Rare Metal Materials and Engineering
Volume 45, Issue 1, January 2016
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2016, 45(1): 0023-0027.

ARTICLE

Oxidation Behavior and Surface Tension of Mg-1.2Ca Alloy with Ce Addition

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Abstract: The effects of alloying element Ce on the oxidation behavior and the surface tension of Mg-1.2Ca alloy were investigated in order to further develop the burn resistant magnesium alloys. Results show that with the increase of Ce content from 0 wt% to 1.5 wt%, the ignition point of Mg-1.2Ca alloy increases rapidly while the surface tension declines. The ignition point of Mg-1.2Ca-1.2Ce alloy can reach 780 °C. It can be melted in atmosphere without any protection method. The oxidation film of Mg-1.2Ca melt becomes smooth and dense with the increase of Ce addition, which can prevent magnesium alloys from further oxidation and burning. According to the test and analysis, the oxide film of Mg-1.2Ca-1.2Ce alloy consists of three layers, that is, loose MgO in the outer layer, MgO-CaO composite oxide film in the middle layer and MgO-Ce_2O_3 composite oxide film in the inner layer.

Key words: magnesium alloy; oxidation; surface tension; calcium; cerium

Magnesium alloys are widely used in aerospace, electronic technology and automotive industry due to their good properties such as low density, high specific strength and stiffness, as will as good processability. However, magnesium alloys are prone to oxidate or even burn as they have high chemical activity and loose oxide film. So fluxes or protective gas methods should be taken to prevent oxidation during melting and casting processes [1]. However, both of two methods would lead to many problems, such as inclusion, environmental pollution and complication of melting process and equipment. So it is necessary to investigate a better burn resistant method.

Alloying is an effective method to improve the burn resistant performance of magnesium alloys. Recently, the effect of rare earth (RE) on properties of magnesium alloys has been investigated. RE is usually used as addition element to enhance the oxidation resistance[2]. It was revealed that Ce content in the solid solution will influence the burn resistant performance of magnesium alloys together with other elements in the alloys, such as Ca. The interactive effect on the oxidation resistance is much more complicated than that of the single element in the solid solution. Sakamoto et al.[3] studied the oxidation of Mg-Ca alloy. The results indicated that the ignition temperature could increase by 250 °C after 5 wt% Ca was added into pure magnesium. They also found that the burn resistant performance was improved at the cost of the decrease of tensile properties, so the content of Ca should be controlled in about 1 wt% for the pure magnesium.

Surface tension is both a fundamental property and an important technological parameter to high temperature alloy[4], which is related to the concentration of active element, the internal stress and the wettability. And above mentioned parameters have a great influence on the formation and the morphology of oxide film of magnesium alloys. However, the surface tension of the magnesium alloy melt was rarely studied. The structure of the oxide film on the molten alloy and its thermodynamic and kinetic mechanisms were far from being understood. In the present paper, the author also studied the oxidation behavior of magnesium alloys by means of surface tension testing.

1 Experiment

Received date: January 24, 2015
Foundation item: Natural Science Foundation of Heibei Province (E2010000121); Science and Technology Research of Hebei Province for Youth Found (2011182)
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Mg-1.2Ca-*x*Ce alloys used in the present investigation was smelted from commercial pure Mg (99.95%), Mg-29.7%Ca and Mg-30.0%Ce master alloys in an SG2-1.5-12 electric resistance furnace under the protection of 99.5vol%CO_2-0.5vol% SF_6 gases. The raw materials were first cut and mixed in a proper ratio, melted and then cast into mould, finally the ingots with composition of Mg-1.2Ca-*x*Ce (*x*=0, 0.3, 0.6, 0.9, 1.2, 1.5) were obtained.

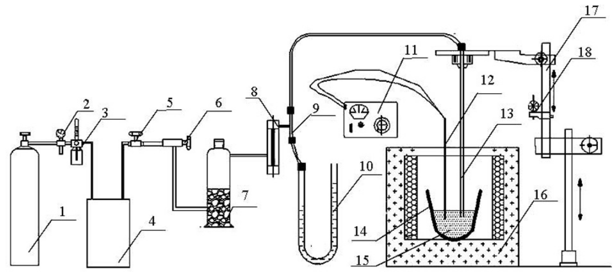
The samples were taken from the central section of the ingots, and then they were machined to cylindrical shape with the dimension of Φ12 mm×15 mm for testing ignition points. Upon testing the ignition points, the samples were continuously heated in the electric resistance furnace at a constant heating rate of 4 °C/min until the ignition occurrance[5]. And the temperature during heating was measured with a multi-channel data acquisition system (with an accuracy of ±2 °C). It is worthy mentioning that neither flux nor gas protection were used in this process. For each alloy, the ignition point was tested for three times and then the average value of ignition point was calculated.

