Effect of cerium on ignition point of AZ91D magnesium alloy

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Abstract: The surface and interior temperature-time curves of blocky cerium modified AZ91D magnesium alloy were measured during a non-protective heating and melting process. Two inflection points with rapid increase in temperature were found on both curves, which corresponded to the formation of "auliflower" oxide on the surface and the occurrence of flame during melting. These two temperatures are therefore defined as oxidation point and ignition point, respectively. The interior temperature-time curve is similar to that measured on the surface except for a comparable time delay. The oxidation and ignition temperatures increase with Ce content, an average increase of 33℃ and 61℃ was found when Ce addition was about 1.0 wt %. However, the increasing rate of the oxidation and ignition temperature decreases with increasing Ce content. An addition of 0.6wt% Ce is recommended for ignition-resistant AZ91 magnesium alloy.

Keywords: AZ91D magnesium alloy; cerium; ignition resistance; ignition point measurement

CLC number: TG146.2+2 Document Code: A Article ID: 1672-6421(2008)01-032-04

Industry scale production of magnesium alloy has been severely limited because of high reactivity of magnesium, which causes oxidizing and flaming during melting, casting, heat treatment and machining. Over decades, a lot of studies have been focused on developing ignition-resistant magnesium alloys by equipment improvement, flux coverage, gaseous protection and alloying [1]. Among them, the alloying method has the greatest potential because it not only resolves the problems of equipment complication, flux inclusion and environmental pollution in melting and casting processing, but also improves materials performances in heat treatment and machining processing [2,3]. Currently, the major elements used for ignition proof of magnesium alloy are Be, Ca and rare earth (RE) [1-8].

Ignition temperature has been used to evaluate the oxidation and ignition resistance of magnesium alloy for years, but the measurement methods and ignition point definitions vary from one study to another [2-11]. People investigated the ignition of magnesium alloy in various forms, such as filings or powder, block, and melt in a protective environment; temperature measurements include the sample temperature, furnace temperature or conducting medium temperature. It has been observed that ignition started with the formation of "cauliflower" oxide and occurrence of flame on the surface of the alloy; and melting followed afterward. The temperature of inflection point on the measured temperature-time curve was usually defined as the ignition point.

The surface and interior temperature-time curves of a blocky AZ91D magnesium alloy were measured with a multi-channel data acquisition system. Two inflection points, corresponding to the formation of "cauliflower" oxide and occurrence of flame, were found in both curves. These two temperatures are defined as oxidation point and ignition point, respectively. The results of ignition point measurement of block AZ91D magnesium alloys added with cerium are discussed in this paper.

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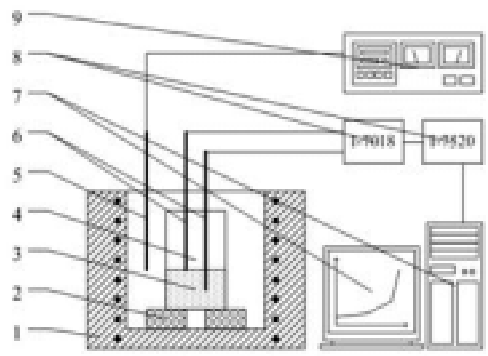
Received: 2007-08-22; Accepted:2007-12-27

1 Experimental procedure

Commercial billet of AZ91D magnesium alloy, commercially-pure aluminum sheet (99.5wt%), analytically-pure zinc granule (99.9wt%) and commercially-pure cerium block (99.0wt%) were used for casting Ce-modified AZ91D alloy. The raw materials were first cut and mixed in a proper ratio, melted and then cast into billet with a composition of 9.5 wt.% Al,1.3 wt.% Zn, 0.0–1.0 wt.% Ce, the rest Mg. Six alloys with Ce concentration of 0.0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0% were made for the current study.

