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NANO SYNTHESIS OF HYDROGEN STORAGE APPLICATION BY MECHANICAL ALLOYING OF MG-TI-X (NB) USING ELECTRON MICROSCOPY

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ABSTRACT

The present research is focused on storing hydrogen in more effective and economical manner. The present work is completely experimental work comprising of mechanical ball milling, XRD machine, SEM (Scanning electron microscope), TEM (Transmission electron microscope) and impedance testing. The scope of this work is to understand the electrochemical behavior of nano-structure particle of magnesium, titanium based alloy through mechanical alloying technique. Also, evaluation of electrochemical properties of nano structure MgTi-based hydrogen storage alloys synthesized by mechanical alloying for hydrogen storage application is performed. The structural characteristics of the powder are evaluated by SEM, EDS (Energy Dispersion X-Ray Spectroscope) and TEM. Hydrogen permeation through metals can be conveniently studied with electrochemical methods like impedance spectroscopy and galvanostatic cycling. Results of SEM and EDS analysis reveal that the clear presence of alloying compounds. Also TEM image indicates a grain size of 30–50 nm for alloy compounds and also confirms the nano-structure. The charge/discharge behavior of the $Mg_{67}Ti_{33}$ based alloy by impedance analysis shows the hydrogen absorption/desorption behavior. It is also thus clear that from the above work, resistance value has been increased with addition of alloying compounds, which indicates alloying is advantageous for the charge-transfer reaction at the electrode/electrolyte interface.

Keywords:
Mg-based alloy, Mechanical alloying, electrochemical properties.

INTRODUCTION

The interest in hydrogen as energy of the future is due to it being a clean energy, most abundant element in the universe, the lightest fuel and richest in energy per unit mass. Hydrogen storage is a key enabling technology for the advancement of hydrogen and fuel cell technologies that can provide energy for an array of applications, including stationary power, portable power, and transportation [1]. Mechanical alloying (MA) is a powder processing technique that allows production of homogeneous materials starting from blended elemental powder mixtures. Mechanical alloying is normally a dry, high-energy ball milling technique that has been employed in the production of a variety of commercially useful and scientifically interesting materials. It has been recognized that powder mixtures can be mechanically activated to induce chemical reactions, i.e., mechano-chemical reactions, at room temperature or at least at much lower temperatures than normally required to produce pure metals, nanocomposites, and a variety of commercially useful materials.

A significant increase of the density and a strong reduction of the necessary volume for a certain amount of hydrogen can be achieved by storing hydrogen atomically in a metal, forming a metal hydride (MH) [2]. Metal hydride provides relatively safe storage as they can be handled without extensive safety precautions. The method of multi-component alloying was also very effective for improving the cycling capacity degradation. Our studies revealed that Scandium and Titanium alloys all had higher cycling stability than many other Mg-based electrode alloys and, the synergetic effect against corrosion was the highest [3-5]. This is very important to develop new magnesium-based alloys with fast hydriding/dehydriding kinetics at ambient temperatures and with good corrosion resistance in the aqueous KOH solution used for the large scale applications of Ni-MH secondary batteries.

Khodaparast et al. [6] has studied the effect of MgH2 powder in the composite material taken as MgH2-5 at % Ti-Mn-Cr with the help of thermal analyzer method and compared with pure un-milled MgH2. Result shows that, finer particle is procured by the addition of Ti- alloy after mechanical alloying. Also, after addition of MgH2 the desorption temperature is decreased significantly.

Martinus et al. [7], have carried out work in regard of enhancing the hydrogen absorption capacity. This is done by mechanical alloying with proper synthesis and characterization of Fe-Ti-Al alloy. Also, X-ray diffractometer is used to analyze milled specimen using rietveld method developed by Fuji Izumi. Result shows the improvement of weight percent capacity of Fe10Ti10Al alloy, which further can be promoted as new hydrogen storage materials. Li et al. [8] have performed study of microstructures, electrochemical properties of Ti–Ni and ternary Ti–Ni–Mg alloy after the processing of high-energy ball milling. Also microstructures have been seen by addition of Mg by XRD and SEM. Results shows that doping of Mg to the starting Ti–Ni powders, FCC Ti-Mg structure was detected with the main BCC phase.

