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WHEC 2014
20th World Hydrogen Energy Conference 2014
June 15[Sun] – 20[Fri], 2014 KDJ Convention Center, Gwangju Metropolitan City, Korea

# The characteristics of Magnesium-Lanthanum alloy obtained by an electrochemical process

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ABSTRACT

In this work, Magnesium-Lanthanum alloy was synthesized by an electrodeposition technique using an aqueous solution, based on Magnesium chloride hexahydrate and Lanthanum(III) Nitrate at a voltage of 4 Volts. A copper cathode plate is used for the deposition of the Mg-La alloy. The as-prepared powder was characterized by scanning electron microscope (SEM) to describe the morphology, energy dispersive spectroscopy (EDS) to determine the chemical composition, X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectra in order to define the chemical structure. Morphological description reveals the formation of heterogeneous chemical structures of very small size on the surface of the sample. EDS analysis indicates the presence of Mg, La and O as major elements and Cl as minor element in terms of weight percentages. X-ray results showed the existence of two distinct phases, Magnesium Hydroxide ($Mg(OH)_2$) and Lanthanum hydroxide ($La(OH)_3$), from the obtained deposit. FTIR analysis confirms the presence of the two phases identified in XRD diffractogram and it can be exhibited by clear peaks.

*Keywords:* Mg-La alloy, Electrodeposition, aqueous solution, analysis techniques, coating.

## 1. Introduction

Magnesium is the eighth most abundant element on the earth and constitutes about 2% of Earth's crust by weight. It is the third most copious element in seawater. It is characterized by various properties for instance a low density, a low cost, a very good malleability and ductility, a high strength/weight ratio and an environmentally friendly nature [1-5]. The high electrochemical potential of magnesium (-2.4 Volts) and a substantial reactivity toward acids and their salts are their two chemical properties [6, 7]. As the lightest structural material, magnesium alloys have been used increasingly for structural compounds for several decades, particularly in the automotive, electronics and aerospace industries and expected to become one of the most promising lightweight materials in the 21st century [8-10]. Recently, many investigations have been made in hydrogen storage materials and magnesium based alloys are considered to be the most promising [10-12]. As benefits of the application of magnesium alloys, Cortés and Cantwell [13] mention improved electromagnetic protective capability and superior corrosion resistance. The addition of rare-earth (RE) elements such as La, Y, Ce and Gd to Mg has received significant attention [14-16]. It has been also reported that Mg-RE alloys exhibit excellent mechanical properties. They are typified by higher specific strength and better creep resistance [17-19]. To fabricate the Mg alloys, three methods have been explored: physical as PVD (Physical Vapour Deposition) [20], mechanical as

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milling techniques [21] and chemical as CVD (Chemical Vapour Deposition) [22]. Besides these methods, metal alloys electrodeposition in aqueous ionic liquids are receiving increased interest [23-27]. It is the most economical method of prepared Mg-RE alloys and can be easily implemented on a large scale. At the same time, this method had other advantages: the phases of alloys could be controlled by electrochemical parameters and could be employed over a large temperature range.

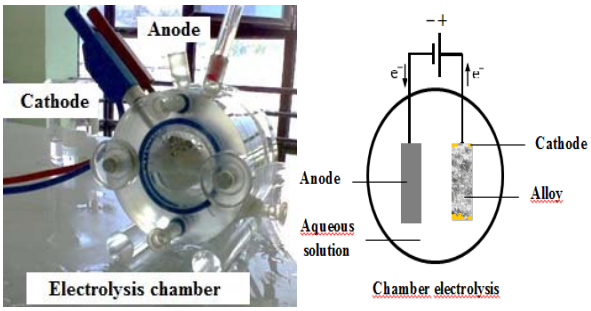
The aim of the work presented in this paper is to study the characteristics of the Magnesium-Lanthanum alloy elaborated by means electrodeposition technique. Section 2 describes the experimental methodology. It includes chemicals and samples preparation and characterization of Mg-La alloys. Section 3 examines the results obtained monitoring with discussions based to the ones found in literature. In the end, conclusions are drawn with some indicators to future analysis.