Samples with the dimension of ϕ60 mm × 60 mm were cut from the ignition-resistant magnesium alloys. Temperature during heating was measured with a multi-channel data acquisition system (with an accuracy of ± 1℃), which is illustrated in Fig.1. Two K-type thermocouples were used for temperature measurement. Both thermocouples were placed close to the surface to measure the temperature rise before melting. Upon melting, one thermocouple stayed on the surface to measure the sample surface temperature and another was pushed into the melt to measure the interior temperature. It is worthy mentioning that neither flux nor gaseous protection was used in this processing. The samples were heated from solid state to melt, oxidize, ignite and form dazzling white light or oxidize completely. The oxidation point and ignition point of magnesium alloy can be determined by comparing the surface phenomena observed and the simultaneously recorded temperature-time curves.



(1) furnace
(2) fire brick
(3) magnesium alloy block/melt
(4) stainless steel crucible
(5) temperature control thermocouple of furnace
(6) thermocouple
(7) computer system
(8) temperature data acquisition and transmission module
(9) temperature controller of furnace

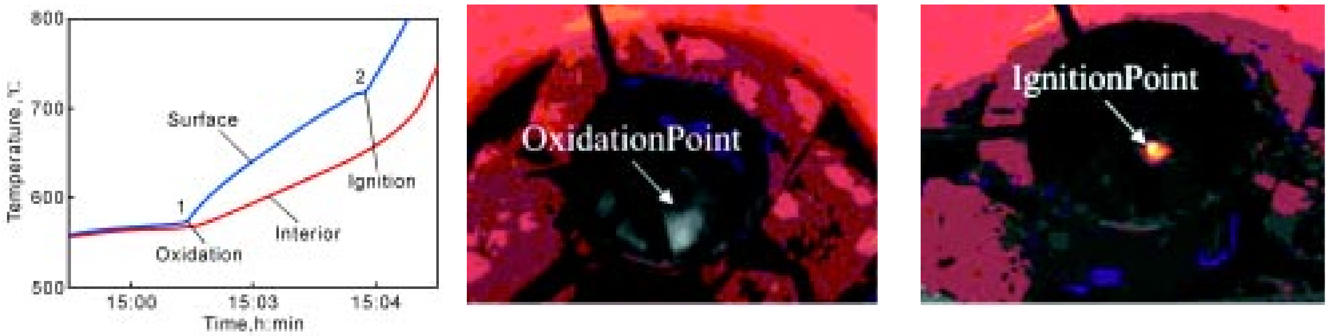
Fig.1 A diagram showing experimental setup and the oxidation and ignition temperature acquisition system

2 Results and discussions

2.1 Oxidation and ignition during heating

In a non-protective continuous heating process, magnesium alloy will undergo three procedures: (1) surface oxidize in a slow and uniform manner; (2) to form the "cauliflower" oxide and then grow quickly; (3) to appear flame and burn up all magnesium finally. Figure 2 shows the typical temperature-time curves (Fig. 2a) recorded and the appearance of "cauliflower" oxide (Fig.2b) and the occurrence of flame ignition (Fig.2c) during heating.

After careful comparison of the observation and experimental data, we concluded that two inflection points of rapid increase in temperature corresponded well with the formation of "cauliflower" oxide and occurrence of flame on the surface respectively. The changes in the rate of temperature increase during heating are because oxidation and ignition are exothermic reactions. Further, the amount of heat produced in ignition process is more than oxidation process indicating the second rapid temperature increase period.



(a) temperature-time curve (b) oxidation (c) ignition

Fig.2 Oxidation and ignition of magnesium alloy and their typical temperature-time curves