Hiroshi Suzuki et al.[9]have analyzed the effects of deformation on hydrogen absorption and desorption properties of titanium to improve such properties, hydrogen was introduced into commercially pure (99.5%) titanium by the electrochemical method. Hydrogen absorption was promoted by applying tensile deformation prior to charging, which leads to hydride formation within a short charging time. Hydrogen was mainly trapped by dislocations followed by hydride formation and that a large fraction of twins hindered dislocation motion, thus reducing dislocation density and decreasing the amount of absorbed hydrogen and by applying in-plane compressive stress to a charged titanium specimen, almost half the hydrogen was released due to hydride decomposition at room temperature.

Yunfeng Zhu et al.[10] have performed hydriding combustion synthesis (HCS) and subsequent mechanical milling (MM) was used to prepare Mg-based hydrogen storage electrode alloy. Mechanical alloying has been used to synthesize amorphous or nanocrystalline magnesium-based alloys. The phase structures and electrochemical properties of the alloys were characterized by X-ray diffraction analysis and galvanotactic charge–discharge cycle test. The XRD results showed that the structure of the as-milled alloys was nanocrystallite or amorphous-like state and electrochemical measurements showed that the discharge capacity was improved greatly for the products of HCS+MM.

Kalisvaart et al.[11] carried out electrochemical hydrogen storage properties of MgxSc1−X alloys are investigated both in thin film and bulk form. A comparison is made between the electrochemical, thermodynamic and structural properties of both systems and is shows that the electrochemical properties of the thin films and bulk materials strongly resemble one another. The formation of a fluorite structure for the bulk hydride was confirmed by X-ray diffraction. The thin films can be regarded as a suitable model system for bulk alloys and electrochemical responses and the trends in storage capacity and kinetics with composition and hydrogen content are quite similar and the thin films can be regarded as a suitable model system for bulk alloys.

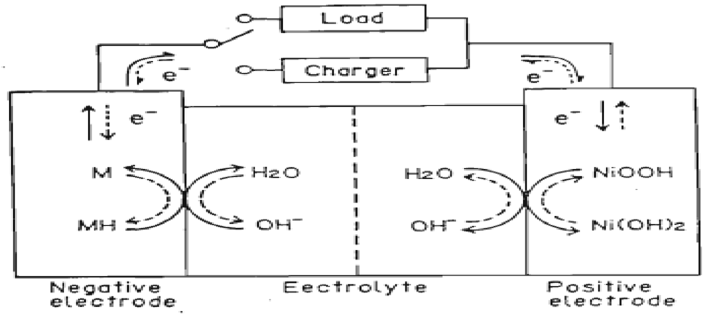
Chuang et al.[12] evaluated pressure composition isotherms and charging–discharging properties of Ti–Zr based alloys. Nickel substitution for Manganese and Chromium in the alloy was found to increase the plateau pressure and the partial substitution of Cr by Vanadium greatly improved the discharge capacity. Here, the six-element alloy, Ti0.5Zr0.5V0.2Mn0.7Cr0.5Ni0.6, degraded rapidly in the gas–solid reaction and also hydrogen contents in the alloy under low pressure were increased during hydrogen absorption–desorption cycling. The composition of an alloy plays an important role in its properties. Storage of the alloy powders under air for two months reduced the discharge capacity significantly and the activation time of charge–discharge reaction has been reduced.

The present article deals with the hydrogen storage in metal hydrides with particular interest in MgTi as it has potential to become one of the most promising storage materials [13]. MgTi-based hydrogen storage alloy is a kind of negative electrode of Nickel-Metal Hydride (Ni-MH) batteries owing to its significant advantages, such as high discharge capacities, abundant reserves, low cost, etc. Ni-MH is a type of rechargeable batteries. These are widely used in all electric plug-in, mobile phones, laptops, remote control cars, telecommunication, power tools etc. The use of Mg–Ti alloy as high-capacity Hydrogen storage materials for batteries. By means of electrochemical loading of Mg0.8-Ti0.2 they found a gravimetrical storage capacity of 6.53 wt% H: which is four times higher than the commercially available Ni-MH batteries. The titanium doping of magnesium greatly enhances the kinetics of hydrogen uptake and release. Mg0.60Ti0.2Sc0.2 composition revealed excellent kinetic properties and the highest reversible hydrogen capacity of 6.7 wt. % of hydrogen.

