Preparation of high-density fused quartz ceramics based on a J₂-optimality mixed orthogonal method

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Abstract: A method for obtaining high-performance fused silica ceramics was investigated in this work. An advanced experimental method was used to prepare green bodies. The optimal experimental scheme was deduced using the hybrid orthogonal experiment method of J₂-optimality. The solid-phase content, the amount of dispersant, the pH and the milling time were used as variables. The effects of various factors related to the processing of fused silica ceramics on the performance of the crucible were studied. The structure and properties of the samples were characterized by using a universal testing machine, a scanning electron microscope, an electron density meter and an X-ray diffractometer. The results show that a solid-phase content of 65 wt%, a pH of 5, a dispersant content of 2.5 wt% and a milling time of 15 led to a green body with a flexural strength of 18.5 MPa and a bulk density of 1.91 g/cm³, resulting in ceramics with improved mechanical properties.

1. Introduction
Like many other ceramic products, fused silica ceramics can not currently meet the requirements for use in a wide range of applications, however, fused silica ceramics show a strong potential for the development of ceramic materials. The preparation of fused silica ceramics by the traditional grouting moulding process leads to a lengthy production cycle and high production costs. Furthermore, the particles are segregated during the grouting process. The obtained green body exhibits layering especially in the case of large, thick-walled products, which leads to uneven structure and performance. Therefore, to meet the strength (bending strength greater than 40 MPa) and overall uniformity requirements of some special applications, the strength and uniformity of quartz ceramics must be improved to reduce the number of generated defects and increase reliability.

2. Experimental procedure

2.1 Materials preparation
In this work, the water-based gel system was selected with acrylamide (AM) as the monomer, N,N-methylenebisacryl (MBAM) as the crosslinking agent, and ammonium persulfate as the initiator.

In the initial stage of slurry preparation, HEMA and TMPTA were added to a certain amount of deionized water in a certain proportion. The fused silica powder was then mixed into a premix, the mixture was ball milled, and citric acid was added to adjust the pH. Finally, the appropriate amount of
the dispersant was added. In the coagulation moulding process, the slurry was vacuum degassed and APS was added to the mould at room temperature; After drying, sintered samples were first degreased and then placed in a microwave sintering furnace. Different sintering temperatures and different heating rates were used; the sintering time was 3 h. The entire experimental process is shown in Fig.1:

![Fig.1 Flow chart of the gel-casting process](image)

2.2 Testing method
Because of the unequal experimental effect of each factor, a reasonable orthogonal experiment scheme was obtained by optimizing the calculation according to an orthogonal experiment and the orthogonality. The method used in this experiment is based on J₂-optimality hybrid orthogonal experiment, and the basic principle is described as:

\[
O(x_i, x_j) = \sum_{k=1}^{m} \delta(X_{ik}, X_{jk})
\]

where \(x_i\) and \(x_j\) are two rows in the experimental design (i.e., two experiments); \(m\) is the number of factors, and if \(x = y\), then \(\delta(x, y) = 1\), otherwise, \(\delta(x, y) = 0\). Thus, the degree of similarity of the two experiments is evaluated.

The orthogonality of the entire experiment is defined as:

\[
J_2(d) = O(x_i, x_j) \quad 1 \leq i, j \leq n
\]

The solid-phase content, the pH, the amount of dispersant and the milling time were used as the influencing factors, and the viscosity of the slurry was used as the reference index. The factors and levels of the orthogonal test design were shown in Table 1. The orthogonal test scheme and the bulk density values of the samples are shown in Fig. 2, and the results of the orthogonal test are shown in Table 2.

| Table 1. Orthogonal experimental factors and levels |
|---------------------------------|--------|--------|-----------------|--------|
|        | Level | Solid content (wt%) | pH value | Amount of dispersant (wt%) | Milling time (h) |
|--------|-------|----------------------|----------|-----------------------------|-----------------|
| 1      | 1     | 50                   | 3        | 1.5                         | 10              |
| 2      | 2     | 55                   | 4        | 2.0                         | 15              |
| 3      | 3     | 60                   | 5        | 2.5                         | 20              |
| 4      | 4     | 65                   | 6        | 3.0                         | 25              |
(1) Range method analysis

The results of the range method analysis are shown in Table 2:

Table 2. Results of the range method analysis

| Factor          | Factor A Solid-phase content (wt%) | Factor B pH value | Factor C Dispersant | Factor D Milling time (h) |
|-----------------|-----------------------------------|-------------------|---------------------|--------------------------|
| $\sum_1/K_i$    | 14.33                             | 43                | 43.75               | 40.5                     |
| $\sum_2/K_i$    | 26.67                             | 30.25             | 37.75               | 45.5                     |
| $\sum_3/K_i$    | 44                                | 55.5              | 47.25               | 42.75                    |
| $\sum_4/K_i$    | 86.67                             | /                 | /                   | /                        |
| $R$             | 72.34                             | 25.25             | 9.5                 | 5                        |

$R$ represents the range method, which is equal to the difference between the maximum and minimum values for each of the corresponding factors.

The results in Table 2 indicate that the order of significance of the orthogonal experiments is A, B, C, D (i.e., solid content, pH value, dispersant, and milling time). A trend graph based on the magnitude of the $\sum_i/K_i$ values was constructed (Fig. 3) to enable a more intuitive selection of the optimal value of each factor:
(2) Variance method analysis

The results obtained using the orthogonal test calculation method are simple, intuitive and show a small range. However, the accuracy of the judgment effect is poor and the experimental error cannot be estimated. A large experimental error can lead to an inaccurate estimation, it often may cause miscarriage of justice. Therefore, we analysed the variance for validation after the analysis of the range method.

