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Pressure Desensitization Influential Factors and Mechanism of Magnesium Hydride Sensitized Emulsion Explosives

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Abstract: Magnesium hydride sensitized emulsion explosives can effectively reduce "pressure desensitization" problems that traditional emulsion explosives encounter in utilization. Shockwave desensitization experiments and underwater explosion experiments show that, compared with traditional glass microspheres (GM) sensitized emulsion explosives, magnesium hydride sensitized emulsion explosives are better at resisting pressure desensitization. The microstructures of GM and magnesium hydride sensitized emulsion explosives before and after compression are studied with scanning electron microscopy, and the pressure desensitization resisting mechanism of magnesium hydride sensitized emulsion explosives is discussed. This work shows that reduction of "hotspots" is the key factor of pressure desensitization of emulsion explosives through comparative research.

Keywords: Emulsion explosives · Hydrogen containing material · Explosion mechanics · Pressure desensitization

1 Introduction

Emulsion explosives are one type of main industrial explosives. They were developed in the 1960s [1]. The matrix material of water in oil (w/o) type of emulsion explosives is not detonator sensitive until sensitized by physical or chemical methods converting it into emulsion explosives. Glass microspheres (GM) are the most common physical sensitizer used in emulsion explosives, and its function is to introduce uniformly distributed bubbles in an emulsion matrix, which can form "hotspots" during explosion process. In engineering blasting practices, millisecond delayed blasting technology divides the blast into parts by delay detonators. This technique is extensively used to improve the blasting quality and lowers the seismic effect, and it can increase blasting scale. However, in millisecond delayed blasting operation, emulsion explosives detonated with delays will be precompressed by shockwaves or detonation waves that earlier detonated adjoining emulsion explosives produce; thus, many sensitization bubbles in the compressed emulsion explosives may be damaged and detonation performance of emulsion explosives will be influenced [2]. This phenomenon is called "pressure desensitization". Pressure desensitization of emulsion explosives not only influences the blasting quality and construction progress but also enables the formation of misfired emulsion explosives and it is likely to result in accidents when dealing with these blind shots, which seriously affect blasting safety.

The pressure desensitization of emulsion explosives has aroused general concern of researchers in the field of industrial explosives, and many important results were obtained [3–6]. In order to improve the pressure desensitization resisting properties of emulsion explosives, magnesium hydride sensitized emulsion explosives was developed. This type of emulsion explosives is sensitized by the hydrogen containing material MgH_2, which acts as both sensitizer and energetic material when added to emulsion matrix.

In this study, the pressure desensitization resisting ability of magnesium hydride and GM sensitized emulsion explosives were studied and key influential factors of pressure desensitization of emulsion explosives are found. The mechanism of pressure desensitization of magnesium hydride and GM sensitized emulsion explosives are also discussed.

2 Preparations of Emulsion Explosives

Magnesium hydride sensitized emulsion explosives were compared with GM sensitized emulsion explosives in order to demonstrate their detonation performance. Through previous experiments [7], it was found that the output energy of each type of emulsion explosive reached a maxi-

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Table 1. Different formulation designs of emulsion explosives.

Emulsion explosives	Emulsion matrix [wt-%]	Glass microspheres [wt-%]	MgH_2 [wt-%]
GM sensitized	100	4	0
Magnesium hydride sensitized	100	0	2

mum when the added amount of GM and MgH_2 had values of 4% and 2%, respectively.

In these experiments, the weight of emulsion matrix samples was 30 g each, so the influence of different amounts of emulsion matrix did not occur. Emulsion explosives samples were made according to mass ratio in Table 1 and kept in ambient temperature (297 K) for about 24 h before experiments.

GM is one of the physical sensitizers that contain inert gas and sensitization bubbles were introduced into emulsion explosives directly (static sensitization); MgH_2 is a chemical sensitizer and reacts with the emulsion matrix because of its weak acidic properties. Thus, hydrogen bubbles are produced, which sensitized the emulsion matrix.

3 Pressure Desensitization Experiments

The pressure desensitization phenomenon of emulsion explosives in millisecond delayed blasting can be simulated by a shockwave dynamic pressure generating equipment, and the pressure desensitization resisting abilities of the two types of emulsion explosives are studied.

