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Effects of Ca addition on microstructure and properties of AZ63 magnesium alloy①

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Abstract: Effects of Ca addition on the microstructure and viscosity as well as electrochemical properties of casting AZ63 magnesium alloy were studied. Testing results show that the viscosity value increases with the increase of calcium content, especially at the higher temperature, and there exists such a relation between the ignition temperature and viscosity of magnesium alloy: when the melt viscosity increases, the ignition temperature increases too. The microstructure of AZ63 magnesium alloy is first refined and then coarsened with the increase of Ca addition. By the addition of 0.15% Ca, AZ63 alloy has more negative open-circuit potential(1.624 5V), bigger anode efficiency (55.65%) and lower corrosion rate(0.214 g/(m^2•h)). AZ63 alloy containing some Ca content is a high driving-potential and high-efficiency sacrificial anodes material.

Key words: magnesium alloy; viscosity; electrochemical properties

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1 INTRODUCTION

Mg-Al alloys have a very wide application because of their excellent properties, low manufacture cost, easy melting technique and no expensive elements content[1]. One of this kind alloys, AZ63 magnesium alloy, is a widely applied magnesium sacrificial anode which is used extensively in underground and freshwater at present. However, compared with that aboard, home sacrificial anode has some demerits: low current efficiency and weak protection function, so investigating the high driving-potential and high efficiency sacrificial anodes is a very significant thing at present[2]. Different alloying elements additions would have different effects on the microstructure and properties of magnesium alloys, so many alloying elements additions have been made to magnesium in an attempt to improve microstructure and properties[3]. These papers[4-6] report that Ca addition can improve the ignition temperature and calcium has the more negative potential than that of magnesium. No investigation has been shown about the effects of the Ca addition on viscosity and electrochemical properties of AZ63 magnesium alloys. The present study is concerned with effects of Ca addition on microstructure, viscosity and electrochemical properties of AZ63 magnesium alloy.

2 EXPERIMENTAL

The experimental alloys were melted in a 45# steel crucible with an electric resistance furnace. RJ-2 fluxes were put on the melt surface to prevent of the oxidation and ignition of magnesium alloys. Ignition temperature of magnesium alloys was tested using ignition-testing equipment designed by ourselves. Cylindrical specimens with a height of 1 mm and a diameter of 5 mm were machined for the ignition testing, and the ignition temperature was determined by the inflexion appearing in the time—temperature curve above the melting point. After melting in furnace, viscosity experiment alloys were cast into cylindrical ingots that were machined into specimens with a height of 48 mm and a diameter of 27 mm. The liquid alloy viscosity was measured using a high temperature viscosity measurement device whose working principle is as the way of oscillating vessel. The system viscosity measurement ranges 0-10 mPa•s, measurement temperature ranges room temperature-1 500 ℃ and measurement precision is ±5%. Microstructure observations and examinations were performed with KH-2200 high-power video microscope and HITACHI S-2500 SEM equipped with EDX fa-

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cility (Oxford Model). Cylindrical specimen (15 mm in diameter and 8 mm in height) was machined from a cast anode to evaluate the performance of sacrificial anode during the 14 d test.

3 RESULTS

3.1 Ignition temperature and viscosity

The effects of Ca addition on ignition temperature and viscosity of AZ63 magnesium alloys are given in Figs. 1 and 2. The results show that Ca addition causes the changes of ignition temperature and viscosity of AZ63 alloys. It can be seen that viscosity gradually increases with the decrease of temperature below 720 ℃, whereas reduces above 720 ℃. Especially at rather high temperature, viscosity increases gradually along with the increase of Ca content. As shown in Fig. 1, the ignition temperature of AZ63 magnesium alloy containing 0.5% Ca (mass fraction) is around 54 K higher than that of AZ63 magnesium alloy. However, the ignition temperature change with increase of Ca content is gradually slow. From what have been discussed above, we can see that the contributions of Ca addition on ignition temperature and viscosity of AZ63 magnesium alloy with the increase of Ca content are similar. So viscosity of magnesium alloys can be regarded as a mark evaluating the ignition tendency.

