Influences of Processing Parameters on Mg-Sr Alloy Prepared by Molten Salt Electrolysis

XIUYUN SUN, GUIMIN LU[*] and SHUDI FAN

National Engineering Research Center For Integrated Utilization of Salt Lake Resources, East China University of Science and Technology, Shanghai, P.R. China

*Corresponding author: Fax: +86 21 64252826; Tel: +86 21 64252065; E-mail: gmlu@ecust.edu.cn

In order to solve the problems in Mg-Sr alloy prepared by direct reaction method , such as oxidation loss, high energy consumption and low electrolytic current efficiency of only strontium, Mg-Sr alloy was prepared by molten salt electrolysis with MgCl$_2$-SrCl$_2$-KCl molten salt. The influences on the electrolytic efficiency and Sr content produced by electrolytic temperature, current intensity and electrolytic time and MgCl$_2$ concentration were studied. The results show that Mg-Sr alloy was feasible at the temperature of 700 °C with 8A/cm^2 cathodic current density, 10 % MgCl$_2$ concentration, 73 % SrCl$_2$ concentration and Sr content is 35 %. The current efficiency of electrolytic process reached 85 % which was much higher than that of only strontium electrolytic preparation. When the Sr proportion of cathode precipitated Mg-Sr alloy increased gradually to about 45 %, the Mg-Sr alloying ability weakened, the Sr loss ratio became larger and the current efficiency reduced.

Keywords: Molten salt electrolysis, Mg-Sr alloy, Co-deposition, Current efficiency, Alloy composition, Thermodynamic properties.

INTRODUCTION

Strontium can be used as a magnesium alloy modificator. Adding a small amount of Sr into magnesium alloy can refine the grain and improve its mechanical properties[1]. Meanwhile, Sr can also be used as an alloying element to improve the heat resistance of magnesium alloys[2]. Strontium is also widely used as efficient modificator in aluminum alloys. Generally, it is added in the form of Al-Sr master alloy. However, Mg-Sr master alloys are superior than Al-Sr master alloys. Al-Sr alloy is mostly eutectic structure containing a lot of thick high-temperature phase Al$_4$Sr. Its dissolved absorption is slow and Sr burns seriously. The melting point of Mg-Sr alloy is lower than that of Al-Sr alloy and does not contain high-temperature phase that can be difficult to break down. The dissolved absorption of Sr is faster and it burns less[3]. Mg-Sr alloys and multi-component alloys have been studied by Argyropoulos *et al.*[4] and they are used in the modification of aluminum alloys.

The main methods to produce Mg-Sr alloys are mixed method and melt-immerse reduction. Mixed method can be used in the Mg-Sr alloys preparation, but it needs preparation of metal Mg and Sr in advance, then remelt and dope into alloys. Therefore, the process is long and the energy consumption is high. The melt-immersion reduction is achieved by adding Sr compounds to the Mg melt and Mg functions as a reducing agent and the Sr concentration gradient of the reaction

interface functions as the thermodynamic and kinetic driving force. Strontium precipitated from Sr compounds diffuses continuously into the Mg melt, forming Mg-Sr alloy. However, due to the slow diffusion rate of reduction, only the Mg-Sr alloy containing a trace amount of Sr (generally not higher than 0.02 %) can be prepared[5]. Molten salt electrolysis co-deposition can prepare metals which are difficult to achieve from an aqueous solution and it has a high deposition rate. Also, it makes the current efficiency higher and the co-deposition and alloying process proceed simultaneously.

