The Effect of the Energetic Additive Coated MgH$_2$ on the Power of Emulsion Explosives Sensitized by Glass Microballoons

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Abstract: Traditional emulsion explosives, in spite of excellent water resistance, safe handling and good storage performance, have low power problems which seriously hinders their use. In order to improve the power of emulsion explosives, a hydrogen based emulsion explosive was devised. Scanning electron microscope pictures and experimental storage results show that the coating effect and stability of coated magnesium hydride (MgH$_2$) are very good. The power of an emulsion explosive sensitized by glass microballoons was significantly increased (24.30 mm compression of lead block) after adding coated MgH$_2$, compared to only 16.10 mm compression when not added. Thus emulsion explosives with coated MgH$_2$ as an energetic additive have many potential applications.

Keywords: emulsion explosive, power, hydrogen storage material, magnesium hydride

1 Introduction

Emulsion explosives are widely used in the engineering blasting and mining industries [1, 2]. Emulsion explosives consist of an emulsion matrix and a sensitizer, the matrix material of water-in-oil type (w/o) of an emulsion explosive is detonator-insensitive until it is sensitized by a physical or chemical method, converting it into an emulsion explosive. Glass microballoons (GM) are one kind
of physical sensitizer to introduce uniformly distributed bubbles into the emulsion matrix, and is commonly used in the emulsion explosive industry [3]. Due to the interaction of these bubbles with the shock wave propagating in the emulsion explosive, so-called “hot spots” are formed and subsequent reaction growth results in detonation buildup [4]. Traditional emulsion explosives have many advantages, such as excellent water resistance, safe handling and storability, but their power is still relatively low [5]. Power can be defined as the ability of an explosive to wreck a solid object in direct contact or in the vicinity of the impacting detonation wave. It is essentially the shattering power of an explosive, which is distinguished from the total work capacity of the explosive [6]. Low power hinders the application range of emulsion explosives, for example in limited space blasting, the power of the emulsion explosive should be high to obtain a good blasting effect. What is more, high power emulsion explosives also can save the quantity of explosive charge or the number of blastholes. Consequently, high-power emulsion explosive research has received attention from researchers in the field of industrial explosives [7, 8].

Magnesium hydride (MgH$_2$) is one of the new promising energetic materials because it stores a large amount of hydrogen (7 wt.%). In our previous research, MgH$_2$ was used as a chemical sensitizer to sensitize the emulsion matrix with “hydrogen bubbles”, and experimental results have shown that MgH$_2$-sensitized emulsion explosives have excellent detonation characteristics and anti-pressure ability [9-11]. However, emulsion explosives sensitized by MgH$_2$ also have problems with foaming and safety. In order to improve the performance of this type of emulsion explosive, MgH$_2$ powders were coated by gel-sol technology to control their chemical foaming effects, and then included in the emulsion explosives along with glass microballoons; the GMs and the coated MgH$_2$ powders play the role of sensitizer and energetic additive, respectively. In this way, the problems encountered with primary MgH$_2$-sensitized emulsion explosives have been resolved, and the power of the emulsion explosive has also been significantly increased. In this paper, we introduce the gel-sol technology for coating MgH$_2$ powders, and then report on our study of the power characteristic of GM-sensitized emulsion explosives with coated MgH$_2$ as the energetic additive.

2 Material and Methods

2.1 Material
The average particle size of the GM (3M, USA) used in the experiments was 55 μm and the bulk density was 250 kg/m$^3$. The average particle size of MgH$_2$ (Alfa Aesar, USA) was 3 μm, and its purity and bulk density were 98% and
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1.45 g/cm³, respectively; its initial decomposition temperature was 573 K. The density of the emulsion matrix was 1.31 g/cm³, and its composition is given in Table 1.

Table 1. Composition of emulsion matrix

<table>
<thead>
<tr>
<th>Component</th>
<th>NH₄NO₃</th>
<th>NaNO₃</th>
<th>C₁₈H₃₈</th>
<th>C₁₂H₂₆</th>
<th>C₂₄H₄₄O₆</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. %</td>
<td>78.0</td>
<td>7.0</td>
<td>4.0</td>
<td>1.0</td>
<td>2.0</td>
<td>8.0</td>
</tr>
</tbody>
</table>

2.2 Coating treatment for MgH₂

There have been many coating methods, such as ball-milling [12], sonoelectrochemistry [13], and gas-phase condensation [14]. However, these methods result in inhomogeneous size distributions for the powders. Ki-Joon et al. [15] used gel-sol technology to coat magnesium nanocomposites and obtained a good coating effect, so we chose the gel-sol method. As for the coating material, it should be waterproof and slightly acid-resistant due to the characteristics of the emulsion matrix; paraffin was chosen as the final one after some comparative experiments [16].

