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Thermal Stability of Mg/TeO_2 Priming Compositions

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The insensitive ignitors with magnesium/tellurium dioxide (Mg/TeO_2) priming composition installed on the spacecraft will experience a harsh thermal environment. Therefore, it is necessary to verify their availability at extreme temperatures. Differential Scanning Calorimetry and Thermogravimetric Analysis (DSC-TGA) were used to analyze the reaction process of the Mg/TeO_2 priming composition. The morphology change of the Mg/TeO_2 priming composition after –70 ℃6d, room temperature, 165 ℃6d were analyze by digital cameras, scanning electron microscope (SEM), as well as the output pressure, ignition time, function time and firing sensitivity of the Mg/TeO_2 priming composition under three temperature conditions were tested. The results show that in a temperature range of –70 ℃ ~ 165 ℃, the temperature conditions have an effect on the output pressure less than 5%, the influence of high temperature conditions on ignition/ function time and sensitivity is greater than low temperature. It can be used as a priming composition for insensitive ignitors at –70 ℃ ~ 165 ℃.

Keywords: Mg/TeO_2 priming composition, thermal environment, thermal stability, function time, firing sensitivity.

1. INTRODUCTION

The priming composition transforms electrical stimulus into the production of flame, pressure and hot particles to ignite or initiate a pyrotechnic action [1]. The priming compositions used for space must meet the requirements of insensitivity and heat resistance. Because of good heat stability, strong ignition capability, and reliable function, the magnesium/ tellurium dioxide (Mg/TeO_2) priming composition can be used as primary explosive of insensitive initiator [2, 3]. Therefore, Mg/TeO_2 priming composition can be pressed or coated on the sealing plug's bridgewire to replace sensitive lead styphnate lead 2,4,6-trinitroresorcinate $C_6HN_3O_8Pb$ (LTNR) for meet 1A/1W/5min no-fire requirement [4].

The pyrotechnics on deep space exploration spacecraft will be exposed to extreme temperature environments [5, 6]. For example, external location pyrotechnic devices (e.g.: ignitor, actuator) on deep-space cruising spacecraft must withstand a large temperature range, typically –100 ℃/+130 ℃ [7, 8]. For some special use, the pyrotechnics will be exposed to severe temperatures ranging from –70°C to +130 °C for 5 days. The following failure modes may occur for priming compositions under high temperature conditions: oxidation of active metal surfaces, melting of oxidizers, deterioration, bulking of charges, accidental firing, cracks, etc.

At present, there are few reports on the thermal stability and output performance of Mg/TeO_2 priming composition after extreme temperature exposure. Therefore, it is necessary to analyze the thermal stability and output performance of Mg/TeO_2 priming composition under extreme temperature. The morphology and thermodynamic behavior of Mg/TeO_2 priming composition were analyzed by Calorimetry and Thermogravimetric Analysis (DSC-TGA) and Scanning Electron Microscopy (SEM) [9, 10]. The influence of the thermal environment on the output performance of Mg/TeO_2 priming composition was verified by three tests of output pressure, time and firing sensibility. The pressure and time of Mg/TeO_2 priming composition under different temperature conditions were tested by a closed bomb. This study can provide a basis for the charging of space pyrotechnic devices.

2. EXPERIMENTAL DETAILS

2.1. Experimental conditions

According to the criteria for explosive systems and devices on space and launch vehicles，test temperatures of ignition composition shall be at least 30℃ higher than the maximum predicted environmental temperature to which the material will be exposed during storage, handling, installation, transportation, launch, flight, and orbit [11]. Since the effect of high temperature on the priming composition is greater, and considering the actual use and test conditions, the test temperature is determined to be 165 ℃6d/–70 ℃6d. There is room temperature (about 25 ℃) samples as check samples in every experiment.

DSC/DTA-TG were carried out using a Perkin-Elmer simultaneous thermal analyzer model NETZSCH STA 449 F5 (Germany). The model of the SEM is HITACHI S4800 (Japan).

High temperature test box was Chongqing SD, model WG2002. Low temperature test box was Chongqing SD, model CT701F.

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Closed bomb was 10 ± 0.5 mL. DC power supply Agilent E3634A was used. Data acquisition system consists of signal conditioner and dynamic analyzer. Signal conditioner was DEWETRON model DEWE-RACK-16; Dynamic analyzer was DEWETRON model DEWE-5001-TR. Sensor parameters are shown in Table 1.

