Effects of CaO and Fe₂O₃ on the Microstructure and Mechanical Properties of SiO₂–CaO–MgO–Fe₂O₃ Ceramics from Steel Slag

Lihua ZHAO,^{1,2)} Yu LI,^{1,2)*} Lingling ZHANG³⁾ and Daqiang CANG^{1,2)}

1) State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, 30 XueYuan Road, Haidian District, Beijing, 100083 China. 2) School of Metallurgy and Ecological Engineering, University of Science and Technology Beijing, 30 XueYuan Road, Haidian District, Beijing, 100083 China. 3) School of Civil and Environmental Engineering, University of Science and Technology Beijing, 30 XueYuan Road, Haidian District, Beijing, 100083 China.

(Received on February 20, 2016; accepted on September 23, 2016; J-STAGE Advance published date: November 26, 2016)

A new SiO₂–CaO–MgO–Fe₂O₃ system ceramics, namely pyroxene ceramics in this paper, was put forward for efficiently utilizing the steel slag. The prepared ceramic with 30 wt% of steel slag has excellent properties with flexural strength of 107 MPa and water absorption rate of 0.045%. Microstructure evolution in the new system ceramics was studied by X-ray diffractometry and scanning electron microscopy. High content CaO in this system contributes to crystallization in low temperature. Diopside (CaMgSi₂O₆) formed at temperature below 800°C, and was predominant at approximately 1 000°C before densification. The main phases of pyroxene have not changed except the solution of ions of Fe²⁺/Fe³⁺, Al³⁺, Mn²⁺, Ti⁴⁺ and so on. Melting of iron-rich andradite, Fe₂O₃ and RO (solution of FeO, MgO, MnO etc.) phases at temperature between 1 100°C to 1 180°C promoted liquid sintering and densification process. The crystallization process at temperature between 700°C to 1 100°C is prior to the densification process at temperature between 1 150°C to 1 220°C, and the formed crystals played an important role of framework during the densification process. Sole interlocking pyroxene phases and less glass phase in the final ceramic are contributed to its excellent mechanical performances.

KEY WORDS: steel slag; pyroxene ceramics; CaO; Fe₂O₃; strength; sintering; microstructure.

1. Introduction

Large amounts of Ca-rich or Fe-rich solid wastes, such as tailing, red mud, metallurgical slag and fly ash, have still not been efficiently utilized in the world. Steel making slag is a typical solid waste with high content of calcium and iron components. In China, 101 million tons steel slag were produced in 2013, with only 22% reused, and the stockpile of steel slag has been accumulated to more than 400 million tons.¹⁾ Such solid wastes have generated crucial problems for environment, because they not only occupy enormous land but also cause various pollutions to groundwater and soil.²⁾ It is of urgency to find solutions of technical and financial feasibility to minimize the impacts of such solid wastes on the environment and also convert them to useful materials.

Steel slag mainly consists of CaO, Fe₂O₃, SiO₂, Al₂O₃, MgO, MnO and P₂O₅.³⁾ There are a number of steel slag utilization methods, which are directed to the use of certain components or characteristic in steel slag, such as utilization in steel enterprise interior (for waste steel and CaO), utilization for production of cement and concrete (for CaO and SiO₂),⁴⁾ utilization for materials of waste water treatment

(for porous structure and large surface area),⁵⁾ utilization for road construction (for strength and shape),⁶⁾ utilization for CO₂ capture (for CaO)⁷⁾ and so on. However, there are some limitations in these utilization methods. For example, steel slag cannot be directly reused in cement or concrete industry and road construction for potential dangers of instability and alkali aggregate reaction resulted from existence of free CaO and free MgO.^{8–10)}

The ceramics appear a promising solution because it is able to convert, at a relatively low cost, complex chemical compositions into stable crystals or glass phase in ceramics.^{11–18)} Moreover, ceramics industry also has the ability to consume these bulk solid wastes besides cement and concrete industries. For instance, 10 billion square meter ceramic tiles were produced in China in 2014, the corresponding raw materials consumption was more than 300 million tons.