Molten salt electrolysis method has been used in the preparation of Mg-Li[6,7], Al-Ca[8], Mg-Li-La[9], Mg-Li-Gd[10] and other alloys[11-13]. As the solubility of Sr in strontium chloride molten salt reaches up to 20 %, the current efficiency of elemental Sr is lower by molten salt electrolysis[14]. Although it is significant, the study of preparation of Mg-Sr master alloy by molten salt electrolysis has not been reported yet. Theoretical decomposition potential difference between Mg^{2+} and Sr^{2+} is nearly 1V, which is generally believed that molten salt co-deposition is very difficult. But because of the formation of binary alloys, the activity of alloying elements reduces effectively. It may promote the dissolution and diffusion of the alloying and has depolarization effect which makes molten salt electrolysis co-deposition possible. In this paper, the electrochemical mechanism of different MgCl$_2$ concentrations of Mg-Sr alloy in electrodeposition process was investigated and the reduction potential and current

parameters of Mg^{2+} and Sr^{2+} in an inert cathode in molten salt system was identified, which provides some theoretical guidance for industrialization preparation of Mg-Sr alloys by molten salt electrolysis co-deposition.

EXPERIMENTAL

The electrolytic experimental apparatus used in the experiment is shown in Fig. 1. Molten salt electrolyte is $MgCl_2$-$SrCl_2$-KCl molten system. A graphite crucible functions as the anode and electrolyzer with 80 mm inner diameter and 90 mm high. The working electrode is a 3 mm diameter cylindrical stainless steel rod which was fixed in an alumina tube. The lower end of the electrode was polished thoroughly using SiC paper and then cleaned in ethanol solution. The immersion depth of the electrode in the molten salt was described as the active electrode area and in this study it was 1.25 cm^2. The $SrCl_2$ and KCl used in the experiment were dehydrated in electric furnace for 24 h at 300 °C to remove residual water before electrolysis, respectively. All experiments were carried out under purified argon atmosphere. The working temperature was measured with a thermocouple protected by an alumina tube inserted into the melt.

Auxiliary techniques such as inductively coupled plasma atomic emission spectrum (ICP-AES, Varian 710ES) analyses was also used.
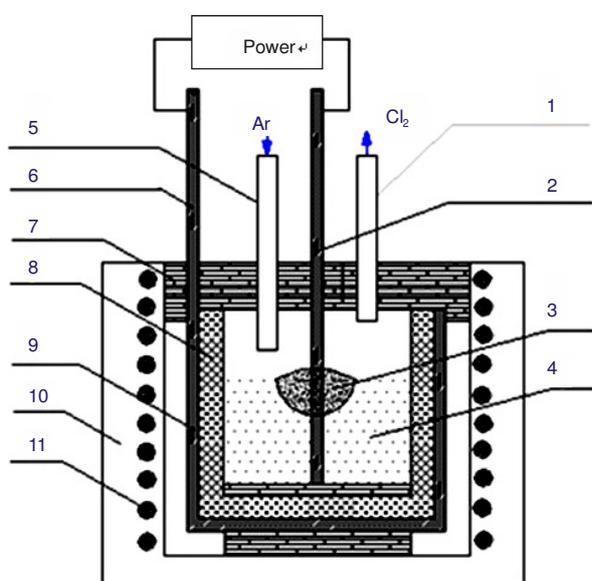

Fig. 1.   Mg-Sr alloy electrolytic equipment: (1) alundum tube (2) stainless steel cathode (3) Mg-Sr alloy (4) molten salt (5) alundum tube (6) anode lead wire (7) insulating brick (8) graphite crucible (9) stainless steel crucible (10) resistance furnace (11) heating resistance

RESULTS AND DISCUSSION

Effects of electrolysis process on current efficiency. The actual amount of power consumed and the theoretical amount of power consumed is called the current efficiency ratio[15]. In this experiment, the current efficiency calculation formula used is as follows:

$$\eta = \frac{Q_{Actual}}{Q_{Theoretical}} \times 100\% \tag{1}$$

$$\eta = \frac{Q_{Mg} + Q_{Sr}}{IT} \times 100\% \tag{2}$$

In which

I–electrolysis current intensity, A;

T–electrolysis time, h;

Q_{Mg}–actual amount of power required in depositing Mg process, A·h;

Q_{Sr}–actual amount of power required in depositing Sr process, A·h.

