Conversion study and mechanical properties of alumina bubble ceramics prepared from a silicone rubber binder precursor

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Alumina bubble ceramics is a light-weight high-strength thermal insulation material of excellent properties with a wide-range application. Binder is the key to its preparation. Binder enables the alumina bubbles to be bonded together to form alumina bubble ceramics with mechanical properties. We report a new method of preparing alumina bubble ceramics with a binder precursor—silicone rubber. The transition of silicone rubber from organic to inorganic substance occurs during the sintering process. Moreover, the binder formed during the transformation coated and bonded alumina bubbles well. Compressive strength of prepared samples was up to 7.5 MPa. For their light weight, high strength, such materials can be adopted as thermal insulations, with prospective application for spacecraft thermal sealing. Due to the good molding characteristic, excellent green body elasticity, and high machinability, this method can be used to prepare samples of complex shapes and precise dimensions.

Key-words : Alumina bubble, Silicone rubber, Precursor, Porous ceramics, Binder

1. Introduction

Incorporating with the strengths taken on by porous material and ceramic material, porous ceramics not only possesses high porosity, high transmittance, and large specific surface area of porous material, but also manifests properties of ceramic material, encompassing high temperature resistance, low heat conductivity, and corrosion resistance. Porous ceramics can be adopted in different situations in virtue of its different properties. The properties of porous material can be adapted to effectuate different applications through changing the composition and pore structure of porous material.¹⁻⁴

Characterized by low density, light weight, thermal shock resistance, prominent thermal insulation property, low thermal capacity, high compression strength, high refractoriness under load, low linear shrinking percentage, etc., alumina porous ceramics has aroused great concern extensively and been employed in a large scale. In contrast with the existing thermal insulation materials of different textures, alumina insulation material is currently deemed as the crucial thermal insulation material as takin on a great variety, high operating temperature, and excellent thermal insulation and energy-saving effect.⁵

The key of preparing alumina porous ceramic is to form porous structure. The common preparative techniques are currently comprised of extrusion molding process, particle accumulation molding process, process of adding pore forming substance, foaming process, impregnation technology of polymeric sponge and gel-casting technology.⁶⁻⁸

The strength of extrusion molding is easy and simple to operate as the shape and size of pore can be precisely designed to be geared into different requirements; the weakness refers to the restriction by preparative technique of molds, and accordingly small-pore sample shall be difficult to prepare. The sample prepared through particle accumulation molding process has high compressive strength and stable performance, whereas its particle size affects pore size distribution. The addition of pore forming substance shall avoid abated porosity triggered by excessively high sintering temperature and get rid of inadequate rigidity stemmed from excessively low temperature. Additionally, the sintered product takes on high porosity and fine mechanical strength, whereas its pore diameter is unevenly distributed. The sample prepared via foaming shall have big pore and high rigidity; this process is geared into the preparation of closed pore sample, and yet its requirements of raw material are high and process conditions are difficult to control. The sample prepared whereby gel-casting technology has controlled size and uniformly distributed pore; this process is suitable for preparing micropore ceramic, whereas its process conditions are difficult to control and quantity production is infeasible.

Alumina ceramic hollow sphere is a tiny hollow sphere
made of inorganic nonmetallic material, and its diameter ranges from tens of micrometers to hundreds of micrometers.\(^9\) Characterized by light weight, low heat conduction, sound insulation, wear resistance, high dispersion, excellent electrical insulating property, excellent heat stability, low preparation cost, etc., it is a light-weight high-strength hollow thermal insulation material of excellent properties with a wide-range application. Binder is an important part of light-weight alumina bubble ceramics. Binder enables the alumina bubbles to be bonded together to form alumina bubble ceramics so that binder determines the mechanical properties of alumina bubble ceramics. Possible negative influence of binder on the high-temperature properties of light-weight alumina bubble ceramic should be reduced or avoided to the greatest extent. Binder can fall into classifications as organic binder, inorganic binder, and mixed binder in line with the difference in chemical composition.

