Evolution of crystals in SiO$_2$-Fe$_2$O$_3$-Al$_2$O$_3$ system ceramics derived from copper slag

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ABSTRACT
Copper slag is a kind of huge metallurgical residue with fayalite as the main phase. Due to the oxidation of fayalite to quartz and hematite during sintering process, quartz became the main phase of ceramics when it contained large proportion of copper slag. The internal stress in the ceramic formed due to the change of α to β increases the potential risk of cracks in the quartz cooling process. In this paper, in order to reduce the precipitation of quartz phase, natural diopside rich in CaO and MgO was introduced into the copper slag-based ceramics. A batch of ceramics were prepared with 50 wt.% copper slag and 5 – 25 wt.% diopside as raw materials at different sintering temperatures. Evolution of crystals and densification process for the ceramics were investigated through physical property tests, including XRF, XRD, SEM, EDS and FACTSAGE calculation. The results indicated that fayalite particles derived from the slag formed a core-shell structure during the oxidation process, with the inner core dominated by silica and the outer shell enriched by iron oxide. It was observed that MgO and Fe$_2$O$_3$ reacted outside the shell to form mafic spinel (Fe, Mg) Fe$_2$O$_4$, which greatly promoted the reaction of Ca$^{2+}$ with SiO$_2$ in the core areas to form anorthite. As the amount of diopside increased, more mafic spinel and anorthite formed, while less quartz appeared. The addition of diopside to the ceramic body did not change its initial sintering temperature at 1170°C but significantly improved its bending strength from 35.8 MPa to 50.3 MPa with 5 – 20 wt.% addition of diopside, and more diopside would result in excessive flux and over firing.

1. Introduction
Copper slag is a waste product during matte smelting and blowing processes, which contains more than 40 wt. % FeO and more than 30 wt.% SiO$_2$ as well as other valuable metals, such as 0.4 ~ 4.5 wt.% Cu. In general, 2.2 tons of copper slag is discharged for every 1 ton of copper product [1]. At present, the annual discharge of copper slag in China reaches nearly 20 million tons [2], and the accumulation of copper slag has exceeded 140 million tons [3]. However, the utilization rate of copper slag in China is quite low, and most of the copper slag is in the state of stockpiling, which not only occupies land with environmental pollution but also wastes slag resources. Therefore, it is imminent to investigate the utilization of copper slag.

Since the main components of copper slag are silicon oxide and ferric oxide, it lacks cementing reactivity and is difficult to be used in cement field. Meanwhile, during the recycling of copper by flotation, most copper slags are required to be ground to below 45 microns, thereby making it hard to be used as an aggregate for concrete and road construction. However, since the raw materials of ceramics need to be ground into fine particle smaller than 45 microns, it is an effective way to convert such finely ground copper slag into building ceramics.

