Effects of Ce concentrations on ignition temperature and surface tension of Mg-9wt.%Al alloy

***Deng Zhenghua[1], Li Huaji[2], Zhao Wanjun[1], and Li Weibin[3]**

1. School of Mechanical Engineering, Chongqing Three Gorges University, Chongqing 404000, China;

2. School of Material Science and Engineering, Chongqing University, Chongqing 400033, China;

3. Department of Mechanical Engineering, Pusan National University, South Korea 605-739

Abstract: Magnesium alloys are well known for their excellent properties, but the potential issues with oxidation and burning during melting and casting largely limit its industrial applications. The addition of Ce in magnesium alloys can significantly raise ignition-proof performance and change the structure of the oxide film on the surface of the molten metal as well as the surface tension values. Surface tension is an important physical parameter of the metal melts, and it plays an important role in the formation of surface oxide film. In this present work, the ignition temperature and the surface tension of Mg-9wt.%Al alloy with different Ce concentrations were studied. Surface tensions was measured using the maximum bubble pressure method (MBPM). Ignition temperature was measured using NiCr-NiSi type thermocouples and was monitored and recorded via a WXT-604 desk recording device. The results show that the ignition point of Mg-9wt.%Al alloy can be effectively elevated by adding Ce. The ignition temperature reaches its highest point of 720 ˚C when the addition of Ce is 1wt.%. The surface tension of the molten Mg-9wt.%Al alloy decreases exponentially with the increase of Ce addition at the same temperature. Similarly, the experiment also shows that the surface tension of Mg-9wt.%Al alloy decreases exponentially with the increase of temperature.

Key words: magnesium alloy; Ce; surface tension; ignition temperature

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Recent developments in the automobile and electronics industries has captivated a broader interest in study of magnesium (Mg) alloys. Magnesium alloys are well known for their excellent properties, such as low density, high specific rigidity, good machinability and damping property. However, the potential issues with oxidation and burning during melting and casting largely limit its industrial applications [1,2]. Fluxes and protective gases have been commonly used to prevent the ignition of magnesium during melting. But both methods have the disadvantages of equipment complexity and atmosphere pollution. Nowadays, alloying elements are added to magnesium alloys to form a compact protective layer to achieve an ignition-proof effect[3,4]. Previously, the effect of Ce addition on the flame-retardant properties of magnesium alloys has been investigated and reported [5,6]. Yet, little study has been done on the effect of Ce addition on surface tension, which is an important physical parameter of the metal melt and plays an important role in the formation of surface oxide film [7-9].

In the present work, we aimed to study the ignition temperature and the surface tension of molten Mg-9wt.%Al alloy with different concentrations of Ce at different temperatures, and further explore the ignition-proof mechanism of magnesium alloy with Ce addition.

*** Deng Zhenghua**

Male, born in 1982, Master of Engineering. His research interests focus mainly on advanced magnesium alloys.

E-mail: dzh1000@yahoo.cn

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1 Experimental detail

1.1 The experimental materials

Materials (by weight) used in this experiment were: 99.5% pure Mg, 99.7% pure Al, and Al-10wt.%Ce master alloy. Home-made flux (by weight) used in the experiments (without crystal water) contained $MgCl_2$ of 60%, KCl of 30%, $BaCl_2$ of 5% and CaF_2 of 5%.

1.2 Measurement of ignition temperature and surface tension of magnesium alloy with different concentrations of Ce

Because the ignition temperature of magnesium alloy decreases gradually when the Ce addition is more than 1wt.% [5,6], Ce addition in the present experiments was controlled in the range of 0–1.2wt.%. Alloys in the Mg-9wt.%Al system with different concentrations of Ce were melted in a graphite crucible placed in an electric resistance furnace. After the Mg-9wt.%Al alloy was melted, Al-10wt.%Ce alloy was added into the molten alloy at about 750 ℃ to obtain the targeted alloys and stirred evenly to ensure the complete melting of the alloys. After removing the covering flux on the surface at 650 ℃, the temperature of the melt was raised to measure the ignition temperature and the surface tension of magnesium alloy with different concentrations of Ce.