3.1 Experimental Methods

3.1.1 Explosive Materials

In the experiments, the average particle size of GM (purchased from Minnesota Mining and Manufacturing Company, USA) is 55 μm and its bulk density is 0.25 $g\,cm^{-3}$. The MgH_2 (purchased from Alfa Aesar, USA) average particle size is 3 μm, and its purity and bulk density are 98% and 1.45 $g\,cm^{-3}$, respectively. The density of emulsion matrix (purchased from Huainan Shun Tai Chemical Co., Ltd) is 1.31 $g\,cm^{-3}$.

3.1.2 Preparations of Samples

The pressed RDX booster is composed of bulk RDX and paraffin wax with a mass ratio of 100 : 5, and its weight and density are 10 g and 1.65 $g\,cm^{-3}$, respectively. The weight of each emulsion matrix that contained the emulsion explosives samples is 30 g. It is made according to Table 1.

The shape of the pressed RDX booster and emulsion explosives samples is cylindrical and spherical, respectively. They are encapsulated by polyethylene plastic bags and entangled by rubberized fabric. In order to achieve a better waterproof effect, the sealing is coated with Vaseline.

3.1.3 Experimental Equipment

Each pressed RDX booster is fixed in the center of the rectangular steel frame and the emulsion explosives samples are placed with different distances to the pressed RDX booster by steel wires. The shockwave dynamic pressure generating device is placed underwater, as shown in Figure 1(a). The emulsion explosives samples at different places were compressed in different degrees by shockwaves underwater, which were produced by detonating the pressed RDX booster. Finally, these compressed emulsion explosives samples were detonated by detonators in the underwater explosion testing tank, and shockwave signals were recorded with an oscilloscope.

The arrangement of the underwater explosion testing tank is shown in Figure 1(b), the depth of water "H" is 5 m and charge position "h" is 2.5 m underwater. The distance between charge and sensor "R" is 0.7 m. The testing instruments are an Agilent5000A digital storage oscilloscope, a 482A22 constant current source and an ICP138A25 PCB pressure sensor (PCB Piezotronics Inc., USA.). The delay time to detonate the compressed emulsion explosives is less than twenty min. The pressure desensitization resisting ability of GM and magnesium hydride sensitized emulsion explosives could be determined by comparing the change of energy output characteristic of emulsion explosives before and after compression.

3.2 Experimental Results

Figure 2 shows the typical shockwave pressure-time curves of compressed emulsion explosives (compressed at different distances) sensitized by GM and magnesium hydride in underwater explosion experiments. It shows that the shock-

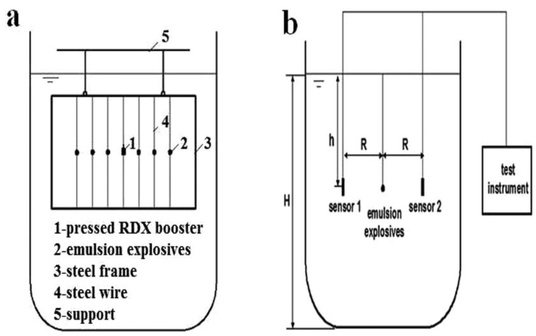

Figure 1. Assembly of the experimental system: (a) emulsion explosives compression device; (b) underwater explosion testing device.

