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Original article

Microwave-assisted processing of graded structural tailing glass-ceramics

Hong-xia Li, Bao-wei Li*, Lei-bo Deng, Peng-fei Xu, Yong-sheng Du, Shun-li Ouyang

Key Laboratory of Integrated Exploitation of Bayan Obo Multi-Metal Resources, Inner Mongolia University of Science and Technology, Baotou 014010, China

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ABSTRACT

Graded structural materials (GSM) with excellent properties exhibit a systematic change in microstructures from one part to another. In this study, we provide a novel, one-step method to prepare enhanced gradient tailing glass-ceramics (TGC). Upon exposure of the different parts to three different microwave susceptors (graphite, active carbon, SiC), effective control of the microstructural evolution of TGC is successfully achieved. The effects of three susceptors on the microstructures and the physicochemical properties of the gradient glass-ceramics are investigated. The results show that the main crystal phase (diopside) is not changed, but the microstructure changes obviously with three susceptors. The crystal morphology evolution occurs from prismatic crystals (graphite layer) to the round-rod-like crystals with fine and small nanowires (active carbon layer) to dendritic crystals (SiC layer). The nanohardness of GSM also varies with the change of microstructures. This method extends the possible applications from TGC to other advanced materials.

1. Introduction

Graded structural materials have evolved over millions of years through natural selection and optimization in many biological systems such as teeth and shells, in which the microstructures gradually change from the surface to the interior. One of the advantages of gradient microstructures is the maximization of physical and mechanical performance at minimal cost. The mechanical performance of materials with microstructure-induced gradients is of considerable interest in multiple disciplines. Graded materials exhibit a systematic change in microstructure along one direction. Such gradient structures with composition or microstructure transition exhibit superior properties to monolithic materials in terms of deformation, fracture toughness, and strength-ductility [1–3]. In the past, graded structural materials were typically designed to withstand a variety of severe in-service conditions, and were mainly based on metals. Two approaches for the formation of these structures have been studied based on either morphology or composition transformation in various matrices. For example, Suresh reported the production of gradient materials by morphology transformation for resistance to contact damage and deformation [4]. The microstructural gradient converts the applied uniaxial stress to multiaxial stresses owing to the evolution of the microstructure along the gradient length. Others have also described different preparation methods of graded materials and the advantages of these changed structures based on metals [5–7]. Recently, great attention has been devoted to ceramic materials due to their attractive properties. Ishikawa described a general process by which functional surface layers with a nanometer-scale composition gradient can be readily formed during the production of bulk ceramic components [8], which imparts superior mechanical properties to the ceramics. In addition, Jaworska reported functionally graded cermets with outstanding plasticity and high hardness that can be used for the fabrication of cutting tools with a hard, wear-resistant surface layer and a ductile body frame using a powder metallurgy method [9]. Overall, the graded materials appeared highly superior to other engineering materials with homogeneous microstructures for meeting complicated working requirements. However, most of the methods used to synthesize these graded materials are very complex and costly, and several process control steps are necessary to achieve ultimate product performance.

In recent years, microwave processing has received significant attention as a highly energy-efficient technique for the volumetric processing of materials. In particular, owing to its selective heating, microwave processing has been used extensively for the fabrication of advanced materials [10–14]. Furthermore, it is known that susceptors can influence the heating mechanism through interactions with target materials. For instance, they can accelerate microwave processing by providing two-way heating and reduce heat losses from the surface of the material. In addition, rapid initial heating via susceptors plays a key role in improving the efficiency of microwave processing for materials with low microwave absorption capacities. These characteristics have been exploited in a wide range of applications including material processing and synthesis and waste treatment [15]. The possibility of using microwaves to induce the crystallization of tailing glasses into glass-ceramics is of significant interest. Tailing glass-ceramics use mineral

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[*] Corresponding author.
E-mail address: hongxialea@163.com (B.-w. Li).

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tailings as the main raw materials [16–18], which represents a resource-efficient use for mining waste to engineer materials with high technological significance. Such glass-ceramics are prepared through controlled nucleation and crystallization of specially formulated glasses [19–21]. They exhibit a unique combination of properties when compared to traditional ceramics. The phase assemblage (i.e., the type and volume fraction of the crystalline and residual amorphous phases) determines the physical and mechanical properties of the final material. Compared to conventional processing, microwave processing of tailing glass-ceramics is expected to be more energy-efficient, environmentally friendly, and economical [22–24]. It is also expected that microwave processing will improve the microstructure of glass-ceramics, thereby extending their mechanical performance. So far, there are few reports about one-step microwave processing methods to produce gradient materials with microstructure transitions.

Based on the above consideration, the construction of gradient materials has significance in applications and theoretical research by use of a microwave fabrication process. In this study, we endeavored to establish a simple, inexpensive, and widely applicable process for creating a novel material with a nano-morphology gradient and excellent functionality. For this purpose, we investigated the feasibility of microwave-assisted heating using a 2.45 GHz multimode microwave cavity. The effect of three different microwave susceptors on the microstructure and physicochemical properties of the glass-ceramics with spatial gradients were also investigated.