Traditional ceramics are a kind of aluminosilicate materials with main phases of mullite, quartz and glass phase. Clay, feldspar and quartz are its main raw materials. In recent years, ceramics prepared from solid wastes or industrial by-production have been studied. The involved solid wastes (industrial by-production) are typically steel slag,¹²⁾ blast furnace slag,^{13,14,18)} municipal solid waste incinerator ashes,¹⁹⁾ and red mud.¹⁵⁾ Part of these studies focused on the experimental verification of possibility of a certain solid

* Corresponding author: E-mail: leeu00@sina.com

DOI: <http://dx.doi.org/10.2355/isijinternational.ISIJINT-2016-064>

waste substituting for traditional raw materials.^{14,18)} However, the traditional ceramics belong to $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--K}_2\text{O}$ (and Na_2O) ternary system, and Fe_2O_3 and CaO are required less than 0.8 wt% and 3 wt% in the raw materials, respectively, because more addition of Fe_2O_3 and CaO would form more low temperature liquid and result in mechanical performance deterioration and sintering deformation. As steel slag has a composition of about 40–50 wt% CaO and 20–25 wt% Fe_2O_3 , utilization of such solid wastes in ceramics with large proportion requires a new ceramics system with high CaO and/or Fe_2O_3 content. The other part of these studies focus on ceramic preparation of a certain or multiple solid wastes without proposing the corresponding ceramic system,^{13,20,21)} therefore limiting their potential applications to utilization of other solid wastes.

Some of authors^{22–24)} prepared high CaO and Fe_2O_3 content ceramics with excellent mechanical properties and its main phases were pyroxene group minerals. There are widely isomorphism phenomena in these minerals between ions, such as Ca^{2+} , Na^+ , Mn^{2+} , Mg^{2+} at position M_2 , Fe^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , Li^+ , Al^{3+} , Fe^{3+} , Cr^{3+} , Ti^{3+} at position M_1 , Si^{4+} , Al^{3+} at position T.²⁵⁾ This means that the pyroxene ceramics can produce in a wide range of composition, which could tolerate the usage of different alternative raw materials or various inorganic industrial solid wastes. Meanwhile, the heavy metal ion, such as Mn^{2+} , Ni^{2+} , Cr^{3+} , Ti^{3+} , could also be solidified in the pyroxene crystals.²⁶⁾ Therefore the pyroxene ceramics have a great economic and environmental prospect in utilization of high CaO and/or Fe_2O_3 content solid wastes, such as steel slag, blast furnace slag, fly ash and red mud. However, as existence of considerable CaO and Fe_2O_3 in $\text{SiO}_2\text{--CaO--MgO--Fe}_2\text{O}_3$ system ceramics, its sintering mechanism especially microstructure evolution related to CaO and Fe_2O_3 was still not clear, which is different from that of traditional $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--K}_2\text{O}$ (and Na_2O) system ceramics. The main purpose of the present study was to investigate the effects of CaO and Fe_2O_3 on microstructure and sintering evolution in the new system porcelain. This study may expand the potential applications to the utilization of other Ca-rich or/and Fe-rich solid wastes. X-ray diffractometry (XRD) and scanning electron microscopy (SEM) techniques were used for phase identification and microstructural study. Physical and mechanical properties were also discussed.

2. Materials and Methods

2.1. Materials

Raw materials used in the present investigation were steel slag (SS, supplied by ShanDong Iron and Steel Group,

China), clay, talcum and pyrophyllite. Main chemical compositions as determined by X-ray fluorescence (XRF, XRF-1800, SHIMADZU, JAPAN) are in **Table 1**. Model porcelain bodies were prepared by mixing 30 wt% steel slag, 50 wt% talcum, 5 wt% pyrophyllite and 15 wt% china clay (kaolin).