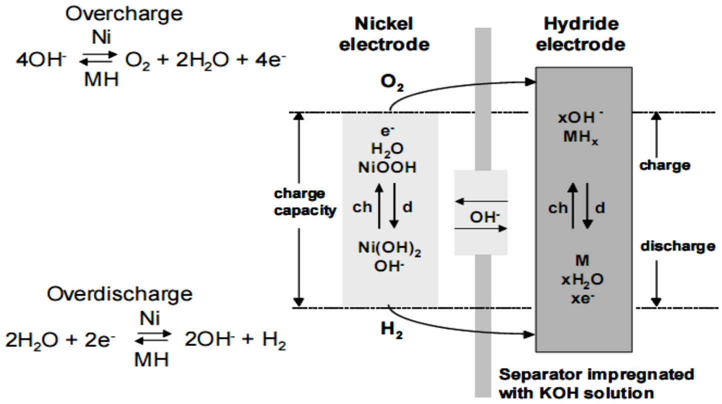
PROBLEM DISCRIPTION

Construction and Principle of operation of Ni-MH batteries

The construction of Ni-MH batteries is very similar to that of Ni-Cd types except for the negative electrode materials. Potassium hydroxide solution is the electrolyte. The negative and positive electrodes are separated by alkali resistant or nylon material. In this battery, the negative electrode is made of a hydrogen storage alloy that can allow electrochemical storage and release of hydrogen during the charge discharge process. The Nickel hydroxide positive electrode is electrochemically reversible between Ni $(OH)_2$ and Nickel oxy-hydroxide. The electrolyte, which is an aqueous solution of potassium hydroxide, has a very high conductivity and usually does not enter into the cell reaction to any significant extent. The electrolyte concentration remains fairly constant over the entire range of state of charge or discharge. These factors lead to a battery with high power performance and long cycle life.



(a) Battery setup



(b) Battery setup with charge-discharge

Fig. 1.Schematic drawing of the charging and discharging reactions

During charging hydrogen is formed at the interface of electrode and electrolyte by an electrochemical reduction of water and is subsequently absorbed by the alloy. During discharging, the hydrogen in the MH is desorbed and oxidized electrochemically at the interface. The process of charging and discharging and the half cell and overall cell reaction on charge and discharge of the battery is shown schematically in the figure. The characteristic of the batteries is that concentration of the electrolyte solution remains unchanged during charging and discharging process because water is not involved in the overall cell reaction.

The excellent durability of the Ni-MH batteries against overcharging or discharging is explained by the following reactions for the case of limited capacity shown by the positive electrode. During overcharging the oxygen gas generated from the positive Nickel electrode is consumed by the hydrogen storage alloy negative electrode.

$$2OH^{-} \rightarrow H2O + \frac{1}{2} O^{2} + e^{-}$$

$$2MH + \frac{1}{2} O_2 \rightarrow 2M + H_2O$$

$$2M + 2H_2O + e^- \rightarrow 2MH + 2OH^-$$

During over-discharging, the hydrogen generated from the polarity reversed Nickel electrode is oxidized into water at the hydrogen storage negative electrode according to the following reactions.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

$$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$$

Material

The objective of this present work is to develop Magnesium-Titanium based Hydrogen storage alloy using mechanical alloying. Elemental Magnesium, Titanium and Scandium with an average particle size of some microns were mechanically alloyed in a high energy ball mill.

