Effect of Calcium on the Combustion Behavior of Molten AZ91 Magnesium Alloy

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In this study, to obtain guidelines for inhibiting the combustion of the molten metal in magnesium alloys, AZ91D magnesium alloy and AZ91 magnesium alloy with added calcium were exposed to the atmosphere, and the surfaces of the alloys were observed. In the case of AZ91D magnesium alloy, aggregated products were observed on the surface of the molten alloy. In the case of AZ91 alloy with added calcium, aggregated products were not observed. A CaO layer was formed on the outermost surface of the molten alloy, and a MgO layer was formed below the CaO layer. With increasing exposure time, the thicknesses of these layers remained almost constant. It was considered that the CaO layer, in which aluminum did not appear, inhibited combustion by limiting the flow of magnesium vapor from the molten alloy to the atmosphere and the oxidation of magnesium over a long time.

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1. Introduction

When a magnesium alloy is melted in the atmosphere, combustion occurs on the surface of the molten alloy. Therefore, the melting of a magnesium alloy is carried out while supplying a gas inhibiting combustion such as SF6 to the surface of the molten alloy in mass production. Because the facilities and the running cost of using such a gas are part of the cost of magnesium alloy products, one of the most important issues for reducing the cost of magnesium alloy products is to melt magnesium alloys without a gas that inhibits combustion.

Several studies on the effect of additional elements on inhibiting the combustion of molten magnesium alloys have been reported. For example, it has been well known for a long time that the addition of beryllium and calcium to magnesium alloys is effective for inhibiting combustion. Akiyama and co-workers quantitatively clarified that the ignition temperatures of pure magnesium and AZ91 magnesium alloy were increased by adding calcium. Moreover, Akiyama and co-workers analyzed a surface film of molten Mg-5%Ca alloy and clarified that there was a thin CaO layer on the outermost surface of the molten alloy. This layer limited the flow of magnesium vapor from the molten alloy to the atmosphere and the oxidation of magnesium, i.e., the CaO layer inhibited combustion. In addition, the inhibition of combustion by adding rare-earth elements has been reported in several studies.

However, the effect of calcium on inhibiting the combustion of Mg-Al alloys, which are mainly used for automobile parts, and the effect of the exposure time on the state of the surface layer of the molten alloy exposed to the atmosphere for a long time were not clarified. In addition, although it is necessary to clarify the combustion behavior of molten magnesium alloys to develop a means of inhibiting combustion, details of the combustion behavior are not yet known.

In this study, to obtain guidelines for inhibiting the combustion of molten magnesium alloys, AZ91D (Mg-9mass%Al-0.7mass%Zn-0.3mass%Mn) alloy and AZ91 alloy with added calcium were exposed to the atmosphere, and the surfaces of the alloys were observed. In addition, the effect of calcium on inhibiting combustion and the effect of the exposure time on the state of the surface layer are discussed.

2. Experimental Procedure

2.1 Observation of the combustion behavior

Commercial AZ91D alloy (Mg-9mass%Al-0.7mass%Zn-0.3mass%Mn) was melted in an SUS430 crucible while supplying SF6 gas to inhibit combustion. When the temperature of the molten alloy reached 963 K, the gas supply was stopped (i.e., the molten alloy was exposed to the atmosphere), and the dross on the surface of the molten alloy was removed using an iron spoon. After the removal, the molten alloy was exposed to the atmosphere for 8 s or 1 min. Then, the films on the surface of the molten alloy were sampled using an iron spoon and were cooled. The surface and the cross section of the films were observed by scanning electron microscopy (SEM) and electron microprobe analysis (EPMA). The SEM observations were conducted using an S-3600N and the EPMA was conducted using a JXA-8500F.

2.2 Effect of calcium addition

Mg-9mass%Al-0.7mass%Zn-1mass%Ca-0.3mass%Mn alloy (AZ91+1%Ca) was melted with commercial AZ91D alloy and pure calcium while supplying SF6 gas. When the temperature of the molten alloy reached 963 K, the molten metal was exposed to the atmosphere for 0, 10, or 30 min. For comparison, the commercial AZ91D alloy was melted at 963 K while supplying SF6 gas, and the films on the surface were sampled without stopping the supply of the gas. The surfaces of the samples were analyzed by Auger electron spectroscopy (AES) using a PHI700, and the atomic concentration distribution in the depth direction of the surface of the samples was measured. In the depth analysis, the SiO2 sputtering rate was used to convert sputtering times into depths. The films of the samples exposed for 30 min were analyzed by transmission electron microscopy (TEM), and selected-area electron diffraction (SAED) patterns were ob-
3. Results and Discussion

3.1 Combustion behavior

Figure 1 shows the appearance of the surface of molten AZ91D alloy exposed to the atmosphere for 8 and 30 s. When molten AZ91D alloy was exposed to the atmosphere, a product began to form after 5 s, and a black aggregated product, shown with an arrow in Fig. 1(a), was clearly observed after 8 s. The area of the product increased, covering half the surface of the molten alloy after 30 s, as shown with arrows in Fig. 1(b). In addition, part of the product changed color from black to white. In other words, the combustion of the magnesium alloy resulted in the formation of a black aggregated product, which increased in size and partially changed color to white.