## 2. Experimental and procedures

### 2.1 Experimental Setup

Magnesium chloride hexahydrate ($MgCl_2{\cdot}6H_2O$) and Lanthanum nitrate ($La(NO_3)_3{\cdot}6H_2O$) from Merck Group were employed as received. The ultra-pure water obtained by means of a MEDICA S/R/D (7/15) purification system was used to prepare the different solutions. A mass of 16.2 g of $MgCl_2{\cdot}6H_2O$ and a mass of 4.3 g of $La(NO_3)_3{\cdot}6H_2O$ were dissolved in 34 mL of ultra-pure water at room temperature. The obtained aqueous solutions with pH=6 were prepared for electrodeposition process.

The electrochemical process consists in a cylindrical electrolysis chamber of an internal volume of 36.6 mL. The plexiglass vessel has as inner dimensions 1.8 cm radius and 3.6 cm height. A copper cathode plate and a tungsten thread anode, with a 2.2 cm gap, connected to a conventional potentiometric power source, were used to ensure the deposition of Mg-La alloy. The potential value selected to study its effect on the characteristics of the Mg-La alloys was 4 Volts. The deposition experiments were performed during 8h at ambient temperature (23 °C). The obtained deposit was scraped from the copper cathode plate, dried for 1h at 110 °C, milled manually in a marble mortar and subjected to further analyzes. Fig. 1 illustrates a photograph and a schematic overview of the defined experimental setup.




(a) (b)

Fig. 1. Illustrations of the electrodeposition experimental setup. (a) Photograph and (b) schematic overview.

### 2.2 Characterization of Mg-La alloy

The morphology and chemical composition of the obtained alloy were investigated by a scanning electron microscope (SEM, LEO 1455 VP, acceleration voltage of 20 kV) at a working distance of 15 mm equipped with an X-ray energy dispersive spectrometer (EDS, Inca X- sight, Oxford Instrument). The phase identification of the alloy were determined by means of X-ray diffractometer (XRD, Philips X' PERT) using Cu Kα radiation source (λ=1.54 Å, 40 kV, 30 mA) at room temperature. The scanning rate of 0.02°/s within the $2\theta$ range going from 10° to 90° was used in order to increase counting statistics and to improve the signal/noise ratio. Thermogravimetric and differential scanning calorimetry analysis of the sample of the scraped deposit was performed by SETARAM apparatus under flowing Argon atmosphere at the heating rate of 10 °C/min in the temperature range of 25 °C to 600 °C. Fourier transform infrared (FTIR) spectroscopy of the alloys samples was carried out with a Nicolet 380 FT-IR spectrometer using the ATR technique. All spectra were collected with the resolution of 4 $cm^{-1}$ in the range of 4000-500 $cm^{-1}$.

## 3. Results and discussion

As mentioned in the previous section, the characteristics of Mg-La alloy will be studied to 4 Volts. This section is structured as follows: a presentation of EDS and X-ray diffraction analyzes as well as the IR absorption spectroscopy studies.

### 3.1 EDS analysis of the as-deposited powders

Fig. 2 shows the surface morphology (SEM) of as-prepared Mg-La alloy. The image exhibits the formation of

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heterogeneous chemical structures and the different phases seem quite imbricated. Interestingly enough, the size of the aggregates found was in the order of nanometers to micrometers.

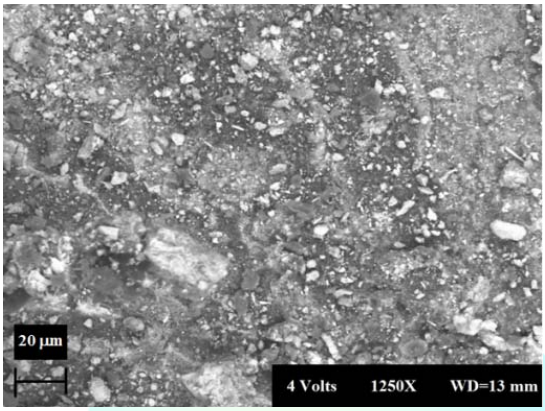


Fig. 2. SEM image of the as-deposited powder

The compositions of Mg-La alloy was examined by EDS, as shown in Table 1. The main elements detected on the surface of the coatings were Oxygen, Magnesium, Lanthanum and a little amount of Chlorine. The existence of O, Mg, La and Cl in the as-deposited powder can be justified by the electrolyte used in electrodeposition experiment. As we can see from this Table, Mg-La alloy in 4 Volts is characterized by high contents of Oxygen (40.7 %) and Lanthanum (31.5 %). The amounts of Magnesium and Chlorine are respectively 21.1 and 6.7 %.