The NiCr-NiSi type thermocouples were located at the surface zone of the molten alloy to monitor and record the change of the temperature via a WXT-604 desk recording device. This temperature started to be recorded as the ignition temperature when the surface temperature of the molten alloy was raised to begin to ignite.

According to the measured results of the ignition temperature, the surface tension of Mg-9wt.%Al molten alloy with different concentrations of Ce was measured at different temperatures, respectively, by using the maximum bubble pressure method (MBPM), which is schematically shown in Fig. 1 [10]. The tubule, made of stainless steel with an inner diameter of 1.4 mm, was perpendicularly inserted in magnesium alloy melt. Argon gas was blown into the magnesium alloy melt through the tubule, thus forming air bubbles. The curvature radius of bubble decreases as it grows. When the diameter of the bubble is equal to the inner diameter of the tubule, the pressure in the bubble is maximum and is given by Eq. (1) [11]:

$$P_m = h_1 g\rho + \frac{2\sigma}{r} \quad (1)$$

where P_m is the gas pressure in the bubble, g is acceleration of gravity, σ is the surface tension of the molten magnesium alloy, r is the inner diameter of the tubule, ρ is the density of the molten magnesium alloy, and h_1 is the insertion depth of the bubble. The surface tension of the molten magnesium alloy can then be calculated according to Eq. (1)

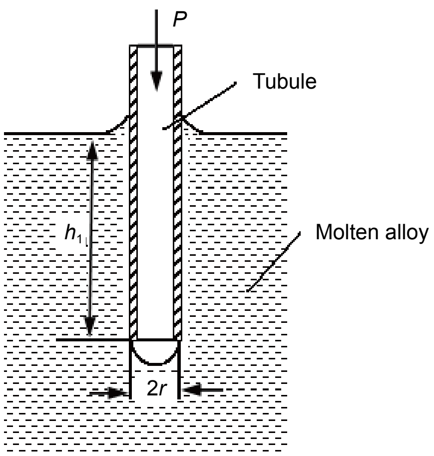

Fig. 1: Schematic diagram of maximum bubble pressure method

2 Results and discussion

2.1 Effect of Ce on ignition temperature of magnesium alloy

The influence of Ce addition on ignition temperature of Mg-9wt.%Al alloy is shown in Fig. 2. Experimental data from current study further verifies the positive influence of Ce on the ignition temperature of magnesium alloy. The ignition temperature of Mg-9wt.%Al alloy without Ce addition is 650 ℃. The ignition temperature rises monotonically with the increase of Ce until the Ce concentration reaches 1wt.%, whose corresponding ignition temperature is about 720 ℃. Further addition of Ce does not significantly raise the ignition temperature. The results are in good agreement with noted references [5] and [6].

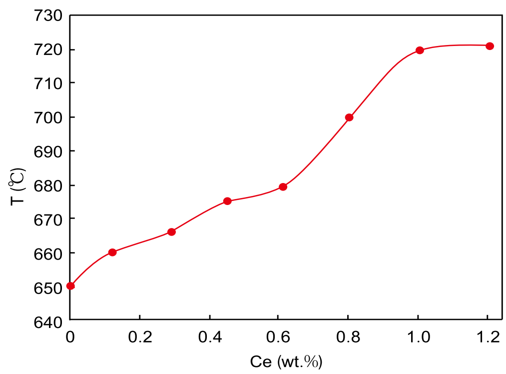

Fig. 2: Influence of Ce addition on ignition temperature of Mg-9wt.%Al alloy

2.2 Effect of Ce on surface tension of molten alloy

According to the results in Fig. 2, the surface tension of the molten Mg-9wt.%Al alloy with different concentrations of Ce was measured from 650 to 720 ℃, and the experiment data was summarized in Table 1. The surface tension of molten Mg-9wt.%Al alloy without Ce is 0.560 $N \cdot m^{-1}$ at 650 ℃ [12]. The surface tension value decreases gradually with an increase in Ce addition at the same temperature. Figure 3 shows an approximately exponential decrease of surface tension in Mg-Al alloys with the increase of Ce concentration at a constant of temperature. Further addition of over 1.2wt.%Ce does not seem to have a significant impact on the surface tension drop.