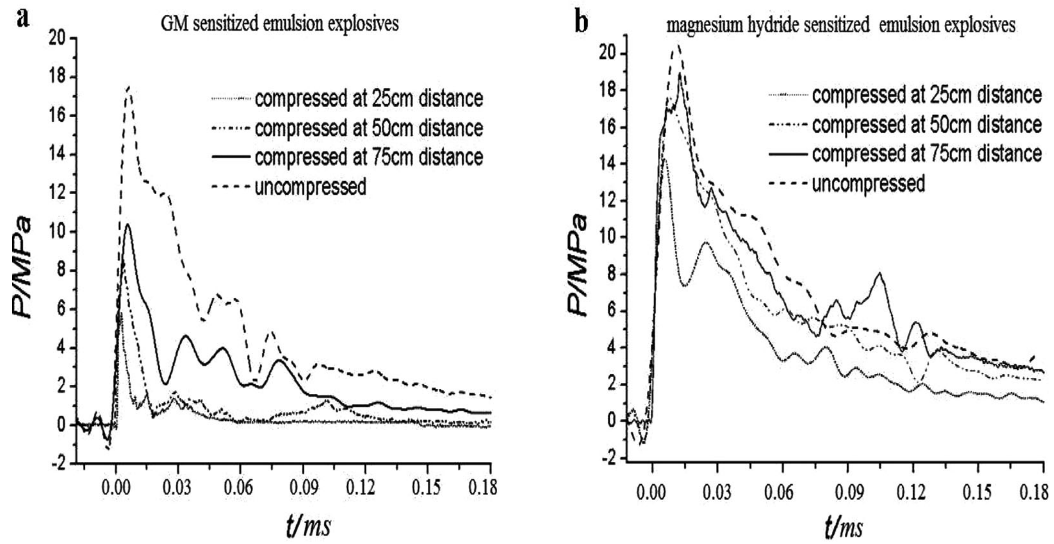

Figure 2. Pressure-time curves of compressed emulsion explosives in underwater explosion: (a) GM sensitized; (b) magnesium hydride sensitized.

Table 2. Shockwave average peak pressures of different emulsion explosives at different compression distances.

	Shockwave average peak pressure [MPa]					
Compression distance [cm]	25	40	50	60	75	Infinite distance
GM sensitized, [MPa]	5.81	7.63	8.42	9.16	10.36	17.99
Magnesium hydride sensitized [MPa]	14.77	17.66	18.63	18.87	18.68	20.37

wave peak pressures of both types of emulsion explosives are decreased after compression, the degree of reduction is inversely proportional to compression distance.

The average values of shockwave peak pressure of emulsion explosives samples compressed at different distances are listed in Table 2 and the uncompressed emulsion explosives samples are regarded as being compressed at infinite distance.

3.3 Influence Degree of Pressure Desensitization

In order to better describe the desensitization degree of emulsion explosives after compression by external shockwaves, a parameter of the "desensitization ratio" is introduced to illustrate the decrement of explosion properties of emulsion explosives before and after compression, which changes the research on pressure desensitization from qualitative expression to quantitative analysis. As is described in Ref. [8], compared with shockwave energy and bubble energy, the shockwave peak pressure is most suitable for calculating the desensitization ratio; it can be obtained by the following equation:

$$D = (P_0 - P_1)/(P_0 - P_d) \qquad (1)$$

The symbol "D" is the desensitization ratio, P_0 represents the shockwave peak pressure of uncompressed emulsion explosives [MPa]; P_l is the shockwave peak pressure of compressed emulsion explosives [MPa]; P_d is the shockwave peak pressure of a detonator at the same testing condition [MPa].

As it is described in Equation (1), when the value of P_l equals that of P_0, it is obvious that the detonation characteristics of compressed emulsion explosives are not influenced by shockwave impact, and the desensitization ratio "D" is 0; when P_1 equals P_d, it is indicated that compressed emulsion explosives misfired, and the desensitization ratio "D" is 100%. A desensitization ratio "D" between 0 and 100% indicates that the pressure desensitization phenomenon has occurred in emulsion explosives, and the smaller the desensitization ratio is, the weaker the detonation performance of emulsion explosives is influenced by pressure desensitization.

In the underwater explosion experiments, the shockwave peak pressures of two detonators under similar testing conditions as emulsion explosives samples are 5.92 MPa and 6.08 MPa, respectively, and the average value is 6.0 MPa. According to Table 2 and Equation (1), desensitization ratios of two types of compressed emulsion explosives in different compression distances could be obtained. They are shown in Table 3.

Table 3. Desensitization ratios of two types of emulsion explosives at different compression distance.

	Desensitization ratio					
Compression distance [cm]	25	40	50	60	75	Infinite distance
GM sensitized [%]	100	86.41	79.82	73.67	63.64	0
Magnesium hydride sensitized [%]	38.97	18.89	12.11	10.45	11.76	0

3.4 Analysis of Experimental Results

Figure 3(a) shows that at the 25 cm compression distance, desensitization ratio of GM sensitized emulsion explosives is 100% which indicates that GM sensitized emulsion explosives misfired, whereas MgH_2 type is only 38.97% at this compression distance. When the compression distance exceeds 50 cm, the desensitization ratio of magnesium hydride sensitized emulsion explosives is close to 10% and approaches equilibrium. However, with regard to GM sensitized emulsion explosives, the desensitization ratio of compressed emulsion explosives at 50 cm compression distance is 79.82%, which is still greater than 60% when compressed at 75 cm.