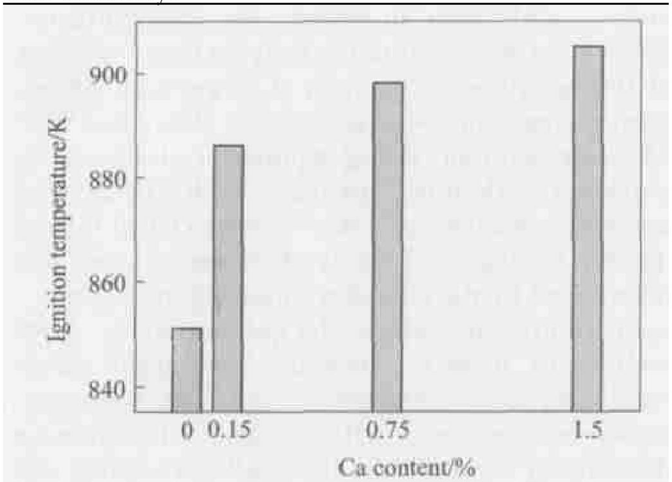

Fig. 1 Effect of Ca addition on ignition temperature of AZ63 magnesium alloy

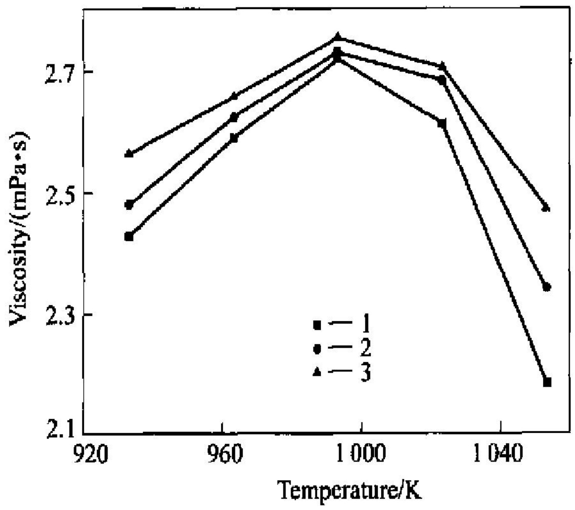

Fig. 2 Effect of Ca addition on viscosity of AZ63 alloy
(1 —0% Ca; 2 —0.15% Ca; 3 —1.5% Ca)

3.2 Microstructure

Fig. 3 shows the microstructures of AZ63 magnesium alloy with different Ca contents. Commercial AZ63 magnesium alloys show that particle and needle shaped substances are rather discontinuously distributed along the boundaries of coarse dendrite crystals. Alloys containing 0.15% Ca have fine structure and particle shaped substances are rather homogeneously distributed on the matrix. The grain size of alloys containing 0.75% Ca is finer than that of commercial AZ63 alloys, whereas coarser than that of the alloys containing 0.15% Ca. In the alloys containing 1.5% Ca, compounds coarsely form on the grain boundaries, and the grain size is coarser than that of the alloys containing 0.15% and 0.75% Ca, whereas finer than that of the commercial AZ63 magnesium alloys. It can be seen from what have been discussed above that the grain refinement is obtained by the addition of a little calcium. AZ63 magnesium alloys containing 0.15% Ca have the finest microstructure under the condition of this experiment.

To understand the effect of microconstituents in detail, AZ63 alloys containing 0.75% Ca are observed under SEM. Selected micrographs are given in Fig. 4. From the EDAX analysis in Fig. 5 it can be found that the compositions of point 1, 2 and 3 in Fig. 4 are about Mg-11.53Al-4.18Zn-0.04Ca, Mg-6.46Al-3.64Zn-0.08Ca and Mg-10.05Al-3.32Zn-0.10Ca (mass fraction, %), respectively. It can be concluded that Ca existed in the Mg-Al-Zn compound phase formed on the boundaries of grains is produced by separated eutectic reaction. Moreover, Refs. [7, 8] studied that calcium can be presented in the form of Al_2Ca compound in magnesium alloys.