2.2. Experimental materials

Magnesium powder used was analytically pure with particle size 40 µm purchased from Tangshan weihao magnesium powder Co., Ltd. TeO_2 powder used was analytically pure, with particle size 5 µm purchased from Beijing chemical works.

Magnesium powder and TeO_2 are mixed in a weight ratio of 1:1 (equivalent to mole ratio of 6.6:1). In order to reduce the firing sensitivity of Mg/TeO_2 priming composition and increase its thermal conductivity, a small amount of boron nitride (BN) is added to the composition. Due to the moderate ignition temperature and the insensitivity to static electricity of magnesium powder, magnesium powder is an ideal flammable agent of insensitive priming composition. TeO_2 is an amphoteric oxide and loses oxygen when heated. It is a strong oxidant [12]. The BN has the advantages of low friction coefficient, good high-temperature stability, good thermal conductivity, and good corrosion resistance [13]. Its role is a thermal conductive material additive to reduce the sensitivity and improve the thermal conductivity. All raw materials have a purity greater than 99 %.

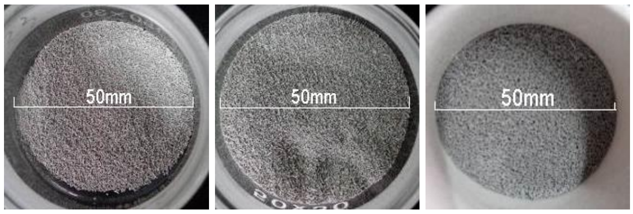
According to the requirements of MIL-STD -1751A (method 1151), the explosive materials should pass through a 325-mesh sieve, therefore, a 40 µm (equivalent to 360 mesh) particle size priming composition was selected for the test [14]. The sieved material was taken, and this was repeated 6 times and then dried at 60 °C for 4 hours. The ignitor for the output performance test was ignited using a φ 0.075 mm nickel-chromium (80/20) alloy bridgewire. with a resistance of 1 ± 0.2 Ohm. The consistency of the ignition state is ensured by detecting the igniter resistance.

3. RESULTS AND DISCUSSION

3.1. Morphology

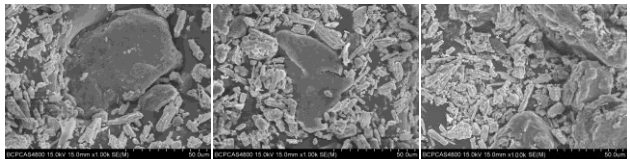
Observing the morphological changes of the Mg/TeO_2 priming compositions after subjected to different temperature conditions, one can intuitively understand the tolerance to extreme temperatures. The result is shown in Fig. 1, Fig. 2.

In the SEM image, the gray ball is a magnesium powder and the white microparticle is TeO_2. The observation results show that the particle size of the composition does not change; the particles also do not have changes such as rupture, expansion, and contraction. From the results of the digital camera photos, there are no obvious color changes in the ignition conditions of the three conditions.



room temperature 165 °C6d –70 °C6d

Fig. 1. Morphology of Mg/TeO_2 priming compositions under different temperature conditions



room temperature 165 °C6d –70 °C6d

Fig. 2. SEM image of Mg/TeO_2 priming compositions

3.2. DSC-TGA

Magnesium powder reacts with nitrogen in the DSC at high temperatures to form solid magnesium nitride (Mg_3N_2) [15, 16]. The thermal analysis of samples was performed under an argon atmosphere instead of nitrogen atmosphere. The heating rate is 10 °C/min and 20 ml/min flow rate. Aluminum oxide vessels with 100 µL volume were used as sample containers. The DSC-TG curves are shown in Fig. 3.

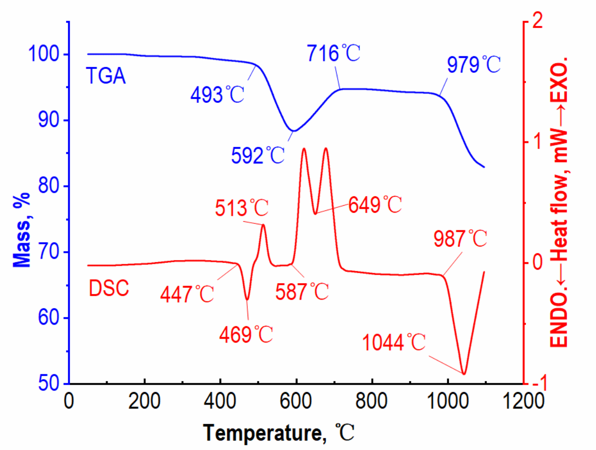


Fig. 3. DSC-TGA curves of Mg/TeO_2 priming composition

The first endothermic peak was TeO_2 sublimation and the first exothermic peak (513 °C) was the main reaction, corresponding to a decrease in the mass of the reactant. The third/fourth exothermic peak is actually a peak, and the exotherm at 649 °C drops because the temperature reaches the melting point of magnesium and therefore endothermic. These two peaks correspond to an increase in the mass of the reactants.

