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MECHANICAL PROPERTIES AND HIGH-TEMPERATURE OXIDATION BEHAVIOR OF Mg-Al-Zn-Ca-Y MAGNESIUM ALLOYS

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Abstract

Ignition resistance and tensile properties of Mg-3Al-1Zn and Mg-6Al-1Zn (wt.%) alloys with combined addition of calcium and yttrium were investigated in the present study. The results of this study clearly show that the combined addition of calcium and yttrium can lead to significant increase in both ignition temperature and tensile properties, comparing to 2 wt.% Ca-added magnesium alloys with lamella-shaped eutectic phases. This is because the reduction of calcium content and the addition of a small amount of yttrium bring about a reduced amount of coarse Ca-containing phases and the formation of duplex protective oxide layers that effectively prevent oxygen penetration into the melt.

Introduction

Magnesium and its alloys are very active, especially in a molten state, and are rapidly ignited or combusted when the clean surface of the melt comes into contact with oxygen in air. Flux or a cover gas has to be used to prevent ignition of magnesium alloys during melting. However, the above methods may cause many problems such as global warming and increased production costs, so many researchers are paying more attention to finding more essential methods to improve ignition resistance. Obviously, it is simple to prevent the ignition of magnesium alloys by the addition of alloying elements. However, it is difficult to select suitable elements, because only some of alloying elements have been proved to benefit the oxidation resistance of magnesium alloys [1-5].

Calcium is one of the promising elements that can improve ignition resistance. The ignition temperature increases by 250 K after an addition of 3 wt.% Ca-added into pure magnesium [6]. You et al. [7] investigated the oxidation behavior of a Mg-xCa alloy (x=0-3 wt.%), and they confirmed that a dense and compact protective MgO/CaO layer formed at elevated temperatures. However, a large amount of calcium addition generally lowers tensile strength and ductility because coarse Ca-compounds precipitate along the grain boundaries. Unfortunately, most of such studies have concentrated on either ignition resistance or tensile properties of magnesium alloys, but there has been no attempt to improve both them.

In fact, increasing both ignition temperature and tensile properties is difficult to achieve because of their contradictory aspects; that is, a large addition amount of ignition resistance improving alloying element is necessary to make ignition-proof magnesium alloys [2, 6-8], but at the same time it causes the deterioration of tensile properties due to the formation of coarse brittle phases. This indicates that instead of a large amount of a single alloying element, the combined addition of two or more alloying elements may suppress the formation of a large fraction of coarse brittle phase without sacrificing ignition resistance. In the present study, we therefore investigate the effect of the combined addition of calcium and yttrium on ignition resistance and tensile properties of magnesium alloys. That is crucial to make magnesium alloys more reliable materials and thus enlarge their application areas, including in advanced transportation vehicles requiring strict stability in a material selection.

Experimental procedures

Mg-xAl-yCa (x=3, 6 wt.%, y=1, 2 wt.%) and Mg-xAl-1Ca-0.6Y (x=3, 6 wt.%) alloys were prepared according to the nominal composition by pure magnesium (99.93 wt.%), pure aluminum (99.9 wt.%), pure zinc (99.9 wt.%), pure calcium (99.9 wt.%) and pure yttrium (99.9 wt.%) in an electric furnace using a low-carbon steel crucible heated to 993 K under a protecting gas (10% SF_6 and 90% CO_2). The melt was poured into a permanent mold preheated to 473 K and then cooled to ambient temperature in air atmosphere. The cast ingots were subsequently heated to 673 K for homogenization treatment and kept at this temperature for 20 hours. The ingots were hot-rolled at 673 K at a reduction rate of 30%/pass with a total reduction of 93%. The rolled sheets with a 1 mm thickness were finally annealed at 523 K for 30 minutes. Ignition tests were carried out by inserting the chipped samples taken from the castings into a tube furnace held at 1273 K. The tests were carried out in air and at least five chipped samples were used. The ignition temperatures were determined as ones associated with both the appearance of flame and a significant temperature increase as shown Fig. 1. Metallographic samples were prepared for microstructure observation according to a standard procedure. The distribution of alloying elements in the surface oxide layer that was formed on the melt was checked using an EPMA (electron probe micro-analyzer). Tensile tests were carried out using an Instron-4206 universal testing machine at a strain rate of 0.001/s at room temperature. Sheet-type tensile specimens with the dimensions of the ASTM E 8M standard were used. All the tensile specimens were taken in parallel to a longitudinal direction of the rolled sheet.