Composition in Weight Percentage-

- $Mg_{67}Ti_{33}$
- $Mg_{34}Ti_{22}Nb_{44}$

METHODOLOGY

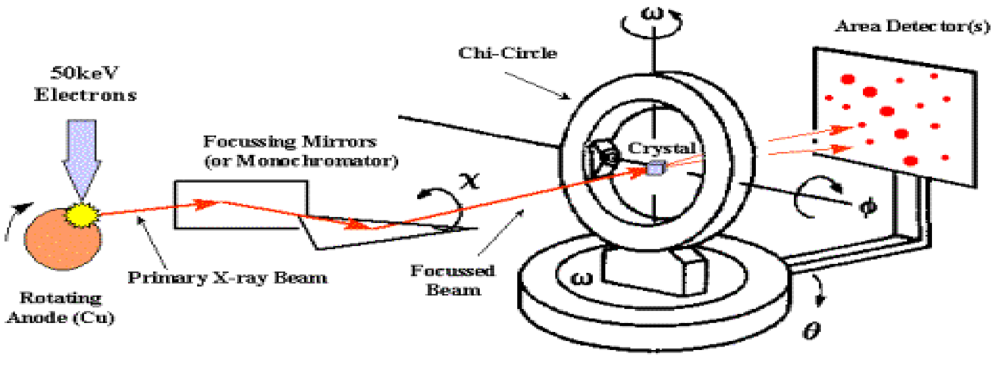
X-ray crystallography is a method of determining the arrangement of atoms within a crystal, in which a beam of X-rays strikes a crystal and causes the beam of light to spread into many specific directions. The X-ray diffraction pattern of a pure substance is, therefore, like a fingerprint of the substance. The powder diffraction method is thus ideally suited for characterization and identification of polycrystalline phases.

In an X-ray diffraction measurement, a crystal is mounted on a goniometer and gradually rotated while being bombarded with X-rays, producing a diffraction pattern of regularly spaced spots known as reflections. The principals of stress analysis by the X-ray diffraction is based on measuring angular lattice strain distributions i.e. we choose a reflection at high angle (2θ)and measure the change in the 'd' spacing with different orientations of the sample. X-rays can be considered waves of electromagnetic radiation. X-ray striking an electron produces secondary spherical waves emanating from the electron. This phenomenon is known as elastic scattering. Inelastic scattering alters the phase of the diffracted x-rays, and as a result does not produce useful data for x-ray diffraction. Rather, in-elastically scattered x-rays contribute to the background noise in a diffraction pattern.

A regular array of scatters produces a regular array of spherical waves. Although these waves cancel one another out in most directions through destructive interference, they add constructively in a few specific directions, determined by Bragg's law:

$$n\lambda = 2d\sin\theta$$

Here d is the spacing between diffracting planes, θ is the incident angle, n is any integer, and λ is the wavelength of the beam. These specific directions appear as spots on the diffraction pattern called reflections.



4-Circle Goniometer (Eulerian or Kappa Geometry)

Fig. 2.XRD Setup

Grain Size determination

Analysis of XRD peak broadening using Scherer formulation is used to find the average particle size of nano crystallites. The peak broadening is due to incomplete destructive interference in scattering directions where the x-rays are out of phase. The observed peak broadening is a convolution of intrinsic broadening due to the instrumental and geometrical conditions and broadening due to sample micro structural features like grain size and lattice strain. From the observed peak width, the other contributions may be eliminated as follows:

$$B_r = [(B_o-B_i) \surd (B_o-B_i)]1/2$$

Where, B_o is the observed peak width (FWHM), B_i is the instrument broadening and Br is the remaining width. The Scherer equation can be written as:

$$\tau = K\lambda / \beta cos\theta$$

Where, τ is the grain size of the material, K is a dimensionless shape factor~ 0.94, λ is the incident wavelength, β is the line broadening at half the maximum intensity (FWHM) and sometimes denoted as Δ(2θ), θ is the Bragg angle.

EXPERIMENTAL SETUP

Biologic SP-150

The SP-150 is a full featured economic research grade potentiostat. With its modular chassis, this instrument can be customized to address all applications in the area of classical electrochemistry. The SP-150 potentiostat configuration can be selected at purchase to include an EIS-capable potentiostat, and a low current option (1 nA full scale range). It is controlled from a PC by a USB or Ethernet. It can also be connected to external high current boosters (2, 5, 10, 20, 80 and 100A). The SP-150 has two analog inputs and one analog output to manage external instrument such as rotating electrode or a quartz crystal microbalance and record the generated data.

