular scanning interval from  $20$  to  $120^\circ$  in  $2\theta$ . A scanning electron microscope (JEOL 5900 LV) equipped with an energy dispersive microanalysis by X-ray (EDAX) system was used to determine the morphology and the chemical composition of the powders. The material was analyzed after 20 h of milling by thermogravimetric analysis both before and after the hydrogenation process using thermoanalyzer equipment (TA Instruments model TGA-51) that had been previously calibrated. The heating system was programmed from ambient temperature to  $500^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ , with nitrogen gas as carrier (high purity  $\text{N}_2$ ).

## **3. Results and discussion**

Figure 1 shows a micrograph of the Ta element utilized in this investigation. The micrograph corresponds to Ta particles; according to the SEM analysis, the scale reported indicated that the particle sizes were larger than 100

microns and possessed a heterogeneous morphology because we started from blades, which were roughly shaped with lime before the mechanical milling process. The image of the particles was obtained at 100X. According to the results of EDAX for elemental composition, only tantalum was identified without any impurity. Generally, with this particle size is difficult to start hydrogenation process; hence the material must be reduced in size to nanometer scale in which the probability of reacting with hydrogen increases.

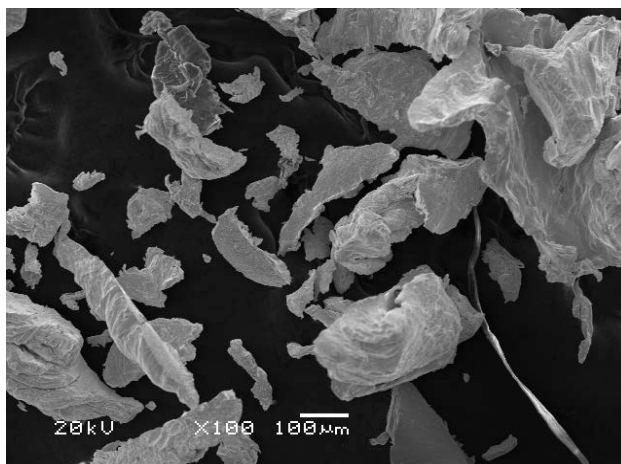


Figure 1. Micrograph of tantalum particles prior to mechanical milling process.

Figure 2 shows two micrographs of Ta powder after 20 h of milling. The image A was obtained at 500X which represents the material which is distributed in general. A large difference in particle size is observed after milling because a submicron scale was achieved, and agglomerate accumulation was almost uniformly distributed. Nanometer sizes were obtained when less powder material was milled with the time intervals used in this research. Image B represents the material in detail, it can see a group of clusters formed by particles whose size is of nanometer order, and with the milling time used to reduce its size is supposed that the powders observed on the images corresponding to the tantalum hydrides, since according to XRD diffractograms only hydride phases were identified. The image was obtained at 30,000X.

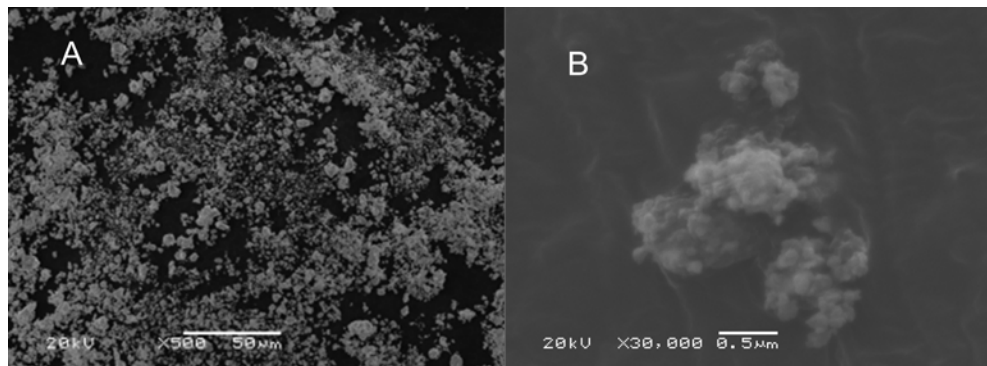


Figure 2. Micrographs of Ta hydride powder after 20 hours of milling.