The copper slag is composed of more than 40 wt.% FeO and 30 wt.% SiO$_2$. Thus, the ceramic derived from a high proportion of copper slag contains much higher iron oxide than the traditional SiO$_2$-Al$_2$O$_3$-Na$_2$O (K$_2$O) ceramic with Fe$_2$O$_3$ content below 3 wt.%, and belongs to the new ceramic system with high iron oxide and silica. In addition, the minerals of copper slag changed with the increase in temperature and additives. The main mineral phase in copper slag is fayalite. When it was heated from 700°C to 870°C, the diffraction peak of fayalite gradually decreases and disappears, while that of hematite and quartz gradually increases, indicating that the conversion of fayalite into hematite and quartz under air conditions. Furthermore, when the temperature continues to rise above 1100°C, the diffraction peak of hematite gradually decreases, while that of magnetite begins to strengthen [4]. Zhang et al. [5] used thermodynamic calculation and derivation to analyze the changes in valence state and component phase occurrence state of iron oxide during the oxidation process of high iron CaO-FeO$_x$ -SiO$_2$(CFS) system, and found that the increase in calcium oxide content in the system could improve the enrichment degree of iron element in magnetite phase. Zhao et al. [6] studied the influence of calcium oxide and iron oxide on the...
slag ceramics of SiO$_2$-CaO-MgO-Fe$_2$O$_3$ system, and found that high CaO content contributed to the low-temperature crystallization of the whole system. In the study of Tan et al. [7], the physical property transformation of magnetite in roasted copper slag was investigated and the results indicated that the addition of CaO promoted the transformation from Fe$_2$SiO$_4$ to Fe$_3$O$_4$ in the slag. When 25 wt. % CaO was added, the Fe$_3$O$_4$ content in the system was the highest, having the best crystal migration and aggregation effect. Blackman et al. [8] showed that the addition of MgO had a positive effect on the formation of Fe$_2$O$_4$ and MgFe$_2$O$_4$ in the MgO-Fe$_2$O$_3$-MgFe$_2$O$_4$ ternary system. Yadav et al. [9] believed that the addition of magnesium oxide could promote the transformation of hematite to Fe$_3$O$_4$ in the system, and further into the spinel family (Mg, Fe) Fe$_2$O$_4$. Jiang et al. [10] studied the influence of MgO content on the solid-phase modification of industrial copper slag. Shi et al. [11] used thermogravimetric method to study the oxidation kinetics of iron olivine. Stoyko et al. [12] analyzed the oxidative thermal decomposition process of copper slag from pyromelting in synthetic air and confirmed that copper slag was separated from iron and silicate by oxidation in synthetic air atmosphere. Meng et al. [13] studied the effect of Na$_2$O addition in copper slag on the recovery and formation of iron slag, as well as the preparation of ceramics with non-magnetic residue. Tsunazawa et al. [14] selectively oxidized the liquid copper slag, which could promote the crystallization precipitation of magnetite particles, and further realize the growth of magnetite particles by controlling the cooling rate. At present, a large number of studies have been conducted on the decomposition behavior of iron olivine in air under different oxygen partial pressures [15,16]. The results showed that Fe$_3$O$_4$ was firstly decomposed into Fe$_3$O$_4$ and amorphous SiO$_2$. With the increase in temperature, Fe$_3$O$_4$ was further oxidized to γ-Fe$_2$O$_3$ and finally oxidized to α-Fe$_2$O$_3$, but amorphous SiO$_2$ had no obvious effect. In the study of Liu et al. [17], the phase transformation of copper slag was studied during the calcination process. With the increase in calcination temperature, amorphous SiO$_2$ is converted into quartz crystal and eventually into cristobalite. It could be seen that during the sintering process of ceramics mixed with copper slag, the oxidation of iron ions in olivine would release silica with different forms, and the mineral phase transformation of quartz was closely related to the occurrence state of iron ions.

For copper slag ceramics, as the temperature rises under air conditions, high iron oxide (magnetite or hematite) and quartz phase are introduced into the ceramic body during the sintering and oxidation process. Due to the high melting point of quartz, it is relatively stable with magnetite or hematite during high-temperature sintering. Only part of the quartz could melt or participate in the sintering reaction, and there are more quartz remaining. During the cooling process of ceramics, if the temperature drops too fast, the residual quartz in the body would generate greater internal stress due to the volume shrinkage effect of crystal transformation from α to β quartz, resulting in micro-cracks and deteriorate its thermal shock resistance and mechanical strength. Therefore, the strategy for avoiding the formation of excessive quartz in copper slag ceramics becomes a key factor in the preparation process, especially for ceramics with high content of copper slag.

Science additives containing CaO and/or MgO present high reactivity with quartz at high temperature, mixing the additives into copper slag ceramics is an effective method to reduce the amount of quartz. Diopside is a commonly used raw material containing calcium and magnesium in the ceramic industry, which has been successfully applied to improve ceramic properties, reduce sintering temperature and shorten the sintering time of tile ceramics [18]. Yu [19] discussed the influence of diopside on the vitrification performance of porcelain tiles, and found that an appropriate diopside content (10 wt. %) was beneficial to increase the vitrification degree of porcelain tiles and reduce the sintering temperature. Bai [20] used 10 wt. % and 20 wt. % diopside instead of alkali feldspar to study the influence of diopside on the microstructure of traditional quartz-clay-feldspar three component ceramics. It is concluded that the diopside replacing about 10 wt. % alkali feldspar could significantly improve the densification.