Fig. 3.SP-150 model

EC-Lab Software

EC-Lab® is an advanced software package for performing electrochemistry measurements. With an easy-to-use straight-forward parameter input window, this unique interface gives a simple overview for the user to create, modify and visualize the experimental setup. The software allows the user to set data sampling and recording conditions without any limit on the number of data points taken. One of the advanced functions of this software is the capability to perform EIS measurements simultaneously on the working and on the counter electrodes.

These techniques can address applications in voltammetry, EIS, corrosion and energy source development. A powerful technique builder can execute a series of different modular techniques, wait and loop features to create complex experimental sequences. Two view modes are available in EC-Lab®. The setup of experiments can be done with a technique menu, or by inputting parameter values into a spread sheet. Many experimental parameters can be modified "on the fly" during the experiment, with the changes stored into the raw data file. The appearance of the software interface is able to be adapted to create the best working environment for the user.

Setup

The method uses a reference electrode, working electrode, and counter electrode which in combination are sometimes referred to as a three-electrode setup. Electrolyte is usually added to the test solution to ensure sufficient conductivity. The combination of the solvent, electrolyte and specific working electrode material determines the range of the potential. Electrodes are static and sit in unstirred solutions during the tests. The samples prepared through cold pressing were used as the working electrode.

In potentiostatic mode, a potentiostat/galvanostat will accurately control the potential of the Counter electrode against the working electrode so that the potential difference between the working electrode and the reference electrode is well defined, and correspond to the value specified by the user. In galvanostatic mode, the current flow between the working electrode and the counter electrode is controlled. The potential difference between the reference electrode and working electrode and the current flowing between the counter electrodes and working electrode are continuously monitored.

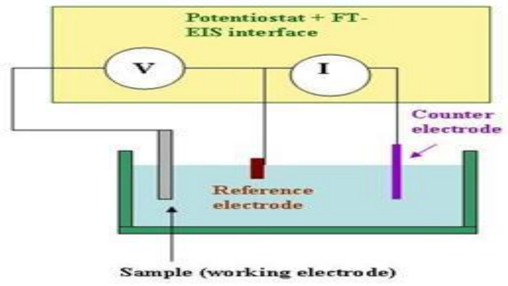


Fig. 4.Three electrode setup

The counter electrode (CE), also known as auxiliary or second electrode, is an electrode which is used to close the current circuit in the electrochemical cell and it is usually made of an inert material and it does not participate in the electrochemical reaction. The counter electrode was NiOOH/Ni $(OH)_2$. A reference electrode (RE) is an electrode which has a stable and well-known electrode potential. The reference electrode was Hg/HgO (Calomel).The working electrode (WE) is the electrode in an electrochemical system on which the reaction of interest is occurring. Common working electrodes can be made of inert materials such as Au, Ag, Pt, glassy carbon and Hg drop and film electrodes etc. The size and shape of the working electrode also varies and it depends on the application. The electrolyte 6M KOH was prepared by dissolving 1.5g KOH pellets in 250ml de-ionized water. Tests were performed using the SP-150 model potentiostat/galvanostat unit.

Sample Preparation

Elemental Mg and Ti, Mg, Ti and Sc, powders were mixed and charged in to stainless steel vials under high purity argon atmosphere. The ball to powder ratio was 10:1 and the diameter of the balls were 5mm. The mechanical alloying process was performed by an attritor ball mill at 260 rpm and the milling duration was 30 hours. At regular intervals argon gas was discharged to prevent possible oxidation of the alloy powders. As a result of ball milling better powder homogeneity was obtained.

The ball to powder ratio (BPR) has a significant effect on the time required to achieve a particular phase in the powder being milled. The higher the BPR, the shorter is the time required. At a high BPR, because of an increase in the weight proportion of the balls, the number of collisions per unit time increases and consequently more energy is transferred to the powder particles so alloying takes place faster. At high speeds, the temperature of the vial may reach higher value. This may be advantageous in some cases where diffusion is required to promote homogenization or alloying in powders. But in some cases, this increase in temperature may be a disadvantage because the increased temperature accelerates the transformation process and results in the decomposition of the supersaturated solid solutions or other metastable phases formed during milling.

Table.1 Parameter and Variables of Ball Milling.