According to Hume Rothery law, the solid solution is difficult to form if the atom radius ratio of A to B (A and B are two different elements) is more than 15%. The atom radius ratio of Ce to Mg is more than 15%, therefore, the solubility of Ce in Mg is small and Ce is called "surface active element"[13,14]. Ce element has a trend to be concentrated on the surface of molten alloy, so that the concentration of Ce element on the surface area could be several times higher than that in the inner area. In theory, the addition of a surface-active element can reduce the surface tension of molten alloy, and such a relationship is

Table 1: Surface tension values of Mg-9wt.%Al alloy with different Ce concentrations at different temperatures

Ce addition (wt.%)	σ (N·m^{-1})							
	650°C	660°C	670°C	680°C	690°C	700°C	710°C	720°C
0	0.560	-	-	-	-	-	-	-
0.12	0.485	0.448	-	-	-	-	-	-
0.30	0.428	0.397	-	-	-	-	-	-
0.45	0.371	0.358	0.341	-	-	-	-	-
0.60	0.337	0.322	0.318	-	-	-	-	-
0.80	0.318	0.296	0.275	0.265	0.247	-	-	-
1.00	0.298	0.268	0.242	0.223	0.212	0.205	0.197	0.193
1.20	0.289	0.257	0.231	0.217	0.208	0.199	0.191	0.190

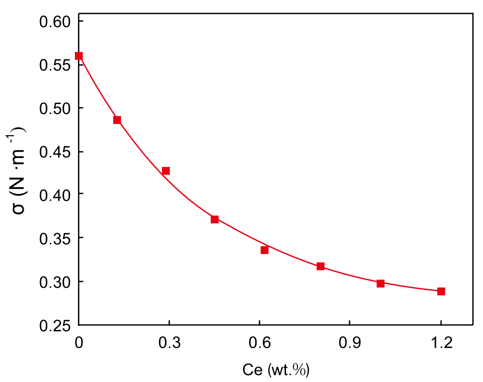

Fig. 3: Effect of Ce addition on surface tension of Mg-9wt.%Al alloy at 650°C

governed by Gibbs absorption equation [15]:

$$\Gamma = -\frac{C}{RT}\cdot\frac{d\sigma}{dC} \quad (2)$$

where C is solute concentration, R is boltzmann constant, T is temperature, Γ is the mass fraction of the enriched solutes per unit area on the surface of the molten metal, σ is the surface tension of the molten alloy.

Ce is a surface-active element for magnesium alloy, Γ of Ce in the Mg-9wt.%Al alloy is positive. According to Eq.(2), as the content of Ce increases, dC >0; considering a positive Γ, one can see that the resultant $d\sigma$ becomes negative, which means the surface tension of molten alloy decreases. However, as Ce on the surface area saturates due to more addition, Γ reaches its maximum, which makes surface tension of molten alloy decrease to the minimum value, as shown in Fig. 3. The influence of Ce on the surface tension of the molten Mg-9wt.%Al alloy at other temperatures shows a similar tendency, as shown in Fig. 3 and Table 1. Because Ce is a surface-active element in magnesium alloy, Ce preferentially combines with O and forms Ce oxides when oxygen infiltrates or diffuses into the melt. Simultaneously, a small amount of Al_2O_3 is generated due to the reaction of aluminum and oxygen. Thus, the oxidation film mainly consisting of MgO, Ce_2O_3 and Al_2O_3 is formed. Because η (η refers to the ratio of the oxide volume to the volume of the original metal that is consumed to form oxide) value of the Ce oxide is greater than 1, Ce oxide tends to expand, which fills the porosities in MgO and forms tightly coherent film, effectively restraining oxygen infiltrating into the molten alloy. As a result, the molten alloy is prevented from further oxidization and the ignition temperature is elevated [2].

