Effect of rare earths (Y, Ce) additions on the ignition points of magnesium alloys

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Magnesium alloys with low density have considerable potential as light-weight structural materials for automobile and aircraft industry, but their extensive application has been limited due to the poor oxidation resistance. As is well known, it is impossible to melt magnesium alloys without any protection because of serious oxidation and even burning. Commonly fluxes or protective gases (CO_2, SO_2, and SF_6) are used to prevent magnesium alloys from burning during melting process [1–4], but the above methods have disadvantages such as environmental pollution, complication of the casting equipments, cost inflation, etc. So, since the 1950s, much interest has been focused on the investigation of ignition-proof magnesium alloys. Beryllium and Calcium proved to be effective elements to improve the oxidation resistance of magnesium alloys [5–12], but ignition-proof magnesium alloys with Beryllium and Calcium additions have not been extensively applied in industry due to their poor mechanical properties and the smart toxicity of Beryllium.

Rare earths are often used as addition elements to improve alloys' properties. Especially Yttrium and Cerium have been used in many alloys to improve the oxidation resistance [13–15]. In the present research, the effect of Yttrium and Cerium additions on the ignition point of magnesium alloys was studied so as to provide a new idea for the preparation of ignition-proof magnesium alloys.

All the magnesium alloys, i.e., Mg-Y, Mg-Ce and Mg-Y-Ce were prepared using commercial pure magnesium (99.9 wt%), pure Yttrium (99.3 wt%) and pure Cerium (99.5 wt%) elements. Magnesium alloys with different contents of Yttrium ranging from 0 to 15 wt% and Cerium ranging from 0 to 15 wt% were melted in an electric resistance furnace under the protection of CO_2-0.5%SF_6 gas. The chemical compositions of the alloys were analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy method (ICP-AES). Samples of about 20 × 20 × 5 mm were cut for ignition points testing directly after mechanical polishing and degreasing in acetone. The crystallographic features were examined mainly by X-ray diffraction with a Cu K_α source. The analyses of microstructural morphologies were completed by using scanning electron microscope with energy dispersive spectrometer (SEM & EDS).

Fig. 1 is the schematic diagram of the ignition point testing device, which can be heated at the rate of 4 °C/s, and the typical temperature vs. time curve is shown as Fig. 2. The combustion heat is large enough to cause the steep rise of the temperature of the samples, which proves the feasibility of the method of the ignition point testing. The inflexion in the curve was defined as the ignition point of magnesium alloy.

The results of ignition point test are shown in Table I. When the contents of Y are less than 8 wt%, there is no notable change in the ignition point of alloys, but with the contents increasing continually, the ignition points were increased, and when the content is more than 10 wt%, the alloys do not burn up to 900 °C. However, magnesium alloys would be very brittle if the content of Y is larger than 8% [16], moreover, large Y addition will make the alloys costly. So Cerium was added to the alloys to reduce the Y content.

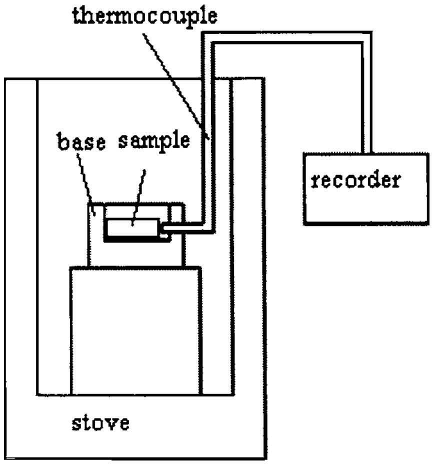

Figure 1 Schematic diagram of the ignition points testing device.

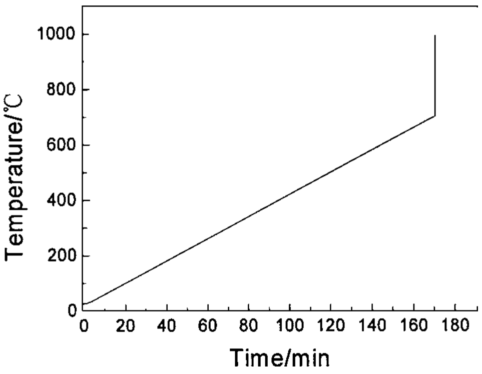

Figure 2 Typical temperature vs. time curve of magnesium alloys.