Figure 2 shows the appearance of the surface of AZ91D alloy solidified after exposure to the atmosphere for 8 s and 1 min. A black aggregated product was observed in Fig. 2(a), shown with an arrow, and both black and white aggregated products can be observed in Fig. 2(b). Thus, it was considered that the aggregated products observed in Fig. 1 can be obtained by sampling the aggregated products formed by the molten alloy followed by cooling.

Figure 3 shows SEM-backscattered electron (BSE) images of the surface of the aggregated products and the molten alloy in Fig. 2(b). Positions corresponding to black parts, white parts, and the molten alloy were observed. Particles of approximately 0.2 μm diameter were observed on the entire surface in the black parts (Fig. 3(a)(b)), and much smaller particles were observed on the entire surface in the white parts (Fig. 3(c)(d)). On the other hand, no particles were observed on the surface of the molten alloy (Fig. 3(e)(f)).

The formation of the aggregated products is related to the oxidation of magnesium as mentioned later. In general, around 10 mass ppm beryllium is added in a commercial AZ91D alloy to prevent the oxidation of magnesium\(^2\). It is thought that beryllium has an effect of limiting the oxidation of magnesium by forming BeO, but its long-term effect has not been demonstrated. Therefore, the part where the aggregated products were not formed immediately (Fig. 3(e)(f)) was the part where the effect of BeO on limiting the oxidation was demonstrated.

Figure 4 shows SEM-BSE images of the cross section of the aggregated products of AZ91D alloy exposed to the atmosphere for 8 s shown in Fig. 2(a). The size of the aggregated product after exposure for 8 s was around 1 mm (Fig. 4(a)). Its outer layer had a fractal-like shape (Fig. 4(b)). It was considered that particles of approximately 0.2 μm diameter, such as those shown in Fig. 3(a)(b), existed on the fractal-like surface. In the aggregated product, the \(\beta\)-phase (Mg\(_{17}\)Al\(_{12}\) intermetallic compound) and a dark-contrast phase were observed in the matrix (Fig. 4(c)). It was considered that this dark-contrast phase was magnesium oxide (see Fig. 6).

Figure 5 shows SEM-BSE images of the cross section of the aggregated products of AZ91D alloy exposed to the atmosphere for 1 min in Fig. 2(b). The positions of black and white parts of the aggregated products are indicated in
Fig. 5(a). Its outer layer had a fractal-like shape and the intervals were approximately 30 μm (Fig. 5(b)). In the interior of the aggregated product, the β-phase and dark-contrast phase in Fig. 4 were observed (Fig. 5(c)). On the other hand, on the surface of the white part, the fractal-like shape appearing in the black part was not observed, but a layer of thickness 5–10 μm was observed (Fig. 5(d)).

Figure 6 shows the microstructures and EPMA maps of the black and white parts shown in Fig. 5. A concentrated layer of aluminum and oxygen with a thickness of μm order was observed at the surface of the black part (Fig. 6(a)). Even though the compound shown with an arrow was inside the black part, oxygen was detected from the compound. Therefore, it was clarified that the compound was magnesium oxide. On the other hand, small particles accumulated on the surface of the white part and formed a layer with a thickness of approximately 10 μm, and magnesium and oxygen were detected from the layer (Fig. 6(b)). It was considered that the particles observed in Fig. 3(c)(d) were MgO, explaining the white color of the layer. In addition, aluminum was partially detected in Fig. 6(b). It was considered that the compound from which aluminum was detected was the β-phase (Mg17Al12). Next, we discuss the mechanism of the formation of the MgO layer with a thickness of approximately 10 μm, which was observed in Fig. 6(b) but not in Fig. 6(a). The temperature locally increases at the surface of the black aggregated product for two reasons: (i) the area of the surface in contact with the atmosphere is large because the surface has a fractal-like shape, (ii) the oxidation of magnesium is promoted by its own oxidation reaction heat. Owing to the local increase in the temperature, most of the surface having a fractal-like shape is oxidized to form a MgO layer with a thickness of approximately 10 μm.