Magnesium and strontium content were measured by inductively coupled plasma mass spectrometer.

$$Q_{Actual} = nzf \tag{3}$$

In which

n–Electrolysis deposition of metals of the amount of material, mol;

z–The number of electrons in the electrode reaction;

f–The Faraday constant, $26.801 \text{ A h mol}^{-1}$.

Effects of electrolysis temperature on current efficiency are shown in Fig. 2. Electrolyte is 10 % $MgCl_2$-73 % $SrCl_2$-17 % KCl, current density is 8 A/cm^2 and electrolysis time is 2 h.

When the temperature is low, the current efficiency increases with the increase of electrolysis temperature and reaches the maximum at 700 °C. Electrolysis temperature rises gradually and the current efficiency decreases.

When the temperature is low, the electrolyte has a high viscosity, poor mobility and ion diffusion speed is slow. Meanwhile, the speed of Mg-Sr alloy precipitation is slow and there will be more losses of the dissolved strontium. With the increase of temperature, the viscosity of electrolyte reduces, ion diffusion accelerates and current efficiency increases. When the electrolysis temperature is over 700 °C, the solubility of metals in the electrolyte increases and a large number of dissolved metals causes deterioration of physical and chemical properties of molten salt. Temperature is so high that the strontium burning increases and causes the current efficiency reduction.
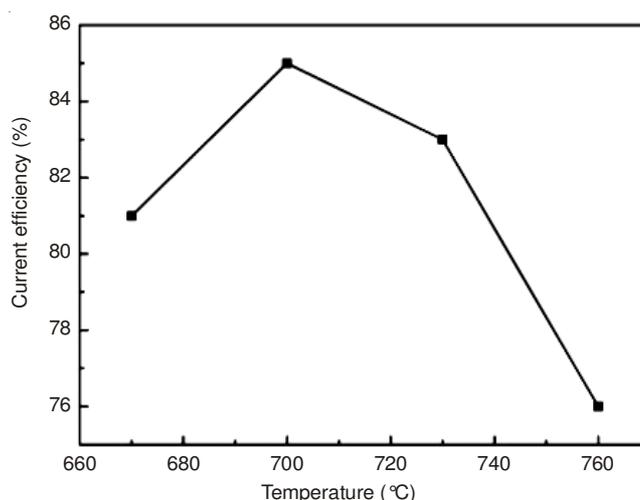

Fig. 2. Relation between current efficiency and electrolysis temperature

Effects of cathode current density on current efficiency are shown in Fig. 3. Electrolyte is 10 % $MgCl_2$-73 % $SrCl_2$-17 % KCl, electrolysis temperature is 700 °C and electrolysis time is 2 h.

With the increase of cathode current density, the current efficiency increases. When the current density exceeds 8A/cm^2, the current efficiency gradually decreases, but the decline is not significant. With the increase of the current density, metal ion deposition on the cathode and the nucleation density is controlled by the current density and the amount of Mg-Sr deposited on the cathode increases gradually. The Mg-Sr alloying rate reaches a maximum value with further increase of the current density. Strontium deposition rate is faster than the diffusion rate of strontium to liquid Mg-Sr alloy. A portion of the metallic strontium is too late to form alloy with the liquid Mg-Sr and has a dissolution loss, so that the current efficiency reduces[16].
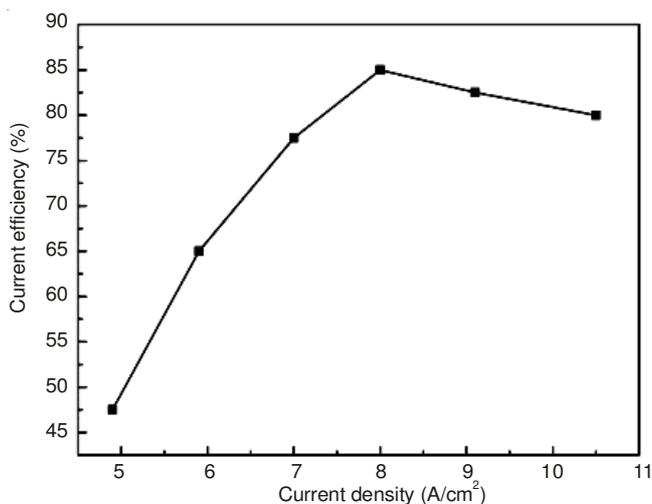