According to Mg-Al and Mg-Ca binary phase diagram[9], the melting temperatures of Al_2Ca and $Mg_{17}Al_{12}$ are 1 079 ℃ and 437 ℃, respectively. So Al_2Ca forms prior to $Mg_{17}Al_{12}$ in the early stage of solidification. The preferentially occurred Al_2Ca can prevent the growth of grains in the late stage of solidification, which results in the grain refinement.

3.3 Electrochemical properties

Electric potential is the driving force between anode and cathode, so the open-circuit potential is one of important parameters for sacrificial anode playing the role of protecting, and anode efficiency

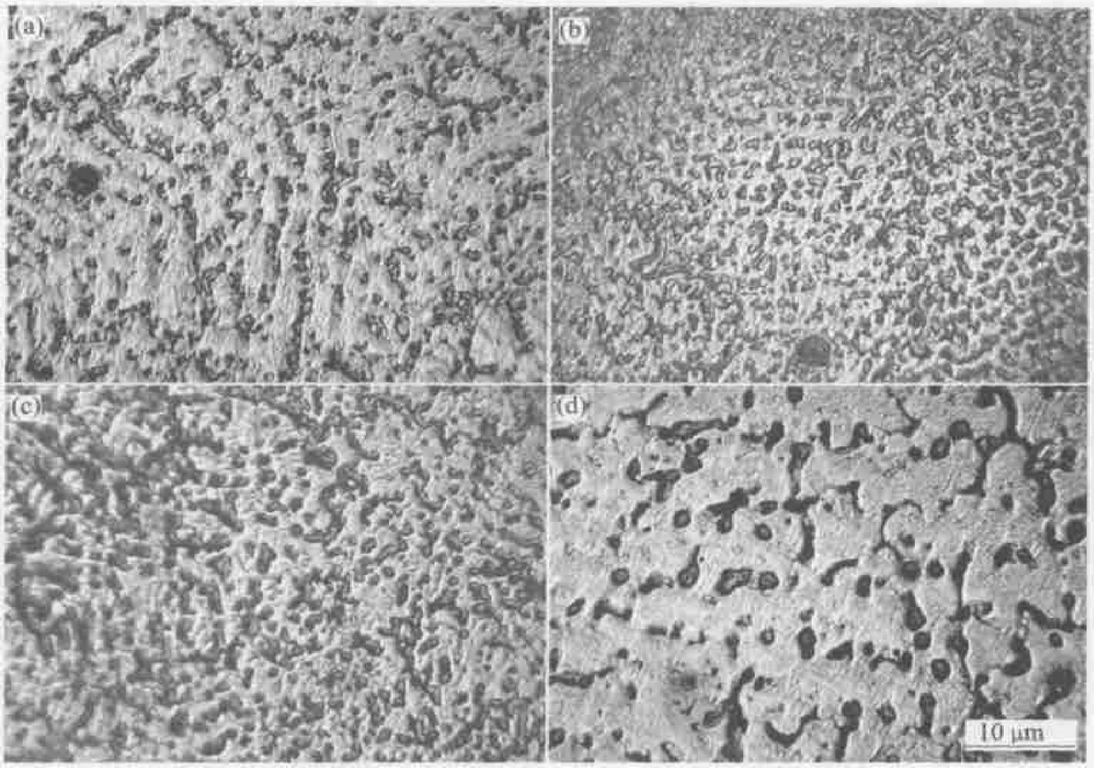

Fig. 3 Microstructures of AZ63 magnesium alloy with different Ca contents
(a)—0%Ca; (b)—0.15%Ca; (c)—0.75%Ca; (d)—1.5%Ca