The surface tension of molten Mg-1.2Ca-*x*Ce alloys were measured at the temperature of 730 °C in open air using the maximum bubble pressure method (MBPM)[6], as shown in Fig.1. The maximum bubble pressure method proposed by Simon[7] is based on the use of a single capillary immersed into the studied liquid. Mg-29.7%Ca and Mg-30.0%Ce interalloys were added after commercially pure Mg melted completely at the temperature of 730 °C, removing the impurities of melt surface. The surface tension were tested after maintaining the melt at the temperature of 730 °C for 15 min.

The surface tension σ can be calculated from the measured maximum capillary pressure P and the known capillary radius r by the Laplace equation[8]:

$$\sigma = Pr/2 \tag{1}$$

The measured capillary pressure P can be expressed via the excess maximum pressure in the measuring system $P_s=\rho_1 g H_{max}$, where H_{max} represent the maximum difference of liquid level between U-tube manometer, and ρ_1 is the density of liquid;



1-argon gas, 2-pressure reducer, 3-flowmeter, 4-pressure stabilizer, 5-needle valve, 6-fine needle valve, 7-drying bottle, 8-flowmeter, 9-three-limb tube, 10-U-tube, 11-temperature controller, 12-thermocouple, 13-capillary, 14-graphite crucible, 15-melt, 16-furnace, 17-bracket, 18-dialgage

Fig.1 MBPM surface tension testing schematic

hydrostatic melt pressure $P_h=\rho_2 gh$, where h is the immersion depth of the capillary into the melt, and ρ_2 is the density of melt. Hence the capillary pressure is given as follows:

$$P = P_s - P_h \tag{2}$$

Together with Eq.(1) we obtained：

$$\sigma = (\rho_1 H_{max} - \rho 2h)gr/2 \tag{3}$$

The analyses of composition and microstructure of oxidation film were conducted by a Hitachi S4800 scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS). The phase of oxidation film was examined by an X-ray diffraction (XRD) system (SmartLab, Rigaku) with Cu Kα radiation.

2 Results and Discussion

2.1 Ignition point testing

A typical temperature-time curve of ignition point testing of pure magnesium is shown in Fig.2. The combustion heat of the samples is large enough to cause a steep rise in the temperature-time curve. The temperature-time curves display a rapid oscillation of rising in burning process and the first inflection point is defined as the ignition point of the sample in the present research[9].

The results of the ignition point testing are shown in Fig.3. And the fitted curve is also drawn up in the figure, which complied with Gaussian function. As can be seen from the graph, the ignition point of Mg-1.2Ca increases rapidly when the content of Ce is in the range from 0 wt% to 1.2 wt%. However, when the content of Ce is more than 1.2 wt%, the ignition point is almost invariable. The average ignition point of Mg-1.2Ca-1.2Ce can reach 780 °C, which is about 77 °C higher than that of Mg-1.2Ca. The data of ignition point of Mg-1.2Ca-*x*Ce alloys can be fitted as the following equation:

$$T = 702.21 + 80.80\exp[-2(\frac{x-1.39}{1.03})^2] \tag{4}$$

where, T is the ignition point (°C) and x is analyzed content of Ce (wt%) in Mg-1.2Ca.

2.2 Oxide film analysis

The oxide films of Mg-1.2Ca and Mg-1.2Ca-1.2Ce can be vividly seen in Fig.4. Both of them are cooled under natural condition from magnesium melt. As can be seen, the oxide

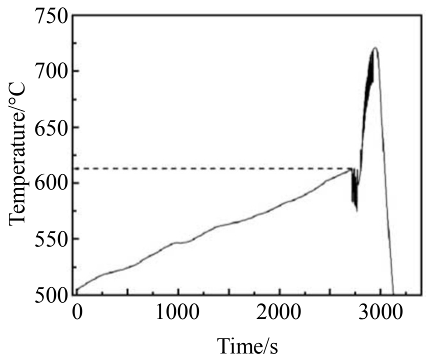


Fig.2 Typical ignition point test of pure magnesium