Crystallization kinetics of diopside glass ceramics

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Abstract—The glass ceramics were prepared by a reaction crystallization and sintering method using waste glass powder and a crystallizing promoter with a main crystal phase of the enstatite. X-ray diffraction(XRD), Scanning electron microscope(SEM), Differential scanning calorimetry(DSC), etc. were used to characterize its phase composition, morphology, and thermal decomposition process. The results show that the main crystal phase of the prepared glass ceramics was diopside and the secondary crystal phase was albite. The precipitated crystals were rod-shaped with a maximum length of about 7 μm and a diameter of about 0.6 μm. Diopside glass ceramics were measured with different heating rates, and it was found that the peak temperature increased with the heating rate. The Kissinger method was used to calculate the crystallization kinetics of diopside glass ceramics, and the crystallization activation energy was 872.4 kJ\cdot mol\textsuperscript{-1}.

1. INTRODUCTION
Using reaction crystallization to prepare glass ceramics is a new technology in recent years\cite{1-3}. It is a type of polycrystalline solid material prepared through low-temperature reaction sintering\cite{4-5}. The glass ceramics may be fabricated through a direct reaction between crystallization promoter and glass powders, so that the cost can be reduced greatly and the processing can be simplified because waste glass can be utilized.

Diopside has interwoven structure, that is, it contains chain structure and other structures (such as frame structure). The slag glass ceramics with diopside as the main crystal phase have good mechanical properties and chemical stability, and the crystallization ability of pyroxene is high, the crystallization process tends to be fully the same crystal, and various cations are easy to form a lattice, so the pyroxene glass ceramics can be synthesized by using slag of various components. Diopside based glass ceramics have many excellent properties, and the sources of raw materials are wide, and the preparation process is simple, which has become a hot spot of this year's research.

At present, many scholars at home and abroad use industrial raw materials and waste residue to prepare diopside glass ceramics with excellent hardness and strength, and explore its heat treatment mechanism and crystallization mechanism. Toya\cite{6-7} have been prepared glass ceramics containing diopside and calcium feldspar by mixing different wastes with Kaolin Tailings. Tulyaganov\cite{8} has made glass ceramics with three crystal phases, i.e. magnesia feldspar, calcium feldspar and diopside, from industrial raw materials.
Karamanov[9] have been prepared the diopside and wollastonite glass ceramics, it had Young modulus of 100 GPa and high bending strength of 130 MPa after only 1 min sinter-crystallization at 900 °C. Qian[10] have been reported the diopside-based glass ceramics can be synthesized by using municipal solid waste fly ash. Its process was as follows: melting at 1500 °C for 30 min, nucleating at 730 °C for 90 min, and crystallization at 880 °C for 10 h.

The process of glass crystallization can be described from two aspects of thermodynamics and dynamics. Compared with crystal, glass in amorphous state has higher thermodynamic energy, and there is always a tendency of crystallization. From the point of view of dynamics, the process of glass to crystal transition becomes slow in time due to the high degree of melting or the high activation energy of ion migration at high temperature, which is common under the natural cooling speed it is too late for the melt to transform the structure to form glass. Therefore, it is necessary to heat treat glass at a suitable temperature for a long time to obtain new materials such as microcrystalline glass.

In the present paper, the diopside glass ceramics were investigated by XRD, SEM and DSC. The crystallization kinetics of diopside glass ceramics were characterized by Kissinger method, and the apparent activation energy of crystallization process have been determined.

2. EXPERIMENTAL

2.1. Preparation of diopside glass ceramics

In this experiment, the main components of the waste glass were as follows (by mass percentage wt%): 71.8 SiO₂, 12.9 Na₂O, 9.5 CaO, 4.6 MgO, 0.9 Al₂O₃, 0.3 K₂O. The waste glass was cleaned, dried, crushed, and sieved to yield powders (200 mesh) in size.