Fig. 3. Relation between current efficiency and current density

Effects of electrolysis time on current efficiency are shown in Fig. 4. Electrolyte is 10 % MgCl$_2$-73 % SrCl$_2$-17 % KCl, electrolysis temperature is 700 °C and current density is 8A/cm^2.
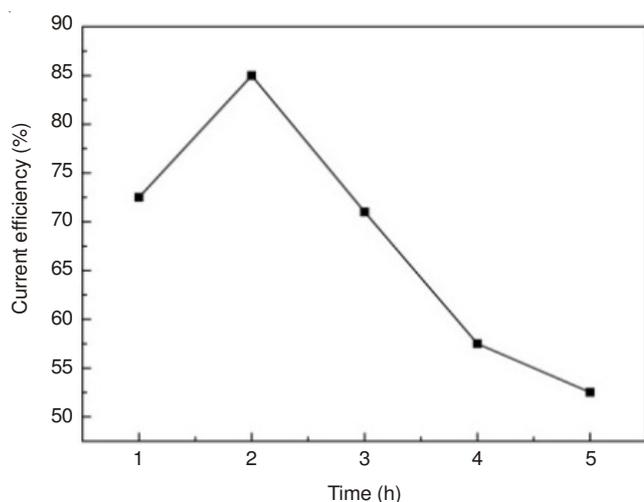

Fig. 4. Relation between current efficiency and electrolysis time

With the extension of electrolysis time, the current efficiency increases gradually and reaches a maximum value at 2 h. As a further extension of the electrolysis time, the current efficiency reduces. In initial electrolysis stage, dissolution rate of the precipitated Mg-Sr alloy in a molten salt is large and current efficiency is low. As electrolysis time extends, the Mg-Sr formation rate reaches a maximum value and the Mg-Sr alloy dissolution rate decreases. With a further extension of electrolysis time, alloying ability reduces. The deposition rate of strontium is greater than the diffusion velocity of strontium to liquid Mg-Sr alloy. A portion of the metallic strontium is too late to form alloy with the liquid Mg-Sr and dissolves into the molten salt. On the other hand, with the electrolysis time extends, the cathode area will gradually increase and the actual cathode current density reduces. It will also lead to a current efficiency reduction[9].

Effects of MgCl$_2$ content on current efficiency are shown in Fig. 5. Electrolysis temperature is 700 °C, current density is 8A/cm^2 and electrolysis time is 2 h.

When the MgCl$_2$ content is 10 %, the current efficiency reaches a maximum value. Too low or too high the MgCl$_2$ content is, current efficiency will reduce. When MgCl$_2$ content is low, the precipitation rate of Sr is greater than the alloying rate of strontium to Mg-Sr alloy which makes the dissolution of strontium loss increase, so that the current efficiency is low. MgCl$_2$ content continues to increase and Sr^{2+} concentration decreases. Therefore, the precipitation of strontium is difficult and the current efficiency reduces.
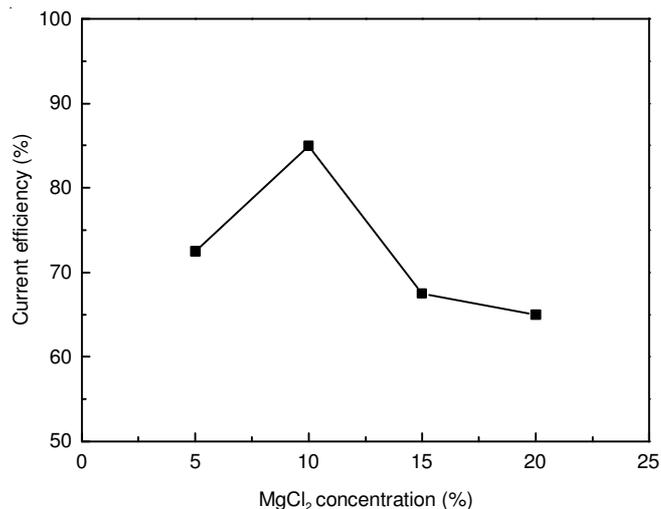