From the above analysis it becomes obvious that magnesium hydride sensitized emulsion explosives have a better pressure desensitization resisting ability. Moreover, as is shown in Figure 3(b), the shockwave peak pressure of magnesium hydride sensitized emulsion explosives is much higher than that of GM sensitized emulsion explosives when compressed by a shockwave of equal strength (at the same compression distance). The error bars represent one standard deviation of the average value obtained from three peering tests.

4 Influential Factors of Pressure Desensitization

De-emulsification of emulsion matrix and reduction of "hotspots" in emulsion matrix are the main reasons for pressure desensitization of emulsion explosives [9,10]. De-emulsification of the emulsion matrix means that the water phase of emulsion matrix is precipitated when compressed by external pressure, which destroys water in oil (w/o) structure of emulsion matrix, and influences the explosion power of emulsion explosives. "Hot spots" play an important role in the detonation process of emulsion explosives, when a shock wave propagates into the emulsion explosive and "hot spots" are created as the shock compresses air bubbles. The reactions initiated in the explosive around the "hot spots" and accelerated to detonation [11], so reduction of "hotspots" affects the explosion power of emulsion explosives.

4.1 Effect of Hotspots

According to the "hotspots" initiation mechanism of emulsion explosives described in the literature [12,13], the quantity of "hotspots" is influenced if micro hollow grains or bubbles (sensitizers) have large displacement, deformations or have been destroyed, which is unfavorable to excitation and propagation of detonation reaction of emulsion explosives.

Figure 4 and Figure 5 show micrographs (SEM) of two types of emulsion explosives samples before and after compression, and the compression distance is 50 cm. Figure 4 shows that lots of glass microspheres in GM sensitized emulsion explosives are collapsed after compressed by shockwaves, and Figure 5 shows that sensitizing bubbles in magnesium hydride sensitized emulsion explosives only

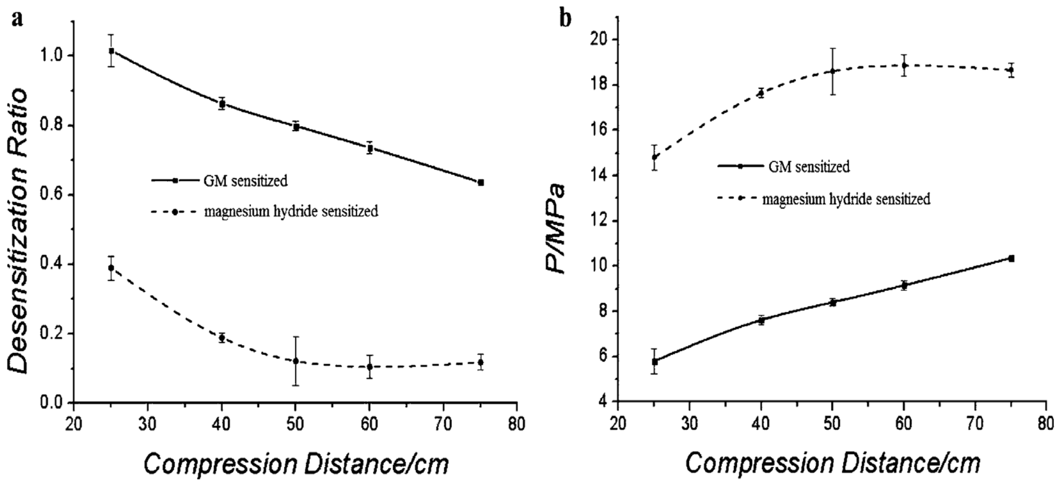

Figure 3. Relationship with compression distances: (a) desensitization ratios; (b) shockwave peak pressures.

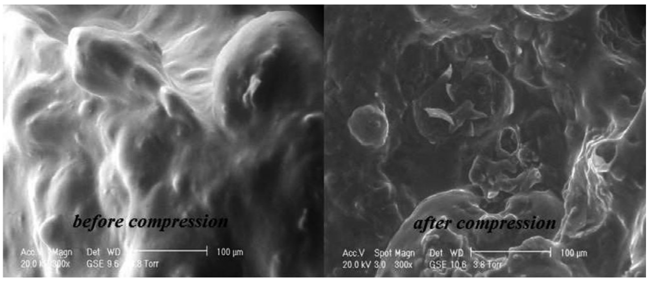

Figure 4. Micrographs of GM sensitized emulsion explosives before and after compression.