2.2. Ceramics Manufacture Process

Batches (400 g each) were wet-milled (with 400 ml water) in a porcelain mill with alumina media for 40 min at 500 rpm. The slurry was passed through an 180 μm mesh. The sieved slurry was then oven-dried overnight at 105°C and moistened by spraying with a fine mist of distilled water droplets (6–8 wt%) and granulated through an 850 μm mesh. The granulates were pressed at 80 MPa in a steel die and the shaped samples (50 mm $\times$ 100 mm $\times$ 7 mm) were dried at 105°C for 12 h. The dried samples were fired in an electrically operated laboratory furnace at constant heating rate of 5°C/min and soaked for 6 h at the highest temperature in order to acquire a complete crystallization and then cooled to room temperature with furnace. These samples are referred to such as Y0 throughout this study, where Y0 is the as-mixed body and the number after Y denotes the relevant firing temperature.

2.3. Physical Properties Tests

The fired samples were subjected to physical tests of weight loss, linear shrinkage, water absorption and flexural strength (three-point bending). Linear shrinkage (LS) was determined the length difference between the green (L_1) and the fired material (L_2) by using Eq. (1):

$$LS(\%) = 100 \cdot (L_1 - L_2) / L_1 \quad \text{..... (1)}$$

The water absorption (WA), measured according to ISO 10545-3,²⁷⁾ expresses the relationship of the mass of water absorbed (M_2) to the mass of dry sample (M_1) as Eq. (2):

$$WA(\%) = 100 \cdot (M_2 - M_1) / L_1 \quad \text{..... (2)}$$

The flexural strength (R), measured according to ISO 10545-4,²⁸⁾ is calculated by Eq. (3)

$$R(\text{MPa}) = 3 \cdot F \cdot l / (2 \cdot b \cdot h^2) \quad \text{..... (3)}$$

Where F is the breaking load (N); l is the span between the support rods (mm); b is the width of the test sample (mm); h is the minimum thickness of the test sample measured after the test along the broken edge (mm).

2.4. Structure and Thermodynamic Analysis

XRD analysis was performed using an automated dif-

Table 1. Main chemical compositions of the raw materials and initial mixture (wt%).

	SiO_2	Al_2O_3	MgO	CaO	Fe_2O_3	K_2O	Na_2O	TiO_2	MnO	Cr_2O_3
SS	14.45	2.03	5.83	53.04	19.20	–	–	0.78	2.36	0.46
Pyrophyllite	76.95	22.13	–	0.03	0.16	0.36	–	0.16	–	–
Talcum	64.07	1.34	30.44	3.64	0.25	0.26	0.12	0.02	0.02	–
Clay	69.15	20.05	0.51	1.43	0.92	4.9	2.69	0.08	0.08	–
Initial mixture	50.59	5.39	17.05	17.95	6.03	0.88	0.46	0.26	0.73	0.14

fractometer (M21X, MAC Science Co. Ltd) at 40 KV and 30 mA utilizing CuK α radiation on powder samples sieved <300 grade mesh. The detector was scanned at a step size of 0.02°, a dwell time of 2 s per step, and a scan range from 15° to 75°. The identification of all crystalline phases was undertaken with JADE6 software (Materials Data, USA) and the PDF-22004 database (International Centre for Diffraction Data, USA).

The fracture surfaces of the fired samples were investigated, using SEM (MLA250, FEI) at 20 KV equipped with EDS (energy-dispersive spectrometry). The polished samples were etched with HF solution (5 vol%) for 90 s at room temperature, immediately rinsed with deionized water in ultrasonic wave cleaner for 3 min. All samples were coated with Pt. Secondary electron images (SEI), back-scattered electron images (BSI) were used to observe the apparent morphology and identify the constituent phases.

The purpose of the calculation of Gibbs free energy changes is to support the analysis of sintering process. Thermodynamic analysis was conducted by *View Data* model of FactSage 6.3 software.

