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Novel preparation of glass ceramics from amorphized tungsten tailings

Kang Peng, Changzheng Lv, Huaming Yang*

Department of Inorganic Materials, School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China

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Abstract

Glass ceramics were successfully prepared from amorphized tungsten tailings after magnetic separation. Samples were characterized by DSC, XRD, SEM, and FTIR. The results demonstrated the main crystalline phases of the as-prepared glass ceramics were gehlenite ($Ca_2Al_2SiO_7$) and hedenbergite ($CaFeSi_2O_6$), and the amount and size of the crystalline phases increased with increase of crystallization temperature. The morphology of crystalline grains varied from tiny granular to plate-like crystals. The crystalline phases would melt again, and hedenbergite would partially transform into gehlenite at a crystallization temperature of 1100 °C. Based on the kinetics analysis for crystallite growth, the activation energy (E_α) and Avrami constant (n) were calculated as 381.16 kJ/mol and 2.04, respectively, indicating that the crystallization mechanism followed two-dimensional growth. The glass ceramics from tungsten tailings at 1050 °C showed proper crystal structure and high performance, which could be considered for potential applications in building materials.

Keywords: D. Glass ceramics; Tungsten tailings; Amorphization; Crystallization behavior

1. Introduction

Tungsten tailings are the solid waste from tungsten ore dressing, and its major constituents commonly contain SiO_2, Al_2O_3, CaO, and Fe_2O_3. Production of 1 t of tungsten concentrates is accompanied by 9 t of tungsten tailings for the low grade tungsten minerals [1,2]. China produces 90.9% of global tungsten, reserves 62.1% of the global tungsten resources [3,4], and generates and retains the most tungsten tailings in the world. Currently, tungsten tailings are simply stored in the tailing pond or backfilled in the mine without effective use. The disposal of tungsten tailings leads to serious pollution of ground waters and soil. The contamination of arsenic and heavy metals from tungsten tailings causes potential health risks [5–8]. To limit the degree of pollution and improve the value of tungsten tailings, many efforts have been made to take advantage of tungsten tailings. Choi et al. used tungsten tailings as a substitute material for cement [9], and acceptable properties of the mortar could be obtained using 10 wt% tailings. The recycling of valuable metals, garnet and fluorite, is also a common use for tungsten tailings [10].

Glass ceramics are polycrystalline materials produced by melt quenching and subsequent crystallization at proper heat treatment. Production of glass ceramics is used in a wide range of fields such as machinable ceramics, bio-ceramics, optical materials, cooking ceramics and building materials [11–14]. The important effects of glass ceramics properties are the crystalline phases and the microstructures, which can be tailored by the chemical composition and heat treatment [15]. The main constituents of glass ceramics are SiO_2, Al_2O_3, CaO, and MgO, provided by various chemically pure materials and minerals. Many tailings contain the constituents required of glass ceramics. Using tailings as the raw material for glass ceramics is an effective approach for the comprehensive use of mining waste [16–18]. For example, Yang et al. made double-layer prepared ceramic/ceramic tiles from bauxite tailings and red mud using a single firing powder processing route [12].

In this work, we demonstrated a strategy for the preparation of glass ceramics from the tungsten tailings from Hunan, China, and investigated the crystallization behavior of glass ceramics.

*Corresponding author. Tel.: +86 731 8871 0804; fax: +86 731 8883 0549.
E-mail address: hmyang@csu.edu.cn (H. Yang).

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Table 1
Chemical compositions of tungsten tailings and the as-amorphized.

Compositions	SiO_2	CaO	Al_2O_3	Fe_2O_3	Na_2O	MgO	Others
Tungsten tailings (wt%)	36.52	28.02	8.70	11.71	0.03	2.28	13.37
As-amorphized (wt%)	38.55	27.24	16.51	9.76	4.74	0.94	2.26
As-amorphized (mol%)	44.24	33.50	11.17	4.21	5.27	1.61	–

To optimize the crystallization temperature, we studied the effect of crystallization temperature on the crystal structure.

2. Experimental

Tungsten tailings were obtained after tungsten ore magnetic separation from Hunan, China. Analytical reagents of SiO_2, Al_2O_3, $CaCO_3$, and Na_2CO_3 were provided by Xilong Chemicals Co. Ltd. 72 wt% of tungsten tailings, 7 wt% of SiO_2, 8 wt% of Al_2O_3, 6 wt% $CaCO_3$, and 7 wt% Na_2CO_3 were used as raw materials to prepare CaO–Al_2O_3–SiO_2–Fe_2O_3 glass ceramics. The chemical compositions of the tungsten tailings are listed in Table 1, and the iron content was calculated from the mass percentage of iron oxide (equal to 70% of the iron oxide content).

