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Preparation of novel ceramics with high CaO content from steel slag

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ABSTRACT

Steel slag, an industrial waste discharged from steelmaking process, cannot be extensively used in traditional aluminosilicate based ceramics manufacturing for its high content of calcium oxide. In order to efficiently utilize such solid waste, a method of preparing ceramics with high CaO content was put forward. In this paper, steel slag in combination with quartz, talcum, clay and feldspar was converted to a novel ceramic by traditional ceramic process. The sintering mechanism, microstructure and performances were studied by scanning electron microscope (SEM), X-ray diffraction (XRD) techniques, combined experimenting of linear shrinkage, water absorption and flexural strength. The results revealed that all crystal phases in the novel ceramic were pyroxene group minerals, including diopsite ferrian, augite and diopsite. Almost all raw materials including quartz joined the reaction and transformed into pyroxene or glass phase in the sintering process, and different kinds of clays and feldspars had no impact on the final crystal phases. Flexural strength of the ceramic containing 40 wt.% steel slag in raw materials can reach 143 MPa at sintering temperature of 1210 °C and its corresponding water absorption, weight loss, linear shrinkage were 0.02%, 8.8%, 6.0% respectively. Pyroxene group minerals in ceramics would contribute to the excellent physical and mechanical properties.

1. Introduction

With the rapid development of the industry, industrial wastes accumulates year by year, not only occupying large amount of land but also causing various pollutions to groundwater and soil, which has raised great attention in many countries in recent years. As one kind of common industrial waste, steel slag is one of the main byproducts produced from the steelmaking process, which accounts for about 12–20% of the steel production. In China, 93 million tons steel slag was produced in 2012, with only 22% reused in the same year. In addition, the amount of deposited steel slag in china has been accumulated to more than 350 million tons. Many scholars have studied the utilization of steel slag in various directions, from recycling in the steel plant, utilizing for road constructing, hydraulic construction and production of cement and concrete to fertilizer in agriculture, materials of waste water treatment [1–4]. Nevertheless, the great amount of steel slag produced all over the world implies that the recycle is presently necessary not only for the pollution and occupation of land but also for the eco-industrial development of human.

Ceramic is a widely used aluminosilicate material, the raw materials mainly include clay, supplemented with feldspar, quartz and other mineral components. Its main phases are mullite, quartz, glass phase and so on. Ordinary ceramics belong to SiO_2–Al_2O_3–K_2O(Na_2O) ternary system, Fe_2O_3 and CaO are required less than 0.8 wt.% and 3 wt.% in the raw materials mixture. The presence of iron and calcium ions promotes the formation of low temperature liquid phase and affects the color of the body or glaze. Therefore, the traditional ceramic is facing a shortage of high-quality mineral resources depletion and the potential threat from rising prices.

Recently, ceramics prepared from industrial waste and have been investigated, such as red mud [5], coal fly ash [6,7], and blast furnace slag [8–12]. This is a promising solution because it can not only decrease the risk of the shortage of high-quality mineral resources, more advantageously, but also convert the industrial waste to useful materials and reduce the pollution of the environment. Reports concerning the application of steel slag in ceramic are not much. Favoni et al. [13] investigated ceramic processing of municipal sewage sludge and two types of steelworks slags in different proportions, obtained the main phase of hematite

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(Fe_2O_3), magnetite (Fe_3O_4), essenite ($CaAlFeSiO_6$) and anorthite ($CaAl_2Si_2O_8$) samples, with the flexural strength about 70 MPa. Badiee et al. [14] introduced the use of electric arc furnace steel slag (EAFSS) as a raw material in the floor tile body, fabricated a floor tile with a maximum amount of 40 wt.% EAFSS, and the sample had a maximum bending strength of 94 MPa, and high water absorption of 1–2%. Glass–ceramics are attractive materials use in various applications [15,16]. Convertion steel slag into glass–ceramic is a another solution. He et al. [17] prepared glass–ceramic materials with 31–41 wt.% steel slag being used. The main crystalline phase was wollastonite ($CaSiO_3$) and the bending strength could reach ~145 MPa. But this needs first of melt-quenching and two-step thermal treatment of nucleation and crystal growth processes for more than 4–7 h. These studies all focused on the ceramic preparation of certain or multiple solid wastes without proposing the corresponding ceramic system, therefore limiting their potential applications to other solid waste utilization.

Until now, limited attention has been paid to study the calcium-rich ceramic system. In this research, pyroxene ceramics based on the $CaO–MgO–SiO_2–Al_2O_3–Fe_2O_3–K_2O$ (Na_2O) system were prepared from steel slag in combination with traditional ceramic materials by traditional ceramic process. Physical and mechanical properties (including linear shrinkage, weight loss, water absorption, flexural strength) were examined in order to compare with the traditional ceramics. In addition, different feldspars and clays were used to verify the influence of ingredients fluctuations on the properties of specimens. This study can also provide the basis for the use of other calcium-rich waste.

