Research on the Preparation and Performances of a New Type of Hollow Glass Microspheres

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Abstract: Hollow glass microsphere is a cross-functional frontier material that can be added to a variety of substrate materials to improve their performances and environmental benefits. In this paper, the characteristics, application fields and development status of hollow glass microspheres were summarized, and the basic formula, preparation process, performance testing equipments and methods of a new type of hollow glass microspheres were expounded. By testing and analyzing the main performances such as micro morphology, chemical composition, particle size, floating rate, bulk density, true density, compressive strength and other indicators of the microsphere samples, the properties and application potential of the hollow glass microspheres that we prepared are comprehensively characterized. The experimental results show that the microspheres have regular morphology and uniform particle size, the floating rate of them is higher than 97%, the bulk density is 0.1~0.4g/cm³, the true density is 0.20~0.65g/cm³ and fluctuates in a reasonable range; besides, the compressive strength is so good that microspheres are barely broken. What’s more, the development prospect of glass microsphere industry is prospected at the end.

1. Introduction
Hollow glass microsphere (HGM) that also known as vitrified small ball is a kind of micron-sized hollow sphere with smooth surface, its main chemical composition is soda lime borosilicate glass, and the natural accumulation state of them is white light inorganic powder[1-2]. Composition and hollow structure endow the microspheres with unique properties different from other inorganic non-metallic or hollow materials. In addition to low density, high compressive strength, high temperature or corrosion resistance, low thermal conductivity, nice fluidity and chemical stability, advantages such as non-toxic, odorless, electric insulation, sound-proofing, anti-radiation, self-lubrication and easy surface modification are also showed by hollow glass microspheres[3-5]. These characteristics make hollow glass microspheres widely used as additives in many fields, such as water-based lightweight building insulation paint, low-density drilling fluids and cementing slurry, lightweight components in aerospace and vehicles, ship floating block and coatings, electronic components, high molecular composite materials, putty powder, artificial marble, and natural / synthetic products[6], etc.

- With the deepening of laboratory research and improvement from the feedback message of practical application, hollow glass microspheres have been industrialized in dozens of domestic enterprises, and become a new inorganic raw material with low price and rich source gradually,
which is of great significance to weight reduction of materials related to the national economy and people's livelihood, as well as to energy-saving and carbon emission reduction strategy of our country[7, 8]. In this paper, based on the experience of interrelated enterprises, the preparation method of a new type of hollow glass microspheres was researched, and a series of performance tests were carried out.

2. Experiments

2.1. Raw materials
Quartz sand powder (SiO$_2$, 200 mesh), Lingshou Shunye mineral products processing plant; Potassium carbonate (K$_2$CO$_3$, industrial grade), Dongguan Qiaoke chemical Co., Ltd; Sodium octaborate (Na$_2$B$_8$O$_{13}$·4H$_2$O, industrial grade), Henan Chengduo chemical Co., Ltd; Sodium carbonate (Na$_2$CO$_3$, industrial grade), Weifang Haizhiyuan chemical Co., Ltd; Calcium hydroxide (Ca(OH)$_2$, industrial grade), Tianjin Jinhuitaiya chemical reagent Co., Ltd; Sodium aluminate (NaAlO$_2$, food grade), Henan Laisheng bioengineering Co., Ltd; Lithium carbonate (Li$_2$CO$_3$, industrial grade), Shandong Hezhan chemical Co., Ltd.

2.2. Preparation of hollow glass microspheres
Referring to the traditional preparation method of hollow glass microspheres, combined with the existing experiences of this industry and interrelated enterprises, the basic formula of the new type hollow glass microspheres is shown in Table 1, and the preparation scheme is elaborated as follows.

| raw material | quartz sand | K$_2$CO$_3$ | Na$_2$B$_8$O$_{13}$·4H$_2$O | Na$_2$CO$_3$ | Ca(OH)$_2$ | NaAlO$_2$ | Li$_2$CO$_3$ | H$_2$O |
|--------------|-------------|-------------|----------------|-------------|-------------|------------|-------------|-------|
| Mass percentage/% | 27 | 14.5 | 15 | 10 | 3.5 | 3 | 0.5 | 26.5 |

- First, mix quartz sand powder and potassium carbonate powder according to the proportion in Table 1, and melt them at a relative high temperature to obtain potassium silicate frit; Then the potassium silicate frit is crushed and dissolved in hot water (80~100℃) to obtain potassium silicate solution (note: the mass concentration is controlled to be 10~40wt%).
- Second, Sodium octaborate, sodium carbonate, potassium carbonate, calcium hydroxide, sodium aluminate and lithium carbonate are dissolved in deionized water and stirred continuously. During the stirring process, the potassium silicate solution above is added into them to prepare potassium sodium borosilicate solution (The molar ratio of potassium and sodium is 0.66~1.32).
- Last but not least, The potassium sodium borosilicate solution should be transported to the spray dryer for drying, and then further dehydrated and spheroidized by sintering in a high temperature (≤620℃), via this way, hollow glass microspheres with 3~108μm average particle size, 0.1~1.9 true density and 3~80MPa compressive strength can be prepared.

