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Mechanical and tribological properties of calcia–magnesia–alumina–silica-based glass–ceramics prepared by in situ crystallization

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Abstract

CMAS glass–ceramics were prepared with natural minerals and industrial slag based on the glass system of CaO–MgO–Al_2O_3–SiO_2. Mechanical and tribological properties of the glass–ceramics were investigated. Results show that the bending strength and the Vickers hardness of the material increased with the increase of crystallization temperature. A glass–ceramics with 12.35 GPa of hardness and 366 MPa of bending strength was obtained by nucleated at 840 °C for 1 h and crystallized at 960 °C for 1 h. The main phases of the glass–ceramics are wollastonite (β-$CaSiO_3$) and diopside ($CaMg(SiO_3)_2$). Friction coefficient of the material is located in the range 0.05–0.6, which is very related to the contact pressure and sliding speed. Under a contact pressure of 0.1 MPa, the friction coefficient is less than 0.1, showing a good self-lubrication. The specific wear rate of the material is in a value of 10^{-3} to 10^{-6} mm^3 $(N\,m)^{-1}$, depending on the test temperature and contact pressure. The wear rate is slowly increased from room temperature to 500 °C, then obviously decreased from 500 to 800 °C. It can reach to less than 10^{-5} mm^3 $(N\,m)^{-1}$ at 800 °C when the contact pressure is 0.1 MPa. Good wear resistance of the material is mainly depending on the ability to create plastic deformation and the critical yield stress to form microcracks.

Keywords: Glass–ceramics; Mechanical property; Friction and wear; Self-lubrication

1. Introduction

Glass–ceramics, as fine-grained polycrystalline materials prepared by in situ crystallization of special glass systems, have receiving wide applications for its advantages of high mechanical strength, good abrasion and corrosion resistance [1–3]. Especially CaO–MgO–Al_2O_3–SiO_2 (CMAS) glass–ceramics, which can be prepared by inexpensive natural minerals and industrial slag, have received great attention of environmentalists for its benefits of recycling of mineral resources [4–6]. Tulyaganov et al. [7] investigated the preparation of CMAS glass–ceramics with natural materials. Result indicates that CMAS glass–ceramics has good mechanical properties which will make these materials very attractive for industrial applications. Furthermore, many studies of CMAS glass–ceramics have been developed on processing schedules, crystallization kinetics and microstructures [8–10]. The results show that diopside, as the main crystals in CMAS glass–ceramics, is confirmed to contribute the mechanical strength, abrasion and corrosion resistance of the glass ceramics. However, no reports were founded on the friction and wear mechanism of CMAS glass–ceramics, especially on elevated temperatures. In this work, CMAS glass–ceramics were prepared using minerals and industrial slag as the major raw materials. The processing schedules for nucleation and crystallization, testing conditions on the mechanical and tribological properties of CMAS glass–ceramics were investigated.

2. Experiments

2.1. Preparation of glass–ceramics

The major starting materials are quartz, feldspar, calcite, dolomite and industrial slag. The chemical compositions of the

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Table 1
Compositions of natural minerals and Ignition loss

Materials	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	KNaO	Cr_2O_3	CrO_3	Ignition loss
Quartz	99.06	0.45	0.15	–	0.32	0.15	–	–	–	–
Feldspar	68.23	19.20	0.18	–	0.23	0.10	14.28	–	–	0.24
Calcite	–	–	0.12	–	55.46	0.12	–	–	–	44.06
Dolomite	–	–	0.16	–	31.68	20.35	–	–	–	47.93
Blast furnace slag	32–35	6–8	2–3	<0.5	36–38	12–14	–	–	–	–
Steel slag	8–10	2–3	24–28	15–18	35–38	6–8	–	–	–	–

materials are listed in Table 1. CaF_2, ZrO_2 and P_2O_5 are selected as the nucleating agents, which are introduced by fluorite, zircon, calcium phosphate, respectively.