3. Results

3.1. Physical and Mechanical Properties

Linear shrinkage, water absorption and flexural strength are monitored because these parameters are related to sintered bodies properties. The variation in linear shrinkage, water absorption and flexural strength with sintering temperature are shown in **Fig. 1**. The linear shrinkages of samples increase with heating temperature. However, the rate of increase in linear shrinkage is slow or nearly constant at low temperatures (below 1 000°C), but increases rapidly beyond 1 100°C, reaches the maximum 12.82% at 1 220°C, decreases at 1 240°C because of overfiring. Dramatically change of linear shrinkage in the temperature range of 1 150°C to 1 220°C illustrates the occurrence of densification process in this temperature range. Generally, water absorption depicts a reverse trend to that of the linear shrinkage. The water absorption is high (above 10%) at low temperatures (below 1 150°C), and nearly constant beyond

1 220°C although the linear shrinkage and flexural strength has been changed at 1 240°C. Tendency of water absorption and flexural strength had confirmed the occurrence of densification process between 1 100–1 220°C, which was in accordance with the linear shrinkage.

As shown in **Fig. 1**, three stages of sintering process of the ceramics were observed according to changes of their properties. Stage I (from 700°C to 1 100°C), which shown high water absorption, low flexural strength and linear shrinkage. Dramatically change in physical and mechanical properties at stage II suggested the densification process happened at temperature from 1 100°C to 1 220°C. Stage III was named over-fired process because of expansion.

For the sample fired at 1 220°C develops the highest flexural strength 107 MPa and the lowest water absorption 0.045%, which are much better than the requirements of porcelain about ≥ 35 MPa for flexural strength and $\leq 0.5\%$ for water absorption.

3.2. XRD Analysis

The phase changes in the fired experimental bodies were investigated by XRD analyses. **Figure 2** shows the XRD patterns of unfired sample and samples fired at different temperatures. The XRD pattern of Y0 shows the complexity of the component, and major XRD peaks correspond to quartz, talcum, calcite, larnite and small peaks correspond to hematite. Quartz peaks shows decreasing trend with sintering temperature and only trace at 1 150°C. Anorthite was detected at 700°C and diopside was seen at 800°C. Akermanite peaks were clearly seen at 900°C, beyond which major akermanite peaks were disappeared and diopside became prominent at the same time. X-ray patterns of Y1000 sample shows diopside as the main phase. No obvious changes among X-ray patterns of samples sintering above 1 100°C, except the main phase changed from diopside in Y1100 to diopside aluminian in Y1150. The above results illustrated that the crystallization process completed at temperature blow 1 150°C. The evolution of calcium-rich and iron-rich crystalline phases will be further discussed below. The main phases and several other small peaks not marked in **Fig. 2** were shown in **Table 2**.

Fig. 1. Linear shrinkage, water absorption and flexural strength of samples sintered at different temperatures.

Fig. 2. XRD patterns of initial powder and samples sintered at different temperatures. Where: (a) 1-Larnite- Ca_2SiO_4 ; 2-Quartz; 3-Talcum- $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$; 4- α -Quartz; 5-Calcite- CaCO_3 ; 6-Enstatite- MgSiO_3 ; 7-Hematite- Fe_2O_3 ; 8-Anorthite- $\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)$; 9-Andradite- $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$. A-Akermanite- $\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$; B-Diopside- $\text{CaMgSi}_2\text{O}_6$. (b) V-Diopside aluminian- $(\text{Mg}_{0.851}\text{Fe}_{0.026}\text{Al}_{0.080}\text{Ti}_{0.003}\text{Cr}_{0.040})(\text{Ca}_{0.720}\text{Na}_{0.027}\text{Mg}_{0.179}\text{Fe}_{0.071}\text{Mn}_{0.003})(\text{Si}_{1.891}\text{Al}_{0.109})\text{O}_6$.

