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Corrosion behaviour of aluminium-magnesium alloys in molten sodium①

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Abstract: The corrosion behaviour of the Al-1 % Mg, Al-3 % Mg, Al-5 % Mg and Al-3 % Mg-0.15 %Zr alloys in molten sodium was investigated. The morphology of the corrosion products and the alloying element distribution of the specimens were analyzed by using OM, SEM and EDS. The results showed that the effects of the magnesium content and the immersion temperature on the corrosion of the specimens are related to β phase (Mg_5Al_8).

Key words: aluminium-magnesium alloy; molten sodium; corrosion; thermo-immersion test **Document code:** A

1 INTRODUCTION

Sodium-sulfur battery, a new-type high temperature battery, has attracted much attention from the international automobile and energy industry since it was developed more than thirty years ago[1~5]. Many problems occurring in the course of commercialization and application consist in the material itself and manufacturing technology[6].

As the interlayer material of standard thermo-compressive diffusion bonding seal for joining metal and α-Al_2O_3 ceramic header, aluminium, though competent in price, mass and manufacturing technology, will be corroded when being immersed in molten sodium for long time. This will lead to sodium leakage. Investigations[7~10] showed that even 99.999 %Al specimen is slightly corroded after 450 ℃, 400 h immersion in molten sodium, and the corrosion products of pure aluminium and aluminium-silicon alloy in molten sodium is AlNaSi phase.

By increasing the purity of aluminium to improve the corrosion resistance of the specimen to molten sodium, the cost of sodium-sulfur battery will increase, and the performance of aluminium will be confined to some extent. The corrosion severity of the specimens from molten sodium is inhibited with the addition of certain amount of magnesium into aluminium[8]. Therefore, in order to promote the commercialization of sodium-sulfur battery, it is necessary to study the corrosion behaviour of the aluminium-magnesium alloy in molten sodium.

2 EXPERIMENTAL MATERIALS AND PROCEDURE

Materials tested were Al-1 % Mg, Al-3 % Mg, Al-5 % Mg and Al-3 % Mg-0.15 %Zr alloys. They were vacuum-smelted from high purity aluminium and high purity magnesium. The specimens were machined into 5 mm × 5 mm × 20 mm rods. First, one surface of every rod specimen was polished. And then, they were put into some specially-made 1Cr18Ni9Ti stainless steel reaction bombs. In an inert atmosphere glove box DRI-TRAINS, chemical purity sodium (≥98 %) was melted and poured into the corresponding bomb. After being cooled to room temperature, bombs were taken out, then immediately sealed with a SP-2 type laser welding machine, and then put into the electric furnace. Isothermal static immersion tests were conducted at 350 ~ 450 ℃ for 25 ~ 400 h. After that, we took out the specimens and remove the sodium attached to the surface of the specimens by ultrasonic washing in alcohol for several times. The corrosion products formed in the polished surface of the specimens after being immersed in molten sodium was observed and analyzed by means of OM, SEM and EDS.

3 RESULTS

3.1 Corrosion behaviour of Al-1 % Mg alloy in molten sodium

The Al-1 % Mg specimens were immersed in molten sodium at 350 ~ 450 ℃ for 25 ~ 100 h. The microscopic photograph of the Al-1 % Mg specimen after 350 ℃, 25 h immersion in molten sodium is given in Fig.1. It can be seen that the Al-1 % Mg specimen is corroded more severely after being immersed in molten sodium at 350 ℃ for such short time.

3.2 Corrosion behavior of Al-3 % Mg alloy in molten sodium

Al-3 % Mg specimens were immersed in molten sodium at 350 ~ 450 ℃ for 25 ~ 400 h. The results

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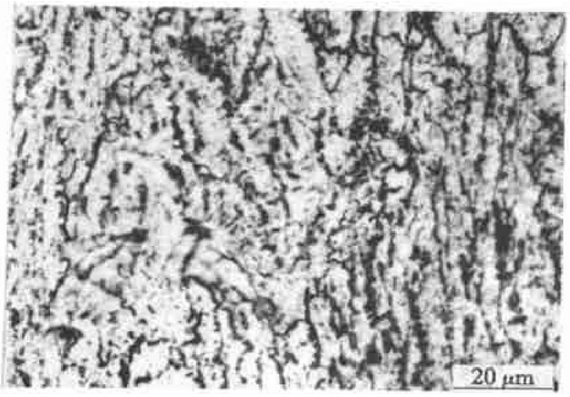

Fig. 1 Micrograph of Al-1 % Mg alloy after 350 ℃, 25 h immersion in molten sodium

showed that the surface of the specimen is very smooth and it possesses considerably high corrosion resistance to molten sodium when the immersion temperature is below 450 ℃, and it is corroded pretty severely when the immersion temperature is up to 450 ℃.

