ELECTROCHEMICAL DEPOSITION OF La-Mg ALLOYS IN LaCl₃-MgCl₂-KCl SYSTEM WITH MOLTEN SALT ELECTROLYSIS PROCESS

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Abstract

La-Mg alloys of different compositions were prepared by electrolysis of LaCl₃-MgCl₂-KCl melts. Different phases of La-Mg alloys were characterized by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). Energy dispersive spectrometry (EDS) and Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) analyses showed that chemical compositions of La-Mg alloys were consistent with phase structures of XRD pattern, and magnesium content in the alloy could be controlled by electrolysis parameters. The effects of various process parameters such as concentration of magnesium chloride in the bath, temperature of electrolysis and cathode current density on the current efficiency have been investigated. A maximum current efficiency of 85% and yield of 80% was obtained from the bath at 12.5A/cm² current density at an operating temp 850⁰C.

Key words: Fused salt electrolysis, La-Mg alloys.

1. Introduction

Magnesium is the lightest among all common metals which finds wide applications particularly as alloying elements in transportation and electronics. Moreover, natural resources for magnesium is abundant both in earth crust and sea water and recognized as one of the potential element to replace aluminum and iron. Magnesium based structural materials exhibit low density and high strength properties which is necessary for applications in aircraft and space industry [1]. Addition of rare earth elements to magnesium significantly improves the physical and mechanical characteristics of the alloy. Rare earth-magnesium intermetallics have attracted increasing interest in the recent past due to their creep, corrosion and high temperature resistance properties. These properties arise in the alloy due to precipitation of rare earths elements in the grain boundaries of magnesium [2-4].

The development of La-Mg intermetallic compounds is significant due to its low cost and superior physiochemical properties compared to other rare earths. The La-Mg compounds show good thermodynamic and mechanical properties [5] .The high hydrogen storage capability of lanthanum-magnesium intermetallic is relevant for hydrogen storage and in anodes for Ni-MH batteries [6-8]. Some La-Mg compounds have enhanced effect on hydrogen absorption and desorption kinetics in

various materials [9-11]. High temperature ductility, corrosion resistance and low temperature superconductivity properties of these compounds are also technologically important [12-13]. The good optical properties exhibited by La-Mg alloys are useful in switchable or tunable mirrors [14].

The traditional method for producing the La-Mg alloy is pyrometallurgical, which involves the metal mixing and thermal reduction processes. Both these processes have their limitations like micro-segregation and small batch size [15]. These problems can be circumvented by employing molten salt electrolysis process. This process has some advantages over pyrometallurgy process in terms of batch size, homogeneity of alloy composition and ease of operation which facilitate inexpensive mass production.

The electrolytic codeposition method involves simultaneous deposition of two ions in the electrolyte on the cathode. Several investigators [18-20] in the past have reported the formation of alloys like Co-Sn Sm-Co and La-Co alloys by electrochemical codeposition in the molten salt media. Soare and co workers [21] investigated the electrochemical preparation of Mg-Nd alloy in molten oxyfluoride media. Recently Cao et al.[22-23] succeeded in preparing Mg-Li-La alloys from LiCl-KCl-MgCl₂-LaCl₃ and LiCl-KCl-KF-MgCl₂-La₂O₃ melts. They carried out basic electrochemical studies to know the reduction behavior of lanthanum and magnesium ions

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in the chloride electrolyte. The electrochemical formation process and phase control of these alloys were investigated. All these studies emphasize on preparing these alloys mostly in dendrite state by operating the electrolytic cell at lower temperature than the melting point of required alloy.

With this background, we studied the preparation of La-Mg alloys by electrochemical co deposition of Mg and La on a molybdenum cathode from $LaCl_3$-$MgCl_2$-KCl melt. The main aim is to see the feasibility in obtaining the intermetallic compounds of La-Mg alloys particularly in molten state. The material has been prepared upto 200 g scale to support practical application. It was attempted to operate the electrolytic cell above 800^0C in order to obtain the intermetallic compounds in molten state preventing the formation of high surface area dendrite products [24]. There is also no substantial loss of La and Mg due to vaporization in this particular temperature region and the solubility of of these elements in molten bath is also negligible. In this paper, the preparation of different phases of La-Mg alloys in $LaCl_3$-$MgCl_2$-KCl melt was investigated. The phase control of La-Mg alloys with variation in $LaCl_3$ and $MgCl_2$ concentration in the electrolyte was studied. The effect of experimental parameters like temperature, cathode current density (CCD) on current efficiency was also investigated.