The coating treatment for MgH₂ was as follows: a certain quantity of paraffin was mixed with ether and heated until completely dissolved. The MgH₂ powder was then added to the paraffin-ether solution and dried at 343 K until the ether had volatilized. The thickness of the covering film for the MgH₂ powder can be controlled by adjusting the mass ratio of paraffin. In addition, the coating experiment was carried out under a nitrogen atmosphere to avoid MgH₂ being oxidized, and the mixture of paraffin-ether solution and MgH₂ powder should be stirred during the drying process to achieve a homogeneous coating.

Figure 1 shows micrograms of MgH₂ before and after coating; the shape of untreated MgH₂ powder is flat and long, and there is a paraffin-film on the surface of the MgH₂ particles after coating. From the Figure 1, it is observed that the MgH₂ powder can be uniformly coated by paraffin; the purpose of the coating is to prevent foaming of MgH₂. Previous experimental results [16] have shown that coated MgH₂ powder has excellent resistance to weak acid solutions, which makes the MgH₂ powder stable in the emulsion explosive. In this paper, GM-sensitized emulsion explosives with the energetic additive of coated MgH₂ powder is called GM-MgH₂ sensitized emulsion explosive. Figure 2 shows the underwater explosion experimental results of the GM-MgH₂ sensitized emulsion explosive; the distance between the explosive sample and the sensor was 70 cm. As shown in Figure 2, the shock wave peak pressures of this type of emulsion explosive before and after storage are 14.60 and 14.50 MPa, respectively, having decreased by only 1.09% after five months.
storage. Therefore, the stability of the GM-MgH$_2$ sensitized emulsion explosive meets the standard requirements.

![Micrograms of MgH$_2$ powders: (a) untreated; (b) coated with paraffin.](image)

**Figure 1.** Micrograms of MgH$_2$ powders: (a) untreated; (b) coated with paraffin.

![Pressure-time curves of the GM-MgH$_2$ sensitized emulsion explosive, before and after storage.](image)

**Figure 2.** Pressure-time curves of the GM-MgH$_2$ sensitized emulsion explosive, before and after storage.

### 2.3 Explosive samples and experimental method

In order to study the power of the GM-MgH$_2$ type of emulsion explosive, we compared it with emulsion explosives sensitized respectively by GM and MgH$_2$. The common GM content in the emulsion explosives industry is 2 wt.%, and the value for MgH$_2$ powder was determined as 2 wt.%, in consideration of performance and cost. The GMs act as physical sensitizers in emulsion explosives, while the uncoated MgH$_2$ powders play the role of chemical
sensitizers in MgH₂ sensitized emulsion explosives. Coated MgH₂ powders serve as energetic additives in the GM-MgH₂ type of emulsion explosives. The formulations of the three types of emulsion explosive are shown in Table 2, and each type of sample was tested at least three times.

Table 2. Different formulations of emulsion explosives

<table>
<thead>
<tr>
<th>Emulsion explosives</th>
<th>Emulsion matrix</th>
<th>GM</th>
<th>Untreated MgH₂</th>
<th>Coated MgH₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>GM sensitized</td>
<td>98</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>MgH₂ sensitized</td>
<td>98</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>GM-MgH₂ sensitized</td>
<td>96</td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

The detonation velocities of emulsion explosives were measured using a detonation testing apparatus with metal probes. The emulsion explosives were charged in PVC tubes of diameter 25 mm and length 300 mm. The friction and heat sensitivity of the emulsion explosives were tested using related experimental equipment.

The power of the emulsion explosives was tested by the lead block compression test method, which is a traditional and widely used method for measuring the power of an explosive [6]. The weight of each emulsion explosive (EMX) sample was 50 g, and the length of the lead block was 60 mm before compression; the power of the emulsion explosive can be characterized by the length reduction of the lead block after detonation.