Figure 3 shown two diffraction patterns corresponding to some Ta phases after 5 hours of milling. The first spectrum at the bottom of the figure corresponds to elemental tantalum, and the peaks indicate that the particle size agrees with that shown in figure 1 prior to milling. Likewise, using the 00-004-0788 JCPDS card, the material was identified as only containing elemental tantalum.

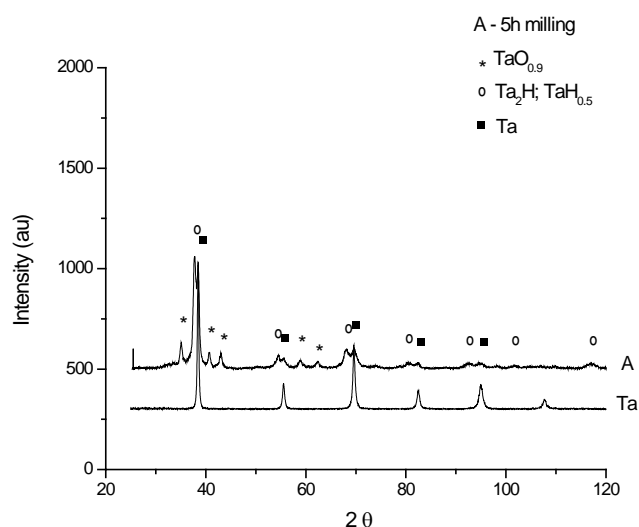


Figure 3. The X-ray diffraction patterns of elemental Ta before and after 5 h of milling. The figure shows the spectra of Ta, as well as different phases (A) of oxides and hydrides formed at this milling time.

The most intense line for  $2\theta$  occurred at  $38.463^\circ$ . The remaining five peaks were perfectly separated at high angle values. Spectrum A corresponds to the material milled for 5 hours in which the peaks indicate that tantalum hydrides are formed “in situ” during the milling process. At this time, tantalum hydrides ( $Ta_2H$  and  $TaH_{0.5}$ ), as well as

tantalum oxide phases ( $\text{TaO}_{0.9}$ ) were formed, which were identified with JCPDS cards 01-089-4074, 00-032-1281 and 03-065-7449, respectively. Elemental tantalum was evenly dispersed and did not react completely after 5 hours of milling. The formation of hydrides “in situ” may be due to the high impact energy generated in the system between the stainless steel balls, and the material (Ta and methanol). In such circumstances, the milling also reaches high temperatures at the atomic level, which causes the dissociation of solvent into its elementary components. Interestingly, the sequence of formation of the tantalum hydride phases during the milling process occurs over a short time (5 h), and Ta oxides as well tantalum metal unreacted were obtained, possibly because the temperature inside the system at short milling times was not high enough to completely dissociate the methanol. Under these milling conditions, it is assumed that the tantalum react with hydrogen so as with oxygen and possibly increasing the milling time is preferably to react with hydrogen, because as shown in the diffraction pattern, the hydride phases appeared with greater intensity than those of the oxides. On the other hand, the diffraction pattern results at 10 hours of milling, different phases were also observed: hydrides, and oxides. In addition, elemental tantalum was not detected, and hydride phases ( $\text{Ta}_2\text{H}$ ,  $\text{TaH}_{0.5}$ ) appeared with greater intensity on the diffractogram. According to the JCPDS cards 00-005-01315, tantalum oxide ( $\text{Ta}_2\text{O}_5$ ) was formed instead of the oxide obtained at 5 h ( $\text{TaO}_{0.9}$ ). It is assumed that after 10 hours of milling tantalum has been completely reacted to form the different phases (hydrides and oxide).

