Preparation of iron tailings glass-ceramics by sol-gel method

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Abstract. For the preparation of glass-ceramics by iron tailings, the sintering and melting methods have been used in the past, but the two methods are short of high energy consumption. In this test, the sol-gel method has been adopted. Because the sol-gel method requires high purity to prepare raw materials, and there are many impurities in iron tailings, which is inconsistent with the preparation requirements of sol-gel method. Therefore, in this experiment, useful elements in iron tailings were extracted. Iron tailings were obtained by thermal-alkali reaction, and Fe was obtained by acid reaction, so as to prepare Ca-Mg-Al-Si system glass-ceramics. After the preparation of sol-gel, the basic glass was obtained, and after nucleation and crystallization, the microcrystalline glass whose main phase was diopside was obtained.

1. Introduction

Microcrystalline glass, also known as glass ceramics, is a new kind of inorganic non-metallic material[1-2]. It is a new material obtained by making full use of the advantages of glass in thermodynamics. It is a new composite phase material composed of micro crystal and residual glass.[3-4]

According to incomplete statistics, more than 10 billion tons of tailings and waste rock are discharged every year around the world. At present, the comprehensive utilization rate of China's tailings is less than 10%, and the amount of iron tailings deposited is as high as over 1 billion tons. There are problems such as occupying a large amount of cultivated land, wasting resources, polluting soil, water and air. Therefore, the comprehensive recycling and utilization of iron tailings has been widely concerned by the whole society[5]. The raw materials for the preparation of glass-ceramics can be pure chemical reagent, tailings, steel slag, quartz sand, glass waste, etc. The application of industrial wastes not only reduces the cost of preparation, but also reuses waste such as tailings, reduces the pressure of waste accumulation and protects the ecological environment[6]. The preparation of sol-gel requires high purity of raw materials and high purity of chemical reagent but high cost. In this experiment, tailings were selected to neutralize the raw material cost. Ethyl orthosilicate, aluminum nitrate, calcium oxide and magnesium oxide were selected as the basic materials. Ethanol as
a solvent, nitric acid as a catalyst and reagent for removal of impurities. Sodium hydroxide is used as raw material for thermal-alkali reaction.

As there are many impurities in iron tailings, sol-gel method is not suitable. Generally speaking, sintering and melting methods are mainly used in the preparation of glass-ceramics from iron tailings. In this experiment, some treatment of iron tailings was carried out to purify the iron tailings, so that they could be used in the sol-gel method \cite{7}. The microcrystalline glass structure is compact, but there is cracking and shrinkage in sol gel process. In order to prevent this adverse factor, dry cracking control agent is commonly used. In this experiment, the method of grinding basic glass into powder is adopted\cite{8}.

### 2 Extraction of useful elements from iron tailings

In this experiment, Ca-Mg-Al-Si microcrystalline glass was prepared by sol-gel method, and the specific process is shown in figure 1.

![Fig.1 Experimental procedure](image)

The main components of iron tailings are SiO$_2$, Fe$_2$O$_3$, and Al$_2$O$_3$, CaO and MgO. The content of SiO$_2$ was the highest. According to the designed Ca-Mg-Al-Si microcrystalline glass, the maximum amount is Si element. Fe$^{3+}$ can be used as a nucleating agent. Considering the purity of raw materials required by sol-gel method, the elements in iron tailings should be extracted first to realize the efficient use of iron tailings\cite{9,10}. The sodium silicate solution was prepared by reaction with acid and alkali, and used as the silicon source to prepare the glass.