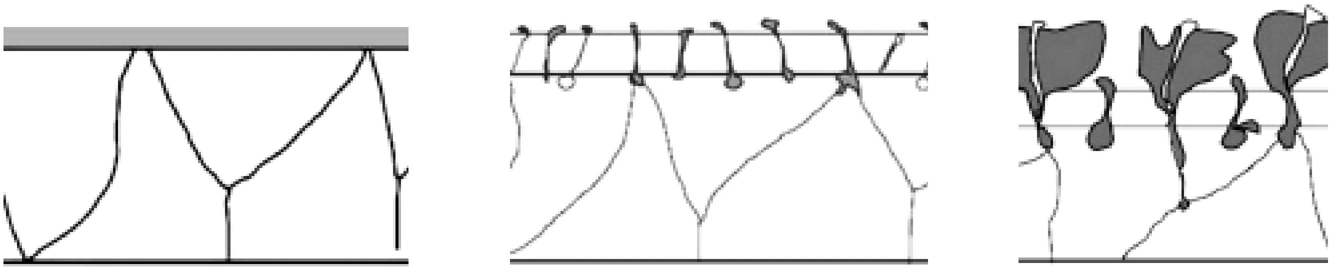
Magnesium alloy begins to oxidize at a lower temperature in a non-protective continuous heating process, accompanying with the surface color change, and the oxide tended to grow on the surface continuously and uniformly. Upon the formation of "cauliflower" oxide, all samples are in their semi-solid or liquid state, so one of the curves in Fig.2a represents the surface temperature evolution and the other represents the inner temperature change. It is apparent that the surface and inner temperature of the alloy melt overlapped before the formation of "cauliflower" like oxide, but differed distinctly thereafter. The interior temperature-time curve is similar to the surface curve but exist a time delay. The rapid increase in surface temperature is due to the fast oxidation and severe ignition reaction, while the interior temperature rise was caused by the heating and heat conducted from the surface in the processes of oxidization and ignition.

Further experiments proved that all other samples including pure magnesium, AZ91D magnesium alloy and their ignition-proof alloys modified with Ce, Y and Ca experienced similar three-staged oxidation and ignition in a continuous heating process without any protection.

2.2 Definition of oxidation and ignition temperature

It has been well-accepted that the ignition of magnesium and its alloy without adding ignition-proof elements occurs at the temperature below liquidus line, and the phenomena associated with the ignition is the formation of "cauliflower" oxide on the surface. Experimentally, the ignition appears at the inflection point on the measured temperature-time curve. The ignition temperature also varies with the heating speed and dwelling time. The ignition point could be increased by several hundreds degrees by adding adequate ignition-proof elements such as Be, Ca and RE.

F Czerwinski considered three stages of the oxidation and ignition procedure in magnesium alloy, as illustrated in Fig.3 [11,12]. The first stage is slow and uniform oxidization, which begins at a lower temperature in solid state. During this stage the alloy reacts with oxygen in the air and form oxide on its surface, but both Mg and O_2 can diffuse through the oxide film because the oxide film is not compact. With time, the oxidization reaction proceeds



(a) compact uniform layer (b) transient to oxide ridges (c) growth of oxide nodules

Fig. 3 Schematic representations showing the development of MgO morphologies at various stages

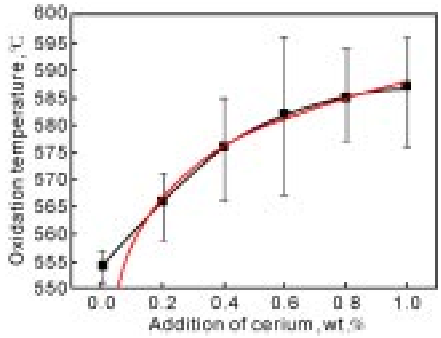
continually and the film thickness increases steadily. Due to the uniform and continuous oxide film on the surface at this stage, the reaction of Mg with O_2 underneath the film is interface-controlled, and therefore the overall progress is slow. Solid-state diffusion of Mg and O_2 through the oxide film dominates the oxidization at this stage. Since Mg has greater diffusion coefficient than O_2 at this stage, the oxidation reaction happens at the oxide/gas interface.

Along with oxidation reaction and the further increase of temperature, the surface of the alloy experiences morphological changes. The outward diffusion of Mg ion leads to the inward vacancy flux, which creates voids at the metal/oxide interface. Those voids act as channels for the transportation of Mg vapor, and also cause the local stress rising contributing to film cracking (Fig. 3b). Another factor causing tensile stresses and formation of fissures is the volumetric difference between the MgO film and metallic substrate. These fissures induce fast Mg and O_2 transportation, especially inward O_2 diffusion through the oxide film, thus the oxidation reaction begins to accelerate and form a fresh oxide at the oxide/metal interface. Then the oxidation reaction becomes non-uniform on the surface followed by an outward growth of ridges at the fissures (Fig. 3c). This is the second fast oxidization stage.