Fig. 5. Relation between current efficiency and MgCl$_2$ concentration

Effects of electrolysis on alloy composition: Effects of electrolysis temperature on alloy composition are shown in Fig. 6. Electrolyte is 10 % MgCl$_2$-73 % SrCl$_2$-17 % KCl, current density is 8A/cm^2 and electrolysis time is 2 h.

The content of precipitated strontium is low at 670 °C. As the temperature rises, strontium content increases gradually and the content of strontium starts to decrease after 730 °C. When temperature is low, the viscosity of electrolyte is high, mobility is poor and diffusion of ions in the electrolyte is slow. The alloying rate of precipitation Mg-Sr alloy is low, which makes the dissolution of strontium appear less, so the strontium content of cathode precipitated is low. As the temperature increases gradually, the electrolyte viscosity reduces, molten salt ion diffusion accelerates and alloying capacity enhances, so that strontium content increases in the cathode. When electrolysis temperature reaches 730 °C, the metal solubility

increases, the cathode dissolution accelerates, physical and chemical properties of molten salt will deteriorate. Therefore, strontium content decreases.
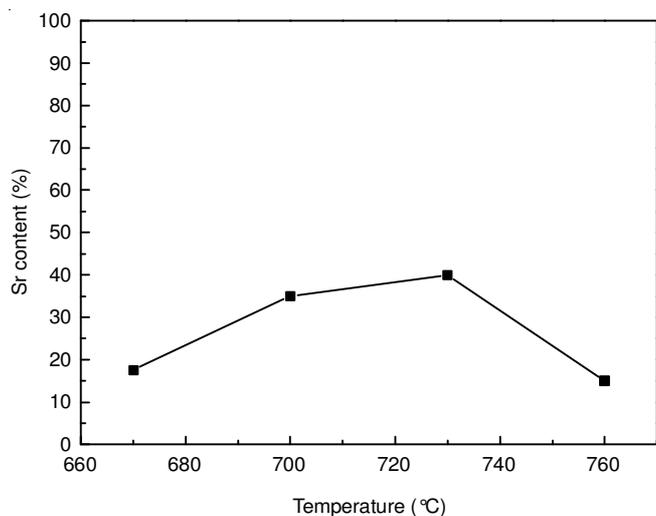

Fig. 6. Relation between alloy composition and electrolysis temperature

Effects of cathode current density on alloy composition are shown in Fig.7. Electrolyte is 10 % $MgCl_2$-73 % $SrCl_2$-17 % KCl, electrolysis temperature is 700 °C and electrolysis time is 2 h.

