CONVERTING STEEL SLAG INTO Si-Ca BASED BUILDING CERAMICS

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Introduction

Steel slag is a by-product of steel making process in steel and iron industry. In China, about 100 million tons of steel slag were produced in 2013, with lower than 25% reused[1]. Steel slag is not only taking up a lot of land, but also polluting the ground water and soil[2]. It is of urgency to find solutions to convert steel slag into useful materials. However, the amounts of f-CaO and low reactivity in steel slag would limited its application into cement, concrete and road bed.

Reusing steel slag in ceramics could help to improve utilisation level of steel slag in quality and quantity, because it is able to convert complex chemical compositions into useful materials with good properties and ceramics which is the third largest silicate materials industry followed concrete and cement has ability to consume a large amount of steel slag. In recent years, many reports[3-9] on sintering mechanism of ceramics from steel slag, and effect of proportion of steel slag on properties of ceramics were discussed.

Research progress of Si-Ca based ceramics from steel slag

Preparation of Si-Ca based ceramics from steel slag

Traditional ceramics belong to a SiO_2-Al_2O_3-K_2O(Na_2O) ternary system and required CaO content of less than 3% in the raw materials. Steel slag has a general chemical composition of 45-60% CaO, which thereby limited its potential applications in traditional ceramics.

Crystals would change in ceramics along with the different dosage from steel slag. When percentage of steel slag in raw materials varied from 0 to 70%, SiO_2 content decreased from 69.1% to 42.8% and CaO content increased from 0% to 25.4%. Mulite, a main crystal in ceramic without slag was disappeared when the proportion of slag reached 25%. Anorthite become dominant crystalline phase in the slag content ranged from 25% to 45%. With the slag ratio increasing to above 45%, pyroxene was the main crystal with more content than anorthite, as shown in Figure 1(left). When main

crystals of the ceramics become anorthite and pyroxene but not mullite or quartz, composition of the ceramics enters into SiO_2-CaO(MgO)-Al_2O_3-Fe_2O_3 system, along with high content of CaO.

Pyroxene group minerals in ceramics would contribute to the excellent physical and mechanical properties. SiO_2-CaO(MgO)-Al_2O_3-Fe_2O_3 system ceramics (Si-Ca based ceramics) ceramics, with 40% steel slag were successfully prepared by traditional ceramic process. The obtained samples had excellent sintering and mechanical properties with water absorption of 0.05%, linear shrinkage of 8.8%. More advantageously, the flexural strength of the samples could reach 100 MPa[3], which is far higher than the requirements of Chinese National Standard for ceramic tiles (35 MPa). High CaO composition of steel slag contributes to crystallisation at low temperature. Akemantite, anorthite and diopside formed at approximately 700°C and diopside were predominant at 1000°C. The resulting crystals played a role of framework in ceramics during the sintering process, and crystallisation process was significantly prior to the densification process[4], which were shown in Figure 1(right). The chemical compositions of the Si-Ca based ceramic in the experiment are as follows: SiO_2 44-55 wt%, CaO 13-28 wt%, Al_2O_3 10-20 wt%, MgO 2-15 wt%. The amount of steel slag in the ceramic can be up to 30-60 wt%.

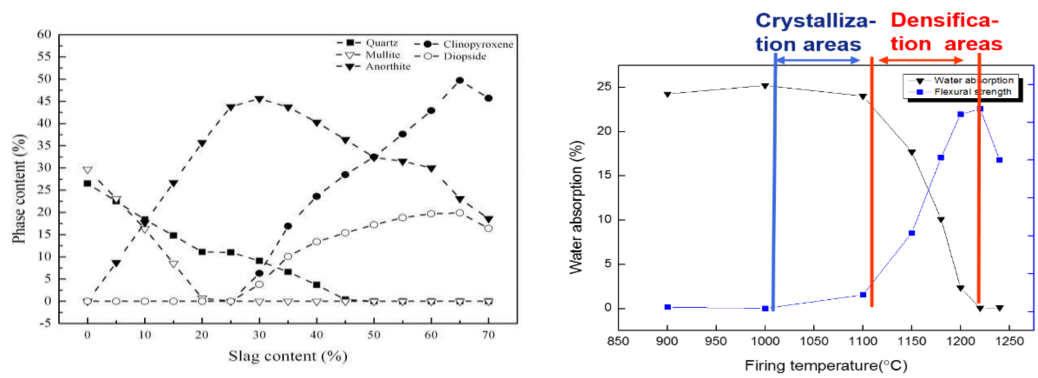

Figure 1: Simulation of the crystal phases with steel slag content (left) by Factsage[4]; Water absorption and flexural strength of fired sample (right)[5]

The Si-Ca based ceramics allow calcium-rich steel slag to be the raw materials. Most of crystal phases in the ceramic were pyroxene group minerals, including diopsite ferrian, augite and diopsite, which were shown in Figure 2(left). Almost all raw materials including quartz joined the reaction and transformed into pyroxene or glass phase in the sintering process, which is different from Si-Al based ceramics. The pyroxenes played an important role of framework during the densification process. Small particles size (2-5 µm) and dense structure of crystals was contributed to its good properties, which was shown in Figure 2(right).