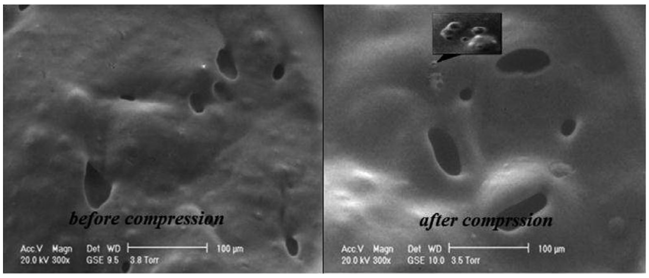

Figure 5. Micrographs of magnesium hydride sensitized emulsion explosives before and after compression.

have slight deformations after being compressed by shockwaves underwater, and the small box in the top of right image of Figure 5 shows unreacted MgH_2 powders in emulsion matrix. In general, the amount of "hotspots" in magnesium hydride sensitized emulsion explosives is much less reduced than that in GM sensitized emulsion explosives after being compressed by external shockwaves.

4.2 Effect of De-emulsification

4.2.1 Preparations of Samples

In order to study the effect of de-emulsification on pressure desensitization of emulsion explosives, the influence of reduction of "hotspots" should be excluded. Therefore, compressed emulsion explosives samples (described in Section 3.1) were mixed with additional sensitizers that form "hotspots" during the detonation process of emulsion explosives to avoid the influence of reduction of "hotspots". These compressed GM sensitized emulsion explosives are mixed with GM in a ratio of 100 : 1, and compressed magnesium hydride sensitized emulsion explosives are mixed with MgH_2 powders of the same mass ratio, and such explosives samples are called "remade" emulsion explosives.

The influence of de-emulsification on pressure desensitization of each type of emulsion explosives can be obtained by comparing the shockwave peak pressures of "remade" emulsion explosives with those of the corresponding compressed emulsion explosives (discussed in Section 3) of similar compression distances.

4.2.2 Experimental Results

"Remade" emulsion explosives samples are tested in an underwater explosion testing tank [see Figure 1 (b)], and the shockwave signals are recorded with an oscilloscope. Each type of the "remade" emulsion explosives samples was tested three times and the average values of experimental results are listed in Table 4. The desensitization ratios of the two types of "remade" emulsion explosives in different compression distances are obtained according to Table 4 and Equation (1). They are presented in Table 5.

In order to better suggest a changing trend of desensitization ratios, the experimental data in Table 5 are illustrated in Figure 6, the error bars represent the standard deviation of the average value obtained from three peering tests.

4.2.3 Discussion of De-emulsification

Figure 6 shows that desensitization ratios of GM sensitized and magnesium hydride sensitized "remade" emulsion explosives are quite small, and changed only slightly with different impact strength (different compression distances) of shockwaves. The desensitization ratios of GM sensitized

Table 4. Shockwave average peak pressures of different "remade" emulsion explosives at different compression distances.

	Shockwave average peak pressure [MPa]					
Compression distance [cm]	25	40	50	60	75	Infinite distance
GM sensitized [MPa]	17.10	17.62	17.38	17.46	17.57	18.27
Magnesium hydride sensitized [MPa]	18.53	18.36	18.99	19.51	19.78	20.75

Table 5. Desensitization ratios of two types of "remade" emulsion explosives at different compression distances.

	Desensitization ratio					
Compression distance [cm]	25	40	50	60	75	Infinite distance
GM sensitized [%]	9.54	5.30	7.25	6.60	5.70	0
Magnesium hydride sensitized [%]	15.05	16.20	11.93	8.41	6.58	0

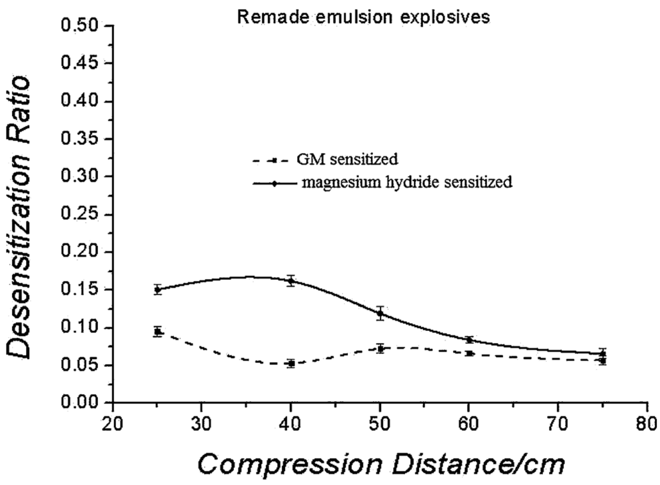

Figure 6. Relationship of desensitization ratios with compression distances of two types of remade emulsion explosives.