The micrographs of the Al-3 % Mg specimens after immersed in molten sodium at 350 ℃ and 450 ℃ for various times are present in Fig. 2, showing that the Al-3 % Mg specimen was just pitting-corroded slightly and its grain boundaries kept smooth after 350 ℃, 400 h immersion in molten sodium (Fig. 2 (a)); its grain boundaries were corroded severely and a large proportion of corrosion products were found after 450 ℃, 100 h immersion in molten sodium (Fig. 2(b)); when the immersion time was up to 400 h, the surface of the specimen became rugged and the corrosion was extended to the entire surface (Fig. 2 (c)).

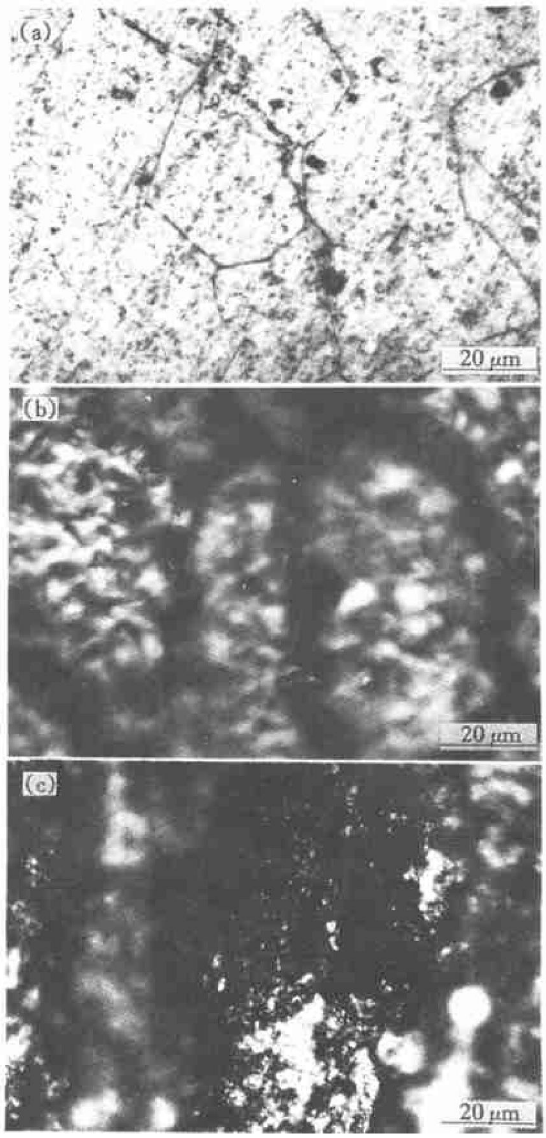

Fig. 2 Micrographs of Al-3 % Mg alloy after immersed in molten sodium
(a) —350 ℃, 400 h; (b) —450 ℃, 100 h; (c) —450 ℃, 400 h

3.3 Corrosion behavior of Al-5 % Mg alloy in molten sodium

The Al-5 % Mg specimens were immersed in molten sodium at 350 ~ 450 ℃ for 25 ~ 400 h to examine further effects of the magnesium content on molten sodium corrosion. The results showed that all the specimens were corroded very slightly and their surfaces were very smooth. The micrograph of the Al-5 % Mg specimen after 450 ℃, 400 h immersion in molten sodium is shown in Fig. 3. It can be seen that, after the Al-5 % Mg specimen was immersed in molten sodium at a temperature of 450 ℃ for 400 h, the grain boundaries kept even and smooth, and the specimen was pitting-corroded fair slightly and homogeneously. This is because there exists a large amount of fine dispersive β phase in Al-5 % Mg alloy, which mostly keeps undissolved after 450 ℃, 400 h immersion in molten sodium.