#### 2.1 Iron tailings react with acid

The main chemical composition of the tailing raw material selected in this experiment is shown in table 1.

| Components | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO | Na$_2$O |
|------------|--------|-------------|-------------|-----|-----|--------|
| Mass percent/% | 68.58  | 2.69        | 13.81       | 3.68 | 4.98 | 0.36   |

#### 2.1.1 Different acids react with iron tailings

HF, HCl, H$_3$PO$_4$, HNO$_3$ and H$_2$SO$_4$ were mainly considered in this experiment. After passing through 200 mesh sieves, the iron tailings were weighed and added with over acid. After reaction for a period of time, filter, wash, dry, weigh the quality of filter residue, and conduct feasibility analysis. It is found that the dissolution of SiO$_2$ in iron tailings by HF is feasible in thermodynamics, but the actual reaction rate is extremely slow, which is not feasible from the point of view of kinetics. Other acids can only react with metal oxides in iron tailings, not with SiO$_2$. It is found that nitric acid is easy to be decomposed, and the decomposition product is poisonous, and has little contribution to the actual reaction. Although sulfuric acid can react, SO$_4^{2-}$ is an impurity ion in the preparation of sol and gel, and is difficult to remove impurities. Other acids can only react with metal oxides in iron tailings, not with SiO$_2$. As FeCl$_3$ can be used as crystal nucleating agent, hydrochloric acid is finally used to acidify iron tailings.

#### 2.1.2 Reaction time with acid

First, 5g iron tailings were weighed and added with excessive dilute hydrochloric acid.
acid to react at room temperature for different times. Then the quality of filter residue was determined by filtration, washing and drying. Finally, formula (1) is used to calculate the dissolution rate. The experimental results are shown in table 2.

It can be seen from table 2 that dissolved percent of iron increases with the prolonged reaction time with acid at room temperature. However, when the time exceeds a certain limit, the dissolved percent starts to grow slowly, which can be regarded as the total dissolution. In this experiment, Fe$^{3+}$ in iron tailings was extracted by reacting 2 days with acid at room temperature.

\[ X = \frac{m_0 - m_1}{m_0} \times 100\% \]  

\( m_0 \) - iron tailings mass before reaction with acid;  
\( m_1 \) - iron tailings mass after reaction with acid.

### Table 2 Dissolved percent of Fe reacted with acid at room temperature

| Time/h | 2   | 4   | 6   | 8   | 24  | 48  |
|--------|-----|-----|-----|-----|-----|-----|
| Dissolved percent/% | 47.6 | 60.1 | 68.4 | 74.5 | 78.6 | 80.3 |

2.2 Iron tailings react with alkali.

In this experiment, the reaction of high temperature with alkali was used to extract Si elements. Firstly, proper amount of iron tailings (mainly SiO$_2$) after reaction with acid was weighed, and a certain amount of NaOH was added. And then mixed evenly, the mixture placed into the muffle furnace heated to 500°C, and the heat preservation for a period of time. Next, the mixture needs to be poured into a certain amount of distilled water and heated to stir for a while. At last, the sodium silicate solution was obtained by filtration and washing.

#### 2.2.1 Effect of holding time on the dissolution rate of SiO$_2$.

Taking 5g iron tailings after reacting with acid and 10gNaOH, and mixing them thoroughly. Put them at the 500°C, heated respectively in 20, 30, 40, 50, 60 minutes, immediately pouring 190 ml water. We will put the mixture at 70°C, heated and mixed 30 min, and then filtered. Equation (2) is used to calculate the influence of the heat preservation time on dissolved percent of Si. The experimental results are shown in table 3 and figure 2.

\[ X = \frac{c_0 - c_1}{c_0} \times 100\% \]  

\( c_0 \) - iron tailings mass before alkali reaction;  
\( c_1 \) - iron tailings mass after alkali reaction.

### Table 3 Dissolved percent of silicon in iron tailings at different time of heat preservation

| Time of heat preservation /min | 20  | 30  | 40  | 50  | 60  |
|-------------------------------|-----|-----|-----|-----|-----|
| Dissolved percent/%           | 26.17 | 30.15 | 34.47 | 39.68 | 39.93 |

![Fig. 2 Dissolved percent curves of silicon in iron tailings at different heat preservation times](image)
It can be seen from the figure that when the heat preservation time is relatively short, dissolved percent of silica increases with the heat preservation time. However, dissolved percent of silica does not change much with the prolonged heat preservation time, and tends to be stable.