In this work, ceramics were prepared with 50 wt. % copper slag, and 0 ~ 25 wt. % diopside as additives were mixed into the ceramics under constant mass ratio of SiO$_2$ and Al$_2$O$_3$ as 3.0. Such copper slag ceramics belong to a novel SiO$_2$-Fe$_2$O$_3$-Al$_2$O$_3$ ceramic system in composition, and its densification process and crystal evolution during sintering process were investigated. Aiming at reducing residual quartz and improving its mechanical properties, the influence of different contents of MgO and CaO on its crystallization and properties were focused on, and the mechanism of controlling the crystallization of copper slag ceramics was discussed. This research is expected to develop SiO$_2$-Fe$_2$O$_3$-Al$_2$O$_3$ system architectural ceramics, so that the copper slag, lead slag, nickel slag, zinc slag and nonferrous slag with high SiO$_2$ and high Fe$_2$O$_3$ could be reused to promote the utilization level of solid waste in nonferrous industry.

2. Experimental

2.1. Experimental materials

Among the experimental raw materials, the copper slag came from FangYuan Nonferrous Metals Group in Shandong. Diopside, clay, bauxite and tailing were
2.2. Sample preparation

The specific steps of sample preparation are as follows: It mainly includes four stages: raw material treatment, powder preparation, press molding and high-temperature sintering. First, according to the formula proportion in Table 2, put the dried raw materials into the planetary ball mill for ball milling and mixing. After drying, the obtained slurry is sieved through 80 mesh sieve, and the sieve residue is less than 1% to obtain the mixed raw materials. Then, the powder was granulated with water and the moisture content of the powder was controlled at 6 ~ 8 wt%. The particles are sieved through 20 mesh sieve and aged for 6 hours to ensure uniform moisture. Then, w put the aged granular material into the mold, press it with a jack, and press it into a 50 mm*10 mm*5 mm spline under the pressure of 25MPa. The pressed green body is dried in a drying oven at 105°C for 2 hours, and the moisture content after drying is less than 1%. After drying, the sample is placed in a gradient crystallization furnace for high-temperature sintering. The heating system is adjusted to the set temperature (1135°C, 1150°C, 1165°C, 1170°C, 1185°C) at the speed of 5°C/min for 30 minutes, and then cooled to 1000°C at the speed of 10°C/min. Finally, it can be removed after cooling to room temperature with the furnace. The obtained samples are tested for subsequent performance and microstructure.

2.3. Sample characterization and evaluation

The basic properties of the sintered samples were tested, including flexural strength, water absorption and shrinkage. The maximum load F of the sample at fracture was tested by using a digital display flexural tester, and the width b, the fulcrum distance L and the thickness h of the sample fracture surface were measured by using a digital display vernier caliper. The flexural strength P (MPa) of the sintered samples was calculated according to formula (2–1).

\[ P = \frac{3F}{2bh^2} \]  

(2–1)

Water absorption of the sample was tested by using a ceramic water absorption device (Ningxia Machinery Research Institute, CXY-A). The mass \( W_0 \) before water absorption and the mass \( W_1 \) after water absorption were measured by an accurate balance, and then water absorption \( W \) was calculated according to formula (2–2).

\[ W = \frac{W_1 - W_0}{W_0} \times 100 \% \]  

(2–2)

The shrinkage \( L \) was measured and calculated according to formula (2–3), in which green length \( L_0 \) and sintered length \( L_1 \) were obtained with a digital display vernier caliper.

\[ L = \frac{L_1 - L_0}{L_0} \times 100 \% \]  

(2–3)

The phase composition of the sintered samples was analyzed by X-ray diffraction (XRD) (Smartlab type, Japan). The test method was continuously scanning with a step of 0.02° using Cu target, a scanning speed

| Table 1. The main chemical composition of raw materials. |
|-----------------------------------------------|
| **Raw materials** | **SiO₂** | **Al₂O₃** | **Fe₂O₃** | **CaO** | **MgO** | **Na₂O** | **K₂O** | **Others** |
|-------------------|----------|-----------|-----------|--------|--------|-----------|--------|----------|
| Copper slag       | 27.29    | 3.71      | 55.45     | 3.06   | 2.69   | 0.98      | 0.64   | 6.18     |
| Clay              | 71.00    | 15.90     | 1.51      | 4.59   | 2.59   | 0.97      | 2.95   | 0.49     |
| Bauxite           | 42.00    | 50.00     | 1.56      | 0.90   | 0.70   | –         | 0.10   | 4.64     |
| Tailing           | 86.70    | 7.50      | 0.20      | 0.60   | 0.34   | 0.86      | 2.97   | 0.83     |
| Diopside          | 61.60    | 0.70      | 0.38      | 19.89  | 16.52  | –         | 0.28   | 0.62     |