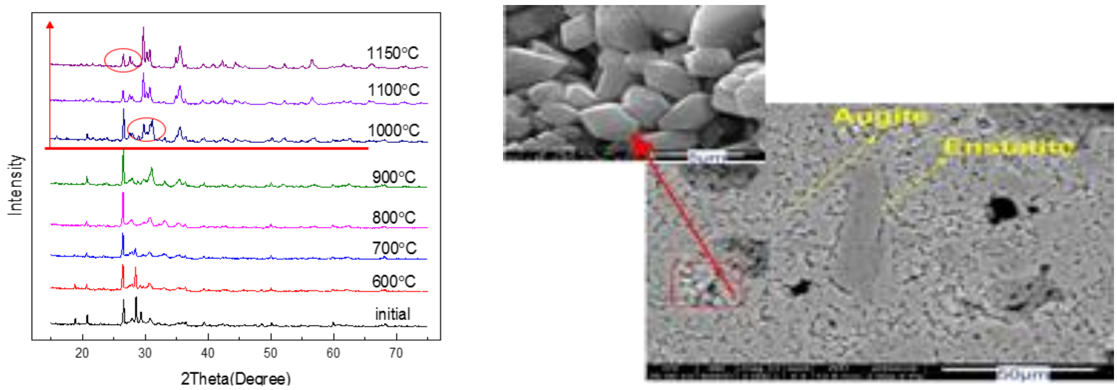

Figure 2: Si-Ca based ceramics prepared from steel slag (30 wt%), XRD analysis(left); SEM photographs (right)

Influences of MgO, Al_2O_3, or Fe_2O_3 content in Si-Ca based ceramics

CaO and MgO in ceramics could promote the formation of anorthite and pyroxene, and adding magnesium-rich materials in ceramics was more beneficial to the formation of pyroxene[4]. Increasing Mg^{2+} content did not significantly change the crystal phases but increases sintering temperature. Fe_2O_3 or RO (solid solution of FeO, MgO, MnO *etc.*) phases in Si-Ca based ceramics did not participate in the sintering at temperature below 1150°C. But melting of iron-rich andradite at approximately 1150°C and Fe_2O_3 or RO phases at approximately 1180°C promoted the densification process[5]. Substitution of Fe^{2+} for Mg^{2+} in augite and enstatite increased amount of Fe^{2+} in crystal, but decreased the amount of liquid which delayed the densification process. Ceramics with high mechanical properties could be obtained at lower temperature with appropriate magnesium ions content[6].

Al_2O_3 first participated in anorthite and then entered into liquid phase with the disappearance of anorthite with a sintering temperature. Diopside would transfer to augite with further spread of part aluminium ion. Increasing alumina content of the ceramics leaded to more glass phase, leading into formation of more internal micro cracks and reducing mechanical properties of final production[7].

Application and Outlook of Si-Ca based ceramics

Si-Ca based ceramics were prepared from adding fixed content of steel slag with variable contents of tailing and other auxiliary materials. Bending strength of the specimens reached 69.4 MPa and the firing temperature decreased by 100°C comparing to the traditional firing temperature[8].

1) Ceramic was produced from 45 wt% stainless steel slag which contained 5.7 wt% of Cr_2O_3. Results of leaching test of Cr, Pb and Cd in ceramics were respectively 25.17, 0.01 and 0.01 mg/kg, much lower than requirements of national standard of 100, 20 and 5 mg/kg (Figure 3). 2) Si-Ca based ceramics was also prepared from red mud (proportion of 10-30 wt% in raw materials) with good mechanical properties, including

high bending strength of 127.39 MPa, low water absorption of 0.07% and good Na^+ solidification behaviour. 3) As a novel method, it has been applied into preparing ceramics from different solid waste, such as steel slag, blast furnace slag, red mud, tailing, fly ash, ferroalloys slag and so on. At present, ceramic tiles from steel slag or tailing have been produced on an industrial line in Guangdong and Guizhou province (Figure 3).

Polished ceramic tiles from 45 wt% stainless steel slag	Polishing and unglazed ceramic tiles from 30-40 wt% BOF steel slag	Applications of glazed tiles from 50 wt% tailing and inferior clay

Figure 3: Ceramic tiles produced on an industrial line

As most of metallurgical solid waste contain trace elements, such as heavy metal elements (Mn, Na, Cr, V and Ti) or alkaline metal ions (Na^+, K^+), effect of these elements on Si-Ca based ceramics system and application of the ceramics should be strengthening. Sintering mechanisms of the ceramics need to be further researched, especially when the ceramics was prepared from different solid waste. Moreover, new properties of Si-Ca based ceramics should be revealed, and not only building ceramics, but also function ceramics would be researched based on the new ceramic system from metallurgical solid waste.

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