Table 1. Alloy element compositions in weight and atomic percentage

| Element | Weight % | Atomic % |
|---|---|---|
| Oxygen | 40.7 | 66.5 |
| Magnesium | 21.1 | 22.5 |
| Chlorine | 6.7 | 5 |
| Lanthanum | 31.5 | 6 |

3.2 X-ray diffraction analysis of the as-prepared powders

The different phases of the as-deposited powder are discerned clearly in Fig. 3 through XRD diffractogram. According to the standard data JCPDS, two significant characteristic peaks are detected, which indicate the existence of Magnesium hydroxide ($Mg(OH)_2$) as a hexagonal structure with lattice constants of a = 3.148 Å and c = 4.787 Å [28] and Lanthanum(III) hydroxide ($La(OH)_3$) as a hexagonal structure with lattice constants a = 6.528 Å and c = 3.858 Å [29, 30]. As can be seen from this Figure, peaks at diffraction angle 2θ of 18.6°, 35.8°, 37.9°, 50.8°, 58.7° and 62.1° are related to $Mg(OH)_2$ whereas those at 2θ of 15.6°, 27.9°, 39.3°, 46.8°, 48.5° and 54.9° are associated to $La(OH)_3$. The peak of $Mg(OH)_2$ can achieve a maximum of intensity value 917 and 207 as minimum. The two others distinct intensity values of the peak $La(OH)_3$ are respectively 895 and 185.

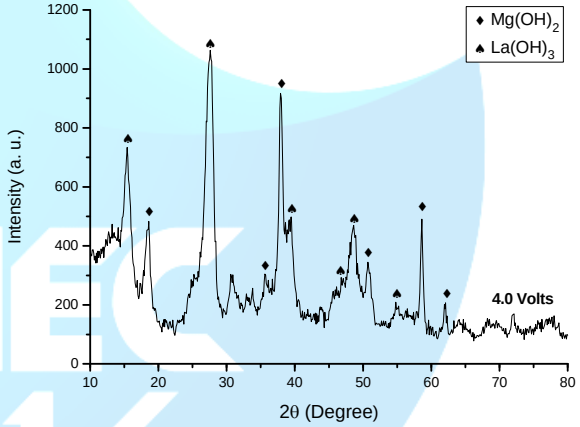


Fig. 3. X-ray diffraction pattern of the sample

3.3 FTIR spectroscopy analysis of the as-deposited powders

Further to the above analyzes, the FTIR spectroscopy study is evident for the structural confirmation of the as-prepared powder. The FTIR transition spectrum of the as-deposited Mg-La alloy in the range of 4000-500 $cm^{-1}$ for 4 Volts is revealed in Fig. 4. A sharp and strong peak at 3696 $cm^{-1}$, which has as transmittance value 75.67, can be ascribed to vibrations and stretching of OH bonds in $Mg(OH)_2$ [31, 32]. The band centred at 3606 $cm^{-1}$, corresponding at 79.37, is associated for stretching mode of $OH^-$ in Lanthanum (III) hydroxide [33, 34]. The bands at 3455 $cm^{-1}$ and 1640 $cm^{-1}$, relating respectively to 79.24 and 81.70, are attributed to the hydroxyl groups in water as mentioned by Aghazadeh and Khosrow-pour [35, 36]. The two other peculiar bands at about 1434 $cm^{-1}$ and 1048 $cm^{-1}$, characterized by the following values; 78.69 and 82.30, can be associated to asymmetric stretching vibrations of the carbonate group, which originate from the reaction of the as-prepared powders with $CO_2$ from air during the FTIR spectroscopy analysis [33, 35, 37].

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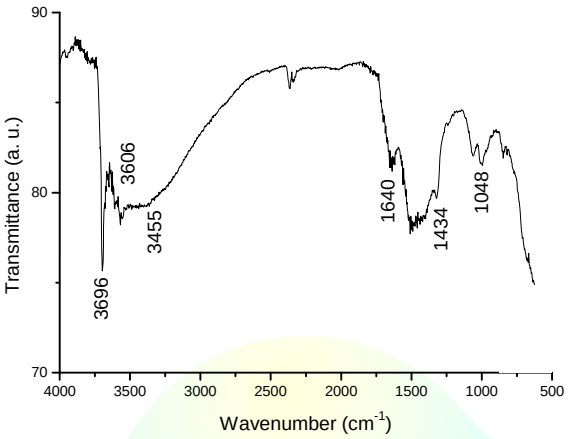


Fig. 4. FTIR transition spectrum of the as-prepared powder

## 4. Conclusion

(1) The synthesis of Magnesium-Lanthanum powder due to an electrodeposition process at room temperature has been successfully treated.