Results and discussion

Fig. 2 shows the as-cast microstructures of the experimental alloys. In Figs. 2(c) and 2(f), the alloys with the combined addition of 1 wt.% Ca and 0.6 wt.% Y contain a small amount of semi-continuous dihexagonal C36-$(Mg,Al)_2Ca$ Laves phase at interdendritic regions and spherical Al_2Y particles inside grains; however, as shown in Figs. 2(b) and 2(e) only 2 wt.% Ca-added

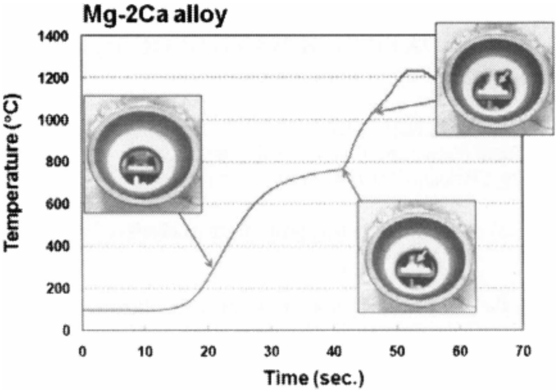

Figure 1. Measurement of ignition temperature. A sudden increase in temperature indicates that the sample begins to be ignited.

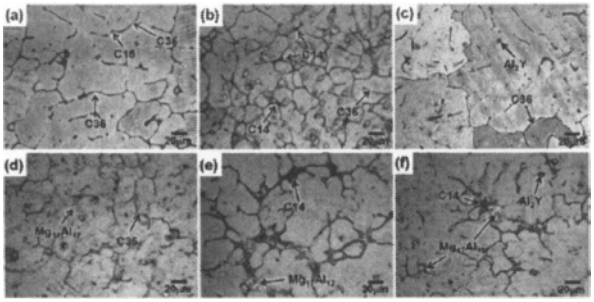

Figure 2. Optical micrographs showing the as-cast microstructures of (a) AZX311, (b) AZX312, (c) AZX311-0.6Y, (d) AZX611, (e) AZX612, and (f) AZX611-0.6Y.

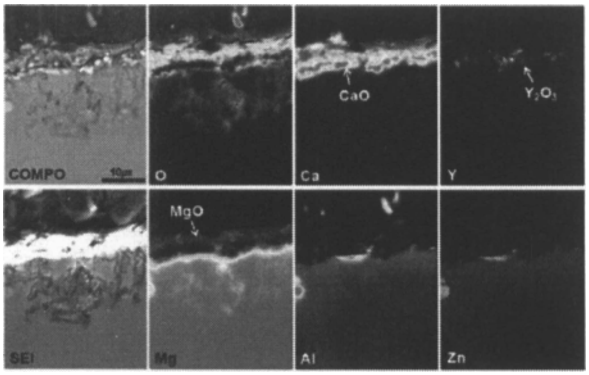

Figure 3. EPMA result showing the surface oxide layer of the AZX611Y alloy held at 950K for 10 min. The white oxide layer in the SEI image is composed of two distinctive layers in the BEI-COMPO image.

alloys contain a large amount of lamella-shaped C14-Mg_2Ca phase [9-10]. According to a thermodynamic calculation, an addition of yttrium does not influence the mass fraction of Ca-containing eutectic phases, namely C14-Mg_2Ca, C15-Al_2Ca, and C36-$(Mg,Al)_2Ca$, but it is involved only in the formation of Al_2Y particles.

Table 1. Ignition temperatures of the castings and tensile properties of the rolled sheets.

	T_{ig} [a] (K)	YS (MPa)	UTS (MPa)	El. (%)	U.El. (%)
AZ31	753	176.4	274.5	25.2	17.4
AZX311	981	191.1	276.1	24.3	16.9
AZX312	1020	255.2	303.6	16.5	9.7
AZX311-0.6Y	1041	175.8	265.2	24.7	18.4
AZ61	794	218.7	324.0	22.0	17.2
AZX611	976	204.4	306.2	19.7	16.0
AZX612	1028	230.0	321.0	16.7	14.1
AZX611-0.6Y	1047	225.7	323.4	19.6	15.5