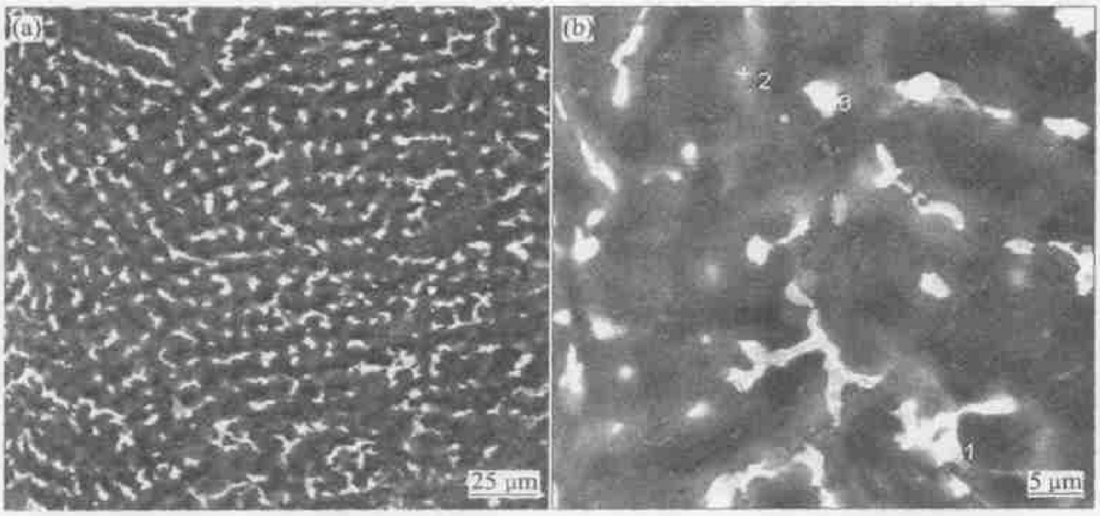

Fig. 4 Microstructures of AZ63 alloy containing 0.75%Ca

is another important technical parameter for anode materials. Definition of anode efficiency is as follows:

$$\eta = \frac{C_E}{C_T} \tag{1}$$

where η is the anode efficiency; C_E is the effective electrical current capacity; C_T is the theoretical electrical current capacity.

Figs. 6, 7 and 8 show the effects of Ca addition on open-circuit potential, efficiency and corrosion rate of AZ63 magnesium alloys. It can be seen that open-circuit potential and corrosion rate first decrease and then increase with the increase of Ca content, however, the anode efficiency first increases and then decreases.

From the analysis of effects of Ca content on electrochemical properties of AZ63 magnesium alloy, we can see such a relation: the higher (more negative) the open-circuit potential, the higher the anode efficiency and the smaller the corrosion rate. In terms of these sacrificial anodes in this paper, the AZ63 magnesium alloys with the addition of 0.15% Ca have more negative open-circuit potential − 1.624 5 V, bigger anode efficiency 55.65%, lower corrosion rate 0.214 g/(m^2·h), which is a high driving-potential and high-efficiency sacrificial anode with good future.