3 Results and Discussion

From Table 3 we can see that the detonation velocity of the emulsion explosive sensitized by GM and MgH₂ is 4689 m/s, and that the safety of the three types of emulsion explosives also meet the standard requirements. Table 3 and Figure 3 show that the value of the lead block compression by the emulsion explosive sensitized by GM and MgH₂ was 24.30 mm, 5 mm more than that of the emulsion explosive sensitized by MgH₂ alone. The power of the GM sensitized emulsion explosive was the smallest, and compressed the lead block by only 16 mm. Compared with the traditional emulsion explosives sensitized by GM, the energetic material MgH₂ considerably improves the power of emulsion explosives, whether it acts as a chemical sensitizer or an energetic additive, and the power of emulsion explosives sensitized by both GM and MgH₂ is the most powerful. Table 3 also shows that the power is not completely dependant on the
detonation velocity for the emulsion explosives studied, which is different from the detonation velocity mechanism for power which is described in Ref. [17].

Figure 3. Power of different emulsion explosives characterized by the compression of a lead block.

Table 3. Parameters of explosion performance of various emulsion explosives

<table>
<thead>
<tr>
<th>Emulsion explosive</th>
<th>Density [g/cm$^3$]</th>
<th>Power* [mm]</th>
<th>Detonation velocity [m/s]</th>
<th>Friction sensitivity [N]</th>
<th>Heat sensitivity [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GM sensitized</td>
<td>1.24</td>
<td>16.10</td>
<td>4534</td>
<td>&gt;358</td>
<td>&gt;503</td>
</tr>
<tr>
<td>MgH$_2$ sensitized</td>
<td>1.25</td>
<td>19.15</td>
<td>4950</td>
<td>&gt;358</td>
<td>&gt;503</td>
</tr>
<tr>
<td>GM-MgH$_2$ sensitized</td>
<td>1.28</td>
<td>24.30</td>
<td>4689</td>
<td>&gt;358</td>
<td>&gt;503</td>
</tr>
</tbody>
</table>

*Compression of lead block

Emulsion explosives are a kind of non-ideal explosive. According to the famous ZND detonation model, there is a chemical reaction zone after the shock wave front during the detonation [4, 18], as shown in Figure 4. GMs are not energetic materials and only act as sensitizers in the emulsion explosive, but untreated MgH$_2$ powder in the emulsion explosive plays a double role as sensitizer and energetic material because of the hydrogen bubbles. The hydrogen participates in the detonation reaction and increases the explosive power of the emulsion explosive, so the power of a MgH$_2$ sensitized emulsion explosive is higher than that of a GM sensitized one. However, either GMs or untreated MgH$_2$ powder in emulsion explosives mainly react in the initiation stage of detonation for their roles as sensitizers.
As for the GM-MgH$_2$ type of emulsion explosive, the so-called “hot spots” in the emulsion matrix created by the GMs in the preliminary phase, and most of the coated MgH$_2$ powder reacts in the reaction zone. MgH$_2$ is a kind of ionic metal hydride and decomposes into magnesium and hydrogen at a high temperature, and these decomposition products would be involved in detonation and release of energy in the reaction zone, which delays the attenuation of the shock wave. In addition, our preliminary studies show that MgH$_2$ can improve the effect of the explosion reaction of emulsion explosives [9], and makes the emulsion explosive explode more completely, thus increasing the detonation pressure.

From the above analysis, the reasons for the high power of the GM-MgH$_2$ sensitized emulsion explosives may be concluded to be the slower attenuation of the shock wave and higher reaction extent of the emulsion explosive because of the coated MgH$_2$. The experimental results are somewhat in accordance with the mechanical impulse mechanism of power for explosives [6, 19], which deems that the power parameter is related to the detonation pressure and the duration of the shock wave. The power mechanism research of the GM-MgH$_2$ sensitized emulsion explosives is a complex but important work, and will be studied further in the near future.

Figure 4. Schematic diagram of the ZND detonation model.
4 Conclusions

High power research is always one of the hot issues in the field of emulsion explosives. In this paper, we report a new type of emulsion explosive with the additive coated MgH$_2$. The gel-sol technology was used for coating MgH$_2$ powders, and paraffin was the coating material. Scanning electron microscope pictures showed that MgH$_2$ powders can be coated homogeneously by paraffin films. Storage and experimental sensitivity results indicate that the stability and safety of the coated MgH$_2$ in emulsion explosives meets the standard requirements. The detonation velocity of a GM-MgH$_2$ sensitized emulsion explosive is 4689 m/s, but its power reaches up to 24.3 mm (lead block compression). The experimental results somewhat conform to the mechanical impulse mechanism of power for explosives, but the typical mechanism of power for GM-MgH$_2$ sensitized emulsion explosive needs to be studied further.

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References

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