Table 1. Sensor parameters

Model	Charge type	Measuring range	Linear error	Sensitivity	Natural frequency	Shock resistance	Overload
KISTLER 601A	Piezoelectric sensor	0 ~ 25 MPa	± 0.27 %	150 pC/MPa	150 kHz	10000 g	50 MPa

This is due to the presence of excess magnesium (if the material is completely reacted, the molar ratio of the reactants should be 2:1, but the actual molar ratio is 6.6:1.) in the reaction system, and magnesium reacts with nitrogen in the DSC at high temperatures to form solid magnesium nitride (Mg_3N_2). Therefore, the TGA data show a weight gain after the step of mass decrease that is attributed to the excess of Mg and conversion of it to as follows [15, 16]:

$$3Mg(g)+N_2(g) \rightarrow Mg_2N_3(s) \quad (1)$$

The last endothermic peak and the corresponding mass decrease are the gasification of the reaction product tellurium (Te). The results show that the Mg/TeO_2 priming composition does not physically change until 447 °C. The LTNR starts to react at around 290 °C [17]. Therefore, Mg/TeO_2 priming compositions has better thermal stability than LTNR.

3.3. Output pressure and time

The output pressure and time is used to characterize the function of the priming compositions and is the primary performance indicator of the ignitor. The time includes the ignition time and function time. The former is the time from the start of the power-on until the pressure begins to rise, the latter being the time from the start of the power-on until the pressure reaches to a peak. The output pressure and time is affected not only by the properties of raw materials but also by the temperature conditions at firing.

The output pressure and time are obtained by a closed bomb test. The test is required to be completed within 5 minutes after removal of the temperature test box. The test results are listed in Table 2.

It can be seen from the results that the influence of temperature conditions on the output peak pressure of Mg/TeO_2 priming composition is 3 % ~ 5 % (compared with room temperature conditions). In addition, the temperature condition has an influence on ignition/ function time of 1 % to 8 % (compared with room temperature conditions). Since the pressure change of LTNR is 3.9 %, and the time change is 16 % ~ 23 % [17]. The comparison shows that the pressure changes of Mg/TeO_2 priming composition and LTNR under different temperature conditions are close, but the time changes are significantly different. Therefore, the output energy of the Mg/TeO_2 priming composition has good stability and consistency in this temperature range. Since the ignition time is directly related to the heating rate, which is affected by the ambient temperature and the input power of the bridgewire. Under the DC 5 A current stimulation, the bridgewire heats up after about 0.005 s, reaching the critical point of the chemical reaction of the Mg/TeO_2 priming composition, and is output by pressure; after about 1ms, the reaction is completed.

The energy consumed to stimulate the reaction is:

$$W = I^2Rt = 5^2 \times 1 \times 0.005 = 0.125\text{J}, \quad (2)$$

where W is the input energy, joule; I is the current, ampere; R is the resistance, ohm; t is the time, second.

Under the DC 3.5A current stimulation, it takes about 0.01 s to reach the critical point, and the reaction is completed in about 3 ms. The energy consumed to stimulate the reaction is:

$$W = I^2Rt = 3.5^2 \times 1 \times 0.01 = 0.123\text{J}. \quad (3)$$

The input energy is very close under both conditions. From the influence of temperature on ignition/ function time, the amount of change under high temperature conditions is about twice that under low temperature conditions (compared with room temperature conditions). Moreover, in a case of large firing current, the amount of change in temperature is significantly lower than the small firing current. This is because when the ignition current is large, the energy is rapidly accumulated, and the influence of the ambient temperature is relatively small.

3.4. Firing sensitivity

Firing sensitivity is a statistical event, the energy that is introduced into the sample must be effectively absorbed by the sample and a temperature rise must occur in at least part of the sample, bringing that portion to its ignition temperature [18]. The firing sensitivity of the insensitive ignitor is an important indicator for evaluating its performance and reliability. The up and down method was used for sensitivity testing, and the quantity of test sample for each condition was 35 [19, 20]. The step size used in the test was 0.1 A. The test results of firing sensitivity are shown in Fig. 4.