Parameter	Variable
Type of mill	Attritor ball mill
Milling container (Vial)	Hardened Tungsten Carbide
Grinding ball	Stainless Steel
Ball diameter (mm)	5
BPR ratio	10:1
Milling speed (rpm)	260
Milling time (hours)	30
Type of Milling	Dry Milling

Because of above reasons the mill was allowed to run for 15 minutes and then rested for the next 10 minutes in order to avoid temperature rise. A process control agent (PCA) is added to the powder mixture during milling to reduce the effect of cold welding. Here toluene is used as the process control agent.

RESULT AND DISCUSSION

Powder analysis

The alloyed powders prepared through ball milling process were sent for characterization using the X-ray Diffraction technique, Scanning Electron Microscope and Transmission Electron Microscope. The phases were characterized by the Cu K α radiation from the source of radiation.

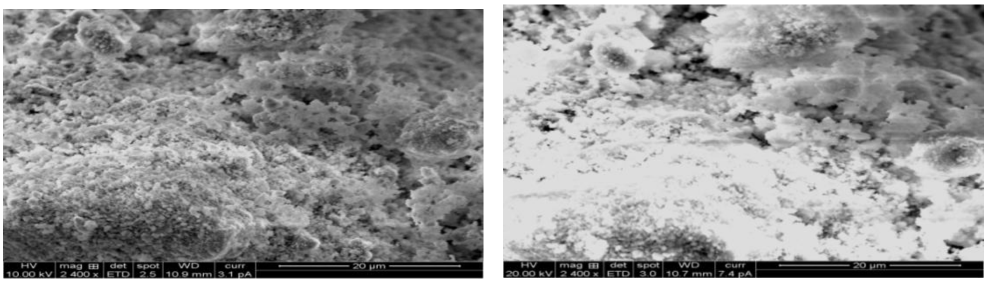


Fig.5. SEM image of $Mg_{67}Ti_{33}$

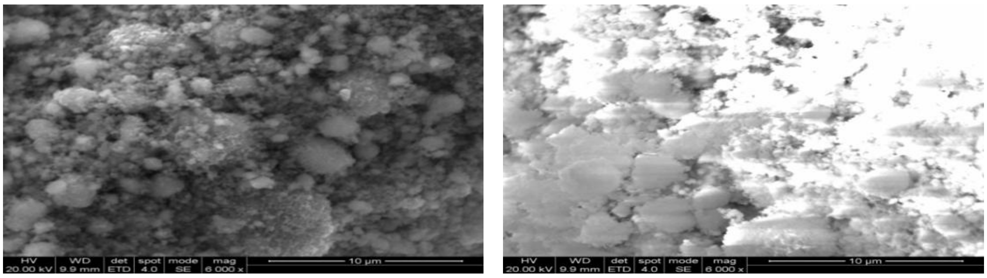


Fig.6. SEM image of $Mg_{34}Ti_{22}Nb_{44}$

The SEM study helps to understand the MA mechanism, particle morphology etc. Fig shows the SEM micrographs of $Mg_{0.8}Ti_{0.2}$ (67wt%Mg, 33wt%Ti) system processed by MA at 30 hrs milling intervals. At 30 hrs of milling, the powder shows nanostructure. This is mainly due to fineness or more surface area of powder particle at 30 hrs. It is believed that the powder particle not only submicron in size, also having Nano grains. The regular particle morphology, submicron size particle with Nano crystals will be more helpful to absorb/ desorb hydrogen. The SEM images of mechanically alloyed (30hrs) $Mg_{34}Ti_{22}Nb_{44}$ powders. Particle size before and after, milling is 25µm and 3µm respectively. The morphology of MA powders is spherical with fine and uniform distribution. The chemical composition of alloy phase MgTi from EDS analysis indicate the presence of Magnesium, Titanium compound. The chemical composition of alloy phase $Mg_{34}Ti_{22}Nb_{44}$ from EDS analysis indicates the presence of magnesium, titanium, niobium compound. Fig. shows a typical TEM image combined with selected area diffraction pattern of $Mg_{67}Ti_{33}$.The crystallite size of the powders is around 30-50 nm. The SAD pattern indicates the Nano-crystalline nature. A typical TEM image combined with selected area diffraction pattern of MgNb. The crystallite size of the powders is around 30-50nm. The SAD pattern indicates the nano-crystalline nature.

