

# Study on ablation behavior of silicone rubber based insulation material under the condition of boron oxide particles erosion

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**Abstract.** Self-designed oxygen-kerosene ablation system was employed to study the ablation characteristics of silicone rubber based thermal insulation materials under the condition of boron oxide particles erosion. The ablation test was designed with a mass fraction of 1.69% boron oxide particles and particles-free, the microstructure and elemental analysis of the specimens before and after ablation were carried out by Scanning Electron Microscopy (SEM) and Energy Dispersion Spectrum (EDS). Experiment results show that the average mass ablation rate of the materials was  $0.0099 \text{ g}\cdot\text{s}^{-1}$  and the average ablation rate was  $-0.025 \text{ mm}\cdot\text{s}^{-1}$  under the condition of pure gas phase ablation; and the average mass ablation rate of the multiphase ablation test group was  $0.1775 \text{ g}\cdot\text{s}^{-1}$ , whose average ablation rate was  $0.437 \text{ mm}\cdot\text{s}^{-1}$ ; during the ablation process, the boron oxide particles would adhere a molten layer on the flame contact surface of the specimen, which covering the pores on the material surface, blocking the infiltration channel for the oxidizing component and slowing down the oxidation loss rate of the material below the surface, but because the particles erosion was the main reason for material depletion, the combined effect of the above both led to the upward material ablation rates of Silicone Rubber.

## 1. Introduction

When solid rocket ramjet engine works, the secondary combustion chamber wall should not only endure the ablation of high temperature and oxygen enriched gas, but also suffer from the erosion and damage of metal particles in multiphase flow gas, which puts forward higher requirements for the ablation/erosion properties of insulation materials. Silicone rubber insulation material is widely used as solid propellant rocket ramjet combustion chamber thermal insulation material because of its better oxygen resistance ablation performance, low manufacturing cost and low thermal conductivity.

A large number of ablation tests had been carried out on the ablation process of silicone rubber at home and abroad in order to study the failure mechanism of silicon rubber based insulation materials. Liu Yang and others studied the ablation characteristics of silicone rubber under the condition of particles erosion by means of bending pipe simulation test motor; Wang Shuxian et al. tested the effect of multiphase flow on the ablative properties of silicone rubber insulation. In all kinds of two-phase flow ablation experiments carried out both at home and abroad, most of the particles used in erosion research are dominated by  $\text{Al}_2\text{O}_3$  particles, Although boron based fuel rich propellants have attracted more and more attention due to their higher calorific value and specific impulse, so far, no boron based oxide ablation/erosion simulation test had been reported. Therefore, it is of great



significance to study the ablation behavior of silicone rubber based insulation material with the particles erosion of boron oxide.

In this paper, the oxygen-kerosene ablation system was used to study silicone rubber based insulation material ablation properties under oxygen enriched condition with particles erosion of boron oxide, after the ablation test, the ablation rates were calculated and then combined with the macro and micro morphology of ablation to analyze the influence mechanism of boron oxide particles on silicone rubber material, the results provided a reference for the study of the failure mechanism of silicone rubber insulation material used to solid rocket ramjet engine using boron propellant.

## 2. Experimental

### 2.1. Materials

The raw materials include PDMS; PMPS SiC; fumed silica (silicon dioxide); ammonium polyphosphate (APP); montmorillonite; carbon fiber; aramid fiber;  $ZrB_2$ ; high silica fiber scrim. Base rubber and various fillers were pre-mixed and infiltrated for more than four hours, then dispersed by high speed dispersion for half an hour. After that TEOS with a mass fraction of 3% and the mass fraction of 0.5% organic tin were mixed into the mixture, the material was stirring evenly and pressed into piece by a mould after discharging air bubbles.

According to the actual experience system demand, the finished product was cut into specimen with size of  $50 \times 50 \times 10$  mm, whose density is about  $1.58 \text{ g/cm}^3$ .