(2) The different results on the behavior of the as-deposited powder are in agreement with those of literature Magnesium-based coatings.

(3) As future analyzes, a wide Mg-based would be studied with the different voltages and make a comparison in order to figure out the potential material for the hydrogen storage.

REFERENCES


[1] L.Zhou et al., "Microstructural characteristics and mechanical properties of non-combustive Mg–9Al–Zn–Ca magnesium alloy friction stir welded joints", Materials & Design, Vol.42, 2012, pp.505-512.

[2] X.Yuan et al., "Microstructural characteristics of joint region during diffusion-brazing of magnesium alloy and stainless steel using pure copper interlayer", Transactions of Nonferrous Metals Society of China, Vol.23, 2013, pp.599-604.

[3] A.Tharumarajah et al., "Is there an environmental advantage of using magnesium components for light-weighting cars?", Journal of Cleaner Production, Vol.15, 2007, pp.1007-1013.

[4] N.Hort et al., "Magnesium alloys as implant materials – Principles of property design for Mg-RE alloys", Acta Biomaterialia, Vol.6, 2010, pp.1714-1725.

[5] Q.S.Zhao et al., "Reversibility of electrochemical magnesium deposition from tetrahydrofuran solutions containing pyrrolidinyl magnesium halide", Electrochimica Acta, Vol.56, 2011, pp.6530-6535.

[6] F.Rosalbino et al., "Electrochemical behaviour assessment of novel Mg-rich Mg–Al–RE alloys (RE = Ce, Er)", Intermetallics, Vol.14, 2006, pp.1487-1492.

[7] J.G.Kim et al., "Development of hight-driving potential and high-efficiency Mg-based sacrificial anodes for cathodic protection", Journal of materials Science Letters, Vol.19, 2000, pp.477-479.

[8] D.S.Mehta et al., "Investigation of wear properties of magnesium and aluminium alloys for automotive applications", Journal of Materials Processing Technology, Vol.155-156, 2004, pp.1526-1531.

[9] L.Wang et al., "Electrochemical behaviour of AZ61 magnesium alloy in dilute NaCL solutions", Materials & Design, Vol.33, 2012, pp.345-349.

[10] R.Alderliesten et al., "The application of magnesium based Fibre Metal Laminates in aerospace structures", Composites Science and Technology, Vol.68, 2008, pp.2983-2993.

[11] M.Jurczyk et al., "Hydrogen storage by Mg-based nanocomposites", International Journal of Hydrogen Energy, Vol.37, 2012, pp.3652-3658.

[12] Y.Fan et al., "Modifying microstructures and hydrogen storage properties of 85 mass% Mg–10 mass% Ni–5 mass% La alloy by ultra-high pressure", Journal of Alloys and Compounds, Vol.596, 2014, pp.113-117.

[13] Z.Gao et al., "Phase structures and electrochemical properties of $La_{0.8-x}Gd_{0.2}Mg_xNi_{3.1}Co_{0.3}$ $Al_{0.1}$ hydrogen storage alloys", Journal of Power Sources, Vol.241, 2013, pp.509-516.

[14] P.Cortés et al., "The fracture properties of a fibre-metal laminate based on magnesium alloy", Composites Part B: Engineering, Vol.37, 2005, pp.163-170.

[15] N.Stanford et al., "The effect of rare earth elements on the behavior of magnesium-based alloys: Part 1 – Hot deformation behaviour", Materials Science and Engineering: A, Vol.565, 2013, pp.459-468.

[16] S.Gavras et al., "Microstructure and property evaluation of high-pressure die-cast Mg-La-rare earth (Nd, Y or Gd) alloys", Journal of Alloys and Compounds, Vol.597, 2014, pp.21-29.

[17] Y.B.Kang et al., "Thermodynamic evaluations and optimizations of binary Mg-light Rare Earth (La, Ce, Pr, Nd, Sm) systems", Calphad, Vol.38, 2012, pp.100-116.