2.3. Equipments and methods for performance testing of microspheres
Micro morphology analysis: The morphology and structure of the microsphere samples should be observed by optical microscope and scanning electron microscope (SEM).

- Chemical composition analysis: The microsphere samples should be total-element chemical analyzed by a Spectro X-ray fluorescence spectrometer.
- Particle size analysis: The average particle size and particle size distribution should be measured by laser particle size analyzer (laser diffraction in wet condition).
- Floating rate test: The cone settling cup should be used to test the floating rate of the samples; The calculation formula is \[ F = \frac{V_1}{V_1 + V_2} \times 100\% \] (1)
  F is the floating rate \(/\%\), \(V_1\) is the volume of floating microspheres /ml, and \(V_2\) is the volume of settled microspheres /ml.
- True density test: The AccuPyc II 1340 automatic true density analyzer should be used to test the true density of the samples; Testing atmosphere is 99.999\% high purity nitrogen, and the physical principle of this test is Boyle Ideal-Gas Law.
- Compressive strength test: The gas comparison gravimeter should be used to test the crushing rate of the samples in a closed container under a certain gas pressure; Testing atmosphere is high purity nitrogen, and the gas pressure range is 2.07~206.8MPa (300~30000 psi).

3. Main performances of hollow glass microspheres

3.1. Micro morphology and chemical composition
The natural accumulation state, micro morphology and main chemical composition of hollow glass microspheres are shown in Figure 1 and Table 2.

![Natural accumulation state of microspheres](image1.png)

(a) Natural accumulation state of microspheres

![Profile structure of microspheres](image2.png)

(b) The profile structure of microspheres

![Morphology under optical microscope](image3.png)

(c) Morphology under optical microscope

![Morphology under SEM (X400)](image4.png)

(d) Morphology under SEM (X400)

Figure 1. Micro morphology of hollow glass microspheres.

- It can be seen from Figure 1 that most glass microspheres are close hollow spheres with regular-looking, high transparency and smooth surface.
Table 2. Main chemical composition of hollow glass microspheres.

| Main composition | SiO₂ | Na₂O | CaO | B₂O₃ | Al₂O₃ |
|------------------|------|------|-----|------|-------|
| Mass percentage/%| 68~75| 5~15 | 8~15| 15~20| 2~3   |

According to Table 2, by controlling the proportion of potassium and sodium in the raw materials for experiments, the water content of microspheres can be controlled to be less than 0.5%, and the samples show low hygroscopicity (hydrophilicity) in the process of storage. For example, when exposed in a room with 45~70% RH for more than three days, the samples are not agglomerate.

3.2. Average particle size and particle size distribution

Add a proper amount of sample into the laser particle size analyzer, and set proper experimental parameters, then operate the equipment according to its prompts; Test for three times, and calculate the average particle size of hollow glass microspheres, and the results are shown in Table 3. By the way, the sample’s particle size distribution curve is obtained, which is as shown in Figure 2.

Table 3. Average particle size of different types of microspheres and the notea.

| Type of microspheres | Test I (µm) | Test II (µm) | Test III (µm) | Average (µm) |
|----------------------|-------------|--------------|---------------|--------------|
| HL20                 | 84.43       | 85.57        | 85.04         | 85.01        |
| HL40                 | 66.77       | 66.21        | 65.23         | 66.07        |
| HL60                 | 57.88       | 59.61        | 62.66         | 60.05        |

Note: in this paper, the True Density is cited to determine the type of microsphere samples, such as HL20 (the true density is 0.20~0.22), HL40 (true density 0.39~0.42), and HL60 (true density 0.58~0.62).

It can be seen from Table 3 that the three test results of any type of the microspheres are almost the same numerical value (fluctuate slightly), which indicates that in steady manufacturing conditions, different types of microsphere samples that we prepared are uniform in particle size.
It can be seen from Figure 2 that the particle sizes of the microsphere samples distribute in the range of 10~100 μm, and most of the microspheres’ size are about 50 μm.

3.3. Floating rate and bulk density

According to JCT 1042-2007 Expanded and vitrified small ball and JCT 2164-2013 Technical specification in application of thermal insulation glazed hollow beads mortar, the floating rate of hollow glass microspheres should be greater than 80%. If not, it means that some microspheres are broken abnormally, or there are impurities mixed in the production process, which always results in low yield rate. The experimental results show that, the floating rate of the hollow glass microspheres that we prepared is greater than 97%.

Figure 2. Particle size distribution curve and relevant experimental parameters.
• According to SYT 5504.6-2009 Evaluation method for well cement additives (Part 6: light-weight additive), the bulk density of microspheres should be less than 0.50g/cm³. Three grams of microspheres are weighed by an electronic balance (the accuracy is 0.0001g), then are slowly dumped into a measuring cylinder, and the volume is recorded to calculate the microspheres’ density under a natural accumulation state; Test for three times, and calculate the average value of bulk density, and the results are shown in Table 4.