2.3 Effect of temperature on surface tension of molten alloy

Generally, the surface tension of molten Mg-9wt.%Al alloy gradually decreases with the increase of temperature, as clearly shown in Fig. 4 for Mg-9wt.%Al alloy with 1wt.%Ce and 1.2wt.%Ce alloy respectively.

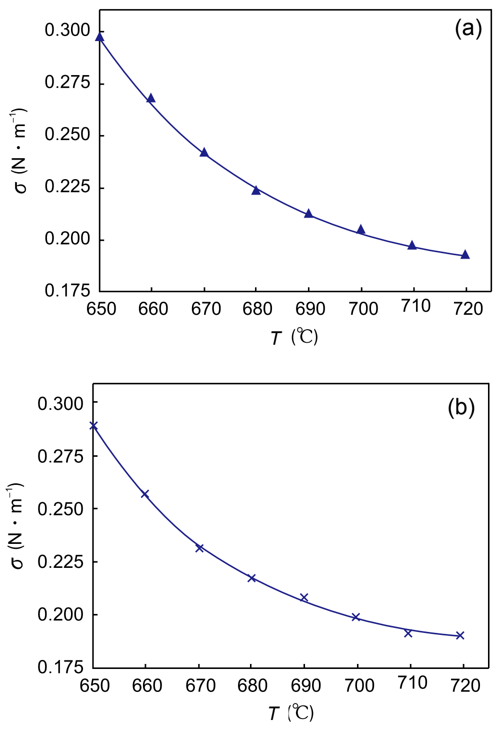

Fig. 4: *T-σ* curve of Mg-9wt.%Al alloy with 1wt.%Ce (a) and 1.2wt.%Ce (b)

The effect of temperature on the surface tension of molten alloy can be described by Eq. (3).

$$\sigma\left(\frac{M}{\rho_1}\right)^{-2/3} = K(T_C - T) \quad (3)$$

where T_C is critical temperature, T is temperature of the melt, σ is the surface tension of the liquid metal, M is the molecular weight of the liquid metal, ρ_1 is the density of the liquid metal, K is constant and $K = 6.4\times10^6$ J·K^{-1} for liquid metal.

According to Eq.(3), the surface tension of molten alloy decreases as the melt temperature rises. This is because the thermal vibration of atoms, the amplitude, and the distance between atoms all increase as the melt temperature rises. When the melt temperature is high enough, diffusion drives the distribution of Ce element on the surface area and in the inner area to be even, which leads to a minimum constant surface tension, as shown in Fig. 4. When the melt temperature rises to the critical temperature, the liquid surface tension is zero since the gas-liquid interface disappears.

A protective oxidation film is formed on the surface when Ce is added into Mg-9wt.%Al alloy. Yet, both the experimental and theoretical studies showed that the surface tension of the liquid metal decreases as the melt temperature increases, so the oxidation film will be finally destroyed. However, the ignition temperature of alloys can be controlled by adding different Ce concentrations into alloys to change the critical temperature of alloys.

3 Conclusions

(1) The ignition point of Mg-9wt.%Al alloy can be effectively elevated by adding Ce. The ignition temperature reaches its highest point of 720 ℃ when the addition of Ce is 1wt.%.

(2) The surface tension of the molten alloy decreases exponentially with the increase of Ce added at the same temperature.

(3) The surface tension of the molten alloy decreases exponentially with the increase of temperature at a constant Ce concentration.

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