Note: the “-” indicates that the component is not detected in the raw material.

| Table 2. Composition and main ratio of raw material. |
|-----------------------------------------------|
| **Experimental formula** | **Main chemical composition of the formula (wt.%)** |
| **No.** | **Copper slag** | **Diopside** | **Si/Al ratio** | **SiO₂** | **Al₂O₃** | **Fe₂O₃** | **CaO** | **MgO** | **Na₂O** | **K₂O** | **Others** |
|-------|----------------|-------------|----------------|--------|-----------|-----------|--------|--------|-----------|--------|----------|
| A1    | 50             | 0           | 3.03           | 44.81  | 14.75     | 31.29     | 2.66   | 2.04   | 0.77      | 1.12   | 2.56     |
| A2    | 50             | 5           | 3.02           | 44.62  | 14.76     | 31.02     | 3.56   | 2.82   | 0.75      | 1.05   | 1.42     |
| A3    | 50             | 10          | 3.01           | 44.22  | 14.66     | 30.69     | 4.49   | 3.60   | 0.70      | 0.91   | 0.73     |
| A4    | 50             | 15          | 3.03           | 43.44  | 14.31     | 30.26     | 5.33   | 4.34   | 0.66      | 0.78   | 0.88     |
| A5    | 50             | 20          | 3.02           | 43.52  | 14.42     | 29.36     | 6.10   | 5.00   | 0.60      | 0.74   | 0.26     |
| A6    | 50             | 25          | 3.02           | 43.33  | 14.35     | 28.21     | 6.84   | 5.69   | 0.56      | 0.64   | 0.38     |
of 10°/min and a scanning range of 10°~90°. After the evaluation of mechanical properties, the general block samples were ground for 2 min and then used for XRD test.

The scanning electron microscope (SEM, FEI, MLA250) was applied for the surface morphology observation. The sample was polished and corroded in 5% HF solution for 90 s, and then washed with distilled water. After that, the sample was dried in oven under 110°C. Prior to SEM test, the sample was sprayed with gold to enhance its electrical conductivity Figure 1.

3. Results and discussion

3.1. Sintering parameters of copper slag ceramics

Figures 2–4 present the variation of flexural strength, water absorption and shrinkage of copper slag ceramic samples with increasing the temperature during sintering. It can be seen from Figure 2 that the flexural strengths of A1-A6 samples generally increase with increasing the temperature. At 1170°C, the flexural strength of A2-A6 samples with diopside increased sharply, while the flexural strength of A1 sample without diopside changed little, indicating that the addition of diopside was beneficial to improve the mechanical properties of ceramics. With the increase in diopside contents from 5 wt.% to 20 wt.%, the flexural strength of the samples significantly increases and all exceed 35MPa, which could meet the national standard (GB/T 4100–2015). The maximum flexural strength of A5 sample with 20 wt.% diopside reached 50.3 MPa. However, when diopside content continually increased to 25 wt.%, the flexural strength of A6 sample dropped to 25.5 MPa.

When the temperature is lower than the sintering temperature of 1170°C, the flexural strength of A6 samples was high, indicating that the introduction of calcium and magnesium ions in the early stage could promote the sintering reaction. However, when entering the liquid phase sintering reaction stage, excessive flux components such as CaO and MgO may cause a large amount of liquid phase to cause the over-burning of A6 sample. As can be seen from the appearance of the sample shown in Figure 5, there were more pores in the internal opening of the blank body, which was the main reason for the decreased strength of the sample. Therefore, the appropriate dosage range of ceramic diopside with high iron (TFi=30 wt.%) component was 10 ~ 20 wt.%, and the alkali earth metal oxide content of CaO and MgO in the corresponding system was around 6 ~ 11 wt.%

Water absorption reflects the densification degree of ceramic body during the sintering process. As can be seen from Figure 3, water absorption of the samples decreased as the temperature increased. Especially in the heating process from 1165°C to 1170°C, the water absorption of A2-A6 samples with diopside dropped rapidly from 9.15% ~9.74% to 3.97%~3.08%, and water absorption of
A5 sample reached the lowest value of 0.52%. However, water absorption of A1 sample without diopside only decreased from 7.48% to 6.92%.