The crystallization accelerator was a self-made material. The specific process was as follows: the kaolin, talc, ZnO and BaCO₃ were mixed evenly, then add water to make the blank, dry it at room temperature until most of the water evaporates, heat it in the resistance furnace to 1100 °C for two hours, let the sample cool at the furnace, crush the calcined sample, put it into the ball mill for 10 hours, and pass the 120 mesh sieve.

The glass powder was mixed with 30% crystallization promoter, added a little binder, then compacted under a uniaxial pressure of 7.5 MPa, and sintered at 1000 °C for 2 hours to obtain the glass ceramics samples.

2.2. Characterization of diopside glass ceramics

The crystalline phase of the crystallization promoter and the glass ceramics was characterized by a x-ray diffraction (2θ=10~70°, Empyrean) with Cu Kα radiation (λ=0.15406 nm). The morphology of the glass ceramics were observed by a scanning electron microscope (JSM-6360 LV). The differential scanning calorimetry was carried out with mixed raw materials of about 10 mg in a temperature range from 30 ℃ to 1000 ℃ at scanning rates of 5°C /min, 10°C /min, 15°C /min, 20°C /min by a SDT 2960 Simultaneous DSC-TGA analyzer.

3. RESULTS AND DISCUSSION

The XRD pattern of the crystallization promoter (Fig.1a) was indexed to the enstatite (MgSiO₃, JCPDS 19-768) and cordierite (Mg₄Al₂Si₅O₁₈, JCPDS 02-0646), in it the main crystalline phase was enstatite. It can be seen from Fig.1b that after sintering at 1000 °C the crystalline phase in the glass ceramics was transformed into diopside (CaMgSi₂O₆, JCPDS 41-1370) and albite (NaAlSi₃O₈, JCPDS 19-1184), in it the main crystalline phase was diopside.

SEM was used to study the morphological characteristics of the diopside glass ceramics (Fig.2). It can be seen that a large number of rod-shaped crystals can be precipitated from the glass phase by adding a crystallization promoter, and the precipitated crystals were closely combined with the glass matrix. The longest crystal was about 7 μm and the diameter was about 0.6 μm.

Fig.3 was the infrared spectrum of diopside glass ceramics. The absorption peak at 1043 cm⁻¹ was caused by the asymmetric vibration of Si-O-Si, the absorption peak at 784 cm⁻¹ was caused by the
symmetric stretching vibration of Si-O-Si, the absorption peak at 637 cm\(^{-1}\) was caused by the symmetric stretching vibration of linear Si-O-Si in diopside, the absorption peak at 602 cm\(^{-1}\) was caused by the bending vibration of Si-O, and the absorption peak at 573 cm\(^{-1}\) was caused by the stretching vibration of Ca-O. The absorption peak of 469 cm\(^{-1}\) was caused by the bending vibration of O-Si-O.

Figure 1. XRD patterns of the crystallization promoter (a) and glass ceramics (b)

Figure 2. SEM photograph of the glass ceramics

Heterogeneous nucleation refers to the process of nucleation depending on the surface, interface, microcracks and other phase boundaries or the structural defects of the matrix. The existence of the interface reduces the interface energy of nucleation and the free energy of the whole nucleation process, which makes the heterogeneous nucleation easier to occur than the homogeneous nucleation.

There were inevitably some defects or impurities in the glass, which can provide a base for the crystal and make the crystal nucleus form on its interface. Therefore, the nucleation mode of the crystal nucleus in the glass ceramics was non-uniform. In order to create the conditions of non-uniform crystallization and to produce a large number of evenly distributed crystal nuclei in the glass melt, the nucleation and growth of glass can be controlled by selecting appropriate glass composition, nucleating agent and heat treatment system.