2. Experimental

The materials used were lanthanum chloride heptahydrate of 99.9% purity (LR Grade), magnesium chloride hexahydrate of 99% purity (GR Grade) and potassium chloride of 99.5% purity (LR Grade) procured from local chemicals suppliers. All these salts were dehydrated under dynamic vacuum. The dehydration of $LaCl_3.7H_2O$ was carried out by stepwise heating to 250^0C for 24 hours and the escaping water vapor was collected by using liquid nitrogen trap [25, 26]. The product obtained was examined by X-ray diffraction (XRD) analysis and found to be $LaCl_3$. The magnesium chloride was also dried by heating in vacuum at 100^0C for 6 hours. The similar dehydration procedure was also followed for potassium chloride at 250^0C for 4 hours. The mixture of anhydrous $LaCl_3, MgCl_2$ and KCl taken in required ratio was used as electrolyte. The electrolytic mixture ($LaCl_3+MgCl_2+KCl$) taken in each experiment was 800 g.

The electrolytic mixture was charged into a graphite crucible of (70mm i.d.×90mm o.d.×250mm height) which served as the container material as well as anode. A molybdenum rod of 6mm diameter (99.9% pure) used as cathode was covered by a close fitting alumina tube stuffed with asbestos rope except the portions required to see the electrolyte in the lower

part and for cathode connection in the upper part. The role of alumina sheath was to give electrical insulation and also to prevent molybdenum rod from getting corroded with Cl_2 gas during the electrolysis process. A schematic diagram of the electrolytic cell assembly is shown in Fig.1. It consisted of a vacuum tight inconel retort (100mm dia) fitted with a stainless steel flange system having provision for placing the cathode ,thermocouple and for gas inlet and outlet. To collect the material deposited at cathode, an alumina crucible was placed below the cathode inside the graphite crucible. Alumina crucible was kept in such a manner that the tip of the molybdenum rod remained just above it . The graphite crucible was placed in the inconel retort which was already kept in a tubular vertical resistance furnace as shown in Fig1.The resistance furnace with electronic control ($\pm 1^0C$) was used to heat the cell up to operating temperature. The electrolyte in the graphite crucible was melted under high pure argon gas. The role of argon gas is also to prevent the oxidation of cell material. The temperature of the bath was measured with a K-type thermocouple protected by an alumina tube inserted into the melt. After equilibrating the bath for 1 hour the cathode was lowered and pre electrolysis was carried out to remove residual water followed by electrolysis applying potential of 5-8 volt from a DC power supply. Electrolysis was continued for specific period of time and after electrolysis, the cell was allowed to cool to room temperature in argon atmosphere. Molybdenum rod, thermocouples were taken above the electrolytic bath to prevent them sticking inside the salt, which solidifies on cooling. The molten alloy collected in the alumina crucible was recovered by washing solidified molten salt with water. The alumina being non conducting helped to protect the alloy from anodic attack as well as reaction with graphite crucible.

Products were analyzed by XRD using CrK_α radiation. The surface appearance and elemental analysis were also carried out by SEM-EDS analysis. Each sample was dissolved in dilute HNO_3 to
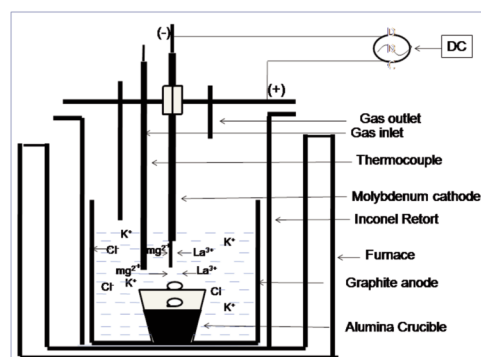

Figure 1. *Schematic of molten salt electrolysis set-up.*

determine Mg and La content and analyzed by ICP-AES. Current efficiency of each experiment was determined using Faraday's law. Current efficiency is the ratio between the actual weights of the material obtained upon the theoretical weight calculated as per Faraday's 1st law. Mathematical equation for current efficiency used in the present study has given below [27].

Current efficiency (h, %): $\eta = m \cdot \dfrac{F}{Q} \cdot \sum_i C_i \cdot \dfrac{z_i}{M_i}$

where m (g) is the mass of deposited alloy, F = 96,485 C/mol the Faraday constant, Q (C) the charge passed during electrolysis, C_i is the mass % of component I in the cathodic deposit, M_i (g/mol) is the molar mass of component I, z_i (dimensionless) is the charge of cation I in the electrolyte.