From the above results, the combustion behavior of molten AZ91D alloy exposed to the atmosphere at 963 K is regarded to be as follows:

1. A black aggregated product is formed on the surface of the molten alloy (Fig. 1). This occurs at random on the
whole surface.
(2) The temperature locally increases at the surface of the black aggregated product.
(3) When the temperature increases at the surface of the black aggregated product, most of the surface having a fractal-like shape is oxidized to form a white MgO layer with a thickness of approximately 10 μm (Fig. 5(d), Fig. 6(b)).
(4) When the surface of the molten alloy vibrates and a new area of the molten alloy is exposed in the white parts, a new black aggregated product is formed while magnesium oxide is taken in by the aggregated product (Fig. 4(c), Fig. 5(c)).
(5) The above steps are repeated, increasing the amount of the aggregated products.

The details of the mechanism of the formation of the black aggregated product are unclear. However, it is assumed that the amount of the aggregated product increases by the repetition of steps (1)–(5) comprising the combustion behavior of the molten alloy. Once a black part is formed, it is difficult to limit the flow of magnesium vapor from the molten alloy to the atmosphere and the oxidation of magnesium. Therefore, to limit the combustion, it is important to prevent the early formation of the black aggregated product. In other words, two measures to limit combustion are (i) to limit the flow of magnesium vapor and (ii) to control the quantity of vapor and limit the temperature increase if it is not possible to limit the flow of vapor.

3.2 Effect of calcium addition

Figure 7 shows the concentration distribution in the depth direction of the surface of molten AZ91+1%Ca alloy exposed to the atmosphere for 30 min. A layer with a thickness of approximately 10 nm was observed at the outermost surface (Fig. 7(a)). Magnesium and oxygen were detected from the surface to a depth of 60 nm. At a depth of more than 60 nm, oxygen was not detected. Thus, it was assumed that the region with depth more than 60 nm was the molten alloy. The concentration distributions after 10 and 30 min have little difference from that after 0 min (Fig. 7(b)(c)). In addition, negligible aluminum was observed at the surface regardless of the exposure time.

Figure 8 shows the concentration distribution in the depth direction of the surface of molten AZ91D alloy melted with SF6 gas. After 0 min, oxygen was detected from the surface to a depth of 60 nm, and fluorine was detected from the surface to a depth of 90 nm. After 10 min, the amount of fluorine at the surface decreased, whereas a peak in the fluorine concentration appeared at a depth of 250 nm (Fig. 8(b)). The oxygen concentration was greatest at the outermost surface, and oxygen was detected from the surface to a depth of 300 nm. When the exposure time was 30 or 60 min, the peak concentration of fluorine was at 450 or 1000 nm, and the peak concentration of oxygen was at 400 or 1000 nm (Fig. 8(c)(d)), respectively. In addition, aluminum was detected at the molten alloy but not at the surface regardless of the exposure time.

Figure 9 shows a TEM image and SAED patterns of the surface of AZ91+1%Ca molten alloy exposed to the atmosphere for 30 min. A layer with a thickness of approximately 30 nm was observed. The SAED patterns of the thin layer are shown in Fig. 9(b)(c). The patterns in Fig. 9(b)(c) were the same, but the compounds identified from the pattern were CaO (Fig. 9(b)) and MgO (Fig. 9(c)). Therefore, this layer was not a ternary compound of Mg-Ca-O but a mixture of two compounds, CaO and MgO. From the above along with the result shown Fig. 7, it is considered that a CaO layer was formed at the outermost surface of the molten alloy and a MgO layer was formed below the CaO layer.
Figure 10 shows a TEM image and SAED patterns of the surface of molten AZ91D alloy melted with SF₆ gas for 30 min. A layer with a thickness of approximately 100 nm was observed at the outermost surface (i.e., layer 1 shown in Fig. 10(a)). In addition, another layer with a thickness of approximately 300 nm was observed below layer 1 (i.e., layer 2 shown in Fig. 10(a)). According to the SAED patterns, layer 1 was MgO (Fig. 10(b)) and layer 2 was MgF₂.
Figure 11 shows the concentration distribution in the depth direction of the surface of molten AZ91+1%Ca alloy exposed to the atmosphere for 30 min at 963 K and molten AZ91D alloy melted with SF6 gas for 30 min at 963 K. In the case of the former alloy, a CaO layer with a thickness of less than 10 nm was formed on the outermost surface and a MgO layer with a thickness of approximately 50 nm was formed below the CaO layer (Fig. 11(a)). On the other hand, in the case of the latter alloy, a MgO layer with a thickness of approximately 300 nm was formed on the outermost surface and a MgF2 layer was formed between depths of approximately 300 and 700 nm (Fig. 11(b)).