* Corresponding author. Tel.:+33-24-848-4065, E-mail address: khaled.chetehouna@insa-cvl.fr (K. Chetehouna).

[18] F.A.Mirza et al., "A modified Johnson-Cook constitutive relationship for a rare-earth containing magnesium alloy", Journal of Rare Earths, Vol.31, 2013, pp.1202-1207.
[19] H.Bayani et al., "Effect of rare earth elements addition on thermal fatigue behaviors of AZ91 magnesium alloy", Journal of Rare Earths, Vol.27, 2009, pp.255-258.
[20] L.Zhang et al., "Microstructure and mechanical properties of as-cast and heat treated Mg-15Gd-3Y alloy", Journal of Rare Earths, Vol.29, 2011, pp.77-82.
[21] G.Garcés et al., "Texture of magnesium alloy films growth by physical vapour deposition (PVD)", Journal of Alloys and Compounds, Vol.309, 2000, pp.229-238.
[22] H.Z.Yan et al., "The influence of ball milling process on formation and electrochemical properties of amorphous MgNi hydrogen storage alloys", Materials Science and Engineering: A, Vol.435-436, 2006, pp.711-716.
[23] Ch.Christoglou et al., "Deposition of aluminium on magnesium by a CVD process", Surface and Coatings Technology, Vol.184, 2004, pp.149-155.
[24] Z.Chen et al., "Electrodeposition of Li and electrochemical formation of Mg-Li alloys from the eutectic LiCl–KCl", Journal of Alloys and Compounds, Vol.464, 2008, pp.174-178.
[25] Y.Liu et al., "A Electro-deposition process for fabrication of biomimetic super-hydrophobic surface and its corrosion resistance on magnesium", Electrochimica Acta, Vol.125, 2014, pp.395-403.
[26] C.Liebenow et al., "The electrodeposition of magnesium using solutions of organomagnesium halides, amidomagnesium halides and magnesium organoborates", Electrochemistry Communications, Vol.2, 2000, pp.641-645.
[27] S.Wang et al., "Electrodeposition mechanism and characterization of Ni-Cu alloy coatings from a eutectic-based ionic liquid", Applied Surface Science, Vol.288, 2014, pp.530-536.
[28] T.S.Sutto et al., "Electochemical and structural characterization of Mg ion intercalation into $Co_3O_4$ using ionic liquid electrolytes", Electrochimica Acta, Vol.80, 2012, pp.413-417.
[29] L.Kumari et al., "Synthesis, characterization and optical properties of $Mg(OH)_2$ micro-/nanostructure and its conversion to MgO", Ceramics International, Vol.35, 2009, pp.3355-3364.
[30] M.Aghazadeh et al., "A novel lanthanum hydroxide nanostructure prepared by cathodic electrodeposition", Materials Letters, Vol.65, 2011, pp.1466-1468.
[31] P.Bocchetta et al., "Template electrosynthesis of $La(OH)_3$ and $Nd(OH)_3$ nanowires using porous anodic alumina membranes", Electrochemistry Communications, Vol.9, 2007, pp.683-688.
[32] A.Xu et al., "A TG-FTIR investigation into smoke suppression mechanism of magnesium hydroxide in asphalt combustion process", Journal of Analytical and Applied Pyrolysis, Vol.87, 2010, pp.217-223.
[33] R.L.Frost et al., "Infrared emission spectroscopic study of brucite", Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Vol.55, 1999, pp.2195-2205.
[34] M.Salavati-Niasari et al., "Synthesis of lanthanum hydroxide and lanthanum oxide nanoparticles by sonochemical method", Journal of Alloys and Compounds, Vol.509, 2011, pp.4098-4103.
[35] M.Aghazadeh et al., "A novel lanthanum hydroxide nanostructure prepared by cathodic electrodeposition", Materials Letters, Vol.65, 2011, pp.1466-1468.
[36] F.Khosrow-pour et al., "Large scale and uniform La(OH)3 nanorods prepared by template-free pulsed electrodeposition method", Materials Letters, Vol.104, 2013, pp.61-63.
[37] J.A.wang et al., "Characterizations of the thermal decomposition of brucite prepared by sol-gel technique for synthesis of nanocrystalline MgO", Materials Letters, Vol.35, 1998, pp.317-323.



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