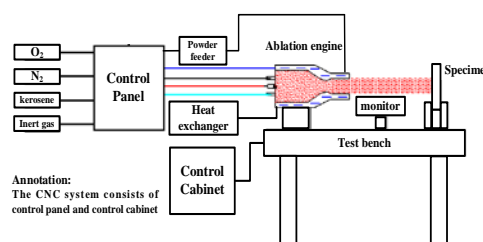
### 2.2. Ablation test system and analytical instruments

The ablation test system used in materials property testing uses aviation kerosene and oxygen gas as combustion agents and oxidizers. The particle concentration of two-phase flow is controllable (0~30%), and the ablation angle can be adjusted between 0~90°, Fig. 1 shows the schematic diagram of the ablation experiment system.

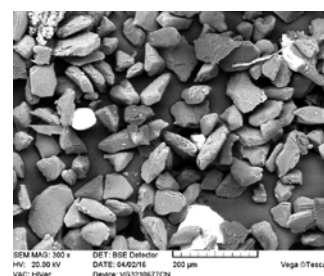
### 2.3. Ablation test parameters

In the experiment, the powder injecting to the flame is boron oxide whose size is  $15 \sim 45 \mu\text{m}$ , and the purity is higher than 99.2%. Fig. 2 is the micro morphology of boron oxide powder, the powder is round in shape and has a uniform particle size.

The analytical instruments used in the experiment include the scanning electron microscope produced by the Czech TESCAN company and the Energy350 INCA energy dispersion spectrum provided by the British OXFORD company.



**Figure 1.** Schematic diagram of the experiment system



**Figure 2.** Morphology of the boron oxide powder ( $\times 300$ )

### 2.4. Ablation test parameters

The oxygen enrichment of the test condition has a great influence on the ablation result, and the value of  $\beta$  is determined by the following formula (1).  $k_0$  means the theoretical mixture ratio of kerosene and oxygen. According to the kerosene brand, the value is 3.3.

$$\beta = \frac{m_1 - k_0 m_2}{m_1 + m_2 + m_3} \quad (1)$$

The particle concentration  $\eta$  of oxygen-kerosene simulation ablation test system is the mass fraction of the particle in the whole flame jet, the calculation formula of  $\eta$  is shown in (2):

$$\eta = \frac{G}{Q_1 \times \rho_1 + Q_2 + Q_3 \times \rho_3 + G} \quad (2)$$

The specific parameter setting is shown in Table 1. Under this condition, the temperature of the jet touching surface of the specimen was about 2000K, the speed was about 470m/s by thermal calculation and simulation analysis, which could meet the practical requirements of the thermal insulation material ablation of the solid ramjet engine. A total of two groups of ablation conditions were designed in the test, with or without particles erosion as contrast variables. Three specimens were set of each group under the ablation condition.

**Table 1.** Ablation test scheme of system for thermal insulation materials

Specimens	A1 A2 A3	B1 B2 B3	Specimens	A1 A2 A3	B1 B2 B3
Oxygen flux/(L·min <sup>-1</sup> )	342	342	Ablation	80	80
Kerosene flux/(kg·min <sup>-1</sup> )	0.138	0.138	Ablation angle/ <sup>o</sup>	45	45
Oxygen-rich condition/%	5	5	Combustion	0.27	0.27
Carry gas flux/(kg·min <sup>-1</sup> )	20	20	Test time/s	20	20
Particle concentration/%	0	1.69			

### 3. Results and discussion

#### 3.1. Ablation rate measurement

The ablation rates of the specimens are calculated, and the final ablation rates are shown in Table 2.

**Table 2.** Average ablation rates of the specimens

No.	Mass ablation rate/(g·s <sup>-1</sup> )	Linear ablation rate/(mm·s <sup>-1</sup> )	No.	Mass ablation rate/(g·s <sup>-1</sup> )	Linear ablation rate/(mm·s <sup>-1</sup> )
A1 A2 A3	0.0099	-0.025	B1 B2 B3	0.1775	0.437