After heating to 1185°C, water absorption of A2-A4 samples continued to decrease from 3.97% ~2.67% to 1.15%~0.58%. At this time, water absorption of A5 sample changed little, while that of A1 sample was still about 5% at 1185°C. The decline slope of water absorption was the largest in the range of 1165 ~ 1170°C, indicating that the densification reaction of ceramic body was severe at this time, and liquid-phase sintering occurred in the body. It is further confirmed that the existence of CaO and MgO in the diopside could make the iron oxide in copper slag easily form a low melting point mineral phase with other components, promoting the densification process of the liquid phase, enhancing the porcelain degree and further reducing water absorption. Therefore, the addition of 5 wt.% diopside could produce the current effect, and the sample displayed the best performance with 20 wt.% diopside addition.

The shrinkage of ceramics represents the size change of ceramics before and after firing at different sintering temperatures. As shown in Figure 4, the shrinkage rates of the samples with diopside raised slowly with the increase in temperature before 1170°C, and were generally higher than those of the samples without diopside after 1170°C, corresponding to the reduction of flexural strength and water absorption. These results indicated that the reaction between diopside and other materials in ceramics mainly occurred after 1170°C.

The samples with a diopside content of 0 ~ 10 wt.% displayed a gentle shrinkage tendency at a temperature of 1135 ~ 1165°C, and the shrinkage rate increased from 2.4%~1.3% to 3.4%~3.1%. However, the shrinkage trend of the samples with a diopside content of 15 wt.%~25 wt.% was quite steeper with the shrinkage rate increasing from 2.1% ~1.3% to 4.2%~4.4%. In the range of 1165 ~ 1170°C, the shrinkage change of A5 sample was the most obvious with the shrinkage rate of 3.5%. Therefore,
the A5 sample had the most eutectic content in this temperature range, with the formation of a more liquid phase and better densification effect. When the temperature exceeded 1170°C, the shrinkage rate of the samples with diopside showed a downward trend, also indicating that the samples were all overburned in the range of 1170 – 1185°C. The presence of overburning would lead to the expansion of ceramic surface and the decrease in shrinkage rate.

### 3.2. Crystal phase evolution of copper slag ceramics

The addition of diopside could improve the physical properties of copper slag ceramics, especially when the diopside content was 20 wt.%. Therefore, in order to compare the regulation of diopside on the inner mineral phase of copper slag ceramics in SiO2-Fe2O3-Al2O3 system with large dosage, the sample without diopside (A1) and the sample with 20 wt.% diopside (A5) were selected for XRD diffraction analysis at the sintering temperatures of 1135°C, 1150°C, 1165°C, 1170°C, and 1185°C, respectively.

According to the X-ray diffraction results of the ceramic samples shown in Figure 6, it can be seen that in the air atmosphere, when the temperature increased from room temperature to 1135°C, there were diffraction peaks of quartz and hematite phase in the copper slag ceramic sample, but there was no diffraction peak of fayalite phase. This indicated that the fayalite in the copper slag had been completely oxidized to hematite phase and quartz phase. In addition, since Fe3O4 and MgFe2O4 had no big difference in crystal structure, the angles corresponding to diffraction peaks on the same crystal plane (220), (311), (400), (422), (511) and (440) were extremely close. Therefore, they could be used as mafic spinel group (Fe, Mg) Fe2O4 for the following discussion.

![Figure 6. XRD patterns of A1 sample at different sintering temperatures.](image)

According to the comparison of XRD patterns of A1 and A5 samples, it could be found that at a sintering temperature of 1135°C, the characteristic diffraction peaks of hematite at 24°, 33°, 49° and 54° in Figure 7 were significantly weakened, while the diffraction peaks of spinel ore phase at 30°, 36° and 57° were obviously enhanced. In addition, when the temperature increased to 1150°C, the characteristic diffraction peak of 33° hematite decreased compared with that of 36° spinel. And hematite was the only iron-bearing phase other than spinel; thus, the increase in spinel came from hematite. This indicated that the spinel phase increased significantly, and part of hematite transformed into spinel phase with increasing the temperature.