3. Results and Discussion

3.1 Molten salt electrolyte system

The molten salt bath used in this study consisted of $LaCl_3$, $MgCl_2$ and KCl where $LaCl_3$ and $MgCl_2$ acted as functional electrolyte and KCl as carrier electrolyte. The function of KCl is to increase the electrical conductivity and reduce the viscosity of bath. Table1 shows the current efficiency with the change in composition of carrier electrolyte. The results show rate of deposition is slow in the composition where $(LaCl_3+MgCl_2)$: KCl ratio is 60:40. Current efficiency starts increasing and reaches maximum where wt% of KCl is 60, when wt% KCl becomes more than 60 there current efficiency starts decreasing due to codeposition of potassium ions. Thus an electrolyte bath of $(LaCl_3+MgCl_2)$: KCl=40:60 was selected for the study.

Table 1. *Effect of electrolyte ratio $(LaCl_3+MgCl_2)$: KCl on current efficiency at 850^0C temperature at current density of $10A/cm^2$ for 3 hours duration.*

Wt% $LaCl_3$	Wt% $MgCl_2$	Wt % KCl	Current Efficiency
45	15	40	42
37.5	12.5	50	64
30	10	60	76
22.5	7.5	70	60

In each experiment, the electrolyte contains 60 weight % of KCl with varying concentrations of $LaCl_3$ and $MgCl_2$. Lanthnum and magnesium deposit simultaneously on the molybdenum cathode. Molybdenum was used as cathode as it is inert to both lanthanum and magnesium in the operating temperature range. It does not form any alloy with either of these elements. The electrolysis was carried out at 800^0C which is higher than melting point of La-

Mg alloys. As the temperature of the operation is higher than the melting point of alloy, it gets collected in the alumina crucible kept below the cathode rod. The standard electrode potential for Mg^{2+}/Mg and La^{3+}/La are not very close in chloride system on molybdenum electrode. P.Cao et.al. have described the simultaneous deposition of lanthanum and magnesium at lower concentration of magnesium at higher current density [23]. They attributed the under potential deposition of lanthanum on predeposited magnesium leads to the formation of La-Mg alloys. The same mechanism is perhaps true in this case i.e. $LaCl_3$-$MgCl_2$-KCl system. This mechanism can be substantiated by implementing transient electrochemical technique like cyclic voltametry and chronopotentionmetry.However this is beyond the scope of this present investigation.

3.2. Formation of alloys

Electrolysis was carried out at a constant current density of $10A/cm^2$ in $LaCl_3$-$MgCl_2$-KCl melt for 3 hours using molybdenum electrode at 850^0 C. Table 2 gives the composition of alloy obtained with varying concentration of electrolyte. Fig. 2 shows typical XRD pattern with La-Mg, $LaMg+LaMg_2$, $LaMg_2$ and La_2Mg_{17} alloy phases. In the sample 'a', the peaks of only LaMg phase were obtained where the concentration of $MgCl_2$ was 10%.The presence of strong $LaMg_2$ phase diffraction peak with small amount of LaMg phase was observed in sample 'b' obtained from the melt having 12% $MgCl_2$ in the electrolyte. The pure $LaMg_2$ phase appears in the pattern where $MgCl_2$ concentration in the melt increased further to 15 weight %. Similarly increasing concentration to 20 weight % resulted in forming a new La_2Mg_{17} phase. From the XRD pattern a-d, magnesium content in the alloy increases with increasing concentration of $MgCl_2$ in the electrolyte.

Table 2. *Phases of products obtained by electrolysis at 850^0C temperature at cathode current density (CCD) of $10A/cm^2$ for 3 hours duration.*

Sample No.	Weight% $LaCl_3$	Weight% of $MgCl_2$	Weight% of KCl	Phase Products obtained after cooling
1	30	10	60	LaMg
2	27.5	12.5	60	$LaMg+LaMg_2$
3	25	15	60	$LaMg_2$
4	20	20	60	La_2Mg_{17}

XRD study which shows the existence of $LaMg_2$ phase at room temperature is an interesting observation. According to phase diagram, $LaMg_2$ phase is only stable above 725^0C temperature. The

existence of LaMg$_2$ phase could be due to the slow decomposition kinetics in presence with molten salt . In the sample 'C', there may be presence of other phase in very low concentration which is beyond the detection limit of XRD.These assumptions need to be substantiated by further studies which is beyond the scope of this paper.
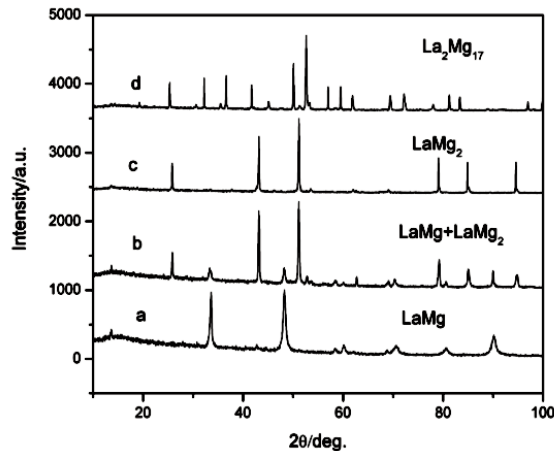