Table 2. Main phase of the samples.

Main phases	Y700	Y800	Y900	Y1000	Y1100	Y1150	Y1180	Y1200	Y1220
Quartz- SiO_2	√	√	√	√	√	√	√	√	—
Protoenstatite- MgSiO_3	√	√	√	√	√	√	√	√	√
Calcium silicate- Ca_2SiO_4	√	√	—	—	—	—	—	—	—
Hematite- Fe_2O_3	√	√	√	√	√	√	√	√	—
Akemanite- $\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$	—	√	√	—	—	—	—	—	—
Anorthite- $\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)$	√	√	√	√	√	√	√	—	—
Forsterite- Mg_2SiO_4	—	—	√	√	√	—	—	—	—
Diopside- $\text{CaMgSi}_2\text{O}_6$	—	—	√	√	√	—	—	—	—
Andradite- $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$	—	—	—	√	√	—	—	—	—
Diopside aluminian- $(\text{Mg}_{0.851}\text{Fe}_{0.026}\text{Al}_{0.080}\text{Ti}_{0.003}\text{Cr}_{0.040})(\text{Ca}_{0.720}\text{Na}_{0.027}\text{Mg}_{0.179}\text{Fe}_{0.071}\text{Mn}_{0.003})(\text{Si}_{1.891}\text{Al}_{0.109})\text{O}_6$	—	—	—	—	—	√	√	√	√

“√” indicates the presence of the phase, while “—” indicates the absence of the phase

3.3. SEM Analysis

The SEM microstructure of Y900 is shown in **Fig. 3**. In Y900, EDS detected only magnesium, silicon and oxygen in the agglomeration with dark contrast (labeled “A”), suggesting that those agglomerates were protoenstatite (MgSiO_3), which is the decomposed product of talc. The lighter contrast reticular area (labeled “C”) contained calcium, magnesium and silicon, suggesting that they were akemanite ($\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$) and diopside ($\text{CaMgSi}_2\text{O}_6$) coupled with the XRD analysis results. Some regions (labeled “B”) appearing bright white in BSI contained only more iron, magnesium and oxygen, suggesting that they were hematite (Fe_2O_3) or/and RO phase (FeO-MgO solid solution from steel slag). In Y900-b (the higher magnification), more aluminum were in the EDS spectra in the agglomerates labeled as “F”, the crystals could be distinguished as clay relict. The granular crystals at the surface of “F”, labeled as “D”, enriched in Si, Ca and Al, suggesting that those crystals were anorthite ($\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)$). EDS of the region “G” and “E” revealed that they were protoenstatite (MgSiO_3) and akemanite ($\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$), respectively.

In Y1000 and Y1100, as BSI shown in **Fig. 4**, three types of agglomerates were observed. The block “A” were protoenstatite (MgSiO_3), and decreased “B” were hematite (Fe_2O_3) or/and RO phase compared with Y900. Region “C”, increased with the increasing sintering temperature, enriched Ca, Mg and Si, suggesting that they were diopside ($\text{CaMgSi}_2\text{O}_6$). Details of “C” were presented at higher magnification (Y1000-b, Y1100-b). These fine crystalline (labeled “H”) ($<2\text{ }\mu\text{m}$) developed from the surface and the interface of the bulk crystals. In Y1100-b, the surface of the bulk were smooth (region “L”), suggesting the formation of a liquid in the matrix.

Figure 5 shows the SEM micrographs of Y1150, Y1200 and Y1220. It is observed starting densification porcelain in Y1150 consisting of club-shaped “A” (protoenstatite, MgSiO_3), bulk “B” (hematite, Fe_2O_3 or/and RO phase), bond “C” (diopside alumina) and irregular pores. Little of iron existed as Fe_2O_3 or FeO could be found in BSI in Y1150-a. However, the bulk “B” were completely disappeared at 1200°C, which means all hematite and RO phases had been transformed into other phases, such as glass phase.