Meanwhile, the diffraction peaks of other mineral phases have also undergone great change. For instance, the characteristic diffraction peaks of quartz at 21° and 27° were obviously weakened, and the characteristic diffraction peaks of anorthite at 28° and 43° were enhanced. The quartz mineral phase was derived from the oxidation decomposition of fayalite into clay minerals and copper slag. The formation of feldspar ore phase was mainly due to the small amount of CaO in ceramic raw materials, which could react and combine with SiO2 and Al2O3 in clay raw materials. Moreover, more CaO was introduced with the addition of diopside, eventually leading to a continuous increase in feldspar ore phase. As a result, the basic physical properties of A5 sample were better than that of A1 sample, which was consistent with the optimal performance of A5 measured previously.

In addition, in order to more accurately analyze the diffraction intensity and content difference of each mineral phase in A1 and A5 samples, the diffraction peak intensity of each mineral phase was calculated with the aid of jade6.0 software. The diffraction peak height of quartz ore phase at 27°, denoted as IQO2, was defined as the diffraction peak intensity of the mineral
phase. Similarly, the diffraction peak intensities of hematite phase at 33°, spinel phase at 36° and anorthite phase at 28° were denoted as $i_{Fe2O3}$, $i_{Fe,MgFe2O4}$, and $i_{CaAl2Si2O8}$, respectively. In order to visually express the change in diffraction intensity of each mineral phase, the diffraction peak intensity of hematite phase at 33° was taken as the benchmark. Then, the ratio of diffraction peak intensity of each crystalline phase to the characteristic peak intensity of hematite phase was defined as K. For instance, the ratio of diffraction peak intensity of quartz phase to hematite phase could be expressed as $K_{SiO2} = i_{SiO2}/i_{Fe2O3}$, and the ratio of diffraction peak intensity of spinel phase to hematite phase could be expressed as $K_{Fe,MgFe2O4} = i_{Fe,MgFe2O4}/i_{Fe2O3}$. The diffraction peak intensity ratio of anorthite phase and hematite phase was expressed as $K_{CaAl2Si2O8} = i_{CaAl2Si2O8}/i_{Fe2O3}$. The calculation results are shown in Figure 8.

It can be seen that the diffraction peak intensity of each mineral phase of A1 sample changed little with the increase in temperature. After adding 20 wt.% diopside, the diffraction peak ratio of the remaining mineral phase and hematite phase of A5 sample changed significantly at 1135°C, such as $K_{SiO2}$ decreasing from 0.81 to 0.64, $K_{Fe,MgFe2O4}$ increasing from 0.75 to 1.38, and $K_{CaAl2Si2O8}$ increasing from 0.14 to 0.36. At the same time, $K_{SiO2}$ decreased with increasing temperature, while $K_{Fe,MgFe2O4}$ and $K_{CaAl2Si2O8}$ showed an upward trend.

In addition, through the comparison of the basic performance results, it can be seen that there was a great difference in the properties of the samples at 1165°C and 1170°C. Therefore, in order to investigate the influence of the change in mineral phase composition and content of the samples on the properties of ceramic green body, the samples under two sintering conditions were selected for X-ray diffraction analysis.

From the X-ray diffraction results shown in Figures 9–10, the mineral phase type of the sample did not change under different sintering temperatures of 1165°C and 1170°C. There was an obvious difference in the mineral phase diffraction intensity of the samples with the same component under two sintering temperatures. Combined with the sharp change of flexural strength, water absorption and shrinkage of the sample in this temperature range, it can be inferred that the liquid-phase sintering process mainly occurs in the sample. Science of the material liquid-phase migration was much faster than the solid-phase diffusion, the densification speed of the sintered body was accelerated and the shrinkage was significant [21], leading to the enhancement of the porcelain strength of copper slag ceramics and the substantial improvement of the basic properties of copper slag ceramics.