"remade" emulsion explosives are less than 10% when compressed by external shockwaves, as for magnesium hydride sensitized "remade" emulsion explosives, their desensitization ratios are also very small, but slightly higher than those of the GM type. The reason for this phenomenon may be described as follows: de-emulsification of magnesium hydride sensitized emulsion explosives will lead to precipitation of NH_4NO_3 in emulsion matrix, and the amount of free water among interfaces of sensitizers and emulsion matrix are limited, so hydrolysis of MgH_2 is influenced, which weakens sensitization effect of magnesium hydride sensitized "remade" emulsion explosives. Whereas GM sensitized "remade" emulsion explosives are sensitized by glass microspheres (GM), which directly introduce sensitization bubbles into the emulsion matrix, the precipitation of NH_4NO_3 in emulsion matrix has only a minor effect on the sensitization of GM sensitized "remade" emulsion explosives.

4.3 Key Influential Factors of Pressure Desensitization

In order to find key influential factors of pressure desensitization, the desensitization ratios of each type of compressed emulsion explosives were compared with corresponding "remade" emulsion explosives of similar compression distance. The amount of de-emulsification of the emulsion matrix is in proportion to the compression distance, the shorter compression distance is, the stronger is the effect on emulsion explosive, and the amount of de-emulsification also increases. As shown in Figure 7(a), the desensitization ratios of GM sensitized emulsion explosives are slightly changed with different compression distance, which indicates that de-emulsification of emulsion matrix has little effect on the pressure desensitization of GM sensitized emulsion explosives, so de-emulsification is not the key factor of pressure desensitization. However, differences of desensitization ratios between compressed emulsion explosives and "remade" GM sensitized emulsion explosives are obvious, the desensitization ratios of GM sensitized compressed emulsion explosives are high, and the desensitization ratios of "remade" GM sensitized emulsion explosives are quite low. In the above analysis, "de-emulsification" could be excluded as the key factor of pressure desensitization of GM sensitized emulsion explosives, whereas de-emulsification of emulsion matrix and reduction of "hotspots" are the two main reasons for pressure desensitization, which suggest "hotspots" are the main reason for pressure desensitization of GM sensitized emulsion explosives.

As shown in Figure 7(b), magnesium hydride sensitized emulsion explosives presents a completely different phenomenon, desensitization ratios at different compression of

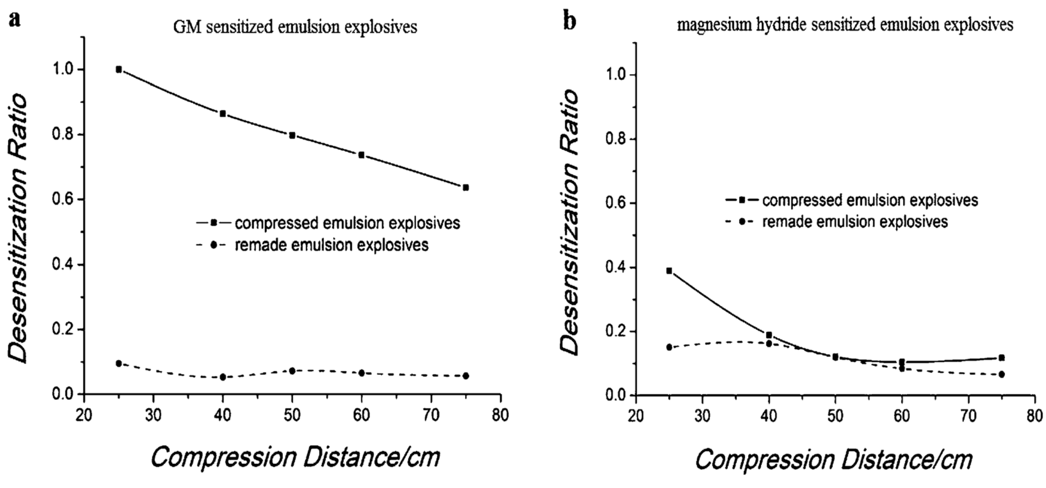

Figure 7. Comparison of desensitization ratios of emulsion explosives with "remade" emulsion explosives at similar compression distances: (a) GM sensitized; (b) magnesium hydride sensitized.

