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Effect of RE on the ignition-proof, microstructure and properties of AZ91D magnesium alloy

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Abstract: The magnesium alloy is prone to burn during die-casting, which limits its applications severely, so the effect of adding rare earth (RE) on the ignition-proof of AZ91D Mg alloy is studied. The results indicate that the addition of mischmetal RE elements has a remarkable influence on the ignition-proof property of the magnesium alloy. It is found that the ignition temperature of the magnesium alloy can be greatly raised by adding a proper amount of RE. When the amount is 0.1 wt%, the ignition temperature reaches 877°C which is 206°C higher than that of AZ91D without RE and the mechanical properties of the alloy are also improved. However, the amount of RE must be properly controlled because too much RE would induce grain coarsening and reduce the mechanical properties.

Key words: AZ91D magnesium alloy; ignition-proof; RE; mechanical properties; microstructure

1 Introduction

The applications of Mg alloys are becoming more and more popular due to their desirable properties such as low density, high specific strength, and high specific rigidity, well cutting and damping [1]. However, it is impossible to melt magnesium alloys without any protection because of serious oxidation or even burning. Fluxes or protective gases have been used to prevent the ignition of magnesium during melting. But both methods have some disadvantages such as the complexity of the equipment and atmosphere pollution, which badly limit the applications of magnesium alloys. So it is critical to solve the problem of oxidation or burning during melting [2-3]. And the ignition-proof method of alloying has been considered and is expected to replace fluxes and protective gases in the future. Thus the study on improving the ignition-proof effect of magnesium alloys and refining their microstructure is of great significance, which can make magnesium alloys melt and cast in the atmosphere without any protection, improve the mechanical properties as well as widen the application field of magnesium alloys [4-5]. Here some exploratory research and theoretical analysis have been done about AZ91D Mg alloy.

2 Experimental

The experimental samples were prepared with a commercial purity of 99.95wt%Mg, 99.97wt%Al, 99.95wt%Zn, Al-10wt%Mn and Al-10wt%RE intermediate alloy, flux (38wt%-46wt%$MgCl_2$, 32wt%-40wt%KCl, 5wt%-8wt%$BaCl_2$, 3wt%-5wt%CaF_2), alternant (C_2Cl_6 or dry $MgCO_3$). The alloys were matched and melted in a plumbago crucible furnace (SG2-5-12) by covering the mixture flux. When the crucible was warmed-up to be dark red, some flux was scattered on the bottom, then Mg and Al ingots warmed beforehand were added into the crucible, covering with some other flux. When the furnace was heated to 720°C, Zn and Al-10wt%Mn ingots were added in the same way. The RE was added when the temperature was about 750°C. The melting was stirred uniformly after all metals have been melted. When the temperature was declined to 650°C, the flux was uncovered and the Ni-Cr/Ni-Si thermocouple (UJ33a with DC potentiometer) was inserted in the melting. Subsequently the temperature was raised till the surface of the melting began to ignite. This temperature was recorded as the ignition temperature (repeated the same experiment two times and got the average data).

As it was done above, the RE addition to the AZ91D alloy was changed, and the ignition temperature were recorded in the same way. The samples were cut from the cooled ingots for metallographic microstructure analysis. Several magnesium alloys were selected for tensile and rigidity tests, the melting process was as follows: all alloy elements were added into

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the crucible according to what had been done above during melting for recording the temperature. The melt was stirred uniformly before being covered with flux. Dry $MgCO_3$ was added to the melting when the temperature fell to 730°C and kept stable for 5-8 min in this state. Then the refining flux was added to the melt and stayed for 4-8 min. The molten alloy heated to about 760°C was kept static for 10 min before it was poured into a mould to gain the specimens for test.

3 Results and analysis

3.1 Effect of RE on ignition-proof of AZ91D magnesium alloy

According to the experimental results, we get the relationship between the ignition temperature of AZ91D and the added amount of RE as shown in figure 1.