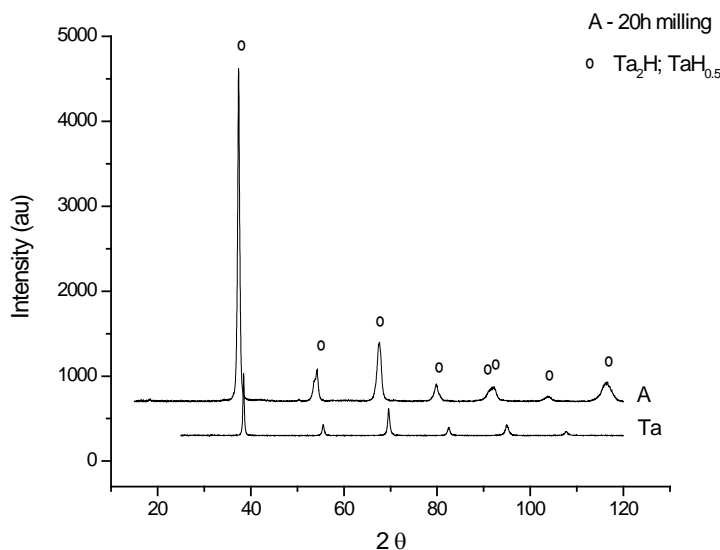


Figure 4. XRD pattern of elemental Ta before milling, and the spectrum showing the tantalum phases formed after 20 h of milling (A) in which only tantalum hydrides were observed.

Figure 4 shows the diffraction spectrum of the hydride phases 20 hours after milling, in which only the tantalum hydride phases were identified and obtained “in situ”. All deflections of the spectrum were obtained and correspond to different tantalum hydrides phases ( $Ta_2H$  and  $TaH_{0.5}$ ), according to the JCPDS 00-032-1281, 01-089-4074 respectively. The spectrum clearly shows that the intensities of the main tantalum hydrides at the  $2\theta$  angle did not interfere with the elemental tantalum intensities, whose values are 37.762, and 38.463, respectively. The shapes of the peaks in the spectrum are relatively wide compared to those in figs. 3A. It is possible that the effect of hydrogen and the thermal activation carried out inside the container transformed the material from a nanocrystalline state back to an amorphous state and that the hydrogenated phases were formed simultaneously. The results of diffraction showed only tantalum hydrides phases, however, it is possible that tantalum oxides are mixed into the main matrix at low concentrations such that diffraction technique can not detect them because there is a limit of detection in order to show the deflections in this case the corresponding oxides. The sample was also examined by X-ray diffraction at a milling time of 30 hours. The same phases of tantalum hydrides were conserved at this long milling time (30 h). Finally, at 20 h of milling or less, only tantalum hydrides phases were obtained. During the mechanical milling process, high energy is generated by the intense impact between the container walls, milling media and material. This energy is high enough to break the chemical bonds of methanol, which is used as a control medium and dissociates into hydrogen, carbon and oxygen. The bonding energies between carbon - hydrogen, oxygen - hydrogen, and carbon - oxygen are 415, 460 and 352 kJ / mol, respectively. It should be mentioned that the values are mean energies because the energy of a given bond depends slightly on the other atoms bonded in a given compound. It is assumed that the temperature in the milling system is higher than the binding energy of the methanol solvent. To dissociate into elemental oxygen, hydrogen and carbon, oxygen and hydrogen most likely remain as negative ions ( $O^-$ ,  $H^-$ ), which react quickly with the tantalum. The carbon remains in the elemental form and mixes with the other compounds without reacting with Ta or oxides, and carbon's concentration is below the detection limit. Under these experimental conditions, hydride formation may be possible because elemental Ta, as well as the compounds subsequently formed during milling, act as catalysts that improve the reaction conditions, thereby causing dissociation of the control medium into its components, H, O and C. Another possibility for the formation of different phases of tantalum may be the reduction in particle size as a function of the milling time. Smaller particle sizes most likely facilitate the formation of tantalum hydrides, as shown in the diffractograms. However, this phenomenon could result from a combination of different events that occur during the milling process and methanol dissociation. On the other hand, the hydrogen content up to 2wt% was measured in the tantalum hydride phases. It is interesting to note that, in this investigation, the hydrogen absorption process was realized “in situ” during over a short milling time. By varying the milling time, different phases of tantalum oxide were formed and changed after 20 h or less of milling. On the other hand, it is also interesting to note that there is an alternative method for preparing metal hydrides at low temperatures and normal pressures, which simultaneously confers a source of hydrogen via conversion of methanol during a mechanical milling process as a hydrogen source.