We first calculate the sum of squares prior to the variance analysis:

\[
SS_T = \sum_{i=1}^{n} (T_i - \bar{T})^2
\]

where \(\bar{T}\) is the mean of all experiments; \(n\) is the total number of experiments; and \(T_i\) is the \(i\)th experimental value. We then calculate the square sum of the factor effects of A, B, C, and D factors: \(SS_A\), \(SS_B\), \(SS_C\), \(SS_D\):

\[
SS_A = \sum_{i=1}^{A} k_{i A} \left( \sum_{iA} - \bar{T} \right)^2
\]

After calculating the square of the factor effect of each factor, the error squared sum \(SS_e\) is calculated as follows:

\[
SS_e = SS_T - SS_A - SS_B - SS_C - SS_D
\]

where \(LA\) is the number of levels of factor A; \(\sum_{iA}\) is the sum of the experimental values at the level of factor A; \(k_{iA}\) is the number of experiments at the level of factor A.

After calculating the sum of squares of squares and \(SS_T\) and the effect of each factor, we can continue to calculate the mean square error and \(F\) test of each factor.

\[
MSE_A = \frac{SS_A}{f}
\]
\[ F = \frac{MSE_A}{MSE_e} \]  

(7)

Table 3. Results of the variance method analysis (1)

| Source of variance | SS    | f    | MSE   | F     | Critical value | Significance |
|--------------------|-------|------|-------|-------|----------------|--------------|
| A                  | 8988.9| 3    | 2996.3| 17.2  | \( F_{0.01}(2, 2) = 9^* \) | (*)          |
| B                  | 1275.2| 2    | 637.6 | 3.7   | \( F_{0.01}(3, 2) = 9^* \) | /            |
| C                  | 184.7 | 2    | 92.3  | 0.5   | \( F_{0.01}(2, 2) = 1^* \) | /            |
| D                  | 50.2  | 2    | 25.1  | 0.1   | \( F_{0.01}(3, 2) = 1^* \) | /            |
| MSE\(_e\)          | 348   | 2    | 174   | /     | /              | /            |

A comparison of the F values and the critical value does not indicate that they significantly influence each factor. The influence of A is largest, followed by (*) . To improve the accuracy of the analysis, we only considered the factor A because factors B, C, D are incorporated into the error. Thus, \( S_g + S_c + S_D + S_e = 1275.2 + 184.7 + 50.2 + 348 = 1858.1 \)

Table 4. Results of the variance method analysis (2)

| Source of variance | SS    | f    | MSE   | F    | Significance |
|--------------------|-------|------|-------|------|--------------|
| A                  | 8988.9| 3    | 2996.3| 12.89| (**)         |
| MSE\(_e\)          | 1858.1| 8    | 232.3 | /    | /            |
| T                  | 10847 | 11   | /     | /    | /            |

\[ F_{0.01}(3, 8) = 9.6 ; \quad F_{0.01}(3, 8) = 7.59 \]

A comparison of the F value and the critical value reveals that factor A is the significant factor. In this case, the order of influence is ABCD, and the selected optimal scheme should be \( A_4B_3C_3D_2 \). That is, the solid-phase content, pH, amount of dispersant, and the milling time should be 65\%, 5, 2.5\%, 15 h respectively.

On the basis of these two methods—the range method and the variance method—we observe that the four factors have a certain influence on the green body density with the solid-phase content having the greatest influence on the density of the green body, followed by the pH and the dispersant content, and with the milling time having the smallest effect; This order of influence of the factors is attributed to the density of ceramic materials and the solid-phase content of their slurry being closely related. To ensure high strength of the body minimize product shrinkage, and avoid deformation, cracking and other defects, the experimental program should be designed to improve the slurry solid-phase content of the powder as much as possible; We deduced that the optimum conditions are: a solid-phase content of 65 wt\%, a pH equal to 5, a dispersant content of 2.5 wt% and a milling time of 15 h.

3. Results and discussion

3.1 Scanning electron microscopy analysis
It can be seen from Figure c, when the solid content of 65%, the sample appeared a lot of larger particles. This shows that in this case there is a liquid phase, the product particles in close contact between the sintering densification uniform, While the other two groups of particles are not close, more pores, so that the strength of burning products, hardness are affected.

3.2 X-Ray Diffraction analysis

It can be concluded from Fig. 4 that the crystallization peak of the fused silica ceramic sample is not much different when the sintering temperature is at 1150 ℃ and 1200 ℃, and there is not much crystal quartz. But the sintering temperature rose to 1250 ℃, the square quartz crystal peak is more obvious, and it will affect the use of fired products performance. Under these conditions, the optimum sintering temperature was chosen to be 1200 ℃.

3.3 Flexural strength test
With the increase of the solid content, the flexural strength of the green body first increases, and reaches the highest value when the solid content is 65%, and then decreases. The reason for this is that the strength of the green body is improved and the strength of the green body is enhanced as the solid content increases. However, as the solid content is further increased, the total amount of liquid to be adsorbed increases and the free-flowing liquid becomes less. At the same time, the distance between the particles in the slurry becomes smaller, the organic chains adsorbed on the surface of the particles are overlapped with each other, so that the movement between the particles is difficult and the flow ability is deteriorated. These are not conducive to the slurry removal and pouring molding, so the intensity decreases.

4. Conclusion
There are many influencing factors of coagulation molding process, and the previous experiments are based on single factor optimization experiment method, control variables to arrange the experiment, making the experimental workload is heavy and heavy. In this experiment, the orthogonal experiment was designed to obtain the parameters of high solid phase and low viscosity slurry. The solid phase content, pH value, dispersant dosage and milling time were used as influencing factors.

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