Whereby the strengths, encompassing low curing temperature, excellent adhesive property, high and low temperature resistance, easy mixing and molding, etc, the aluminum phosphate system is currently the most frequently-employed binder of alumina bubble ceramics, whereas pure aluminum phosphate binder involves high brittleness, and shall be readily cracked during sintering. Accordingly, the requirement for adhesive property is failed to meet. In virtue of strengths, comprising high curing rate and high bonding strength, organic binder has already been adopted extensively, whereas its application is confined arising from its poor temperature resistance and ageing resistance performance to a large extent.\(^10\)

In silicone rubber, -O-Si-O-chain refers to the predominated chain, and silicon atom in the primary chain can be connected to some organic side bases. In this regard, it is an elastic high polymer material whose molecular chain possesses organic and inorganic nature in the meantime. Organic silicon rubber takes on not only preferable water resistance and weather resistance performance, but also excellent elasticity and comparatively high bonding strength.\(^11\) It has already been extensively employed in industrial production and aviation sealing. Yet like other organic binders, silicone rubber binder is also defective in thermal endurance.

Precursor ceramics aims to obtain the organic polymer which can be transformed into ceramic material after splitting decomposition in heating through chemical synthesis method. On that basis, the ceramic material shall be gained whereby pre-forming and thermal treatment for the polymer. Strengths taken on both by organic polymers and ceramic materials are incorporated into this method. Multiple flexible forming methods, inclusive of solid forming, liquid forming, and micro injection molding, can be adopted to realize near-net-shaping of ceramics. As a high polymer material, the precursor after forming presents the feature of easy machining owned by the high polymer material. At present, most studies about precursor ceramics concentrate on the utilization of precursor to prepare non-oxide ceramics of silicon nitride, silicon carbide, alumina, boron nitride, SiOC, SiON, and SiBCN systems under reducing atmosphere,\(^12\)\(^,\)\(^13\) involving extremely high technological requirement and high cost, so mass production cannot be realized.

The ceramic precursor method was adopted to prepare alumina bubble ceramics. Cheap silicone rubber was set as binder precursor. The alumina bubble ceramics setting siliccon dioxide as binder was prepared through sintering under oxidizing atmosphere after injection molding. Ceramic body with a complicated shape can be prepared at a comparatively low cost with this method. Displaying first-rate elasticity and machinability, the green body obtained can be employed to prepare thermal insulation components of complicated shapes and high dimensional requirements.

## 2. Experiment

### 2.1 Raw material

Raw materials adopted in this study are comprised of alumina bubble, simethicone (50 cst, added as diluent of the silicone rubber), and condensed dimethyl silicone rubber (end capped with hydroxide radical, binder precursor). SEM photograph and particle size distribution of the alumina bubble adopted are exhibited in **Fig. 1**. The particle size distribution range is 0.21–0.50 mm, and the particle size is 0.34 mm on the average.

### 2.2 Sample preparation

Alumina bubble, simethicone, and silicone rubber were weighed abiding by the proportion of 2:1:9, mechanical agitation was conducted in the beaker, and 1% curing agent was added into the uniformly mixed sizing agent. After being stirred evenly, the sizing agent was poured into

![Fig. 1.](image-url) (a) SEM image and (b) particle size distribution of the alumina bubble.
the mold of 10 × 10 × 30 mm for curing at room temperature, and alumina bubble–silicone rubber composite body with excellent elasticity was gained after demolding two hours later. Rubber discharging was conducted for the green body in air atmosphere under 270–330°C for 6 h. On that basis, the temperature was increased to 900, 1100, 1300, and 1500°C at the rate of 2 °C/min. Sintered sample was obtained after heat preservation for 2 h. The preparation flow is presented in Fig. 2.

2.3 Property test
Thermo gravimetric differential scanning calorimeter (TG-DSC, STA 449C, Netzsch, Germany) was employed to analyze the thermal weight loss process of samples under high temperature; air atmosphere was adopted as the test condition, the heating rate was 10 °C/min, and the test temperature ranged from room temperature to 1500°C.