2. Experimental section

2.1. Sample preparation

The glass samples were prepared by a melting method using mineral tailings as the main raw materials. The chemical composition of the raw materials and the preparation process for glass matrix have already been described in our previous work [24]. These chemical compositions are given in Table 1. In the present study, the mixture used to prepare glass-ceramics contained 57.4 wt.% iron tailings, 19.3 wt.% gold tailings, as well as lab-grade oxide powders of 11.8 wt.% SiO_2, 4.2 wt.% CaO, 1.3 wt.% MgO, 2.9 wt.% Al_2O_3, 2.8 wt.% Na_2CO_3, and 0.45 wt.% Cr_2O_3. The chemical composition of the glass matrix material was calculated accordingly, and the results are presented in Table 2. The final mixture underwent milling, melting, casting and annealing to form glass samples with dimensions of ~60 mm in length, ~40 mm in width, and ~10 mm in height, respectively.

The glass samples were crystallized using a hybrid microwave process. A 2.45-GHz microwave furnace (DLGR-06S, Zhengzhou DLG Microwave Technology Co., Ltd, 450001, China) was used for the microwave crystallization experiments. A schematic of the hybrid microwave heating system used in this study is presented in Fig. 1. Because of their low dielectric loss factors at RT, tailing-based glasses are not easily heat-treatable via microwave radiation. Therefore, in the present work, the glass sample was placed in a mullite crucible; three different types of powders were used as susceptors (graphite, active carbon, and SiC) for different parts of the sample to increase the temperature; the annealed glass samples were subjected to microwave irradiation for 50 min at a 2-kW power input; and the measured local temperature of the sample was 770 °C as determined by a regular type-K thermocouple. The three parts are referred to as L1, L2, and L3, and the schematic of the hybrid microwave heating system is shown in Fig. 1.

Table 2
Predicted the chemical composition of the glass matrix prepared from the tailings wt%.

SiO_2	Al_2O_3	CaO	MgO	R_2O	Cr_2O_3	Fe_2O_3
49.5	8.2	17.5	3.9	4.4	0.45	6.9

2.2. Characterization

The phase constitution was identified by a PANalytical X'Pert Powder X-ray diffraction (XRD) spectrometer (Cu-Kα radiation 40 kV, 30 mA).

The bonding states of samples were analyzed by Fourier-transform infrared (IR) and Raman spectroscopy. IR spectra were recorded using a Nicolet 360 spectrophotometer at a resolution of 4 cm^{-1}. Raman spectra were collected by a Raman spectrometer (Jobin Yvon, HR 800) equipped with an Ar^+ laser (514.5 nm) with an output power of 25 mW and an instrumental resolution of 1 cm^{-1}.

The microstructure of the sample was observed using field-emission scanning electron microscopy (FE-SEM, Carl Zeiss SUPRA55, Germany). The surfaces of the glass-ceramics were first polished using a typical polishing machine and then etched with a 5 vol.% hydrofluoric acid solution for 75 s. Etched samples were successively rinsed with water and alcohol, dried, and finally coated with a thin film of gold.

2.3. Mechanical measurements

The physical, chemical, and mechanical properties of the glass-ceramic samples, including density, Vickers nanohardness, Young's modulus, acid resistance, and alkali resistance, were assessed. The density measurement was performed by the Archimedes method. Vickers nanohardness and Young's modulus were assessed by the nano-indentation technique (Keysight Technologies G200, China). The chemical durability of the glass-ceramic samples, which were manually crushed into powder (< 9.00 mm), was evaluated by treating about 1 g of powder in 50 mL of a leaching solution (20 wt.% NaOH and 20 wt.% H_2SO_4) at 98 °C for 1 h, measuring the weight of the glass-ceramic samples before and after leaching. The acid/alkali resistance values were calculated by Eq. (1):

$$w\% = \frac{m_1 - m_2}{m_1} \times 100\% \tag{1}$$

where w is the acid/alkali resistance, and m_1 and m_2 are the mass before and after leaching, respectively.

3. Results and discussion

Representative FE-SEM micrographs of the middle of tailing-based glass-ceramic samples are presented in Fig. 2. Different parts of the same sample exhibited different microstructural features. Fig. 2(a) presents a macroscopic image of the sample. The morphology of the left side of the sample (L1), which was prepared by microwave-processing using graphite as the susceptor, is shown in Fig. 2(b). In the L1 sample, prismatic crystal grains formed, with a grain size of ~600 nm. Fig. 2(c) presents the middle part of the sample (L2), for which active carbon was used as a susceptor, indicating crystal grains had a round-rod-like shape with fine and small nanowires dispersed between the grains. Fig. 2(d) presents the third part, L3, of the sample, for which SiC was

Table 1
Chemical composition of the gold and iron tailings used as raw materials wt%.

Raw materials	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	Fe_2O_3	CaF_2	Rest	Total
Gold tailing	67.20	11.04	3.86	1.64	5.66	1.44	2.30	–	6.86	100
Iron tailing	43.00	5.60	21.90	4.00	1.20	1.20	11.30	0.30	11.50	100