Fig. 3. SEM micrographs of Y900. Where: “A”- Protoenstatite (MgSiO_3), “B”- Hematite (Fe_2O_3) or/and RO phase, “C”- Ca-rich crystals, “D”- Anorthite ($\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)$), “E”- Akemanite ($\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$), “F”- Clay relict, “G”- Protoenstatite (MgSiO_3).

Fig. 4. SEM micrographs of Y1000 and Y1100. Where: “A”- Protoenstatite (MgSiO_3), “B”- Hematite (Fe_2O_3) or/and RO phase, “C”- Ca-rich crystals, mainly Diopside ($\text{CaMgSi}_2\text{O}_6$), “H” showing the fine Diopside crystalline developed from the surface and the interface of the bulk crystals, the smooth surface of “L” region suggesting the formation of a liquid in the matrix.

An almost uniform distribution of the club-shaped protoenstatite and diopside aluminian appeared in micrographs of Y1200-b and Y1220-b in Fig. 5. Higher magnification showed the presence of interlocking microstructure with average crystallite width of about $<5 \mu\text{m}$. Clear glassy matrix were seen in Y1220, which etched under the same condition, suggesting more liquid formation. The circular trend pores also proved this.

4. Discussion

A magnified XRD patterns of Y700 to Y1150 at $2\theta=20^\circ-50^\circ$ were shown in Fig. 6 in order to more clearly illustrate the changes of calcium-rich and iron-rich crystalline phases with increasing sintering temperature. The Ca-rich crystals including anorthite, akermanite, diopside and diopside aluminian were indicated as down solid arrow, and the Fe-rich crystals including hematite and andradite were indicated as up hollow arrows. All Ca-rich crystals, akemanite, anorthite and diopside start forming at temperature from 700°C

Fig. 5. SEM micrographs of Y1150, Y1200 and Y1220. Where: “A”- Protoenstatite (MgSiO_3), “B”- Hematite (Fe_2O_3) or/ and RO phase, “C”- Ca-rich crystals, mainly Diopside ($\text{CaMgSi}_2\text{O}_6$).

Fig. 6. Changes of Ca-rich and Fe-rich crystals at different sintering temperatures.

to 800°C. High CaO composition derived from steel slag contributes to crystallization in low temperature. With diffusion of components in ceramics, akemanite transformed into diopside at approximately 1 000°C, which obviously increased the amount of diopside, as shown in the changes of peaks from Y900 to Y1000 in Fig. 6.

In a view of the above analyses, the sintering process at lower temperatures (below 1 100°C) may be described as Eqs. (4) to (12). Gibbs free energy changes (ΔG) of Eqs. (8) to (12) in the range of 700°C to 1 300°C were calculated and shown in Fig. 7. The thermodynamic calculation indicated that the ΔG of Eqs. (8) to (12) reactions were all of negative values at temperature above 700°C, illustrating the existence of these reactions.

Fig. 7. Gibbs free energy changes (ΔG) of Eqs. (8) to (12) in the temperature range from 700°C to 1300°C.

Considering the Fe-rich crystals, hematite derived from steel slag, but andradite generated at 1000°C from Fe-rich areas in ceramics. Peaks of andradite and Fe_2O_3 or RO phases disappeared at approximately 1150°C^{29,30} and 1180°C, respectively, and no other Fe-rich crystal formed except the solution of some iron into diopside aluminian. So it could be inferred that most Fe-rich crystals melted and became liquid in ceramics at temperature above 1150°C. BSI and EDS analysis also proved that Fe_2O_3 or/and RO phases were not involved in the sintering reaction at temperature below 1100°C, but decreased from 1100°C to 1150°C.