Based on the eutectic compositions in the $CaO–Al_2O_3–SiO_2$ system and $MgO–Al_2O_3–SiO_2$ system [11], batch compositions were prepared in the following composition regions (in mass%): SiO_2 45–60:Al_2O_3 5–10:CaO 20–30:MgO 5–15. The raw materials were carefully weighted to form a batch of desired glass compositions. After thoroughly mixing, the batches were melted at 1350–1450 °C for 1–2 h in a Pt crucible and quenched in preheated graphite moulds for obtaining square glass samples with a size about 80 mm × 80 mm × 8 mm and specimens for wear tests with the special geometry as shown in Fig. 1. Then the glasses were annealed at 650–700 °C and cooled freely to room temperature. At last, nucleation and crystallization of the glasses were carried out under designed schedules of heat-treatment for obtaining fine-grained microstructure.

2.2. Characterization

Differential thermal analysis (DTA) measurements of powdered glasses were performed in a Netzsch STA449C calorimeter. Crystal phases of reheated samples were analyzed by X-ray diffraction (XRD) using Cu Kα radiation with a Siemens D5000 equipment. Scanning electron microscopy (SEM) investigations of the microstructure of the glass–ceramics were carried out using a JEOL JSM-5600LV electron microscope. The flexural strength was measured by the three-point bending method with a specimen size of 5 mm × 5 mm × 40 mm, span at 30 mm and loading speed at $9.8 \pm 0.1\,N\,S^{-1}$. The volume density was measured by Archimede's method. The Vickers hardness of the glass–ceramics was carried out by HX-1000 equipment.

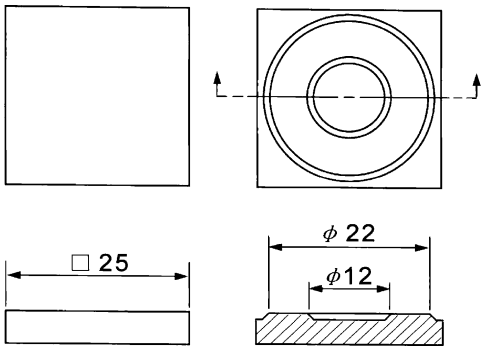

Fig. 1. Specimen geometry: (a) plate specimen; (b) annular specimen

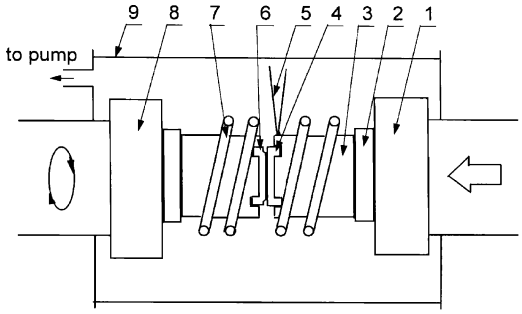

Fig. 2. Schematic of the test section of wear test rig: (1) stationary rod; (2) insulator; (3) sample holder; (4) plate specimen; (5) thermocouple; (6) annular specimen; (7) RF coil; (8) rotatory rod; (9) vacuum chamber.

Wear tests of the plate-on-plate type were conducted with a dry friction test rig as shown in Fig. 2. The annular specimen was rotated on the square specimen under a constant load provided by a servo-controlled pneumatic cylinder. Specimens were fixed on the stainless steel holders and heated by high-frequency induction coils to the testing temperature. The temperatures were determined by the thermocouple welded on the holder. The sliding speed was adjusted by the rotational speed of the ring specimen. The wear tests were conducted for a sliding distance of 200 m under constant conditions of temperature, contact pressure and sliding speed. The wear loss was measured as a change in mass of the specimens before and after test.

3. Results and discussion

3.1. Processing schedules of nucleation and crystallization

Fig. 3 shows the DTA curve of the glass sample. The transformation temperature is about 710 °C, while the crystallization temperature lies at 980 °C. Table 2 summarizes the properties of the glass–ceramics prepared under different nucleation and crystallization temperatures for 1 h. Bulk crystallization was observed in all glass samples. XRD patterns of the glass–ceramics are shown in Fig. 4. Crystallization appeared after reheated at 840 °C. When the glass nucleated at 840 °C and crystallized at 960 °C, the major crystals are wollastonite (β-$CaSiO_3$) and diopside ($CaMg(SiO_3)_2$). With the increase of crystallization temperature, diopside increases and wollastonite decreases. This indicates that the increase of crystallization temperature is helpful for the formation of diopside, which is