[a] Ignition temperature of chip sample

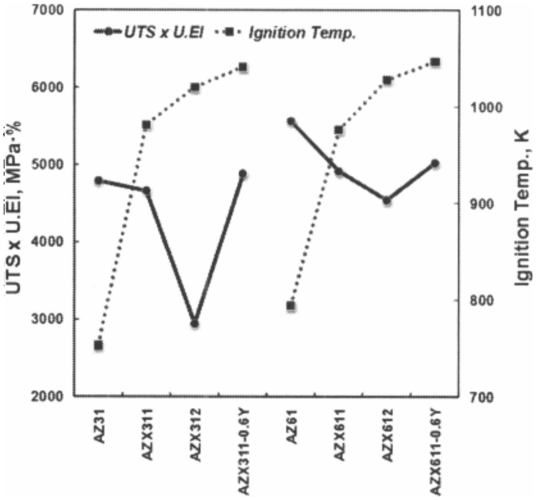

Figure 4. The changes in ignition temperatures and tensile properties with additions of Ca and Y. The combined addition of a small amount of calcium and yttrium improves both ignition resistance and tensile properties of magnesium alloys.

Despite the small amount (no more than 1 wt.%) of calcium and yttrium, the ignition temperatures of the AZX311-0.6Y and AZX611-0.6Y alloys in Table 1 are 1041 K and 1047 K, respectively, and they are approximately 20 K higher than those of the AZX312 and AZX612 alloys and moreover more than 60 K higher than those of 1 wt.% Ca-added alloys. These results of chip ignition tests demonstrate that the alloys with the addition of 1wt.% Ca and 0.6wt.% Y have better ignition resistance than those with the addition of only 2wt.% Ca. The studies in Refs. [6-8] suggest that an individual addition of calcium and yttrium to magnesium alloys should be larger than at least 2 wt.% and 4.3 wt.%, respectively, to obtain practically acceptable ignition-proof performance. Compared to the alloys with an individual addition of calcium or yttrium, our study confirmed that the alloys with a combined addition of those alloying elements exhibited much more superior ignition-proof performance, even by a small addition of no more than 1 wt.%.

Fig. 3 clearly shows that the surface oxide of the AZX611-0.6Y sample held at 950 K for 10 minutes is composed of two distinctive layers. An addition of yttrium to Ca-added magnesium alloys can make a dense and protective oxide layer that contains Ca and Y elements on the surface contacting with a Mg alloy melt in addition to an outer oxide layer that contains Mg, Al, and Ca elements.

The tensile properties of the hot-rolled sheets are shown in Table 1. As calcium content increases from 1 wt.% to 2 wt.%, both yield and tensile strengths increase, but at the same time elongation drops due to a large amount of brittle Ca-containing phases. In particular, the total elongation of the AZX312 alloy decreases approximately 8% compared with the AZX311 alloy. We can infer from Table 1 that such a deterioration of elongation can be restored by reducing the calcium content and adding a small amount of yttrium. In Table 1, the elongations of the AZX311-0.6Y and AZX611-0.6Y alloys are 24.7% and 19.6%, respectively, which are similar to those of the AZX311 and AZX611 alloys. Furthermore, the ignition temperatures of the AZX311-0.6Y and AZX611-0.6Y alloys are higher than those of the AZX312 and AZX612 alloys, respectively. As an increase in elongation commonly gives rise to a decrease in strength, the multiplied values of ultimate tensile strength by uniform elongation are better to represent the overall tensile properties of the samples. In Fig. 4, the values significantly decreased in 2 wt.% Ca-added magnesium alloys, but they were restored to those of 1 wt.% Ca-added magnesium alloys by the combined addition of calcium and yttrium. This is because the reduced amount of brittle and coarse Ca-containing phases is attributed to the improvement in tensile properties of those alloys. On the other hand, compared with 2 wt.% Ca-added magnesium alloys, the large decrease in yield strength of the alloys with the combined addition of calcium and yttrium was caused from only a small amount of fine C15-Al_2Ca precipitates, which can form at grain interiors in alloys with excess calcium content of more than 2 wt.%, and thus contribute to strengthening matrix [10].

Conclusions

In this study, the combined addition of calcium and yttrium has a very attractive beneficial effect on the ignition resistance and tensile properties of magnesium alloys. The duplex protective oxide layers of CaO-Y_2O_3 at the inner part and MgO-$MgAl_2O_4$–CaO at the outer part are attributed to further improvement in ignition resistance, compared to the only Ca-added magnesium alloys. In addition, the reduced amount of brittle and coarse Ca-containing phases in the alloys with the combined addition of a small amount of calcium and yttrium contributes to a large increase in tensile properties, especially elongation. Our approach to improve both ignition resistance and tensile properties provides a strong impact on the development of clean manufacturing technology for reliable magnesium alloys, which in turn will lead to an expansion of their application areas.

Acknowledgements

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