Magnesium alloys have been used widely since the recent years in automotive, electric and aerospace industries for their high specific properties [1-3]. Despite such properties, the use of magnesium alloys is still relatively limited due to the severe composition segregation and coarse grains produced in the course of traditional casting. Spray forming is a promising rapid solidification technique, which has been used to manufacture magnesium alloys because of its grain refinement effect, leading to improvement over their poor workability [4-6]. During spray forming process, the liquid metal must be atomized into droplets by inert gas (argon, helium or mixed gas). However, the manufacturing cost of magnesium alloys is increased with the use of inert gas in large measure. If nitrogen can be used instead of the inert gases, the manufacturing cost will be greatly reduced. The problem is that the heat from the reaction between magnesium alloys and nitrogen makes magnesium alloy burn easily in the spray forming process. Therefore, it is critical to investigate the ignition points of magnesium alloys under nitrogen atmosphere at static conditions.

It has been reported that addition of Ca has much influence on ignition-proof [7, 8] of pure Mg in air. In this paper, the effects of nitrogen gas purity on ignition point of Mg-Ca alloy were also discussed.

1 Experimental details

1.1 Sample preparation

Pure Mg (99.995%) and intermediate alloys (Mg-10wt.%Ca) were melted using a resistance furnace (SX2-4-12) under the protection of covering flux. After being held for 20 min at 720°C, the melt was then poured into a steel mold (φ25mm) and cooled with the mold in air. The bulk ignition tests were carried out on cylindrical samples with size of φ15 mm × 20 mm, polished with angular 320 grit SiC particles.

The Mg-5Ca samples were cut with lathe and then filtered, the powders of the samples were collected with standard sieves to obtain the powders (as show in Fig.1) in the size ranges of ~45, 45–75, 75–106 and 150–250 μm, respectively.

![Fig.1: 45–75 μm Mg-5Ca powders](image)
1.2 Ignition point test
The ignition point of Mg-Ca alloy under nitrogen atmosphere was tested using a home-made experimental device (as shown in Fig.2). Samples placed in a steel crucible were put into a tube resistance furnace at room temperature in nitrogen. The purity of nitrogen was 99.5% and the flow rate was 2 L/min. Temperatures of test samples were recorded every 2 min during heating process.

2.2 Effect of Ca content on ignition point
The effect of Ca content on ignition point of bulk Mg-Ca alloy in nitrogen is shown in Fig.5. It can be seen that in the figure, the ignition point of pure bulk Mg is 670 ℃. Increasing the Ca content from 0.5wt.% to 5wt.%, the ignition point of the bulk Mg-Ca alloy increases gradually. With the 0.5wt.% Ca addition, the ignition point is 910 ℃, reflecting an improvement of 230 ℃; and when Ca content reaches 5.0wt.%, the ignition point even exceeds 1,030 ℃. It is indicated that the effect of ignition-inhibition of Ca on the ignition point under nitrogen atmosphere is evident.

2 Results and discussion
2.1 Definition of ignition point of magnesium alloy under nitrogen atmosphere
At present, two mature methods are usually used to define the ignition point of Mg alloy in air. The first one is through observation. When magnesium alloy burns in the combustion process, the burning point emerges and then spreads along the surface one by one. When the burning covers the surface completely, the alloy will burn violently or even explosively. Generally, we define the temperature when the sample emerges one or two burning points as the ignition point [9, 10].

Another method is by means of the temperature-time curve. In the combustion process, thermocouples are used to record temperature changes with time. The temperature-time curve is shown in Fig.3. By making two tangents at the inflection point of the curve, the temperature corresponding to the tangent intersection can be used as the ignition point [11-12].

It was found that the combustion process of Mg alloy under nitrogen atmosphere was similar to that in the air. According to the definition of the ignition point of Mg alloy in air, the ignition point of bulk Mg alloy under nitrogen atmosphere can be determined by the consideration of the temperature when the first burning point occurs at the inflection point temperature.

The ignition point of powder Mg alloy was obtained through the inflection point of exothermic curve and weight gain curve on the DSC-TG curve (shown in Fig.4).