2. Materials and methods

2.1. Materials

Raw materials used in the present investigation were steel slag, clay, talcum, feldspar and quartz. steel slag after being crushed and magnetic separated used in this study was supplied by ShanDong Iron and Steel Group. Steel slag was already ground into particles less than 150 μm after magnetic separation process, so the problem that the steel slag is generally hard to grind is solved. Other materials including two different feldspars and clays were taken from Shandong province of China. Main chemical compositions as determined by X-ray fluorescence (XRF) are shown in Table 1.

It can be seen that mainly CaO, Fe_2O_3, SiO_2 and MgO constitute the slag .The quartz has almost no impurities, although SiO_2 content is higher in talcum, the MgO is the principal component. SiO_2 and Al_2O_3 are the main components of clay and feldspar, however alkali metal oxides are also important. The composition of two different feldspar and clay are also shown in Table 1, labeled A and B respectively. As it can be seen from the table, the differences between A and B mainly exists in CaO, MgO and alkali metal oxides content.

Table 1
Main chemical compositions of the raw materials.

	SiO_2	Al_2O_3	MgO	CaO	Fe_2O_3	K_2O	Na_2O
Steel slag	14.45	2.03	5.83	30.04	19.20	–	–
Quartz	97.66	1.52	0.06	0.05	0.16	0.36	–
Talcum	64.07	1.34	30.44	3.64	0.14	0.03	–
Clay A	67.87	18.1	4.09	5.35	1.38	2.17	0.33
Clay B	69.15	20.05	0.51	1.43	0.92	4.9	2.69
Feldspar A	74.01	15.18	0.51	2.19	0.81	3.8	3.04
Feldspar B	71.79	15.31	0.28	2.85	1.11	5.28	2.95

2.2. Ceramics manufacturing process

40% Mass fraction slags were used in this experiment, sample numbers and the corresponding raw materials used are shown in Table 2.

300 g Of a batch was prepared according to batch composition, which contained an amount of 40 wt.% slag. The batch was mixed and wet grounded in a pot mill for a duration of 20 min to get desired fineness (proportion of particles with size greater than 20 μm is less than 10%). The slurry obtained was screened, dried at 105 °C for 12 h, powdered to break the agglomerate and granulated to small particles for better compaction with 6–7% moisture. Samples of 50 mm × 100 mm × 7 mm were hydraulically compacted using uniaxial pressing at 20–25 MPa. The shaped samples were dried at 105 °C for 12 h till the moisture content reduced to less than 0.5%. The dried samples were fired at different temperatures in an electrically operated laboratory furnace. The heating rate was 7 °C/min and the holding period was 20 min. Finally, the fired samples were subjected to physical tests such as linear shrinkage, water absorption (**ASTM:C 373-14**) and flexural strength.

The crystallized samples obtained from the heat treatment were then studied by XRD using a Mac M21X powder diffractometer. The microstructure characterization was performed in the scanning electron microscope (SEM) in an EVO18 Special Edition (Carl Zeiss, Germany) operating at 25 kV. Right before SEM test, the samples were etched with HF 0.5% for 1.5 min at room temperature and coated with carbon to be analyzed.

3. Results and discussion

3.1. Physical and mechanical properties

The variation in linear shrinkage and weight loss of the heated samples with sintered temperature is presented in Fig. 1. Fig. 2 demonstrates the water absorption and flexural strength of the samples sintered at different temperatures. It can be seen that the densification starts at about 1195 °C, while the beginning of overfiring is observed at about 1225 °C. The highest flexural strength is 143 MPa at 1210 °C, and the corresponding water absorption, weight loss, linear shrinkage are 0.02%, −8.8% and −6.0% respectively.

As can be seen from Figs. 1 and 2, a drastic change of water absorption and flexural strength, indicate that the sample quickly complete densification in this temperature range. The reasons possible lie in the fact that a certain amount of liquid phase generated at this temperature range, and the liquid promoted the sinter reaction and fills the gap between the crystal phases. While at 1230 °C, since the amount and viscosity of the liquid phase reached the certain boundaries, gas began to swell, and the samples started to deform, which can be proved by the linear shrinkage curve. In general, the production has high flexural strength, even sintered at 1190 °C, the water absorption is about 7%, that is to say in the absence of complete densification, the flexural strength also can reach 60 MPa or more, which exceeds ASTM standard specification for pedestrian traffic paving bricks (**ASTM:C902-14**) and for building bricks (**ASTM:C62-13a**).

Table 2
Sample No. and the corresponding raw materials.

Types of raw materials	Clay A	Clay B
Feldspar A	1#	2#
Feldspar B	3#	4#