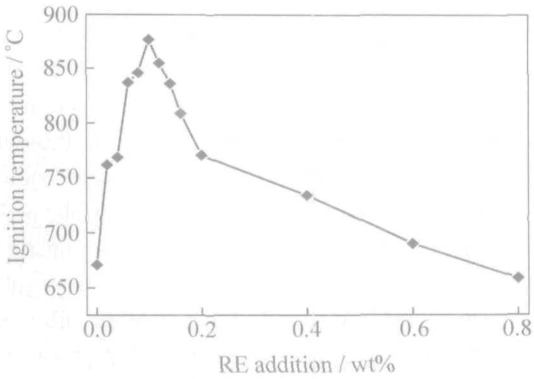

Figure 1 Effect of RE addition on ignition temperature.

It can be seen from figure 1 that the ignition temperature (T_I) of AZ91D changes with the added amount of RE. The T_I of AZ91D is 671°C without RE addition, and raises gradually with the adding of RE. But when the addition is 0.1 wt%, the T_I reaches its highest point at 877°C which is 206°C higher than 671°C. The liquid alloy appeared to be silvery white by uncovering the surface oxide film. But the surface quickly turned brightly red because a great deal of heat was given out by oxidation. The new oxide film covered the melt again and prevented the alloy from further oxidation. And the surface turned dark. When we kept on adding RE to the alloys, the T_I became lower. When the addition of RE is 0.6wt%, there is hardly any effects on ignition-proof or even lose the function of ignition-proof, which illuminates that the effect of ignition-proof can be improved only with a proper amount of RE.

The effect on the ignition-proof of magnesium alloys depends on the ability of the surface segregating the reaction elements. It was found that there was a thin layer on the melt surface by cutting the solidification alloy. Also there were many rumples on the surface of the oxide film **(figure 2). It** seems like a layer of waves as a whole.

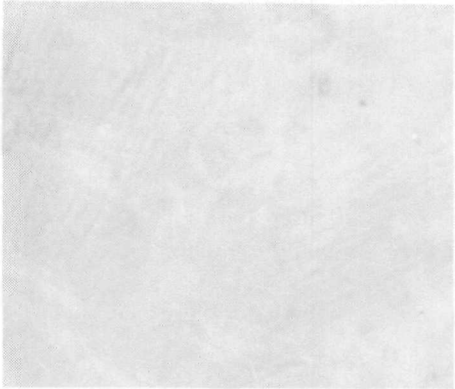

Figure 2 Oxide film with wrinkles on the solidified sample.

RE elements are prone to concentrate on the surface of the molten alloys because all RE elements are surface-active [6]. Moreover, their appetency to oxygen is greater than that of Mg to oxygen. Consequently, a thin layer of oxide film forms on the surface of AZ91D Mg alloy, and the surface is smooth in the liquid state. Whereas the oxide film of the solidification alloy forms some stripe-like rumples in virtue of the different shrinkage extent between the oxide film and the matrix metal. The oxide film with RE has good plastic property and has nice adhesiveness to the matrix metal. So the oxide film does not rupture even if there are so many rumples. This kind of oxide film is very dense, so it has protective property and can prevent Mg alloys from burning.

In order to know more about the film, the sample was cut along the depth direction and observed **(figure** 3). The thickness is about 2.5 μm.

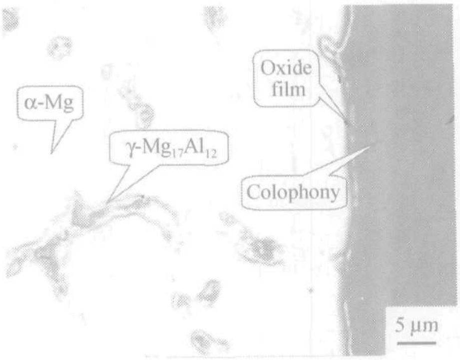

Figure 3 Oxide film on AZ91D alloy with 0.1wt% RE.