2.2.2 The influence of water consumption (NaOH concentration) on dissolved percent of SiO\(_2\). Firstly, taking 5g iron tailings after reacting with acid, and mixing well with 10gNaOH. Secondly, heated 50 min at 500 °C, and were respectively put into the 240, 190, 90, 57, 40ml (NaOH concentration were 4%, 5%, 10%, 15%, 20%) water. Thirdly, the mixture was stirred and heated 30min at 70°C and then filtered. Finally, it was found that the difference of water consumption resulted in dissolved percent of Si. The experimental results are shown in table 4 and figure 3.

| The concentration of NaOH /% | 4        | 5        | 10       | 15       | 20       |
|-----------------------------|----------|----------|----------|----------|----------|
| Dissolved percent/%         | 26.69    | 39.69    | 39.36    | 38.15    | 35.21    |

Fig. 3 Dissolved percent curves of silicon with different NaOH concentrations

According to the figure, when sodium hydroxide concentration is low, Si dissolution percentage increases with the increase of mass fraction of NaOH concentration. When sodium hydroxide concentration is high, Si dissolution percentage decreases with the increase of mass fraction of NaOH concentration. When the concentration of sodium hydroxide solution is large, the viscosity of the solution system increases, thus reducing the reaction rate.

2.2.3 The influence of temperature on dissolved percent of SiO\(_2\) during stirring. Firstly, taking 5g iron tailings after reacting with acid, and mixing well with 10gNaOH. Secondly, heated 50 min at 500 °C, and were respectively put into 190ml water. Thirdly, the mixture was stirred and heated 30min at 30, 50, 70, 90, 100 °C, and then filtered. Finally, dissolved percent of Si can be calculated at different temperatures. The experimental results are shown in table 5 and figure 4.

| Temperature/℃ | 30 | 50 | 70 | 90 | 100 |
|---------------|----|----|----|----|-----|
| Dissolved percent/% | 33.39 | 35.92 | 39.68 | 39.23 | 35.21 |

Fig. 4 Dissolved percent curves of SiO\(_2\) at different temperatures when stirred
The temperature of solution system has great influence on the reaction rate and process. Basically, as the temperature of the solution increases, the speed of the reactant molecules in the solution increases. The number of effective collisions per unit time increases and the reaction rate increases. By the figure that, as the temperature increases, Si dissolution percentage reached the maximum at 70°C. But when the temperature exceeds 70°C, dissolution percentage decline. The reason is that, although the reaction speed increases from a thermodynamic perspective, the viscosity increases as the temperature increases. From the kinetic point of view, the viscosity inhibits the reaction rate, and dissolved percent decreases.

### 2.2.4 Influence of different stirring time on dissolved percent of SiO2.

Firstly, taking 5g iron tailings after reacting with acid, and mixing well with 10gNaOH. Secondly, heated 50 min at 500 °C, and were respectively put into 190ml water. Thirdly, the mixture was stirred and heated 30,40,60,80min at 70°C, and then filtered. Finally, dissolved percent of Si at different stirring time can be calculated. The experimental results are shown in table 6 and figure 5.

**Table 6** Dissolved percent of SiO2 at different stirring time

| Stirring time/min | 20 | 30 | 40 | 60 | 80 |
|-------------------|----|----|----|----|----|
| Dissolved percent/% | 34.48 | 39.68 | 39.76 | 40.13 | 40.22 |

**Fig. 5** Dissolved percent curves of SiO2 at different stirring time

The dissolved percent of silicon increased with the increase of stirring time. It did not change significantly after 60min. The reason was that with the increase of reaction time, the concentration of NaOH decreased, the content of SiO2 decreased, the reaction speed decreased, and the reaction was basically completed. The reason is that with the increase of reaction time, the concentration of NaOH decreases and the content of SiO2 decreases.

The reaction rate is reduced and the reaction is basically completed. In summary, when iron tailings react with alkali. Under the following conditions: 500 °C heating 50 min, pour 190 ml water, heated at 70°C and stirred 60 min., Then you can filter. The dissolved percent of SiO2 in iron tailings is higher.

