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Red mud and fly ash-based ceramic foams using starch and manganese dioxide as foaming agent

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Abstract: Ceramic foams were prepared using red mud and fly ash as raw materials with sodium borate as sintering aid agent, starch and MnO_2 as foaming agent, respectively. The influence of the amount of starch or MnO_2 on the crystalline phase, pore morphology and physical–chemical porosities was studied. The results showed that the main crystal phases of samples with starch addition and MnO_2 addition were sodalite phase $Na_6(AlSiO_4)_6$ and $Na_8(SiAlO_4)_6MnO_4$, respectively. The SEM images showed that the variation of porous structure was mainly dominated by the addition of foaming agent. With the increase of foaming agent, the samples exhibited better comprehensive properties: bulk density of 0.59−0.96 g/cm^3, porosity of 41.82%−63.51%, water absorption of 3.16%−9.17%, compressive strength of 4.22−8.38 MPa, flexural strength of 2.44−5.82 MPa, acid resistance of 95.59%−99.60%, alkali resistance of 99.82%−99.99%. Based on these properties, the ceramic foams can be used in building field.

Key words: red mud; fly ash; starch; manganese dioxide; ceramic foam

1 Introduction

Industrial solid waste pollution from the metallurgical industries has become an increasingly serious problem all over the world. Every year, large quantities of metallurgical wastes are generated from the production of various metals. In these solid wastes, red mud from alkali leaching [1] of bauxite by the Bayer process for producing aluminum oxide (Al_2O_3) [2] and fly ash generated through coal-based thermal power plants have been heavily accumulated and continuously increased [3] for a long time. These residues are considered as hazardous wastes due to their soluble metal content which induces many social problems such as contaminated water [4,5], dust-laden air [6,7] and alkalized soils [8,9], as well as human and animal health [10,11] and security risks from the collapse of wastes. In China, fly ash is generally stored at coal-fired power plants or placed in landfills. About 40% of fly ash is recycled, which was used to supplement Portland cement [12] in concrete production. As for red mud, filling and stacking are yet two major means of its maximizing utilization until recently [13,14].

In recent years, intensive research and development efforts have been directed towards finding compatible solutions for red mud minimization and utilization [15], including decreasing quantities of emissions, maximizing levels of utilization and developing of high value products. Many new kinds of materials have been developed by using red mud as major raw materials, such as soil amendment for pollutants in liquid and solid phases [16], water treatment [17,18], metal recovery (Fe, Al and Ti) [19], radio-opaque materials [20], glass-ceramics [21] and ceramics [22]. The authors believe that the preparation and application of building ceramic foams may be an effective solution for the minimization of wastes and utilization of high value. On one hand, construction industry has an enormous market need for building ceramic foams. Mass production of ceramic foams will obviously decrease the total of wastes which can be used as raw materials, resulting in the alleviation of environmental problems. On the other hand, ceramic foams are high value products with multi-functions such as thermal insulation, acoustic insulation, fire-proof, and freezing tolerance. The wide applications of ceramic foams would lead to a significant reduction of energy consumption and fire disaster in buildings. In our previous studies, foam glasses containing 70% of fly ash [23,24] and ceramic foams with 80% of red mud

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and fly ash [25] have been prepared by using sodium silicate solution (commonly known as water glass) with 2:1 of SiO_2:Na_2O molar ratio as foaming agent. According to Ref. [25], sodium silicate could be used as an excellent forming agent in the production of porous materials. As a viscous foaming agent, however, there are some problems existing in its application such as inconvenient weighing and difficult to guarantee the uniformity of batch mixing. Thus, the dry solid particle foaming agent was chosen for avoiding the inconvenient of weighing raw materials and guaranteeing the uniformity of batch mixing. Generally, starch and MnO_2 are used as common foaming agent to prepare porous materials in Res. [26−28]. However, few reports have been discussed on the preparation of ceramic foams combining fly ash and red mud as raw materials with starch and MnO_2 as foaming agent.

In this work, red mud and fly ash based ceramic foams were investigated by using starch and MnO_2 as foaming agents respectively, and sodium borate as sintering aid agent. The effects of foaming agent content on the crystalline phase, microstructure, physical–mechanical porosities and chemical stability of glass ceramic foams were investigated.