X-ray diffractometer (XRD, Rigaku D/Max-2500, Rigaku, Japan) was employed to ascertain the phase composition of samples. Kx ray of Cu target was adopted as the emission source in the test, the operating voltage was 30 kV, the operating current was 40 mA, the scanning speed was 10 °/min, and the scanning step was 0.02°.

The molecular structure changes of samples were anamolized with Fourier transform infrared spectrometer (FT-IR, WQF-510, Mitech Instrument, China).

Electro-mechanical universal testing machine (EUTM, CSS-44100, MTS System, China) was adopted to ascertain the compressive property of the samples at room temperature and high temperature abiding by the national standard GB/T 4740-1999. Load was adopted at the rate of 0.5 mm/min till the sample was destroyed. Compressive strength of the sample can be calculated by Eq. (1), where \( \sigma_c \) denotes the compressive strength of the sample (MPa), \( F \) denotes the maximum force hypothesized by the sample (N), \( S \) is the compression area (m²).

\[
\sigma_c = \frac{F}{S} \quad (1)
\]

3. Results and discussion
3.1 Transformation in sintering process
3.1.1 Mass loss
At first, the mass variation of silicone rubber in the temperature-rise period was analyzed in the experiment. The TG-DSC curve of silicone rubber is presented in Fig. 3. Four evident weight loss phases exist in the thermogravimetric curve. At the first phase, the mass loss at temperature ranging from 100–380°C is about 8%, which might result from water evaporation triggered by condensation of Si–OH bond. The following condensation reaction happens to silicone rubber in the curing process [Eq. (2)].

\[
\text{Si–OH} + \text{HO–Si} \rightarrow \text{Si}–\text{O}–\text{Si} + \text{H}_2\text{O} \quad (2)
\]

Water produced in the reaction process evaporates in the form of vapor, resulting in mass loss of the sample. At the second phase, the mass loss of silicone rubber at temperature ranging from 380–450°C is about 13.9%, in contrast with the exothermic peak at 422.2°C in the differential thermal curve, which might be associated with volatilization and decomposition of silicone oil. Low-viscosity simethicone (50 cst) was added in the experiment as diluent of the silicone rubber. Its molecular chain is comparatively short, and the decomposition temperature is lower than that of silicone rubber. Small molecules in the silicone oil shall volatilize in the temperature-rise period, and be decomposed before the molecular chain of silicone rubber is decomposed, resulting in mass loss of the sample. At the third phase, the mass loss at temperature ranging from 450–600°C is about 51.46%. The silicone rubber is converted from organic matter into inorganic matter at this phase; methyl of most Si–H bonds, C–H bonds, and side chain cracks, CO₂ gas escapes, and some powders produced after molecular chain breaking are taken away, resulting in mass loss of the sample. To abate the impact exerted by fast mass loss on the material properties, a comparatively
low heating rate should be maintained for the sample in the sintering process at this phase. At the fourth phase, the mass loss at temperature ranging from 1100–1300°C is only 0.03%, bespeaking that the silicone rubber has completely converted into ceramics before this temperature range, and the mass loss might result from the overflow of a small amount of SiO in gaseous state.

3.1.2 Molecular structure

In the course of sintering, the precursor is transformed from organics to inorganic substances, and the molecular structure changes substantially. The molecular structures of green body and sintered sample are analyzed with FT-IR in the experiment. The infrared spectrogram of green body and sintered sample is exhibited in Fig. 4. Infrared absorption peaks of alumina in the sample composition are concentrated in the far infrared region (50–400 cm⁻¹). Accordingly the infrared absorption peaks in the figure primarily stem from the silicone rubber and its ceramic product. In the infrared spectrogram of green body, the peak around 2900 cm⁻¹ is the absorption peak of methyl in silicone rubber; the peak at 1270 cm⁻¹ is the absorption peak of Si–CH₃ in silicone rubber; the peak at 1030 cm⁻¹ is the absorption peak of Si–O–Si in silicone rubber; the peak around 760 cm⁻¹ is the absorption peak of Si–C in silicone rubber. In the Infrared spectrum of the sample after sintering under 600 and 1500°C, only absorption peak of Si–O–Si at 1030 cm⁻¹ and absorption peak of Si–C around 760 cm⁻¹ are left. Hence, silicone rubber has completely converted into ceramics at 600°C, and the ceramization product is silicon oxide. Meanwhile, a small amount of C not completely oxidized exists in the form of Si–C. The residual C is oxidized in the case of 1500°C sintering temperature, where it is not oxidized completely.