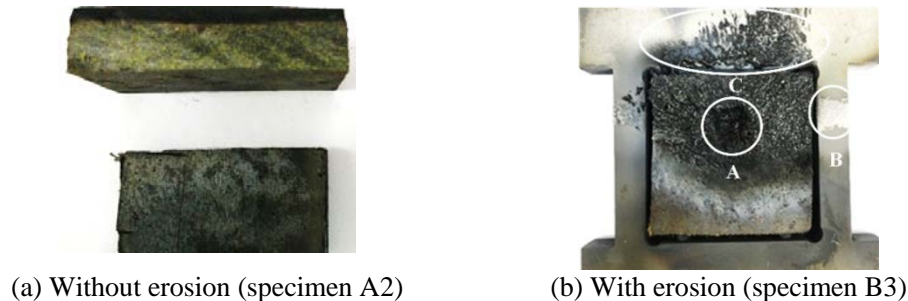
Under the condition of pure gas ablation, the linear ablation rate of the material is negative. With the addition of particles, the two kinds of ablation rates of the specimens have been greatly increased, which shows that the erosion of particles is the main reason for the insulation material consumption.

#### 3.2. Macroscopic ablation morphology analysis

After ablation, the three specimens in the A group overall expanded, whose flame contact surface became rough and turned black. No ablation pit appeared in the center of the specimens in the A group, the macroscopic morphology of A2 specimen is obtained as shown in Figure 3(a) after it was cut. The section morphology shows that the specimen formed a layered morphology after the ablation of the insulating materials, and the reaction layer (ceramic layer and pyrolysis layer) at the center of the ablation is slightly thicker than the edge, the naked eye can directly see the interface between the reaction layer and the virgin layer, but the ceramic layer and the pyrolytic layer in the reaction layer were not easy to distinguish.

After ablation, the ablation pits were observed in the center of the group with particle, Figure 3(b) shows B3's overall appearance (including specimen holder). The ablation pit is circled out shown as the A area in this figure. There were bundle ablation gully morphology below the ablation pit of specimens along 45° direction that was the ablation jet spray direction, because of the high temperature, high speed and high heat flux of the jet center, the damage to the center of the material was stronger than the jet edge, and finally the pit was left on the surface of the material; Partial white

crystal was retained in the specimen B area, and the upper half of the specimen and the C area of the specimen holder were covered with dark brown substance.



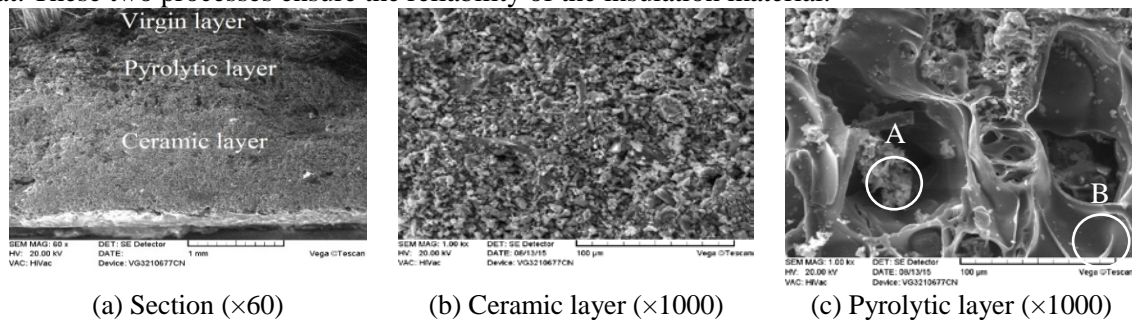
**Figure 3.** Ablation morphology of the specimens

### 3.3. Microscopic morphology analysis

In order to investigate the ablation mechanism of silicone rubber based insulation material under particles erosion of boron oxide condition, the micro morphology and material composition of the material were analyzed by SEM and EDS.