Figure 2. *X-ray diffraction pattern of the products obtained by electrolysis in LaCl$_3$-MgCl$_2$-KCl (60wt %) melt containing: a) 10wt%, b)12.5wt%, c)15wt% and d)20wt% of MgCl$_2$.*

The ICP results are shown in table 3 which confirms the elemental composition of the alloys are consistent with the phase revealed by XRD. Increasing concentration of magnesium ion enhances the Mg^{2+} deposition rate leading to formation of alloys having higher magnesium content. Experiments were also carried out to study the effect of electrolysis time on the phase pattern of the alloys. Table 4 gives the phase structure of La-Mg alloys with varying duration of electrolytic process. It is evident from the table that the duration of electrolysis process doesn't have any effect on the phase structure of the alloy. It therefore appears that phase composition of the alloy can be controlled by varying concentration of LaCl$_3$ and MgCl$_2$ in the electrolyte.

Table 3. *ICP-AES analysis of the samples obtained by electrolysis at 850^{0}C temperature at cathode current density (CCD) of 10A/cm^2 for 3 hours duration.*

Sample No	Phase	La Content (wt %)	Mg content (wt %)
1	LaMg	84.5	Bal.
2	LaMg+LaMg$_2$	78	Bal.
3	LaMg$_2$	74.3	Bal.
4	La$_2$Mg$_{17}$	40.1	Bal.

Table 4. *Effect of electrolysis duration on composition of the alloy obtained in the melt containing 25wt% of LaCl$_3$ and 15wt% MgCl$_2$ at 850^{0}C temperature at CCD of 10A/cm^2.*

Duration of electrolysis (hours)	Phase obtained
2	LaMg$_2$
3	LaMg$_2$
4	LaMg$_2$

3.3. Microstructure Evolution

The SEM images of the identified products are shown in the figure 3. The product shows uniform distribution of particles in the alloy powder. The average grain size of the alloys is around 30μm indicating the absence of grain growth. The mapping analysis shows that magnesium and lanthanum distribute homogenously throughout the alloys.
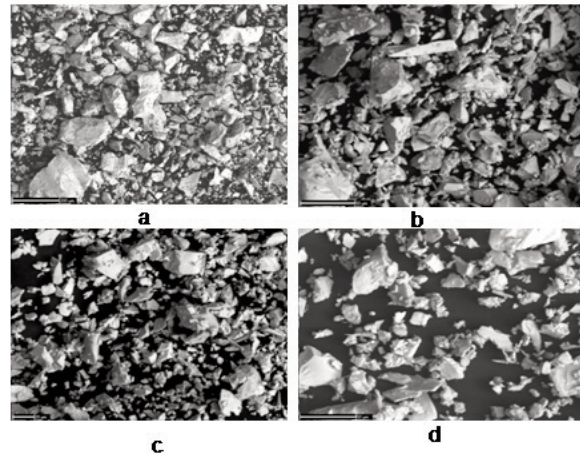

Figure 3. *SEM images of samples a-LaMg, b-LaMg+LaMg$_2$,c-LaMg$_2$ and d-La$_2$Mg$_{17}$ obtained by electrolysis in LaCl$_3$-MgCl$_2$-KCl electrolyte at 850^{0}C temperature at current density of 10A/cm^2 for 3 hours duration. Electrolytic Composition: a) 30 wt% LaCl$_3$+10 wt% MgCl$_2$ + 60wt% KCl; b) 27.5 wt% LaCl$_3$+12.5 wt% MgCl$_2$+60wt% KCl; c) 25 wt% LaCl$_3$+15 wt% MgCl$_2$+60wt% KCl; d) 20 wt% LaCl$_3$+20 wt% MgCl$_2$+60wt% KCl*