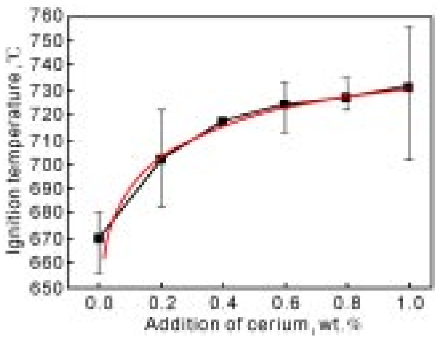
Oxide with loose and shaggy structure formed on the surface during uniform oxidization stage, followed by a second stage oxidization featured with faster oxidation reaction and rapid surface temperature rising. When heat from oxidization reaction accumulates to certain level, the magnesium vapor starts to burn. Based on Czerwinski's model [11,12] and experimental observation, it is rational to define the temperatures corresponding to the two inflection points in Fig.2a as oxidation temperature and ignition temperatures, respectively.

2.3 Effect of Ce on oxidation and ignition of AZ91D magnesium alloy

Figure 4 shows measured data of oxidation and ignition temperature of magnesium alloy as a function of Ce addition. It can be seen from Fig. 4 that magnesium alloy begins to oxidize at the temperature below the melting point, and the oxidation and ignition temperatures increase steadily with cerium content. An average increase of 33℃ and 61℃ for oxidization and ignition temperature has been found for the AZ91 alloy after 1wt% Ce addition, and the highest temperatures were 596℃ and 756℃, respectively. However, the increasing rate of the oxidation and



(a) oxidation temperature



(b) ignition temperature

Fig.4 Effect of Ce on oxidation and ignition temperature of AZ91D magnesium alloy

ignition temperature decreases with cerium content, and the advisable content is about 0.6wt% for developing ignition-resistant AZ91 magnesium alloy.

Experimental data were further regressively analyzed using three mathematical models, i.e. $T=a+b\times w_{ce}$, $T=a+w_{ce}^{\ b}$, $T=a-b\times c^{w_{ce}}$ and the analytical results are listed in Tab.1, where Ce represent the content of Ce and r is correlation coefficient. Based on the correlation coefficient, we concluded that there is an approximately exponential increase in the oxidation and ignition temperatures of magnesium alloys as a function of Ce addition. The regression results of $T=a+w_{ce}^{\ b}$ fit the experimental data well and are also included in Fig.4 as smooth curves.

3 Conclusions

(1) Magnesium and its alloys undergo three stages of surface or bulky reactions, such as early protective oxidation stage (slow), middle non-protective oxidation stage (fast) and late ignition stage, in a non-protective heating process. Oxidation and ignition correspond to the formation of "cauliflower"oxide and

Table 1 Regressive results of oxidation and ignition temperature of magnesium alloy contain Ce

Model	Oxidation temperature				Ignition temperature			
	a	b	c	r	a	b	c	r
$T=a+b \times w_{ce}$	558.7	32.6	-	0.954	684.2	55.3	-	0.904
$T=a+w_{ce}^{b}$	587.9	0.023	-	0.996	731.9	0.025	-	0.993
$T=a-b \times c^{w_{ce}}$	591.9	38.3	0.118	0.999	731.5	61.4	0.028	0.999

occurrence of flame on the surface of the alloy and its melt, respectively. The fast oxidation stage occurs at a temperature below liquidus line.

(2) Rare-earth element Ce can effectively improve the oxidation and ignition resistance of magnesium alloy. The oxidation and ignition temperatures increase with cerium addition, an average increase of 33℃ and 61℃ has been found for AZ91 alloy modified with 1.0wt.% Ce. The increasing rates of oxidation and ignition temperatures decrease with Ce content, and the advisable content is about 0.6wt.%.

(3) The effect of rare-earth element Ce on the oxidation and ignition temperatures of magnesium alloy can be quantitatively described by $T=a+w_{ce}^{b}$.

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This work was supported by the Hi-Tech Research and Development Program of China (grant No.2002AA336080), the National Basic Research Program of China (grant No. G2000067202) and Jiangxi Provincial Department of Education.