The results show that the stimulation energy is negatively correlated with temperature at the same firing sensitivity. There are some reasons for this phenomenon. First, due to the lower temperature of the bridgewire, more heat is needed to heat the bridgewire to reach the ignition point; second, because the temperature of the composition is low, the heat conduction to the surroundings during the temperature rise of the bridgewire is faster and more, the main reason is the increased reactivity of the priming composition under high temperature conditions.

Table 2. Pressure and time test results

Exposure conditions	Sample sizes, piece	Charge mass, mg	Firing current, A	Peak pressure		Ignition time		Function time	
				Average value, MPa	Standard deviation	Average value, ms	Standard deviation	Average value, ms	Standard deviation
room temperature	15	190 ± 5	3.5	1.21	0.15	10.68	0.65	13.50	1.07
	15		5	1.24	0.23	5.23	0.05	6.26	0.31
165 °C,6d	15		3.5	1.27	0.14	9.78	0.70	13.04	1.59
	15		5	1.19	0.09	5.18	0.13	6.21	0.12
–70 °C,6d	15		3.5	1.16	0.25	10.97	0.77	13.65	1.25
	15		5	1.28	0.16	5.57	0.16	6.48	0.28

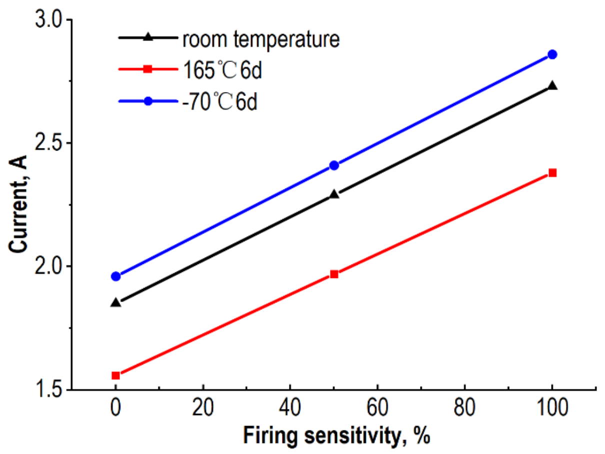


Fig. 4. Firing sensitivity of different temperature

In contrast, under high temperature conditions, the firing stimulus of the Mg/TeO_2 priming composition is significantly reduced (the firing current is reduced by 0.29 ~ 0.35 A with a temperature increase of 140℃, change rate 12.8 % ~ 15.7 %). The stimulation energy change of the high temperature sample group is about three times that of the low temperature sample group. Therefore, high temperature conditions have a sensitizing effect on the Mg/TeO_2 priming composition, and as the temperature increases, this effect tends to increase gradually. Under the three temperature conditions, the Mg/TeO_2 priming composition can meet the 1 A/1 W/5 min no-fire requirement. Subsequent safe current tests (35 samples) also confirmed that the Mg/TeO_2 priming composition under all three conditions passed the 1.2 A/1 W/5 min safety test. Therefore, it can be seen that the safety and reliability of the Mg/TeO_2 priming composition in a high and low temperature environment is guaranteed.

4. CONCLUSIONS

The temperature condition has little effect (< 5 %) on the output pressure of the Mg/TeO_2 priming composition in a temperature range of –70 °C ~ 165 °C. It sublimes at 447 °C and reaches the main reaction peak at 513 °C. The influence of temperature on the output pressure is 3 % ~ 5 %, and the influence on ignition/ function time is 1 % ~ 8 %. The influence of temperature on ignition/ function time, the amount of change under high temperature conditions is about twice that under low temperature conditions. Under low temperature conditions, the firing stimulus of the Mg/TeO_2 priming composition slightly increased (the firing current is increased by 0.11 ~ 0.13 A, change rate 5.2 % ~ 5.9 %). In contrast, under high temperature conditions, the firing stimulus is significantly reduced (the firing current is reduced by 0.29 ~ 0.35 A, change rate 12.8 % ~ 15.7 %). 1.2 A/1 W/5 min no-fire can be satisfied at –70 °C ~ 165 °C. The thermal stability of Mg/TeO_2 priming composition is superior to that of LTNR. Overall, the Mg/TeO_2 priming composition is a kind of heat-resistant insensitive pyrotechnic composition, and it can be used as a priming composition for insensitive ignitors at –70 °C ~ 165 °C.

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