As the current density increases, the strontium content in Mg-Sr alloy increases gradually. When the current density is low, the current density exceeds that of magnesium ion diffusion. The cathode mainly precipitates magnesium as the current density increases. The cathode begins to precipitate strontium. According to the strontium content changing, it can be seen that strontium content is more than 45 % and the alloying ability of Mg-Sr alloy reduces.
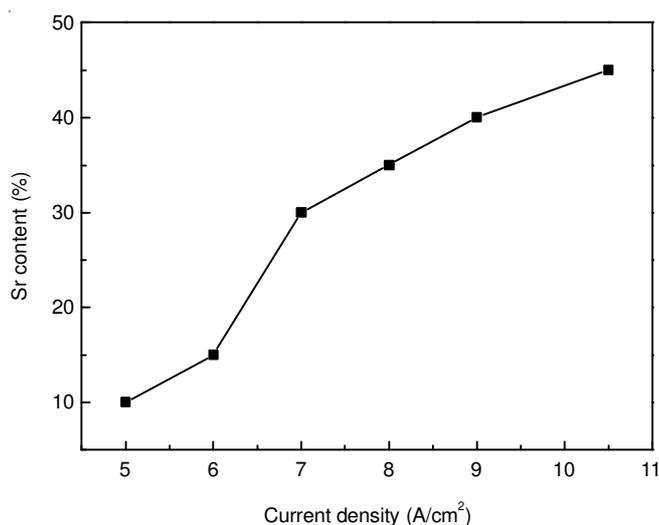

Fig. 7. Relation between alloy composition and current density

Effects of electrolysis time on alloy composition are shown in Fig. 8. Electrolyte is 10 % $MgCl_2$-73 % $SrCl_2$-17 % KCl, electrolysis temperature is 700 °C and current density is 8A/cm^2.

As electrolysis time extends, strontium content gradually increases and it increases rapidly within 1-2 h, then stabilizes gradually. At the beginning of electrolysis process, the precipitated Mg-Sr alloy has a large dissolution in molten salt, strontium content is low. As the electrolysis time extends continually, the alloying rate of magnesium and strontium increases, the dissolution rate of Mg-Sr alloy decreases, so strontium content increases rapidly. With a further extension of electrolysis time, the cathode strontium content achieves a higher value, the ability of forming alloy reduces in liquid Mg-Sr alloy. The precipitation rate of Sr is greater than the alloying rate of strontium to Mg-Sr alloy, which makes the dissolution of strontium less increase.
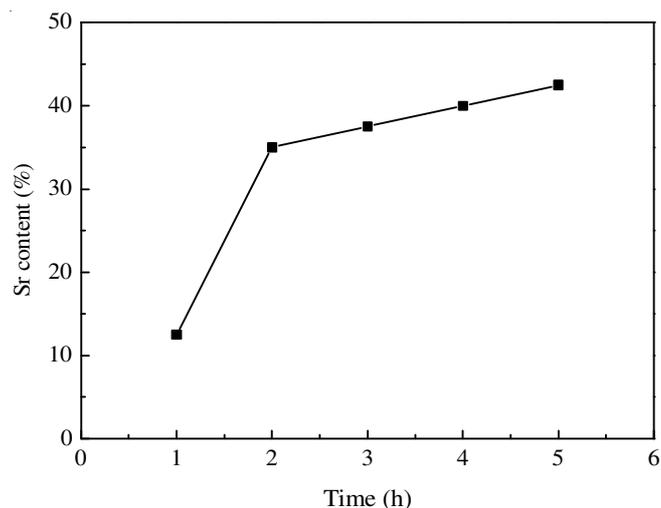

Fig. 8. Relation between alloy composition and electrolysis time

Effects of $MgCl_2$ content on alloy composition are shown in Fig. 9. Electrolysis temperature is 700 °C, current density is 8A/cm^2 and electrolysis time is 2 h.