Table 4. Bulk density of different types of hollow glass microspheres.

| Type of microspheres | Test I (g/cm³) | Test II (g/cm³) | Test III (g/cm³) | Average (g/cm³) |
|----------------------|----------------|-----------------|-----------------|-----------------|
| HL20                 | 0.1171         | 0.1181          | 0.1155          | 0.1169          |
| HL40                 | 0.2203         | 0.2165          | 0.2187          | 0.2185          |
| HL60                 | 0.3347         | 0.3160          | 0.3265          | 0.3257          |

• According to people’s experiences, the higher the bulk density is, the smaller the microspheres’ particle sizes will be. It can be seen from Table 4 that with the increase of the true density of the microspheres, the bulk density increases regularly too, and the average particle size of the corresponding type of sample decreases, which is consistent with the results in Table 3.

3.4. True density
In addition to the floating rate, the true density is a major indicator to judge the level of microspheres, which is of great guiding value to the production and application of hollow glass microspheres. According to SYT 5504.6-2009, the true density of microspheres should be less than 0.80g/cm³ (usually in the range of 0.12–0.70g/cm³). A proper amount of microspheres are weighed by a precision electronic balance, and then safely placed in a cover-tighten true density analyzer; Input the sample’s weight, then operate the equipment according to its prompts, to test the true density of the microspheres, and the results are shown in Table 5.

Table 5. True density of different types of hollow glass microspheres.

| Type of microspheres | Test I (g/cm³) | Test II (g/cm³) | Test III (g/cm³) | Average (g/cm³) |
|----------------------|----------------|-----------------|-----------------|-----------------|
| HL20                 | 0.2069         | 0.2084          | 0.2077          | 0.2076          |
| HL40                 | 0.4076         | 0.4038          | 0.4056          | 0.4050          |
| HL60                 | 0.6076         | 0.6088          | 0.6095          | 0.6086          |

• According to people’s experiences, if the true density of microspheres fluctuates too obviously, the experience of the downstream users of this material will be unpleasant. It can be seen from Table 5 that the three test results of any type of the microspheres fluctuate in a reasonable range (±0.02g/cm³); Besides, the lower the microspheres’ true density is, the lighter-weight they will be with the same volume. If the hollow glass microspheres are used in other mature substrate materials, the weight-reduction of that material would be more effectively realized.

3.5. Compressive strength (Crushing rate)
As one of the most important physical properties of many materials, compressive strength greatly affects the application field of hollow glass microspheres. Test the compressive strength (Crushing rate) of different types of microsphere samples by the equipments and methods mentioned in “Section 2: Experiments”, and the experimental results are shown in Table 6.
According to JCT 1042-2007, cylindrical compressive strength of the vitrified small balls should be greater than 200KPa. According to this data, under the corresponding air pressure, the crushing rate that can reflect the compressive strength of hollow glass microspheres should be less than 20%. It can be seen from Table 6 that under different air pressure, the average crushing rates of different types of microspheres are all about 13%, and the three test results fluctuate in a reasonable range.

Table 6. Crashing rate of different types of hollow glass microspheres.

| Type of microspheres | Air pressure (MPa) | Test I (%) | Test II (%) | Test III (%) | Average (%) |
|----------------------|-------------------|------------|------------|-------------|-------------|
| HL20                 | 3.45 (500psi)     | 12.32      | 13.25      | 10.86       | 12.14       |
| HL40                 | 27.58 (4000psi)   | 11.25      | 13.45      | 12.56       | 12.42       |
| HL60                 | 82.74 (12000psi)  | 13.51      | 14.56      | 12.21       | 13.42       |

4. Conclusion and Prospect

The new type of hollow glass microspheres prepared in our method show regular morphology and uniform particle size, the floating rate of them is higher than 97%, the bulk density is 0.1~0.4g/cm³, the true density is 0.20~0.65g/cm³ and fluctuates in a reasonable range; besides, the compressive strength is so good that microspheres are barely broken.

To sum up, this new type of hollow glass microspheres are low in density and high in strength, which are able to resist high temperature and acid / alkali corrosion, and show low thermal conductivity and nice electrical insulation. Hollow glass microsphere is a cross-functional frontier material that can be added to a variety of substrate materials to improve their performances (such as weight-reduction) and environmental benefits (such as building thermal insulation). Especially under the background of striving to achieve the "carbon peak" and "carbon neutralization" goal, researching and promoting the application of multi-specification hollow glass microspheres in building paints, industrial coatings, cementing slurry, sealants and adhesives, modified plastics, rubber-based products, epoxy tooling board, emulsion explosives, artificial stones and other fields, is of great strategic significance to carbon emission reduction, chemicals storage, aviation and aerospace, petroleum and natural gas mining, 5G communications and military industry for our country.

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