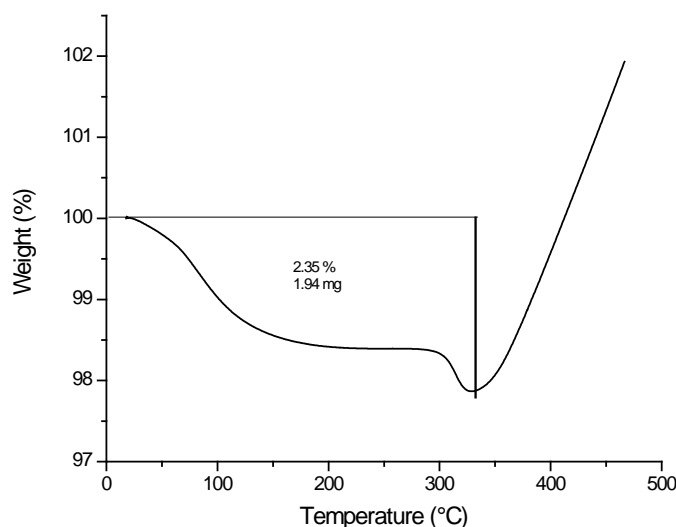


Figure 5. Shows the thermograms of Ta after 20 h of milling process, indicating that hydrogen desorption is a function of temperature.

Figure 5 shows the thermogram of Ta powder hydrogenated from mechanical milling process. The spectrum corresponds to hydrogen desorption from the material after 20 hours of milling. The hydrogen in the structure of the tantalum material was reacted “in situ” during milling. Hydrogen liberation occurs from room temperature to 320°C approximately. It is possible that there a correlation between the two mass losses on the thermogram curve and hydride phases identified, unfortunately at this time we can not know which of the two hydrides are desorbed at low temperature. The shape of the curve implies that hydrogen slowly diffused with increasing temperature, and a second hydrogen desorption event occurred between 275 and 320°C. The percentage obtained directly in the thermogram corresponded to the hydrogen that was liberated by the tantalum hydride materials, which was 2.35% by weight. The formation process of tantalum hydrides by mechanical milling was reproducible and in this temperature interval the percentage of hydrogen released was  $2.1 \pm 0.5$  by weight. Furthermore, at a higher temperature of approximately 275°C, at these conditions, hydrogen is released according to thermogram and after the material increased in weight and moves to the top. In the TGA system the Ta element begin to react with oxygen and tantalum oxide possibly is formed. The reaction takes place with oxygen, which is an impurity in the nitrogen carrier gas into the TGA system. Under these experimental conditions, with 20 h of milling process used in this work, Ta hydrides were obtained. Based on these results, it can be confirmed that the hydride phases of tantalum were formed “in situ” during the milling process. Hydrogen storage in solid materials is the long-term goal. During the last two decades, a number of promising new lightweight materials have been developed and studied. However, no materials satisfying each of the main targets with respect to storage capacities thermodynamics and kinetics have been found, and further research in



this field is required. These efforts will involve combinations of theory and experiments, development and improvement of novel methods for synthesis and finally, “in situ” methods and the development of strategies that combine different preparation techniques. Many research efforts are currently under way to develop new technologies for hydrogen storage. Metal hydrides are attractive candidates for a safe way to store hydrogen for a broad range of practical purposes, such as portable, mobile or static applications. However, more research is needed to develop metal hydrides that meet all industry requirements.

#### **4. Conclusions**

The tantalum hydrides were formed “in situ” during the mechanical milling process. Due to the high impact energy process within the mechanical milling system, the methanol used as a control medium was dissociated in carbon, hydrogen and oxygen. The oxygen and hydrogen were reacted with tantalum for producing the corresponding oxide and hydride phases, respectively after 20 h or less of milling. The mechanical milling process can be used as an alternative method for some hydride preparation such as the tantalum hydride which was readily formed.

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