2.2 Effect of Ca content on ignition point
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<table>
<thead>
<tr>
<th>Ca content (%)</th>
<th>Ignition point (℃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>670</td>
</tr>
<tr>
<td>1</td>
<td>910</td>
</tr>
<tr>
<td>5</td>
<td>1,030</td>
</tr>
</tbody>
</table>

The holding time of Mg and Mg alloys without burning at high temperatures is shown in Table 1. It is apparent that pure magnesium can hold for 15 min at 650 ℃ without burning, but as the temperature rises to 700 ℃, it starts burning within 5 min. Both Mg-1Ca and Mg-5Ca can keep no-burning for over 600 min at 700 ℃, and the Mg-5Ca alloy can even hold for 30 min at
Table 1: The holding time of Mg alloy without burning at high temperature

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temperature (℃)</th>
<th>Holding time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>650</td>
<td>15</td>
</tr>
<tr>
<td>Mg-1Ca</td>
<td>700</td>
<td>≤5</td>
</tr>
<tr>
<td>Mg-5Ca</td>
<td>700</td>
<td>&gt;600</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>30</td>
</tr>
</tbody>
</table>

For the powders, the smaller the particle size, the larger the specific surface area. In contrast, the larger the particle size, the lower the specific surface area (as shown in Table 2). During the heating process, the powders with larger surface area are easier to react with the nitrogen due to the stronger chemical activity, generating large volume of heat and lowering the ignition point. Thus, the ignition point of Mg-5Ca alloy powders increases with the increasing particle size.

Table 2: The specific surface area of Mg-5Ca alloy powders

<table>
<thead>
<tr>
<th>Powder size (μm)</th>
<th>~45</th>
<th>45–75</th>
<th>75–106</th>
<th>150–250</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area (m²·kg⁻¹)</td>
<td>92.45</td>
<td>63.86</td>
<td>34.56</td>
<td>10.29</td>
</tr>
</tbody>
</table>

In the atomization process of the spray forming, the metal drops are continuously getting smaller and the ignition point is also reduced. Therefore, it is necessary to study the ignition point of alloy with different particle/droplet sizes to control melting temperature during the spray forming process.

2.4 Effect of nitrogen gas purity on ignition point

In order to find out the influence of nitrogen gas purity on the ignition point of magnesium alloy, the ignition points of Mg-Ca alloy powder under different atmospheres were investigated. Figure 8 shows the ignition points of Mg-5Ca alloy powder under the standard nitrogen (99.5%) and the high-purity nitrogen (99.99%). Under the high-purity nitrogen, the ignition points of Mg-5Ca alloy are respectively 603 ℃ with particle size of ~45 μm and 617 ℃ with size range of 75–106 μm. As shown in the figure, the ignition point under the high-purity nitrogen is lower than that under the standard nitrogen.

Fig. 6: Effect of Ca content on ignition point of 150–250 μm Mg-Ca alloy powders under nitrogen atmosphere

The results of ignition points of Mg-Ca alloy bulk and powder under nitrogen atmosphere indicate that the shape of the samples has significant influence on the ignition points of the alloy. The ignition points of powders are obviously lower than that of the bulk.

2.3 Effect of alloy powder sizes on ignition point

The ignition points of Mg-5Ca alloy powders with different particle sizes under nitrogen atmosphere are shown in Fig.7. Clearly, the ignition points of Mg-5Ca powders increase with the increase of particle sizes.
The results of ignition points of Mg-Ca alloy under different atmospheres show that the purity of nitrogen must be in a certain scope, and the ignition point of Mg-Ca alloys under the (standard) nitrogen atmosphere (with a purity of 99.5%) is obviously higher than that in air or high-purity nitrogen (99.99%). According to this discovery, it is safer and lower cost to use nitrogen as the atomizing gas during spray forming process.

3 Conclusions

1) The ignition point is significantly increased by adding Ca. Adding 0.5wt. %Ca to Mg enhances the ignition point by about 230°C. The ignition point of bulk Mg-5Ca alloy even exceeds 1,030°C, and it can even hold for 30 min at 900°C without burning. In the size range of 150–250 μm, the average ignition point of powders is 685°C, which is much lower than that of the bulk alloy.

2) The ignition point of Mg-5Ca powders increases with the increasing particle size, and the specific surface area of powders plays a more important role in the effect on the ignition point.

3) The purity of nitrogen must be in a certain scope, and the ignition point of Mg-Ca alloys under the (standard) nitrogen atmosphere with a 99.5%-purity is obviously higher than that in air or the high-purity nitrogen.

References


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