The oxide film on the surface of the alloy was composed of three layers including the outer layer, mid-layer and inner layer, the compositions of each layer are different. The cause leads to the variety of composition is very complicated [7]. It is known that the content of Mg matrix is around 90wt%, so there is a great deal of Mg vapor above the melting and quite high vapor tension forms when the alloy is melted, the Mg steam reacts with oxygen to form MgO that covers on the surface of the melt. According to the theory of density coefficient a of the oxide film by Pilling-Bedworth, we know that MgO ($\alpha_{MgO}<1$) film is quite loose and has no protective function to the melt. But the RE oxide, with an a of greater than 1, is very dense and has good function of protection, so it can reduce the oxidization speed of the molten alloy. As a result, the oxygen can easily pass through the loose MgO film and reacts with RE, forming $(RE)_2O_3$. In addition, a small amount of Al reacts with oxygen, forming Al_2O_3. The solubility of RE in Mg alloys is very low $(K<<1)$ because the atom radius of RE are 15% bigger than that of Mg. And RE is regarded as a so-called surface-active element [6]. Therefore, when the crystals grow, the RE enriches on the interface of phases, there is a tendency for RE to concentrate on the surface of the melting AZ91D alloy. With the melting of the ignition-proof Mg alloy, the surface of the melting AZ91D alloy will be oxidized firstly, because MgO has loose structure that can not prevent the oxidization of the inner liquid AZ91D alloy. Oxygen will pass the MgO film and react with Mg to form MgO. During the melting, the surface reactions occur as the following with adding RE to the Mg alloys.

$$2Mg\ (l) + O_2\ (g) = 2MgO(s) \tag{1}$$

$$4RE + 3O_2 = 2(RE)_2O_3 \tag{2}$$

$$RE = [RE] \tag{3}$$

$$3MgO + 2[RE] = 3Mg\ (l) + 2(RE)_2O_3 \tag{4}$$

The result shows that MgO is eliminated from Mg alloys. The process of ignition-proof is essentially the reacting course between RE and MgO. The RE oxide and a little of Al_2O_3 which are formed by the oxidization reactions keep on filling the cavities of MgO and make the loose film become dense, which is called the mid-layer. So the consistency of oxygen sharply declines because of the dense mid-layer which can segregate the molten and air. This leads to the content of RE being extremely little. The amount and the rate of RE gathering on the surface play a very important role in the function of ignition-proof of AZ91D Mg alloy.

According to the analysis above, it can be seen that what mostly prevents the alloy from burning is the dense mid-layer composed of MgO, Al_2O_3, $(RE)_2O_3$ and $Mg_{17}Al_{12}$. The molten alloy and oxygen can be segregated by the mid-layer during the melting process, thus the alloy is hard to burn, so the function of ignition-proof is improved and the ignition temperature of Mg alloys are raised. However, as shown in figure 1 that the ignition temperature varies with the addition of RE, we can see that good effect on ignition-proof is not equal to large amount of the RE addition; by contraries, the effect will decline if too much RE is added to the alloy. That means only appropriate amount of RE can effectively elevate the ignition temperature. This is probably because there is a certain proportion relation among the amounts of the oxide film composition. A proportion may be homologous to a kind of effect on the ignition-proof. The congregating degree of RE to the surface varied with the increasing RE addition, this results in the varying content of RE oxide in the oxide film. We can obtain the best effect of the ignition-proof when the proportion reaches a certain balance. If this balance is broken, the function of preventing burning will decline.

3.2 Effect of RE on **microstructures** of Mg **alloys**

It is shown in **figure 4** that the addition of RE plays an important role in fining the grains of AZ91D Mg alloy. In a certain range, the structures are fined gradually with the increasing of RE. The grains are fined obviously when the addition of RE is 0.06wt%. But the grains will coarsen with an excessive addition of RE. It is known that RE elements are surface active. Therefore, if some RE is added to the alloy during the melting process, the RE will enrich to the front of the solidification interface and prevent other alloy elements from diffusing, and the growth of β-phase is restrained. Thus the solid solubility is reduced, which manifolds the quantity of eutectic, enhance the disparity and fine the alloy structure. In addition, the degree of super cooling turns greater with the increasing of RE. As a result, the secondary dendrite crystal interval of a-Mg dendrite crystal turns small and as-cast structure becomes fine. The consistency of RE in the molten AZ91D Mg alloy reaches a certain value with the adding of RE, RE first integrates with Al to form Al-RE compound because the electronegative difference between RE and Al is greater than that between RE and Mg [8-9]. According to the duality alloy phase diagram [9], it can be seen that the compound forms during melting should be $Al_{11}RE_3$ *etc.* [10-11]. So the increasing of RE leads to two aspects of effects, on the one hand, it leads to the consumption of Al and reduces the β phase at the same time. On the other hand, it promotes the formation of new phase like $Al_{11}RE_3$ and its growth, which make the alloy structure coarsen.