magnesium hydride sensitized compressed emulsion explosives and "remade" emulsion explosives are both very low. As for magnesium hydride sensitized "remade" emulsion explosives, desensitization ratio does not change with compression distances like de-emulsification, they keep stable when the compression distance changes, so we can exclude "de-emulsification" as the key factor of pressure desensitization of magnesium hydride sensitized emulsion explosives. Therefore, "hotspots" is also the key factor for pressure desensitization of magnesium hydride sensitized emulsion explosives. What is more, desensitization ratios of magnesium hydride sensitized compressed and "remade" emulsion explosives at the same compression distance are very close to each other, which manifests that decrements of "hotspots" in magnesium hydride sensitized emulsion explosives after compression are very small.

From the above analysis, we can draw a conclusion that "hotspots" is the key factor of pressure desensitization for both GM and magnesium hydride sensitized emulsion explosives, and decrement of "hotspots" in magnesium hydride sensitized emulsion explosives after compression is very small.

5 Discussion of Pressure Desensitization Mechanism

Experimental results of pressure desensitization experiments shows that the desensitization ratios of magnesium hydride sensitized emulsion explosives when compressed by shockwaves at similar compression distance are smaller than those of the GM type. This indicates that magnesium hydride sensitized emulsion explosives have a much stronger pressure desensitization resisting ability.

When compressed by external shockwaves, the glass microspheres in GM sensitized emulsion explosives shows certain resistance to pressure and will not be crushed if external shockwaves is not strong enough, and de-emulsification among micro interfaces of glass microspheres and emulsion matrix occurs immediately, and many glass microspheres will be destroyed when the intensity of shockwaves reaches a certain level (see Figure 4). Furthermore, the damage extent to glass microspheres is increased as the external shockwaves become stronger, and led to the structures which can form "hotspots" in emulsion matrix decreased.

Emulsion explosives are sensitized by the hydrogen containing material MgH_2 and hydrolyzed to produce evenly distributed hydrogen bubbles in the emulsion matrix. Micro bubbles in the emulsion matrix make the sensitized emulsion explosives elastic and flexible, since the bubbles can absorb shockwave energy when compressed by external shockwaves. Figure 5 shows that sensitization bubbles in both uncompressed and compressed magnesium hydride sensitized emulsion explosives have a similar size, and MgH_2 powders in emulsion explosives did not react completely due to limited free water in the emulsion matrix. In addition, as the reaction process goes on, the generated $Mg(OH)_2$ would restrain hydrolysis reaction of MgH_2 powders. However, these unreacted MgH_2 powders play an important role in resisting pressure desensitization problem of magnesium hydride sensitized emulsion explosives. When compressed by external shockwaves, the internal temperature and pressure of hydrogen bubbles will increase and these unreacted MgH_2 powders may release dissociated H_2 when the temperature and pressure reach a certain level [14]. This could weaken the external shockwaves effects on sensitization bubbles shrinkage and, moreover, in the detonation process of magnesium hydride sensitized emulsion explosives, the unreacted MgH_2 powders will release H_2 with a detonation wave. Then, new hydrogen bubbles are produced to form new "hotspots". These processes are called "dynamic sensitization".

Due to the special "dynamic sensitization" method, "hotspots" in magnesium hydride sensitized emulsion explosives are reduced much less than those in GM sensitized emulsion explosives, which makes magnesium hydride sensitized emulsion explosives much better in resisting pressure desensitization.

6 Conclusions

The hydrogen containing material MgH_2 significantly improves the pressure desensitization resisting performance of emulsion explosives. Compared with GM sensitized emulsion explosives, the desensitization ratio of magnesium hydride sensitized emulsion explosives is much smaller when compressed by external shockwaves of the same impact intensity. This suggests less influence of the explosion power by external shockwaves. The decrease of "hotspots" is the key factor of pressure desensitization for both GM and magnesium hydride sensitized emulsion explosives. It is noteworthy that the "dynamic sensitization" function of MgH_2 reduced the decrement of "hotspots" to a minimum: This is also one of the main reasons for the better pressure desensitization resisting ability of magnesium hydride sensitized emulsion explosives.

Acknowledgments

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