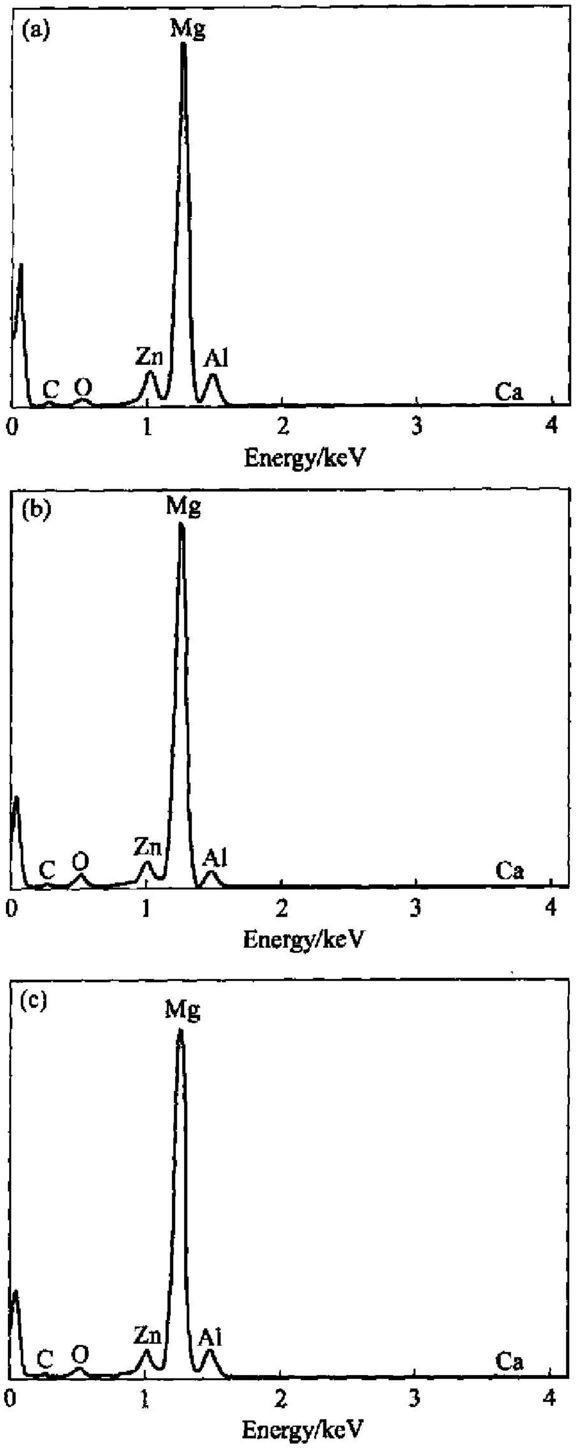

Fig. 5　EDAX curves of point 1, 2 and 3 in Fig. 4
(a) —Point 1; (b) —Point 2; (c) —Point 3

4 DISCUSSION

A well-known formula describing the temperature dependence of melt viscosity is the Andrade equation[10]:

$$\mu = A\exp(C/T) \qquad (2)$$

where A and C are constants. Fig. 2 isn't consistent with the relation apparently. Increasing content of Ca makes the viscosity of AZ63 magnesium alloys more increase, and viscosity first increases above 720 ℃ and then reduces below 720 ℃ with the decrease of temperature. Viscosity