With the content of $MgCl_2$ increasing, metal strontium content decreases in the same electrolysis time. When $MgCl_2$ concentration is 15 and 20 %, the cathode strontium is mostly undetectable. As $MgCl_2$ content is low, Mg^{2+} has a low limited diffusion current density. The precipitated current will increase at the same cathodic current density, so strontium content has a high level in the cathode alloy. However, when $MgCl_2$ content exceeds 15 %, only magnesium precipitates instead of strontium.
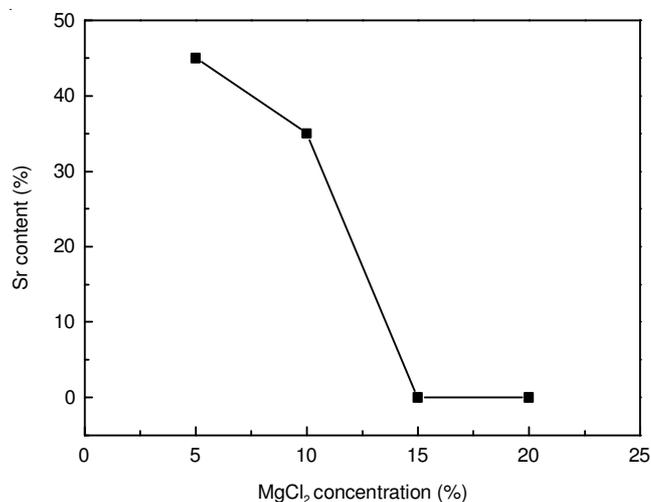

Fig. 9. Relation between alloy composition and $MgCl_2$ concentration

Calculation of thermodynamic properties: The activity curves of the components in the Mg-Sr alloys are presented in Fig. 10. It can be seen that the activities of Mg and Sr show a negative deviation from the ideal solution in the whole range of concentration, the deviation of Mg is small up to approaching the ideal solution and the deviation of Sr is obvious.
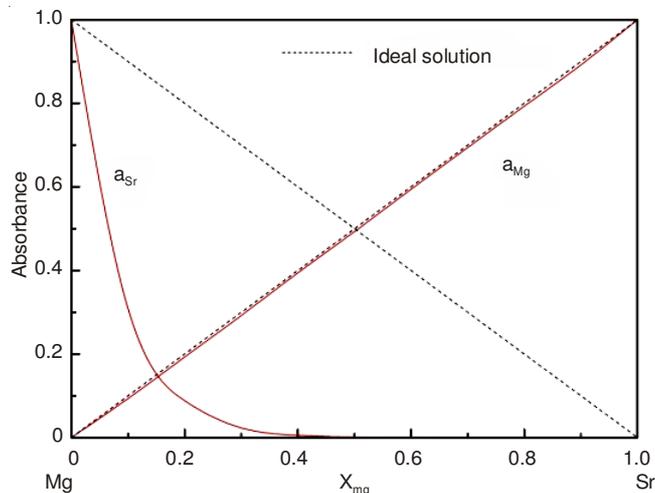

Fig. 10. Activities of Mg and Sr *vs* X_{mg} in Mg-Sr alloys

Various thermodynamic property curves at 973 K are presented in Figs.11-13. The values of mixing enthalpy, excess entropy and excess free energy of the melts are all negative, the minimum value of mixing enthalpy is -3.7937 kJ/mol, the minimum excess free energy is -3.0394 kJ/mol and the excess entropy of the alloy melts approximately approaches zero. On the assumption that $S_E = 0$ and $S_E \neq 0$, There is little effect on the calculation results. Therefore, S_E can be nearly regarded as 0 in practical applications.
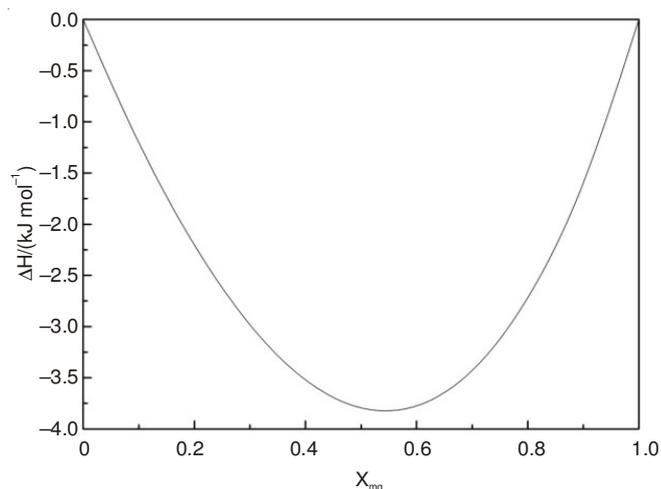