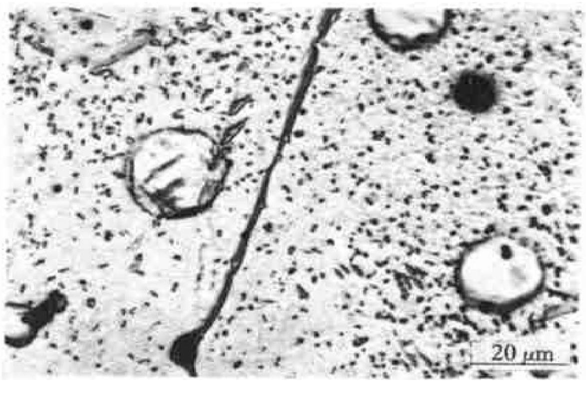

Fig. 3 Micrograph of Al-5 % Mg alloy after 450 ℃, 400 h immersion in molten sodium

3.4 Effects of grain refiner on molten sodium corrosion of aluminium-magnesium alloy

To study the effects of the grain size on molten sodium corrosion of the aluminium-magnesium alloy, 0.15 % zirconium was added as the grain refiner into the Al-3 % Mg alloy. The specimens were immersed in molten sodium at 350 ~ 450 ℃ for 100 ~ 400 h, and then the surface smoothness as well as the quantity and distribution of the corrosion products formed on the surface layer were observed. The results showed that the entire surface of the specimen was smooth and the ability of the specimen to resist molten sodium corrosion increased. The micrograph of the Al-3 % Mg-0.15 %Zr specimen after 450 ℃, 400 h immersion in molten sodium is shown in Fig.4, from which we can see that the Al-3 % Mg-0.15 %Zr alloy is corroded very slightly after being immersed in molten sodium at 450 ℃ for 400 h.

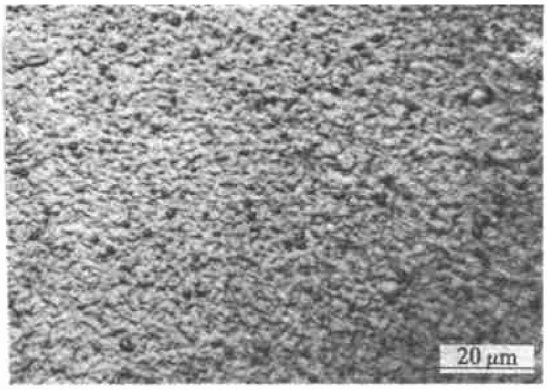

Fig.4 Micrograph of Al-3 % Mg-0.15 %Zr alloy after 400 ℃, 400 h immersion in molten sodium

3.5 Constituent analysis of corrosion products of aluminium-magnesium alloy in molten sodium

To study the constituent elements of the corrosion products formed in the aluminium-magnesium alloy after being immersed in molten sodium, the Al-3 % Mg specimen after 450 ℃, 400 h immersion in molten sodium was cut perpendicularly to the polished surface by a steel saw and then the constituent elements of the corrosion products on the cross-section were analyzed. Fig.5 is its SEM micrograph. Fig.6 is obtained by the EDS results of the point *A* ~ *F* on the corrosion products illustrated in Fig.5. It can be seen that the content of silicon and sodium in the corrosion products are high and their trends of enrichment and impoverishment are identical, while magnesium was not detected in the aluminium matrix. In other words, the corrosion compound consists of Al, Na and Si.

4 ANALYSES AND DISCUSSION

4.1 Effects of magnesium content on molten sodium corrosion

From above experimental facts, it can be concluded that the ability of aluminium-magnesium alloy to resist molten sodium corrosion increases with

Fig.5 SEM micrograph of cross-section of Al-3 % Mg alloy after 450 ℃, 400 h immersed in molten sodium

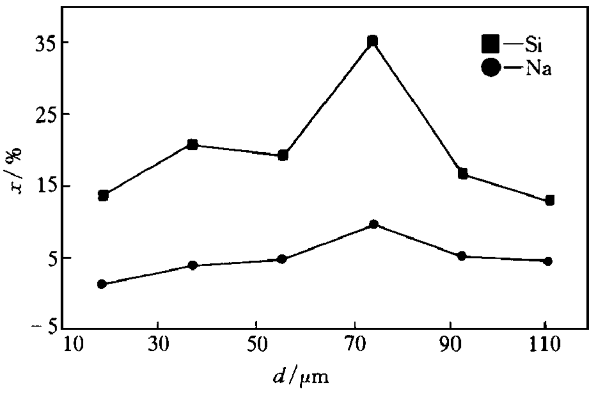

Fig.6 Plots of content of silicon, sodium and magnesium versus distance from polished surface