Similarly, in order to more accurately characterize the change of mineral phase diffraction intensity in the samples with different diopside contents at 1165°C and 1170°C, the diffraction peak intensity of each mineral phase was quantitatively analyzed and calculated by jade6.0 software, and the calculation results are shown in Figure 11. It can be seen that as the temperature increased from 1165°C to 1170°C, the mineral phase diffraction peak intensity of the samples with the same component changed little at different sintering temperatures. However, the main difference exists in the influence of different diopside contents in the sample on the mineral phase diffraction peak intensity. For instance, at 1170°C, with the increase in the diopside content, the $K_{SiO2}$ of A1–A5 samples decreased from 0.70 to 0.49, and the $K_{Fe,MgFe2O4}$ increased from 0.75 to 2.38, and the $K_{CaAl2Si2O8}$ increased from 0.08 to 0.64, indicating that the increase in diopside content not only greatly reduced the quartz content in the green body but also significantly increased the magnetite, magnesite and anorthite contents. The increase in spinel phase such as magnetite and magnesite was mainly due to the change of hematite phase in the billet, due to the reduction of the hematite phase content. Accordingly, the addition of diopside introduced more flux components, such as CaO, leading to the formation of a low melting

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**Figure 8.** The mineral phase diffraction peak ratio (K) of A1 (left) and A5 (right) samples with different temperatures during the sintering.

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point substances such as anorthite in the copper slag ceramic body. This would reduce the content of high melting point substances, such as quartz, and form a large amount of liquid phase, which promoted the liquid-phase sintering process and finally improved the properties of copper slag ceramics, in consistent with the previous results of basic properties of copper slag ceramics.

**Figure 9.** XRD patterns of A1-1165–A6-1165 samples.

**Figure 10.** XRD patterns of A1-1170–A6-1170 samples.

**Figure 11.** The mineral phase diffraction intensity ratio (K) of the samples at 1165°C (left) and 1170°C (right).
3.3. Morphological characteristics of copper slag ceramics

Figure 12 displays the microstructure of copper slag ceramics at 1170°C. It can be seen that crystal structures with different sizes appear in the sample. An appropriate amount of glass phase formed between the crystals to bond the grains together filled the gap among the crystals and promoted the densification of the green body. At the same time, SEM images showed that at 1170°C, the sample formed a core-shell structure dominated by internal silicon oxide and enriched with external iron oxide. Typically, a bright white outer layer was wrapped with a dark gray inner layer, and the A1 sample presented the densest structure. According to the surface scan of EDS shown in Figure 13(a), the bright white area was mainly Fe, O and a small amount of Mg, while the dark gray area was mainly Fe, O and Si. Based on the mineral phase analysis results in the copper slag ceramic system, it can be inferred that the crystal phase in the bright white area was Fe₂O₃, Fe₃O₄ or MgFe₂O₄ mineral phase, and the dark gray crystal phase was SiO₂ and Fe₂O₃ mineral phase. Although the main mineral phase fayalite in copper slag was oxidized and decomposed into iron oxide and quartz, this quartz mineral phase was wrapped inside by iron oxide mineral phase, which was not conducive to the reaction between quartz components and other components in the system. These would easily induce the excessive quartz in the green body, resulting in a decline in ceramic properties. However, with the addition of diopside, the external iron oxide in the core-shell structure gradually appears to be a certain dispersion phenomenon, especially when the diopside content is 20 wt.%. The external iron oxide structure was basically dissociated into a more discrete type, and the internal quartz phase was gradually exposed. As a result, the internal quartz ore phase could easily contact and react with other components. According to the above XRD patterns, there were more ferromanganese spinel in the green body, and more CaO in the green body, which could react with Al₂O₃, SiO₂ in clay raw materials and SiO₂ in fayalite to form more anorthite phase. These could greatly reduce the quartz mineral phase in the green body and finally improve the mechanical properties of copper slag ceramics, in consistent with the results of mineral phase evolution analysis and performance analysis.

3.4. Analysis and discussion

Based on the above analysis, it can be seen that there are a variety of crystal phases in the copper slag ceramics. Therefore, the reaction module of FCATSAGE8.0 software was employed to analyze the change of Gibbs free energy (ΔG) of the main crystal phases in the temperature ranging from 700°C to 1200°C. As can be
seen from Figure 14, the thermodynamic calculation results showed that the reaction formula $\Delta G$ was below zero, indicating the existence of the reaction process.