3.3 Effect of RE on the mechanical properties

The applications of Mg alloys not only need good high temperature property but also ask for their good mechanical properties. The results shown in **figures 5** and **6** are obtained by doing mechanical experiments on the Mg alloys with different additions of RE.

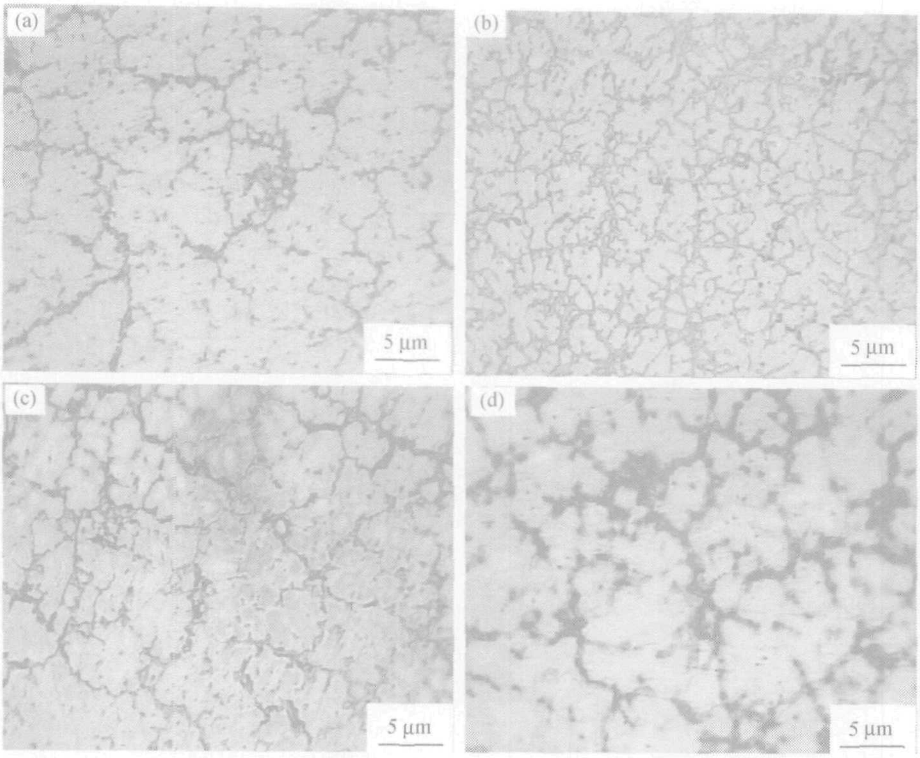

Figure 4 Microstructures of AZ91D alloy with different additions of RE: (a) 0wt% RE; (b) 0.06wt% RE; (c) 0,10wt% RE; (d) 0.12wt% RE.

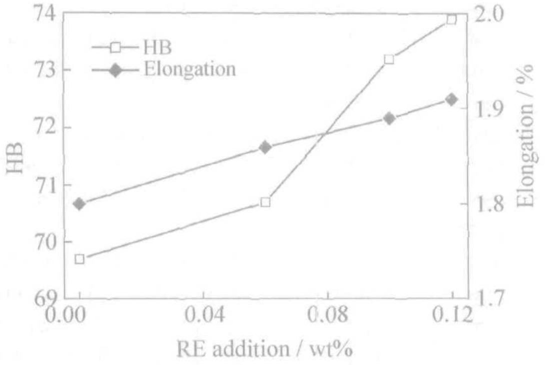

Figure 5 Effect of RE addition on the hardness and elongation of AZ91D alloy.