the increasing of the content of magnesium in aluminium and depends on the quantity, the morphology and the distribution of β phase(Mg_5Al_8) in the aluminium-magnesium alloy. The microstructures of the Al-1 % Mg alloy and Al-3 % Mg alloy vacuum-smelted and cold-rolled are shown in Fig.7. According to the aluminium-magnesium binary phase diagram, the maximal solid solubility of magnesium in aluminium is about 2 %. Because the magnesium content of the Al-1 % Mg alloy is lower, there exist the black Mg_2Si phase elongated along the direction parallel to the rolling axis and a very small amount of light-colored non-equilibrium fine dispersive β phase in aluminium matrix, as shown in Fig.7(a). In the Al-3 % Mg alloy, however, there is a lot of fine dispersive round β phase, which can prevent silicon in aluminium from segregating at the grain boundary, and subsequently, it was corroded slightly after being immersed in molten sodium at 350 ℃ for 400 h, as can be seen in Fig.2(a). The cold-rolled Al-5 % Mg alloy was cor-

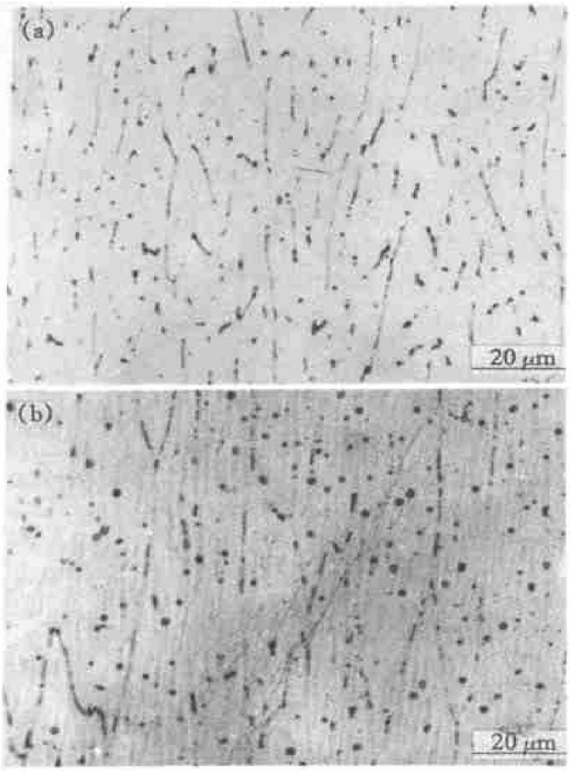

Fig.7 Micrographs of cold-rolled state aluminium-magnesium alloys
(a) —Al-1 %Mg; (b) —Al-3 %Mg

roded more slightly for it possesses a huge amount of fine dipersive β phase.

4.2 Effects of immersion temperature on molten sodium corrosion of aluminium-magnesium alloy

The effects of immersion temperature on molten sodium corrosion of the Al-3 %Mg alloy are related to the behaviour of the fine dispersive β phase in α(Al) matrix. It is known from the aluminium-magnesium binary phase diagram that there is an eutectic reaction at 450 ℃: liquid → Al + Mg_5Al_8(β phase). When the immersion temperature is lower than 450 ℃, β phase will keep undissolvable after the Al-3 %Mg specimen is immersed in molten sodium for a long time; when the immersion temperature is increased to 450 ℃, β phase will dissolve into α(Al) solid solution and a large amount of corrosion products occur at the grain boundaries after the Al-3 %Mg alloy specimen is immersed in molten sodium for 100 h. The specimen is subjected to more severe corrosion(Fig.2(b)). With the prolongation of immersion time, corrosion will gradually extend from the grain boundary to the whole surface layer of the specimen(Fig.2(c)).

5 CONCLUSIONS

1) Al-1 %Mg alloy possesses inferior ability to resist molten sodium corrosion and is corroded considerable severely after being immersed in molten sodium at lower immersion temperature for a shorter time.

2) The corrosion behaviour of the Al-3 %Mg alloy in molten sodium is related to the immersion temperature and immersion time. When immersion temperature is lower than 450 ℃, the specimen is initially corroded; when immersion temperature is up to 450 ℃, with the prolongation of immersion time, the corrosion of the specimen will gradually extend from the grain boundary to the whole surface layer.

3) The Al-3 %Mg alloy is pitting-corroded extremely, slightly after immersed in molten sodium at 450 ℃ for up to 400 h.

4) The corrosion behaviour of the aluminium-magnesium alloy in molten sodium is related to β phase in the specimen.

5) The addition of 0.15 % grain refiner, zirconium, into the Al-3 %Mg alloy will greatly improve the corrosion resistance of the specimen to molten sodium.

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