Figure 12 shows the relationship between the exposure time and the thicknesses of the layers. The thickness of the MgO layer was calculated as the difference between the depths where half the maximum amount of oxygen was observed. The thicknesses of the CaO layer and the MgF2 layer were calculated similarly. In the case of AZ91+1%Ca alloy exposed to the atmosphere, the thickness of the CaO layer at the outermost surface was almost constant with increasing exposure time, whereas that of the MgO layer slightly in-
creased (Fig. 12(a)). Meanwhile, one result for MgO (exposure time of 10 min) was away from a dashed line in Fig. 12(a). The MgO layer was thinner in this case and it is considered that the layer was formed with reaction control. Therefore, a dashed line of MgO was drawn in the figure.

On the other hand, in the case of AZ91D alloy melted with SF$_6$ gas, the thicknesses of the MgO layer at the outermost surface and the MgF$_2$ layer below the MgO layer increased with increasing exposure time (Fig. 12(b)).

We now compare the cases of AZ91D alloy and AZ91+1%Ca alloy. At the surface of molten AZ91D alloy melted while supplying SF$_6$ gas, fluorine in the gas and magnesium vapor from the molten alloy reacted and formed MgF$_2$. The magnesium vapor from the molten alloy passed through the MgF$_2$ layer and formed MgO owing to the presence of oxygen above the molten alloy. In this process, if magnesium vaporizes continuously and forms a large amount of MgO, the molten alloy will undergo combustion. However, the MgF$_2$ layer limits the flow of magnesium vapor through the layer to some extent, so the molten alloy does not undergo combustion. At the same time, because fluorine from the SF$_6$ gas passes through the MgF$_2$ layer formed on the MgF$_2$ layer, the thickness of the MgF$_2$ layer increases with increasing exposure time.

On the other hand, at the surface of molten AZ91+1%Ca alloy exposed to the atmosphere, the calcium in the alloy and the oxygen in the atmosphere react and form a CaO layer. The CaO layer more strongly inhibits the flow of magnesium vapor through the layer to the atmosphere than the MgF$_2$ layer. However, the CaO layer allows the diffusion of a small amount of oxygen in the atmosphere to reach the molten alloy, so the thickness of the MgO layer under the CaO layer increases slightly with increasing exposure time.

It was concluded that the CaO layer inhibited combustion by limiting the flow of magnesium vapor from the molten alloy to the atmosphere and the oxidation of magnesium over a long time. At the same time, the CaO layer allowed the diffusion of a small amount of oxygen. Further verification of the combustion over a longer time is necessary.

4. Summary

Molten AZ91D alloy was exposed to the atmosphere and the aggregated products were analyzed. In addition, the alloy with added calcium was exposed to the atmosphere and kept at a high temperature while supplying a gas to inhibit combustion. Moreover, the outermost surface films of the two alloys were analyzed. The results obtained are summarized as follows:

1. When AZ91D molten alloy was exposed to the atmosphere, a black aggregated product was formed on the surface of the alloy. Then, the amount of the product increased and part of it changed color to white.

2. The outer layer of the black aggregated product had a fractal-like shape with particles of approximately 0.2 μm diameter on the surface. The outer layer that partially changed color to white was flat, and no such particles were observed in this region. The white layer had a thickness of approximately 10 μm and consisted of MgO particles.

3. When molten AZ91D alloy was exposed to the atmosphere, a black aggregated product with a fractal-like shape was formed in the outer layer, then such regions were oxidized, resulting in the formation of thick white MgO layers. Then, new areas of the molten alloy were exposed in some of the white parts, and the black aggregated product was newly formed. By repeating this process, the aggregated product increased in size. These behaviors are regarded as the combustion behavior at the surface of the molten magnesium alloys.

4. The causes of the combustion of the molten alloy are the presence of magnesium vapor and a local increase in temperature. In other words, two measures to control combustion are suggested: (i) limiting the flow of magnesium vapor, (ii) controlling the quantity of vapor and limiting the temperature increase if limiting the flow of vapor is not possible.

5. In the case of AZ91+1%Ca alloy, a CaO layer was formed on the outermost surface of the molten alloy and a MgO layer was formed below the CaO layer. With increasing exposure time, the thickness of the CaO layer was almost constant, whereas that of the MgO layer slightly increased. The CaO layer had a thickness of less than 10 nm and the MgO layer had a thickness of approximately 50 nm when the exposure time was 30 min. Aluminum did not appear in these layers.

6. In the case of AZ91D alloy melted with SF$_6$ gas, a MgO layer was formed on the outermost surface of the molten alloy and a MgF$_2$ layer was formed below the MgO
layer. The thicknesses of both the MgO and MgF₂ layers increased with increasing exposed time. The MgO layer had a thickness of approximately 500 nm and the MgF₂ layer had a thickness of approximately 400 nm when the exposure time was 30 min. Aluminum did not appear in these layers.

(7) It was concluded that the CaO layer inhibited combustion by limiting the flow of magnesium vapor from the molten alloy to the atmosphere and the oxidation of magnesium over a long time.

REFERENCES