DSC was widely used in the study of solid phase transition kinetics, including glass ceramics. During the reheating process, glass will release energy and crystallize, and there was a corresponding exothermic peak on DSC curve. The results show that the peak temperature \(T_m\) of exothermic peak depends on the heating rate \(\alpha\). When \(\alpha\) increases the displacement of \(T_m\) to high temperature, the crystallization activation energy \(E\) of glass ceramics can be calculated according to the existing theoretical formula to understand the crystallization mechanism.
The data obtained from glass crystallization kinetics can be analyzed by using the JAM (Johnson-Mehl-Avrami) transformation equation of Johnson and Mehl et al. This deduces the basic formula of the Kissinger method was [11]:

\[
dlg\left(\frac{\beta}{T_m^2}\right) = \left(-\frac{E}{2.303R}\right)d\left(\frac{1}{T_m}\right)
\]

Fig. 4 showed the DSC curves of the samples heated in air at several heating rates of 5°C/min, 10°C/min, 15°C/min, 20°C/min. The temperature \(T_m\) of the crystallization peak of the glass ceramics was affected by the heating rate of DSC. When the heating rate was slow, the crystallization time of the glass ceramics was sufficient, and the crystallization could occur at a lower temperature, that was, the \(T_m\) was lower. The instantaneous transition rate was small, and the crystallization transition peak was relatively gentle. When the heating rate was faster, the crystallization temperature \(T_m\) of the glass ceramics increases, the instantaneous transition rate increases, and the crystallization heat peak was sharp.

The values of crystallization temperature (\(T_m\), \(1/T_m\) and \(\lg\beta/T_m^2\)) at different heating rates (\(\beta\)) were listed in Table 1. Based on these data, the crystallization kinetic curve of diopside glass-ceramics prepared by reactive crystallization was drawn.

Fig. 5 presents the changes of \(\lg\left(\frac{\beta}{T_m^2}\right)\) values for the \(T_m^{-1}\) at different heating rates. According to the Kissinger method, the value of \(E\) was obtained from the slope of the straight line of \(\lg(\beta/T_m^2)\) versus \(1/T_m\). The calculated value of \(E\) was 872.4 kJ/mol. The correlation coefficient of the straight line was 0.9963, indicating that it had a good linearity.

The transformation of glass into crystal includes two factors: thermodynamic and dynamic conditions. Based on the consideration of different influencing factors, there were two different views on the effect of crystallization activation.
energy. Generally speaking, the crystallization activation energy was the barrier to be overcome when the particles in the glass were adjusted to crystal. The crystallization activation energy was larger, the stability of the glass ceramics was higher.

The higher activation energy indicates that the diopside glass ceramics need more energy to realize crystallization. Previous studies on the activation energy of wollastonite glass ceramics prepared under the same conditions by using the Kissinger method show that the activation energy of wollastonite glass ceramics was only 261.9 kJ·mol⁻¹[12], so the glass ceramics was more prone to crystallization. The study on the crystallization kinetics of glass ceramics was helpful to understand the crystallization characteristics of different glass ceramics and lay a theoretical foundation for its further application.

### Table 1. Related Values Calculated by Kissinger Method

| $\beta$ (K·min⁻¹) | $T_m$/K     | $T_m^{-1}$/K⁻¹ | $\lg(\beta/T_m^2)$ |
|-------------------|-------------|---------------|--------------------|
| 5                 | 1223.177    | 8.175×10⁻⁴    | -5.4776            |
| 10                | 1231.965    | 8.117×10⁻⁴    | -5.1812            |
| 15                | 1237.596    | 8.080×10⁻⁴    | -5.0091            |
| 20                | 1243.196    | 8.044×10⁻⁴    | -4.8880            |

### 4. Summary

The diopside glass ceramics were prepared by reacting and sintering a crystallization promoter whose main crystal phase was enstatite with waste glass powder. The main crystal phase was diopside and the secondary crystal phase was albite. The precipitated crystals were rod-shaped and tightly bonded.
to the glass matrix. The longest crystal was about 7 μm and the diameter was about 0.6 μm. DSC tests were performed on the samples using heating rates of 5 °C/min, 10 °C/min, 15 °C/min, and 20 °C/min. The crystallization activation energy of diopside glass ceramics obtained by Kissinger method was 872.4 kJ·mol⁻¹.

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