As shown in Fig. 2, in stage I, the crystallization process was preliminary completed. Therefore, stage I was named as primary crystallization process. It is obvious that a crystallization process in stage I is significantly prior to the densification process in stage II (as shown in Fig. 1). This is in favor of stable sintering because the resulting crystals

Fig. 8. Box diagram of phase evolution in pyroxene porcelain, based on XRD, SEM, physical and mechanical results.

would play a role of framework in ceramics during the densification process.

As analyzed above, Ca-rich crystals generated at lower temperatures, and akemanite is an intermediate phase and will be converted into diopside due to the surplus of MgSiO_3 and SiO_2 .

Stage II showed that the densification process started at 1 100°C and finish at 1 220°C, which is owing to the formation of liquid in ceramics. Meanwhile, a secondary crystallization would happen in stage II. Diopside ($\text{CaMgSi}_2\text{O}_6$) changed into diopside aluminan at 1 150°C with ions of Na, Fe, Al, Ti, Cr and Mn coming into crystal structure due to the promoted diffusion of ions under liquid sintering process. Therefore, sole well crystallized pyroxene phases composed the final ceramics, which was contributed to their excellent mechanical performances. The solution of metal ions in stage II process is also a good news for the solidification of heavy metals.

Clay and pyrophyllite dehydroxylated at 550°C and 662°C, respectively.³¹⁾ They ensure the strength of the green body, and were the main sources of silicon element. The dehydroxylation of talc began at approximately 600°C and gradually decomposed to MgSiO_3 and SiO_2 at temperature between 800 and 900°C. The rod-shaped MgSiO_3 played a supporting role to prevent sample deformation during the sintering process. The main reaction of steel slag at temperatures below 900°C was calcium carbonate decomposition. High active CaO decomposed from CaCO_3 contributed to crystallize at lower sintering temperature, facilitated the formation of akemanite, anorthite and diopside. The latter is an inosilicate of a simpler structure with respect to the tectosilicate. Consequently, the formation of diopside requires lesser structural rearrangements.³²⁾ Akermanite, which is an interim nonequilibrium phase, formed at approximately 900°C and then transformed to diopside at approximately 1 000°C. Andradite formed at approximately 1 000°C and melted at approximately 1 150°C, prompting the densification process, at the same time diopside transferred to diopside aluminan with more ions solution. At temperatures above 1 220°C, samples began to swell, sample completely lose shape at temperatures above 1 250°C. A box diagram of phase evolution in pyroxene porcelain, based on the present XRD and SEM study, is shown in Fig. 8.

5. Conclusion

Ceramics with high CaO and Fe_2O_3 content were prepared from steel slag and the samples sintered at 1 220°C had good properties with flexural strength of 107 MPa and water absorption of 0.045%. High CaO composition of steel slag contributes to crystallization at low temperature. Akemanite, anorthite and diopside formed at approximately 700°C and diopside were predominant at 1 000°C. The resulting crystals played a role of framework in ceramics during the sintering process. Fe_2O_3 or RO phases did not

participate in the sintering at temperature below 1 150°C. However, melting of iron-rich andradite at approximately 1 150°C and Fe_2O_3 or RO phases at approximately 1 180°C promoted the densification process. As a consequence, the crystallization process is significantly prior to the densification process. Diopside was predominant since approximately 1 000°C and transformed to diopside aluminan at temperature above 1 150°C. Sole pyroxene phases composed the final ceramic, which were contributed to their excellent mechanical performances.

Acknowledgement

This work was financially supported by the National Natural Science Foundation of China (No. 51474027).