3.1.3 Phase analysis

There’s no evident difference in the infrared spectrum above 600°C. Therefore, the phase transformation of samples above 600°C is studied by XRD analysis. The XRD patterns of samples sintered at 900, 1100, 1300, and 1500°C are exhibited in Fig. 5. The figure indicates that the principal crystalline phase of the four samples is α-Al₂O₃, as the content of alumina bubbles occupies 75% of the raw material, and other raw materials undergoes severe mass loss in the sintering process. Consequently, the alumina bubbles take up over 90% in the final product. Amorphous ceramics are produced in the sample in accordance with the previous analysis results. And yet the “bulge” peak characterizing amorphous ceramics is not shown up in the XRD spectrogram. This is likely because its content is too low to be detected. Apart from the characteristic peak of alumina, however, characteristic peak of SiO₂ appears at about 22° in the XRD spectrogram, while this peak does not exist in the sample sintered under 900°C. This characteristic peak turns up under 1100°C with the rise of sintering temperature, and apparent characteristic peak exits under 1500°C. Hence, after silicone rubber is converted into ceramics, it shall exist in an amorphous form first, and amorphous ceramics begins to crystallize when the temperature reaches above 1100°C.

3.1.4 Morphology

The SEM photographs regarding green body and sintered sample are presented in Fig. 6; the structure diagrams of green body before and after sintering are sketched as in Fig. 7. As the SEM photograph regarding green body is denoted in Fig. 6(a), and the interspaces between alumina bubbles are filled with silicone rubber. The SEM photograph regarding sintered sample is indicated in Fig. 6(b). As the SEM photograph shows, the surface of alumina bubble is uniformly coated with a layer of glass phases; glass phases near the cervical region between alumina bubbles are bonded together; closed pores are in the bubbles, and considerable amount of open pores are left between the bubbles. In contrast with Fig. 6(a), Fig. 7(a) sketches the structure diagram regarding green body. The small bubbles are scattered in the silicone rubber, and the silicone rubber packs the pores formed by stacking of small bubbles. Compared to Fig. 6(b), Fig. 7(b) sketches the structure diagram regarding sintered sample. Alumina bubbles are clad uniformly with the high-temperature
ceramization products of silicone rubber which plays a bonding role.

Figure 8 is SEM photograph of sintered samples at different temperatures. Figure 8(a) shows the microstructure of samples after 2-h of heat preservation at 900°C, in which silicone rubber is indicated to have become ceramic whereas not yet softened at 900°C. Figure 8(b) shows the microstructure of samples after 2-h of heat preservation at 1100°C. It is indicated that bonding phase have been softened and the bonding strength begins to be improved at 1100°C. Figure 8(c) shows the microstructure of samples after 2-h of heat preservation at 1300°C. The bonding phase is bespoken to have been sintered and bonding phase at the neck of bubbles begins to be sleek at this temperature. Figure 8(d) shows the microstructure of samples after 2-h of heat preservation at 1500°C. The binder between bubbles in samples is presented to be liquefied and incorporated with bubbles closely. As the temperature rises, the silicone rubber is oxidized to amorphous silica. During the cooling process after 1500°C, most of the silica forms bonding glass and a small part of the silica crystallizes. This is why peaks of cristobalite are
shown in the XRD pattern while the bonding glass is shown in the SEM image.