During the sintering process of copper slag ceramics, because the iron oxide in copper slag mainly exists in the form of fayalite, fayalite is unstable at high temperature and is easily oxidized and decomposed into quartz and high-valence iron oxides, such as $\text{Fe}_2\text{O}_4$ and $\text{Fe}_2\text{O}_3$. Therefore, in the high-temperature sintering process, there are reactions (1) and (2). According to the calculation results of FactSage, the Gibbs free energy of reaction (1) is the lowest. Therefore, it can be inferred that reaction (1) has priority to the reaction (2) under this condition, $\text{Fe}_3\text{O}_4$ will be gradually generated, followed by reaction (2) with the formation of $\text{Fe}_2\text{O}_3$. In addition, in the process of sintering, part of $\text{Fe}_2\text{O}_4$ is able to be oxidized to $\text{Fe}_2\text{O}_3$ as shown in reaction (3), resulting in a continuous increase of $\text{Fe}_2\text{O}_3$. With the precipitation of $\text{Fe}_2\text{O}_3$ and the introduction of more $\text{MgO}$ derived from diopside, the reaction process of $\text{MgO}$ and $\text{Fe}_2\text{O}_3$ will occur shown in reaction (4), so as to form $\text{MgFe}_2\text{O}_4$. As $\text{Fe}_2\text{O}_3$ is mainly distributed in the outer shell areas, the formation of solid solution destroyed the core-shell structure, weakening the blocking effect of crystals of iron oxide (magnetite and hematite) on diffusion of ions, and promotes the progress of reaction (5) with $\text{CaO}$ and internal silicon oxide in the core-shell structure. When the formation of anorthite consumed a large amount of quartz, internal stress in the ceramic body was greatly weakened and its properties were improved.

$$3\text{Fe}_2\text{SiO}_4+\text{O}_2\rightarrow 2\text{Fe}_3\text{O}_4+3\text{SiO}_2$$ (1)

$$2\text{Fe}_2\text{SiO}_4+\text{O}_2\rightarrow 2\text{Fe}_2\text{O}_3+2\text{SiO}_2$$ (2)

$$4\text{Fe}_3\text{O}_4+\text{O}_2\rightarrow 6\text{Fe}_2\text{O}_3$$ (3)

$$\text{MgO}+\text{Fe}_2\text{O}_3\rightarrow \text{MgFe}_2\text{O}_4 \quad \text{(Solid solution)}$$ (4)

$$\text{CaO}+\text{Al}_2\text{O}_3+2\text{SiO}_2\rightarrow \text{CaAl}_2\text{Si}_2\text{O}_8$$ (5)

### 4. Conclusion

In this work, more quartz is formed in the ceramics derived from 50 wt.% copper slag, which increases the potential risk of cracking. Investigation has been conducted to reduce quartz in batches of ceramics by adding 5 ~ 25 wt.% of $\text{MgO}$ and $\text{CaO}$-rich diopside. Compared with clay minerals, diopside with more calcium and magnesium ions could react with $\text{Fe}_2\text{O}_3$ and $\text{SiO}_2$ components at the same time to accelerate the sintering and reaction. Adding 5 wt.% diopside exerted a significant effect on the improvement of sintering density, strength, and shrinkage. At 1170°C, the strength increased from 19.2 MPa to 35.8 MPa, and the shrinkage increased from 3.6% to 6.0%. The ceramics with 20 wt.% diopside in its raw materials at 1170°C possessed the best performance with flexural strength of 50.3 MPa, and water absorption rate of 0.52%, which meets the requirements of the ceramic tiles national standard (GB/T 4100~2015). In addition, the introduction of diopside can significantly reduce the quartz content in copper slag ceramics. Moreover, reactions between $\text{MgO}$ and $\text{Fe}_2\text{O}_3$ in shell outside to form mafic spinel (Fe, Mg)$\text{Fe}_2\text{O}_4$ were observed, which greatly promoted the reaction between $\text{Ca}^{2+}$ and $\text{SiO}_2$ in core areas to form anorthite. With increasing diopside content, more mafic spinel and anorthite formed with less quartz, which effectively solved the problem of excessive stress caused by excessive quartz and improved the basic properties of high-content copper slag ceramics.

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### Disclosure statement

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