3.4. Effect electrolysis temperature on current efficiency

Fig. 4 shows the relationship between current efficiency and electrolytes temperature. The alloys were obtained by electrolysis in the electrolytic bath containing 60 wt % of KCl, 30wt % of LaCl$_3$ and 10 wt % of MgCl$_2$.All these experiments were carried out at an constant current density of 10A/cm^2 for 3 hours in the temperature range of 800 to 900^{0}C.The products

obtained after each experiments were consisting of only La-Mg phase having lanthanum content of 84wt%.This shows the composition of products does not change within the temperature range studied here. From Fig. 4 it is clearly seen that with increase in electrolysis temperature, current efficiency increases and reaches maximum of 85% and thereafter started falling. This trend can be attributed to the fact that incomplete coalescence at lower temperature resulted in lower current efficiency [29]. But after an optimum temperature (as 850^0C in this case) the current efficiency decreases due to increase solubility of cathode product in the melt as well as higher volatilization of the electrolyte [25, 28].
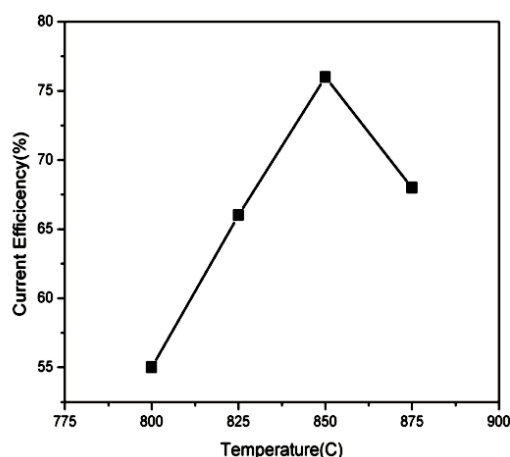
Figure 4. *Effect of electrolysis temperature on current efficiency (CE) in the electrolytic bath containing 60wt % KCl,30 wt % LaCl$_3$ and 10 wt % MgCl$_2$.*

3.5. Effect of cathode current density on current efficiency

The relationship between cathode current density (CCD) and current efficiency is shown in Fig. 5. The effect of cathode current density (CCD) on current efficiency were studied for CCD from 5-15A/cm^2 in the electrolyte consisting of 60 wt % of KCl,10 wt % of MgCl$_2$ and 30 wt % of LaCl$_3$.La-Mg alloys were prepared by electrolysis at 850^0C for duration of 3 hours at different CCD. Here also, it was found that the product composition does not change with current density.

The current efficiency increases with increase in CCD from 5-12.5A/cm^2 and thereafter decreases. With increase in current density, the transfer of metal ions toward cathode increases which enhances the alloy forming process.so,the current efficiency increases with increase in current density and reaches maximum of 85% in 7.5-12.5A/cm^2.However at a very high current density the co deposition of solvent ion and oxidation of metal ions resulted in lower
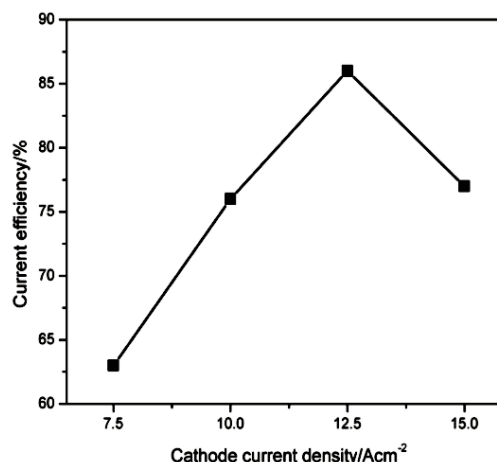
Figure 5. *Effect of cathode current density (CCD) on current efficiency (CE) in the electrolytic bath containing 60 wt % KCl, 30 wt% LaCl$_3$ and 10 wt% MgCl$_2$.*

current efficiency.Incresed CCD means less time for electrolysis, so more time for secondary rections to happen. As a result of incomplete discharge of metal ions at cathode, the recombination of anode and cathode products takes place and hence there is a fall in current efficiency.

4. Conclusion

La-Mg alloys were successfully prepared in the molten state in 150-200g scale by electrochemical co-deposition of lanthanum and magnesium ions in LaCl$_3$-MgCl$_2$-KCl electrolyte**.** Different phases of La-Mg alloys were prepared by varying LaCl$_3$ and MgCl$_2$ concentration in the electrolyte. Typical phases of LaMg, LaMg+LaMg$_2$, LaMg$_2$ and La$_2$Mg$_{17}$ were obtained by by varying concentration of functional electrolyte at 850^0C at a current density of 10A/cm^2.Surface morphology and distribution of elements have been studied by SEM-EDS analysis. The electrolytic process has been studied in the temperature range of 800 to 900^0C at constant current density of 10A/cm^2 and in the CCD of 5-15A/cm^2 at constant temperature of 850^0C.The optimum conditions were established to have high current efficiency of the process.

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