3.2 Performance characterization
3.2.1 Compressive strength

The impact exerted by sintering temperature on the compressive strength of samples is ascertained in this experiment. Figure 9(a) is indicative of the compressive strength of samples sintered at different temperatures. The figure explicitly indicates that the compressive strength taken on by samples shall increase with the rise of sintering temperature ranging from 900–1500°C. The strength of samples is very low, viz. 0.6–0.7 MPa, within the range; the samples start to be sintered, and the compressive strength is elevated to 2.1 MPa approximately at 1300°C; samples gains 7.5 MPa of compressive strength at 1500°C, a data nearly 3.5 times of the strength at 1300°C, bespeaking that sintering of samples can be performed at 1500°C. The formation of bonding glass can greatly enhance the compressive strength of the sample, whereas the crystallization of silica reduces the strength of the sample. As the amount of bonding glass formed far exceeds that of crystallization, the compressive strength of the sample after sintering at 1500°C is, in general, enhanced. The sintering temperature above 1500°C is not ascertained in this work given the limited laboratory equipment. The sintering temperature of samples can be perceived as 1500°C in line with the foregoing data of compressive strength.

Figure 9(b) is indicative of the compressive strength of samples sintered at 1500°C, tested at room temperature, 800, 900, and 1000°C, respectively. The figure explicitly bespeaks that the compressive strength taken on by samples confining to room temperature to 1000°C is basically 7.5 MPa factoring in slight variation. SiO2 and Al2O3 in samples can hardly be softened below 1000°C. In this regard, the strength of samples shall not be lowered confining to room temperature to 1000°C. It’s concluded that the compressive strength taken on by samples shall be lowered at higher temperatures because of softening of binder phase between alumina bubbles. The compressive strength of samples at higher temperature is not ascertained due to the confined operating temperature of universal testing machine.

3.2.2 Fracture action

The stress–strain curve of samples and the typical fracture appearance of samples are exhibited in Fig. 10. The stress–strain curve of samples bespeaks that the elastic deformation of samples can make up 6%, the stress–strain curve of samples denotes a phase similar to yield, and no devastating brittle fracture happens, which might be bound by the fracture mechanism. Accordingly, the fracture appearance of samples was observed in this experiment. The typical fracture appearances of samples are denoted in Fig. 10. Bubbles at the fracture are observed to be severely damaged, and are penetrated into by the fracture. As a result, alumina bubble counts as the weak link of samples.

3.2.3 Flexibility and machinability of green body

Sizing agent with fluidity was adopted in the experiment before modification of the raw material, and molding techniques, inclusive of liquid forming and injection molding, can be employed to prepare samples of complex shapes.

In the meantime, containing silicone rubber of excellent elasticity, the green body is provided with excellent elasticity and machinability, which can satisfy various requirements regarding processing craft, comprising twining and cutting. For this reason, it can be adopted to prepare samples of complex shapes and precise dimensions. Pictures of the samples are exhibited in Fig. 11. Figure 11(a) indicates that the green bodies prepared through adopting this method take on excellent elasticity, and all samples in Fig. 11(b) are obtained through processing sheet or nubby green bodies without the help of molding.

4. Conclusions

Through sintering under oxidizing atmosphere and adopting cheap silicone rubber as binder precursor, alumina bubble ceramics was prepared whereby precursor method in this study. As the results bespeak, organic matter
is converted into inorganic matter as silicone rubber is being sintered, and the binder formed in the conversion can effectively coat and bond alumina bubbles. The compressive strength taken on by samples reached approximately 7.5 MPa. Within the test temperature range (RT~1000°C), the compressive strength taken on by samples hardly decreased. In virtue of preferable molding characteristic, excellent green body elasticity, and high machinability of the object, such method can be employed to prepare samples of complex shapes and precise dimensions. Whereby its strengths, inclusive of light weight, high strength and low heat conductivity, it can be adopted as thermal insulation material. In this regard, a wide-range application of this brick is manifested for spacecraft thermal sealing.

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