Fig. 11. Variation of ΔH in Mg-Sr binary alloy melts with X_{mg}

Conclusion

Mg-Sr alloy was successfully prepared by co-deposition from molten salts. The content of strontium can reach 45 %. The dissolution loss of strontium is the main factor which effects current efficiency of salt electrolysis deposition. Electrolytic
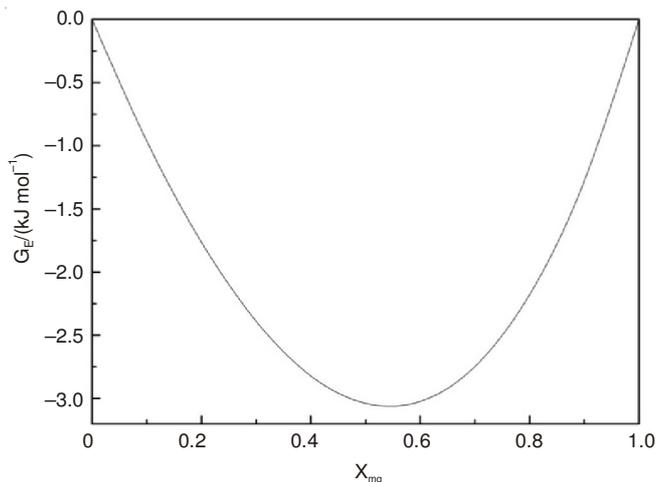

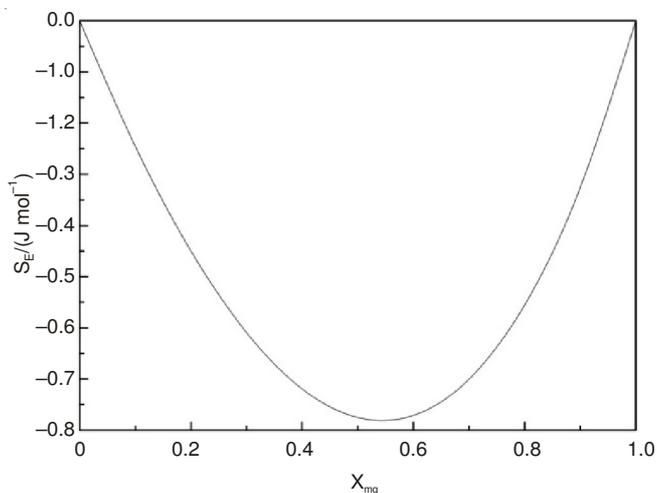Fig. 12. Variation of G_E in the Mg-Sr binary alloy melts with X_{mg}

Fig. 13. Variation of S_E in the Mg-Sr binary alloy melts with X_{mg}

deposition process consists of co-precipitation, alloying process and strontium dissolution in molten salt. The optimum system of Mg-Sr alloy prepared by molten salt electrolysis is 10 % $MgCl_2$-73 % $SrCl_2$-17 % KCl molten salt system in which the electrode pole distance is 4 cm, cathode current density is 8 A/cm^2 and electrolysis temperature is 700 °C. Thus, Sr content is 35 %. The current efficiency of electrolytic process will reach 85 % which is ahead of the current efficiency of electrolytic preparation of only metal strontium. When the content of strontium in Mg-Sr alloy is more than 45 %, the alloying ability reduces, the dissolution loss of strontium increases and the current efficiency decreases. In order to ensure a high current efficiency during the electrolysis, the cathode alloy should export in order to avoid excessive concentration near the cathode. As Mg and Sr form a binary alloy, the activity of alloying elements reduces effectively, which makes Mg-Sr alloy prepared by molten salt electrolysis possible.

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