

## Effect of CaO addition on ignition behavior in molten AZ31 and AZ91D Magnesium alloys

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**Abstract:** Mg alloys have been widely used in automobile and electronic industries because of high specific strength, good castability, etc. However, molten Mg alloys will burn rapidly in air if not protected. To solve this problem, the molten metal should be protected from oxidation by blanketing the surface with flux or protective gases. SF<sub>6</sub> gas is widely used for Mg alloys as a cover gas and has proved to be a successful inhibitor. However, the use of SF<sub>6</sub> gas is limited because of its high cost and its significant impact on non-global warming potential. Therefore, SF<sub>6</sub> gas is being replaced by alternative protection gases. Recent studies show that there has been another attempt by adding CaO into Mg alloys. The aim of this study is to evaluate the effect of CaO on the minimum amount of protective gas, which is necessary not to make ignition in the molten AZ31 and AZ91 Mg alloys.

**Key words:** AZ91; AZ31; CaO; clean production; ignition resistance

### 1. Introduction

Mg alloys have been widely used in automobile and electronic industries because of high specific strength, good castability, etc. [1-5]. Despite these advantages, Mg alloys are used with precautions of high chemical reactivity. Molten Mg alloys will burn rapidly in air if not protected. To solve this problem, the molten metal should be protected from oxidation by blanketing the surface with flux or protective gases. SF<sub>6</sub> gas is widely used for Mg alloys as a cover gas and has proved to be a successful inhibitor. However, the use of SF<sub>6</sub> gas is limited because of its high cost and its significant impact on non-global warming potential (GWP). Also, the Kyoto Protocol proclaims for a reduction in SF<sub>6</sub> gas use. Environmental and economical concerns have caused the magnesium industry to look for possibilities to replace or re-

duce the outlets of SF<sub>6</sub> gas. Therefore, SF<sub>6</sub> gas is being replaced by alternative protection gases such as tetrafluoro ethane (HFC-134a) and 3M™ Novec™ 612. These gases are less expensive and have lower GWP, compared with SF<sub>6</sub> gas. Research has been done to improve these properties by alloying. It is well known that calcium and strontium, though their high cost, are effective for oxidation resistance and elevated temperature properties [6]. However, the relatively high cost of these materials might prevent widespread industrial applications. Furthermore, the handling of calcium and strontium is not easy. The aim of this study was to manufacture CaO added AZ31 and AZ91D Mg alloys with the goals of eliminating or reducing use of protective gases during melting, ingot casting/continuous casting, forming and heat treatment. CaO is cheaper than calcium and easy to handle due to its stability. This paper discussed the effect of CaO on ignition behavior and the opti-

imum amount of protective gas not to make ignition in the molten AZ31 and AZ91D Mg alloys.

## 2. Experimental

The materials employed in the present study were AZ31 and AZ91D Mg alloys, the chemical compositions of which are given in Table 1. Molten AZ31 and AZ91D Mg alloys were prepared in a steel crucible heated to 700 °C in an electric resistance furnace under SF<sub>6</sub> and CO<sub>2</sub> protective cover gas. The desired fraction of CaO particles was added with a feed rate 10 g·min<sup>-1</sup>. CaO particles, which were dehydrated, pulverized and stored in vacuum with average diameters of under 50 μm, were used. In order to avoid a big temperature change during the addition of the particles, the particles were heated to 200 °C prior to addition. The CaO added melts prepared by conventional melting and casting were cast into a 103 mm diameter cylindrical mold preheated at 200 °C. Chemical compositions were determined by ICP-mass spectrometry. Sections of CaO added AZ31 and AZ91D Mg alloys billets were polished and examined using an electron probe micro analysis (EPMA). The alloys chips were prepared from the as-cast billets by drilling without cutting oil for ignition test. Chips on a copper boat were inserted into an electric resistance furnace at 700 °C in an ambient atmosphere. Temperature change was monitored by a thermocouple equipped with a copper boat and the ignition was detected by abrupt temperature rise. The obtained ignition temperatures were based on the average of 10 tests. The effect of CaO on the minimum amount of protective gas required was examined for CaO added AZ31 and AZ91D Mg alloys as shown in Fig. 1. CaO added Mg alloys were melted at a given temperature at 680 and 720 °C under SF<sub>6</sub> / air

(50-3000 ppm, 10 L). Oxide film on the surface of molten Mg alloy was removed by a scraper through the hole of steel cover to react the molten Mg alloy under controlled atmosphere. The minimum amount of protective gas to prevent burning of the melt was evaluated.

## 3. Results and discussion

Fig. 2 shows the surface of the as-cast billets of four materials in cylindrical mold without protective gas. It can be seen that a lot of oxides appeared on the surface of AZ31 as shown in Fig. 2(a). Generally, MgO could not act as a barrier to prevent the further oxidation of Mg because the structure of MgO was loose. Therefore, MgO formed continuously in the ambient atmosphere. Molten Mg melt erupted from cracks in the oxide layer and reacted with the surrounding air to carry out the main reaction of  $2\text{Mg} (l) + \text{O}_2 (g) = 2\text{MgO} (s)$ ,  $\Delta G_f = -962.516 \text{ kJ} \cdot \text{mol}^{-1}$ , accompanied by ignition. However, the 0.14 wt.% CaO and 0.45 wt.% CaO added AZ31 alloys displayed a regular surface, probably associated with the development of a protective oxide layer compared with AZ31 and 0.07 wt.% CaO added AZ31 alloys as shown in Fig. 2.

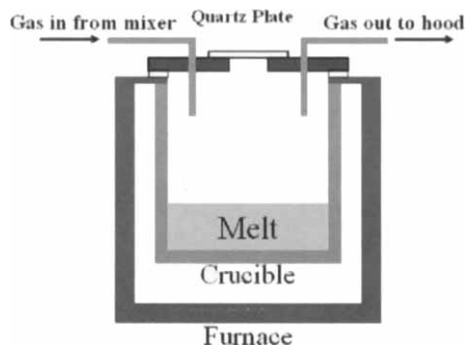


Fig. 1. Schematic of experiment apparatus for optimum protective gas condition.

Table 1. Chemical compositions of AZ31 and AZ91D Mg alloys (wt. %)

Alloy	Al	Zn	Mn	Si	Fe	Cu	Ni	Mg
AZ31	3.00	0.83	0.31	0.01	0.003	0.001	0.001	Bal.
AZ91D	8.29	0.68	0.12	0.011	0.006	0.001	0.003	Bal.

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