TABLE I Ignition points of magnesium alloys with different composition

Composition (wt%)	Mg	Mg0.39Y	Mg1.11Y	Mg1.58Y	Mg2.24Y	Mg3.80Y	Mg4.40Y	Mg5.79Y
Ignition points (°C)	615	660	643	660	641	660	661	665

Mg10.56Y	Mg1Ce	Mg2Ce	Mg3Ce	Mg5Ce	Mg7Ce	Mg9Ce	Mg11Ce	Mg13Ce	Mg2.83Y1.74Ce.
No ignition	636	635	630	647	630	636	647	640	680

Mg2.83Y1.74Ce	Mg2.89Y4.41Ce	Mg2.95Y2.49Ce	Mg3.08Y0.68Ce	Mg3.42Y2.21Ce
680	No ignition	700	No ignition	865

The data in Table I indicate that the effect of Ce on the ignition temperature of magnesium alloys is very little, however, to our surprise, when Y and Ce are added into Mg alloys together, the ignition points of Mg alloys increase rapidly and with no burning up to 900 °C.

Fig. 3 shows X-ray diffraction patterns of the surface of magnesium alloys. Fig. 3a is the spectrum of the surface of Mg-Y-Ce alloys directly after grinding, and Fig. 3b is that of the oxidation film formed on the Mg-Y-Ce alloys held for 0.5 hrs at 1173 K in the air. The surface before oxidation includes mainly Mg, but the oxidation film formed at high temperature contains a majority of Y_2O_3. The difference is obvious although there are still strong Mg peaks in the spectrum (Fig. 3b) because X-ray penetrates the thin film into the alloy matrix. According to the calculation results, the oxidation free energy of Y is much larger than that of Mg at high temperature. Distinctly, the selective oxidation