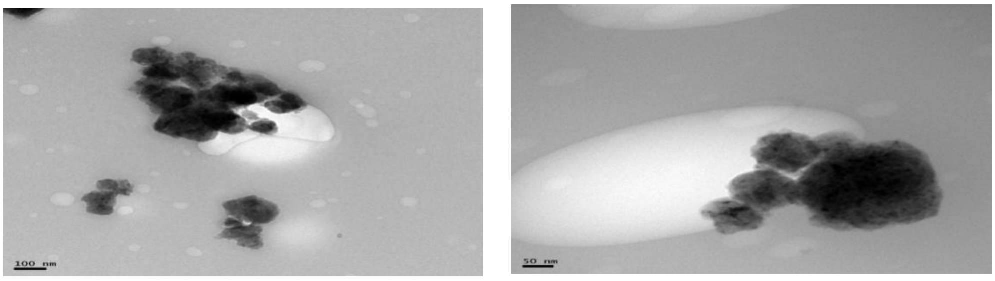


Fig.7. TEM image of $Mg_{67}Ti_{33}$

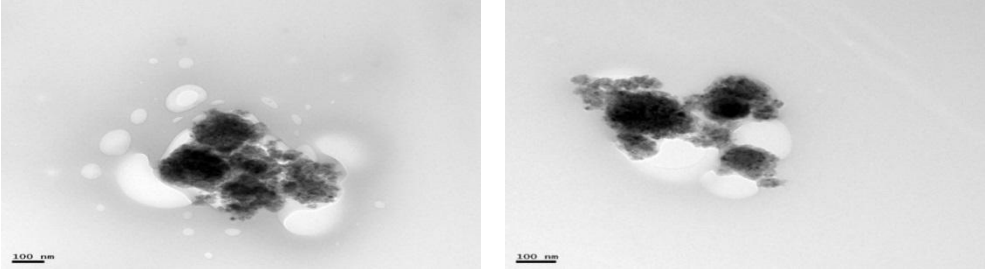


Fig.8. TEM image of $Mg_{34}Ti_{22}Nb_{44}$

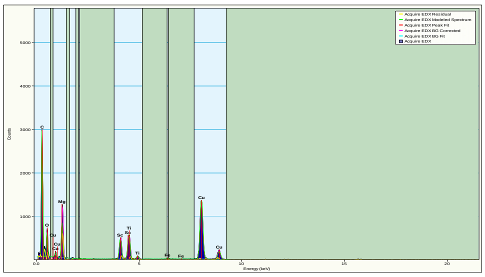


Fig.9.EDS image of $Mg_{67}Ti_{33}$

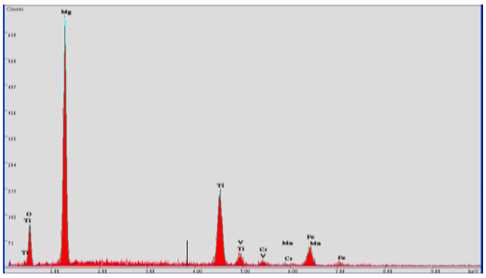


Fig.10. EDS image of $Mg_{34}Ti_{22}Nb_{44}$

CONCLUSION

The above results may be concluded in below mentioned pattern: -

1. $Mg_{67}Ti_{33}$ based alloys were successfully prepared by using a high energy mechanical milling. SEM images confirm that the particle size of 1-15 µm. SEM and EDS analysis reveal that the presence of alloy compounds like Mg, Ti, Nb. TEM image indicates a grain size of 30–50 nm for alloy compounds and also confirms the nano structure.
2. The charge/ discharge behavior of the $Mg_{67}Ti_{33}$ based alloy shows the hydrogen absorption/ desorption behavior. Titanium has the high absorption/ desorption value.
3. The redox reaction shows that Niobium has the good absorption among the entire alloy.
4. It is also clear that resistance value has been increased with addition of alloy, which indicates addition of alloy is advantageous for the charge transfer reaction at the electrode/electrolyte interface.

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