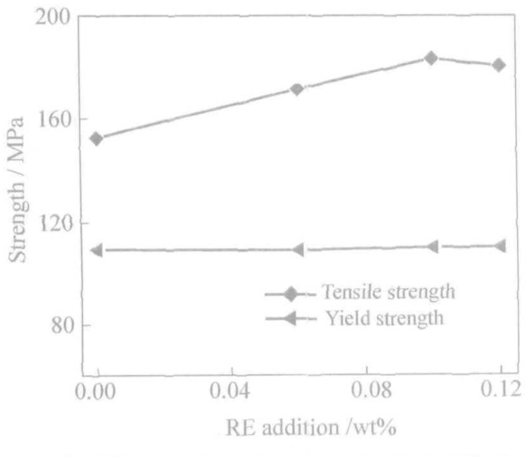

Figure 6 Effect of RE on the strength of AZ91D alloys.

Figure 5 shows that the hardness of AZ91D alloys raises with the increasing of RE addition, but the extent is small. This is mainly caused by the strong combining power between RE and oxygen, sulfur, *etc.* which restrains the function of loosening structure led by these impure elements. The RE elements react with the hydrosphere and hydrogen of the Mg liquid and make RE hydride and oxide during the melting so that it can get rid of hydrogen, reduce the defects of shrinkage porosity and shrinkage void, improve the quality of casting. Furthermore, the RE elements can cleanse the grain boundary and strengthen the crystal boundary. In addition, $Al_{11}RE_3$ newly formed in the alloy structure has high microhardness, which leads to improvement of the hardness of Mg alloys. But excessive RE only leads to the coarsening of $Al_{11}RE_3$ phase and further decreases the solid solubility of Al in the matrix of α-Mg, which dose no good to solution strength. So the hardness has grown but not too much.

Figures 5 and 6 indicate that the tensile strength and elongation are greatly improved with the addition of RE. This is mainly caused by two aspects. On the one hand, the range between the forming temperature (600-500°C) of $Al_{11}RE_3$and the freezing point (660-550°C) of AZ91D is so small that the previous $Al_{11}RE_3$ heterogenic-nucleates with α-Mg while the later $Al_{11}RE_3$ crystallines. In the case, the α-Mg is prevented from growing during solidification. Thus the melt gets refined by adding RE. Furthermore, $Al_{11}RE_3$ can strengthen the matrix element and prevent the crystal boundary from slipping. On the other hand, the alloy structure is obviously fined by adding RE, and the original $Mg_{17}Al_{12}$ net-like distributed along the crystal boundary turns to be shortly rod-shape or grainy and distributing in dispersion. Consequently, the tensile strength and specific elongation of AZ91D are improved, but there is little effect on the yield strength.

According to all the analysis above, we can conclude that the RE addition to AZ91D Mg alloy not only play a significant part in the ignition-proof effect and improving the ignition temperature but also improve the alloy's mechanical properties such as tensile strength, specific elongation and hardness. The best application effect of AZ91D with RE can be obtained by putting all factors together. The best ignition-proof effect can be gotten by adding 0.1 wt% RE to the alloy, and good mechanical properties can be obtained as well.

4 Conclusions

(1) Appropriate amount of RE can elevate the ignition temperature of AZ91D Mg alloy. With increasing the amount of RE, the ignition temperature appears the distribution tendency as a parabola. When the addition of RE is 0.1 wt%, the burning point reaches its peak of 877°C which is 206°C higher than that of the original alloy without RE addition.

(2) The effect on the microstructure of AZ91D Mg alloy varies with increasing the amount of RE. Appropriate amount of RE can obviously fine the grains of AZ91D Mg alloys.

(3) With adding the RE to AZ91D Mg alloy, the specific elongation and tensile strength can be greatly elevated while the hardness can be slightly improved, but there is no effect on the yield strength.

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