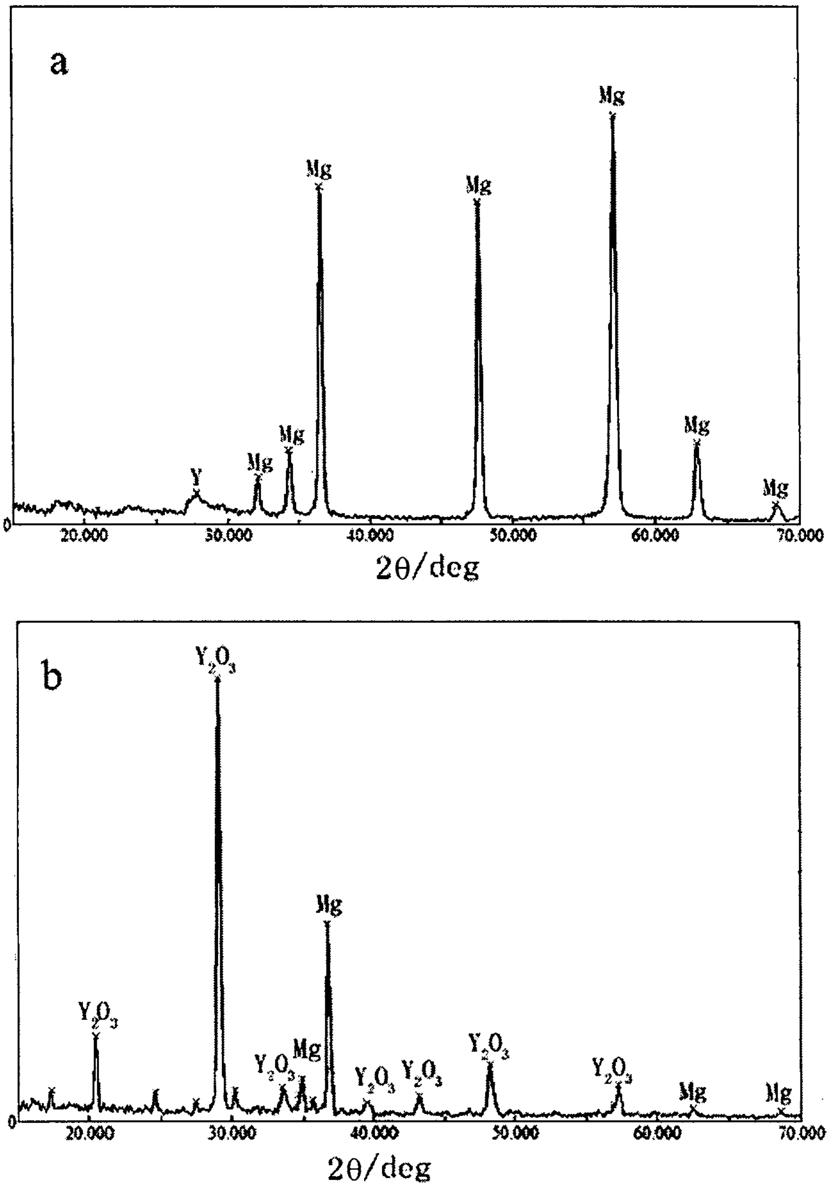

Figure 3 X-ray diffraction patterns of the surface: (a) Spectrum of the surface of Mg-Y-Ce alloys directly after grinding and (b) spectrum of the oxidation film formed on the Mg-Y-Ce alloys held for 0.5 hrs at 1173 K in the air.

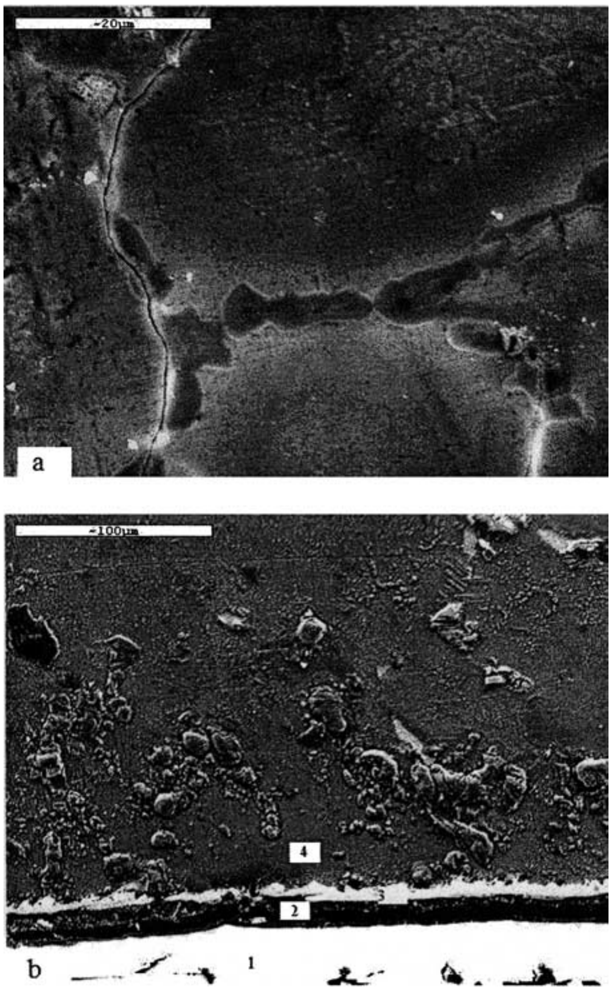

Figure 4 SEM morphologies of the oxidation surface of Mg-Y-Ce alloy at 900 °C for 0.5 hrs: (a) The oxidation surface and (b) the cross-sectional images of the oxidation film: (1) epoxy, (2) the outer layer film, (3) the inner layer film and (4) the substrate.

took place and the Y_2O_3 formed preferentially, which prevents Mg alloys from further oxidation and even ignition.

Fig. 4 is the SEM morphologies of the oxidation surface of Mg-Y-Ce alloy at 1173 K for 0.5 hrs. From Fig. 4a, the surface of Y_2O_3 film is rugged and compact because the Pilling-Bedworth ratio of Y is larger than 1. Fig. 4b is the cross-sectional image of the oxidation film. Referred to EDS analysis, the oxidation film includes two layers. The outer layer (symbol 2) is the mixture of Y_2O_3 and MgO and the inner layer (symbol 3) is mainly MgO with a little Y_2O_3. The addition of Ce reduced the content of Y_2O_3 in the oxidation film, and increased the content of MgO, but Ce_2O_3 did not present itself in the film.

In summary, because of selective oxidation, the compact Y_2O_3 film formed on the surface of Mg-Y and Mg-Y-Ce alloys at high temperature, and the film can prevent alloys from further oxidation and burning. When Y and Ce are added solely, the effect on the ignition points is little, but when they are added together, there will be notable change. Some Mg-Y-Ce alloys can melt safely at 1173 K in air without any protection.

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