#### 3.3.1 Microscopic morphology of specimens after ablation under pure gas ablation

Fig. 4 is the morphology of the ceramic layer and the pyrolysis layer of the specimen A3 at different magnification. The phenomenon of delamination in the ablation region can be clearly observed in Fig. 4(a). Figure (b) and (c) in the Fig. 4 respectively are the local amplification morphology of the ceramic layer and the pyrolysis layer. The structural features of the ceramic layer and the pyrolysis layer are obvious, and the ceramic layer structure is much compact, which can play a better role in protecting the parts under ceramic layer, at the same time, heat passes through the ceramic layer and passes inwards, Pyrolysis of internal polymeric materials brings the formation of a large amount of gas, which results in larger internal pressure in the material. With the overflow of gas, a unique hole in the pyrolysis layer is formed. The area A and B of Figure 4(c) and whole area shown in 4(b) are analyzed for atomic percent by EDS, and the results obtained as Table 3 shown, as we can see, the main elements of ceramic layer are carbon, silicon and oxygen, it is inferred that the main component is fused silicon dioxide with a small amount of silicon carbide which has not been oxidized and pyrolysis by flame gas, they are densely covered with particles on the specimen surface. The material in pyrolysis layer is mainly silicon dioxide, some of which are as the wall surface of pores in the form of molten state. Some of them are attached to the wall of holes in the form of particles, with the release of a large amount of gas from pyrolysis process of polymer materials, material expand and the expansion process cannot be effectively restrained, so the final linear ablation rate is negative value. The ceramic layer effectively blocks the erosion of the pure gas jet, and the pyrolysis process takes away a lot of heat. These two processes ensure the reliability of the insulation material.



**Figure 4.** Micro-morphology of different structural layers

**Table 3.** The atomic percent of the ceramic layer and pyrolytic layer

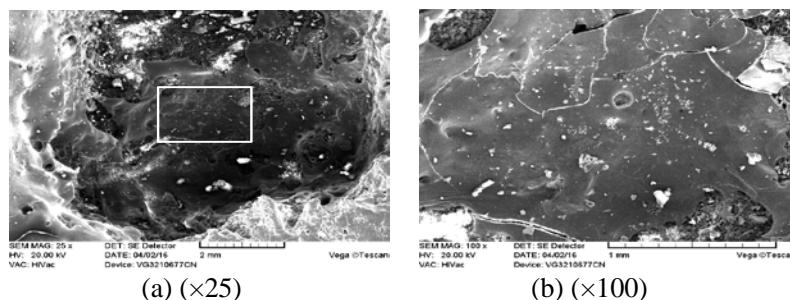
Element	Ceramic layer	Pyrolytic layer(A)	Pyrolytic layer(B)
C	6.17	8.51	5.13
O	51.95	66.44	74.37
Si	37.88	24.61	20.50

### 3.3.2 Microscopic morphology of specimens after ablation under boron oxide erosion condition

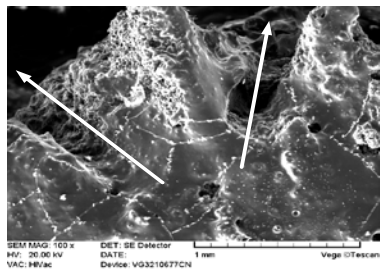
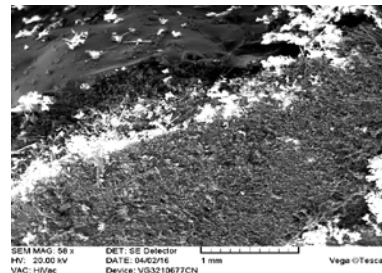
The addition of boron oxide particles causes a large change to the ablation morphology. At the center of specimen morphology is shown in Figure 5(a), the specimen surface attached with a laminar like molten material, which illustrates that the flame temperature reaches the melting point of material under the test conditions, after further amplifying white frame area in the figure 5(a), we can get the morphology shown in figure 5(b), it is observed that molten material have a certain degree of rupture and have not completely covered on the material surface with partial ceramic layer areas exposed to flame and touching to the particles when ablated; at the same time, some large volume particle are not fused completely, and embedded in the molten layer by solid state by the driving of high velocity flame stream, as shown by the white particles on the surface in the figure 5(b). Table 4 is the results of elemental analysis, which shows that the surface white particles are mainly oxygen and boron elements, it can be preliminarily judged that the white particles are boron oxide powder.

The morphology of 45° jet scouring area near the ablation pit is shown in Figure 6. Compared with the central area, the coverage of the melt in the scouring area for the material is more complete, and the cracks are more small. The reason is that the central area is subjected to the positive impact of particles and its force environment is worse than scouring area. But in the scouring area, particles fly following the arrow shown in the fig.6, leading to the gully morphology.