### 3 Basic glass was prepared by sol-gel method

According to table 7, the CaO, FeCl3 and MgO needed can be weighed. Add the nitric acid to dissolve and form the calcium nitrate solution and magnesium nitrate solution. Since Al2O3 did not react thoroughly with acid at room temperature, Al(NO3) 3·9H2O was substituted for Al2O3. Al(NO3) 3·9H2O is highly soluble in water, and the weighed Al(NO3) 3·9H2O was slowly added to the solution.

**Table 7** Base glass chemical composition

| Components | SiO2 | Al2O3 | CaO | MgO | FeCl3 |
|------------|------|-------|-----|-----|------|
| Mass percent/% | 55   | 5     | 22  | 15  | 3    |

As it is difficult to prepare the gel from a single sodium silicate, ethyl orthosilicate is used instead of 30% sodium silicate. According to the molar ratio of TEOS: H2O=1:1, TEOS: ethanol =1:3 and TEOS: HNO3=1:0.04, H2O, ethanol, nitric acid and TEOS were respectively weighed. After mixing them, they...
were stirred for 1h at room temperature to complete the pre-hydrolysis of ethyl orthosilicate. In the prepared sodium silicate solution, ethanol was added according to the molar ratio of 1:3, and HNO₃ was added to adjust the pH value to about 10.5. Let it sit for a while. The prehydrolyzed ethyl orthosilicate was added to the salt solution. After that, sodium silicate solution was added under the effect of magnetic stirring, and the pH value of the solution system was maintained at 8-9 to form the gel. Place the gel in 80 °C oven aging for 6 h. A clear homogeneous dry gel was obtained. DSC detection was performed and the DSC figure was obtained as shown in figure 6.

![Fig. 6 The DSC test chart of the sample](image)

![Fig. 7 XRD diffraction pattern of the sample](image)

**4 Heat treatment**

It can be seen from the graph that a tiny endothermic peak at 80 °C. The ethanol in the dry gel may evaporate from the system. There is a larger endothermic peak appears at 120 °C. It is mainly the elimination of the combined water in the system. A heat absorption valley appears at 720 °C. It could be that the glass phase begins to nucleate. A larger exothermic peak appears at 850 °C. This crystallization exothermic peak is significant. However, there is a large heat absorbing valley before the peak, which is not nucleated heat absorbing peak. It is caused by the softening deformation, microstructure rearrangement and heat absorption of the products in the heat treatment process. So the actual crystallization temperature needs to be higher than that.

Therefore, in the process of heat treatment need to slowly heat up to 120 °C, and then heat preservation for a period of time. Ensure all organic solvents and water are drained. It quickly heats up to 830 °C and keeps 2 h. Then, it needs to raise the temperature to 950 °C, and wait for 2 h. The glass samples can be obtained by cooling them to room temperature.

**5 Microscopic detection**

After the sample is cooled, the samples were taken out and analyzed by XRD and SEM.

1 X-ray diffraction analysis (XRD)

The XRD diffraction pattern of the sample is shown in figure 7.

2 Scanning electron microscope analysis (SEM)

The sample of microcrystalline glass was corroded with 1% HF solution for 2 min. Then wash it, dry it and spray gold. Its microstructure was observed by scanning electron microscopy. The SEM diagram of the sample is shown in figure 8.
Fig. 8 SEM diagram of the sample

It can be seen from Fig 8 that it meets the requirement of microcrystal size. Diopside crystal is short columnar, belongs to monoclinic system, complete crystal is rare, cross section is similar to square, aggregate can be columnar, dense block or radial shape. The morphology of the precipitated crystals was observed to be columnar or lamellar, which was consistent with the morphology of diopside crystals. At the same time, the analysis results are consistent with the previous XRD analysis results.

6 Conclusion
(1) When iron tailings reacted with acid, made it react at room temperature for 2d. The iron elements in iron tailings were dissolved more under this condition.
(2) When iron tailings reacted with alkali, the way to dissolve more silicon is that the mixture heated at 500 °C for 50min, then immediately poured 190 ml water, finally heated and stirred at 70 °C for 60 min.
(3) Through XRD analysis of the glass, it can be known that the samples are mainly diopside. The microscopic morphology seen by SEM is consistent with XRD analysis.

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