REFERENCES

- China Resources Comprehensive Utilization annual report, National Development and Reform Commission, Beijing, (2014), 12.
- B. Dhal, H. Thatoi, N. Das and B. Pandey: *J. Hazard. Mater.*, **250** (2013), 272.
- E. A. Oluwasola, M. R. Hainin and M. M. A. Aziz: *Jurnal Teknologi*, **70** (2014), 117.
- P. Tsakiridis, G. Papadimitriou, S. Tsivilis and C. Koroneos: *J. Hazard. Mater.*, **152** (2008), 805.
- C. Barca, C. Gérente, D. Meyer, F. Chazarenc and Y. Andrès: *Water Res.*, **46** (2012), 2376.
- G. Wang, Y. Wang and Z. Gao: *J. Hazard. Mater.*, **184** (2010), 555.
- J. Yu and K. Wang: *Energy Fuel*, **25** (2011), 5483.
- D. Mombelli, C. Mapelli, S. Barella, A. Gruttadauria, G. Le Saout and E. Garcia-Diaz: *J. Hazard. Mater.*, **279** (2014), 586.
- Z. Li, S. Zhao, X. Zhao and T. He: *J. Hazard. Mater.*, **199** (2012), 448.
- Q. Wang, P. Yan and J. Feng: *J. Hazard. Mater.*, **186** (2011), 1070.
- S. Qin and B. Wu: *J. Hazard. Mater.*, **198** (2011), 269.
- E. Furlani, G. Tonello and S. Maschio: *Waste Manag.*, **30** (2010), 1714.
- E. Karamanova, G. Avdeev and A. Karamanov: *J. Eur. Ceram. Soc.*, **31** (2011), 989.
- K. Dana and S. K. Das: *J. Eur. Ceram. Soc.*, **24** (2004), 3833.
- V. M. Sglavo, S. Maurina, A. Conci, A. Salvati, G. Carturan and G. Cocco: *J. Eur. Ceram. Soc.*, **20** (2000), 245.
- T. Yoshikawa, S. Hirano, N. Hirai and T. Tanaka: *ISIJ Int.*, **48** (2008), 1322.
- W. Dai, Y. Li, D. Cang, Z. Liu and Y. Fan: *ISIJ Int.*, **54** (2014), 2672.
- I. Ozdemir and S. Yilmaz: *J. Mater. Process. Technol.*, **183** (2007), 13.
- L. M. Schabbach, F. Andreola, L. Barbieri, I. Lancellotti, E. Karamanova, B. Rangelov and A. Karamanov: *J. Eur. Ceram. Soc.*, **32** (2012), 2843.
- N. Y. Mostafa, A. A. Shaltout, M. S. Abdel-Aal and A. El-maghraby: *Mater. Design*, **31** (2010), 3677.
- H. Badiee, A. Maghsoudipour and B. Raissi Dehkordi: *Adv. Appl. Ceram.*, **107** (2008), 111.
- X. B. Ai, H. Bai, L. H. Zhao, D. Q. Cang and Q. Tang: *Int. J. Miner. Metall. Mater.*, **20** (2013), 379.
- X. B. Ai, Y. Li, X. M. Gu and D. Q. Cang: *Adv. Appl. Ceram.*, **112** (2013), 213.
- L. Zhao, Y. Li, Y. Zhou and D. Cang: *Mater. Des.*, **64** (2014), 608.
- M. Cameron and J. J. Papike: *Am. Mineral.*, **66** (1981), 1.
- F. J. Torres and J. Alarcón: *J. Non-Cryst. Solids*, **347** (2004), 45.
- ISO 10545-3:1995, Ceramic tiles -- Part 3: Determination of water absorption, apparent porosity, apparent relative density and bulk density.
- ISO 10545-4:2014, Ceramic tiles -- Part 4: Determination of modulus of rupture and breaking strength.
- Y. Suwa, Y. Teltal and S. Nere: *Am. Mineral.*, **61** (1976), 26.
- R. K. Eby, R. C. Ewing and R. C. Birtcher: *J. Mater. Res.*, **7** (1992), 3080.
- Y. Iqbal and W. E. Lee: *J. Am. Ceram. Soc.*, **83** (2000), 3121.
- L. Barbieri, F. Bondioli, I. Lancellotti, C. Leonelli, M. Montorsi, A. M. Ferrari and P. Miselli: *J. Am. Ceram. Soc.*, **88** (2005), 3131.