Section morphology of the specimen B3 is show as figure 7. Compared with the section morphology of the specimen A2 that was ablated under pure gas condition, the morphology shown in the fig. 7 has a thinner reaction layer that can still be observed clearly, which shows that the addition of solid particles in the gas has a strong erosion and destruction to the surface ceramic layer. Besides, a layer of molten boron oxide is also deposited over the reaction layer to reduce permeation of the oxidizing components and slow down the rate of oxidation depletion of materials that is below surface. However particle erosion is the main cause of material depletion, the combined effect of the above both led to the upward material ablation rates of silicone rubber.

**Figure 5.** Morphology in the central area of specimen



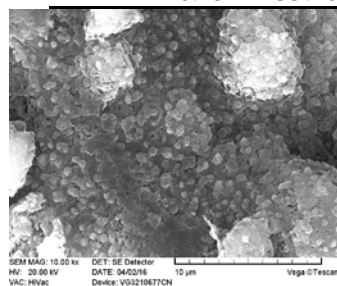
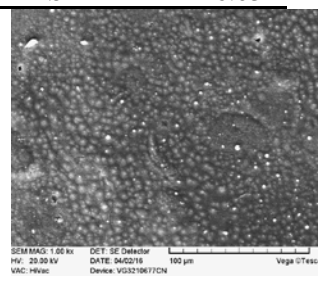
**Figure 6.** Morphology in the scour area ( $\times 100$ )**Figure 7.** Section ( $\times 58$ )**Table 4.** The atomic percent of the central area of specimen

Element	Atomic percent	Element	Atomic percent
B	36.14	O	44.87
C	15.39	Si	3.60

Microscopic of the area B and C in Fig. 3 are shown in fig. 8. The white crystalline in the area B is boron oxide according to the EDS analysis results shown in Table 5. After recrystallization, powders condensed into balls and pile together with small tiny bumps attaching to the balls surface. The overall size of the balls is slightly less than boron oxide powder of addition, the shape of the particles changed from irregular to spherical, this process of change shows that the particles are fully molten in the flame gas, which indirectly proofing the flame under this experimental condition has a similar thermal environment to the secondary combustion chamber of solid rocket ramjet engine using boron propellant; And EDS result of the area C show that the main elements in this area is boron, oxygen and carbon elements, referring to the B area result, the dark brown material in the area C includes not only the molten boron oxide in the gas stream but also the small amounts of silicon dioxide and unoxidized silicon carbide that migrated from the surface of the specimen.

**Table 5.** The atomic percentage of the element in the area B and area C in specimen handle

Element	Area B	Area C	Element	Area B	Area C
O	59.55	39.26	C	—	21.60
B	40.45	33.10	Si	—	6.03

(a) Area B ( $\times 10000$ )(b) Area C ( $\times 1000$ )**Figure 8.** Microscopic morphology of corner ceramic coatings under different oxygen – enriched conditions

#### 4. Conclusion

(1) In this paper, the ablation test of silicone rubber based insulation materials under the condition of Boron Oxide particle erosion is carried out. After calculation, the average mass ablation rate of the material under the multiphase flow test is  $0.1775 \text{ g} \cdot \text{s}^{-1}$ , the average linear ablation rate is  $0.437 \text{ mm} \cdot \text{s}^{-1}$ . In the pure gas phase contrast test, the linear ablation rate is negative value, and the addition of erosion particles is the main factor affecting the depletion of the material.

(2) Boron oxide particles after heating and accelerating attached to the surface of the material and formed a layer of molten material, which covering material pores leading to blocking the infiltration passage of the oxidizing component and slowing down the rate of oxidation depletion of materials below surface. However particle erosion is the main cause of material depletion, the combined effect of the above both led to the upward material ablation rates of silicone rubber.

(3) The boron oxide particles doped in the high temperature flame flow of oxygen kerosene have reached the molten state, which is close to the actual combustion flame flow of solid rocket ramjet engine using boron propellant. The simulated ablation method is better for the reconstruction of the ablation environment. The simulated ablation method used in this article has high application value in the reconstruction of ablation environment.

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