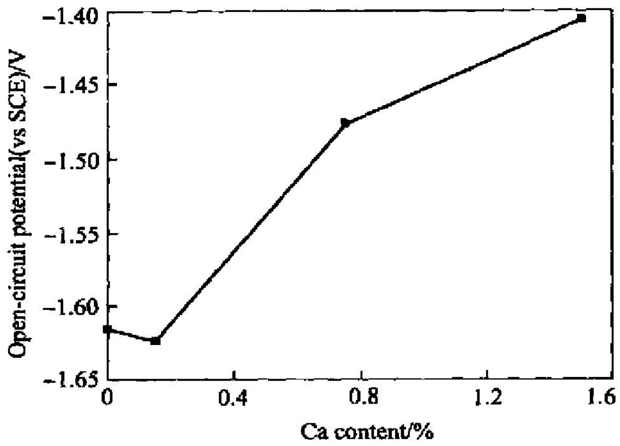

Fig. 6　Effect of Ca content on open-circuit potential of AZ63 magnesium anodes

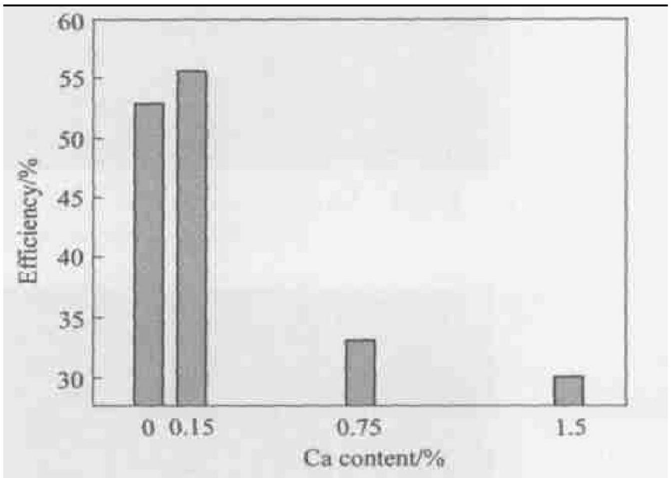

Fig. 7　Effect of Ca content on efficiency of AZ63 magnesium anodes

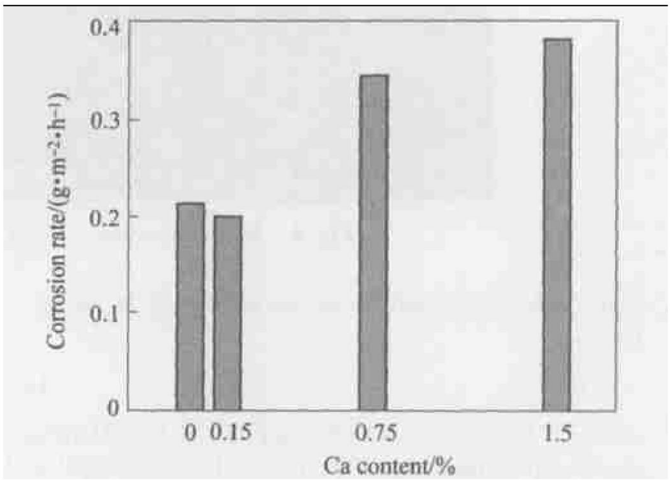

Fig. 8　Relation between Ca content and corrosion rate of magnesium alloy

reaches a maximum at about 720 ℃, which may be related to the change of the liquid structure. This results in the change of strength of the interactions among these atoms or atom groups in the alloy melt.

According to the results of ignition temperature experiment and analyses of oxide film on the alloy surface, the ignition prevention mechanism of calcium has been discussed[11, 12]. Dense and thin calcium oxide film forms on the surface of magnesium alloy oxidized at 973 K. The CaO/MgO film prevents the reaction of magnesium with oxygen. It is known that, in general, when solute atom volume is bigger than solvent atom volume, solute atom would be pushed to the surface of solvent[13]. Calcium atoms will be rich on the surface of AZ63 magnesium alloy for the bigger calcium atom volume than magnesium atom volume, which reduces surface tension of liquid. Oxide film containing calcium makes the film on AZ63 alloy surface more thick and dense, which increases the strength of the interaction among magnesium alloys. On the other hand, according to theories that atoms with different diameters arrange themselves more close than same atoms and close arrange may reduce the transfer momentum of atoms. The bigger atom diameter of calcium than that of magnesium, aluminum and zinc makes the liquid containing calcium element have low viscosity. From what have been discussed above, we can see that there exists a corresponding relation between viscosity of liquid and ignition trend of magnesium or magnesium alloys.

5 CONCLUSIONS

1) The ignition temperature and viscosity of AZ63 magnesium alloys increase with the increase of calcium content. There exists such a relation between ignition temperature and viscosity of AZ63 magnesium alloys: when viscosity increases, the ignition temperature increases.

2) Grains of AZ63 magnesium alloys are first refined and then coarsened with the increase of calcium content. The best grain refinement is obtained by the addition of 0.15% calcium.

3) By the addition of Ca, there exists such a relation among open-circuit potential, anode efficiency and corrosion rate of AZ63 magnesium alloy: the higher (more negative) the open-circuit potential, the higher the anode efficiency and the smaller the corrosion rate. The AZ63 magnesium alloy with the addition of 0.15% Ca has more negative open-circuit potential − 1.624 5 V, bigger anode efficiency 55.65% and lower corrosion rate 0.214 g/(m^2·h).

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