The tungsten tailings and additives were mixed together after grinding. The mixed powders were melted in an alumina crucible at 1400 °C for 3 h to form homogeneous melts and water-quenched to obtain the as-amorphized sample. The as-amorphized sample was ground and sieved to less than 200 mesh (74 μm). The as-amorphized sample was mixed with 3 wt% polyvinyl alcohol solution (the mass ratio of polyvinyl alcohol and water is 1:10) as the binder, and uniaxially pressed into discs with a 20 mm diameter under 30 MPa pressure. The green discs were heated at the proper nucleation temperature for 2 h with the heating rate of 3 °C/min to eliminate the binder. Following nucleation, the temperature was raised to various temperatures (950, 1000, 1050, and 1100 °C) for 2 h to produce the final product glass ceramics.

X-ray diffraction (XRD) was performed with a DX-2700 X-ray diffractometer using Cu Kα radiation (λ=0.15406 nm) at a scanning rate of 0.02 deg/s with a voltage of 40 kV and 40 mA. DSC was performed in air using a NETZSCH STA449C thermal analyzer at various heating rates. SEM was performed with a Quanta-200 scanning electron microanalyzer with an accelerating voltage of 5 kV. FTIR, over the range of 4000–400 cm^{-1}, was recorded on a Nicolet Nexus 670 FTIR spectrometer, where the samples were ground with KBr crystals and the mixture was pressed into a pellet for IR measurement. The samples sizes were measured by vernier caliper, and the samples densities were calculated through mass divided by volume. The compressive strength of samples was measured using a universal testing machine (CMT-5305, China).

3. Results and discussion

Fig. 1 shows the XRD patterns from tungsten tailings to glass ceramics. The major mineralogical constituents of the tungsten tailings were grossular (PDF no. 72-1491) and quartz (PDF no. 65-0466). The iron content of tungsten tailings was 8.20 wt%. However, the iron-bearing mineral was not found by XRD, which might be because the iron element is soluble in grossular and replaces the aluminum element [19]. The as-amorphized sample presented the typical XRD characteristic of an amorphous structure (Fig. 1), which proved that the sample had been amorphized completely. The XRD patterns of glass ceramics crystallized at various temperatures indicated that two crystalline phases, gehlenite ($Ca_2Al_2SiO_7$, PDF no. 35-0755) and hedenbergite ($CaFeSi_2O_6$, PDF no. 41-1372), could be identified for the glass ceramics (Fig. 1). The major phase was gehlenite, which was attributed to the melilite group, and the secondary phase was hedenbergite.

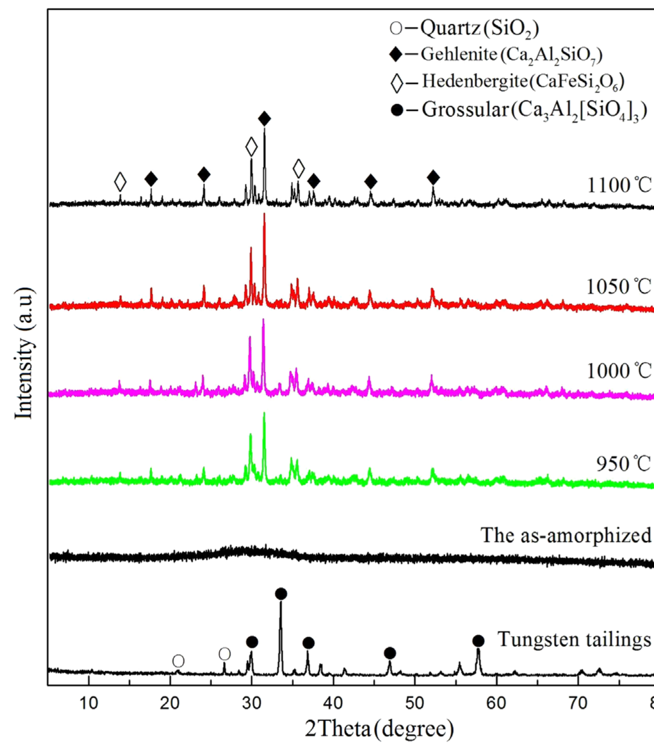

Fig. 1. XRD patterns of tungsten tailings, the as-amorphized sample and correspondingly prepared glass ceramics crystallized at different temperatures.

The SEM images showed that the particles of the tungsten tailings had irregular shapes and smooth surfaces, with sizes from 10 to 100 μm (Fig. 2a and b). The fractured surface of the glass ceramics crystallized at 1050 °C clearly presented plate-like crystals with sizes from 300 to 500 nm (Fig. 2e). The glass ceramics crystallized at 1050 °C had the bending strength of 47 MPa and the compressive strength of 330 MPa. The comparison with the