2 Experimental

2.1 Raw materials

The starting materials used in this work were red mud, fly ash and analytically pure sodium borate $Na_2B_4O_7$ (99%), as well as soluble starch $(C_6H_{10}O_5)_n$ (99.5%) and MnO_2 (97.85%). Fly ash and red mud used in the present experiments were supplied by Leiyang Power Plant and Henan Aluminum Co., Ltd, respectively. The pure sodium borate and soluble starch were provided from Xilong Chemical Co., Ltd, as well as manganese dioxide. The chemical compositions of red mud and fly ash were determined by X-ray fluorescence spectroscopy (XRF, Rigaku, ZSX Primus II) and the results are listed in Table 1. According to the results from XRD analysis, the crystalline phases of the two wastes are shown in Fig. 1.

Table 1 Chemical composition of fly ash and red mud (mass fraction, %)

Material	SiO_2	Al_2O_3	Na_2O	K_2O	MgO	CaO
Fly ash	54.37	24.47	1.44	1.71	0.99	4.85
Red mud	20.53	21.76	12.06	1.76	1.04	17.23

Material	Fe_2O_3	P_2O_5	MnO	TiO_2	LOI
Fly ash	5.50	0.27	0.04	1.45	4.27
Red mud	10.47	0.16	0.01	4.10	10.8

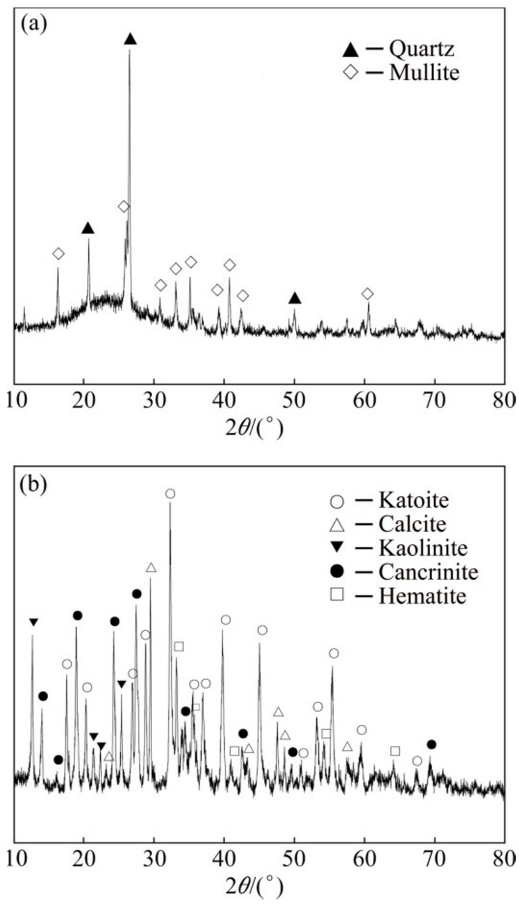

Fig. 1 XRD patterns of fly ash (a) and red mud (b)

From Table 1, both fly ash and red mud contain higher contents of SiO_2 and Al_2O_3 which are commonly used as network formers of glasses and framework compositions of ceramics. The main crystalline phases of fly ash are mullite ($Al_2O_3 \cdot SiO_2$, PDF No. 15−0776) and quartz (SiO_2, PDF No. 85−0798), while amorphous silicate glassy phase is also detected, as shown in Fig. 1(a). Compared with fly ash, the mineral phases of red mud are identified as katoite ($Ca_3Al_2(SiO_4)(OH)_8$, PDF No. 38−0368), kaolinite ($Al_2Si_2O_5(OH)_4$, PDF No. 29−1488), calcite ($CaCO_3$, PDF No. 64−9630), cancrinite ($Na_{7.6}(Al_6Si_6O_{24})(HCO_3)_{1.2}$ $(CO_3)_{0.2}(H_2O)_{2.28}$, PDF No. 70−5030), and iron oxide (Fe_2O_3, PDF No. 87−1164), as shown in Fig. 1(b). Sodium borate was added into the batches of foam ceramics as sintering aids. Starch and manganese dioxide were respectively introduced into the samples.

2.2 Sample preparation

The components of samples were mixed in a ball mill (Xianyang Jin Hong General Machinery Co., Ltd, KQM-X4Y/BC) with alumina balls (Shandong Zibo Win Chi Ceramics New Material Co., Ltd.) at speed of 180 r/min for 4 h and were sieved through 48 μm sieve after drying, and different amounts of starch (1%, 3%,