

Article Relation between Viscosity and Conductivity of CaO-MgO-FeO-Al₂O₃-SiO₂ System for Copper Smelting Slags

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Abstract: The viscosity and conductivity of the smelting slag of copper oxide concentrate are important for reducing the operating temperature. In this study, seven slag samples were prepared by the reductive smelting of copper oxide concentrate with different ferrous oxide contents. The viscosity and conductivity data of these CaO-MgO-FeO-Al₂O₃-SiO₂ samples were measured in the temperature range of 1290~1410 °C. Based on the structural features of aluminosilicate melts, the change and dependency relationships of their viscosity and conductivity were analyzed. The results show that there is a strong tendency to form orthosilicate even when the slag composition is acidic. The formation of fayalite would allow more Al³⁺ to form pyroxene with the six-coordinated structure. As a result, the polymerization degree and viscosity of the melt will be reduced. The [AlO]₄⁵⁻ as a network former will reduce the bonding strength of the structural units, thus reducing the slag viscosity at high temperature. In the experimental range, the logarithm of viscosity of each slag sample has a good linear relationship with its logarithm of conductivity. However, there is no uniform linear equation for these complex slags with wide composition variations. These results have potential guiding significance for the copper smelting process.

Keywords: copper smelting slag; aluminum oxide; viscosity; conductivity; structural unit



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). 1. Introduction

The African Copperbelt is the second-largest and most important copper source in the world [1]. Its gangue component is mainly silica, in addition to a small amount of alumina, magnesium oxide, calcium oxide, and iron oxide. Blast furnace reduction smelting is very suitable for this high-grade copper oxide with Cu > 15% [2]. It has been used in the industrial practice of metal extraction from copper oxide concentrate in Africa. Enhancing the reductive atmosphere in the blast furnace is beneficial for improving production efficiency but will strengthen iron reduction [3]. Therefore, the slag type must be improved to reduce iron reduction.

The crude copper produced by the high-calcium slag has a high grade, but the slag has a high viscosity and requires a higher operating temperature. Although the appropriate addition of iron oxide will reduce the slag viscosity and operating temperature, the reduction degree of iron and the slag viscosity need to be controlled. The study of slag viscosity under different calcium oxide and ferrous oxide contents has important guiding significance for reducing operating temperature. In addition, when the slag viscosity is high, the product of blast furnace smelting needs to be pumped into the front bed to further separate copper from the slag. Generally, direct current power is used to maintain the temperature of the slag. Therefore, the conductivity of slag and its variation characteristics are also important for the separation of copper. When the alumino-silicate melt is completely melted, it can be regarded as a Newtonian fluid, and the relation between the slag viscosity and temperature is in accordance with the Arrhenius relation (1) [4,5].

$$ln\eta = A_{\eta} + E_{\eta} / RT \tag{1}$$

The hole theory of melts considers that the liquid has solid-like structural units (SU), oscillating near the average position in their energy cells (potential wells) [6,7]. Oscillations of magnitude above the barrier cause structural units to move into adjacent empty units, or "holes", provided the latter is empty. Thus, the viscosity of the liquid is determined by the ability of the structural units to jump over the barrier and the presence of "holes" in the liquid. E_{η} and η^0 are related to the activation energy of structural units jumping into adjacent holes and the probability of hole formation, respectively.

The viscosities of alkaline earth silicate or aluminosilicate melts are determined by the polymerization degree of their networks [5]. It has been widely accepted to classify all cations into three behaviors, including glass former (Si⁴⁺, Ge⁴⁺, etc.), modifier (Na⁺, Mg²⁺, Ca²⁺, etc.), and amphoteric gelling agents (Al³⁺, Fe³⁺, etc.). However, the addition of basic oxides can transform the random network structure into a more depolymerized structure containing chains and rings [8–10]. Fincham and Richardson [11] suggested that there are three types of oxygen in silicate melts, including bridging oxygen (BO, O^0), non-bridging oxygen (NBO, O⁻), and free oxygen (FO, O²⁻). Schramm et al. [12,13] suggested that the Qⁿ notation can be used to describe the different coordinated states of molten silicates and aluminates. Based on the Raman spectroscopy and deconvolution technique, Mysen et al. [14] evaluated the degree of polymerization of the melts by distinguishing Q^0 , Q^1 , Q^2 , and Q^3 units and their relative abundance. Structural depolymerization occurs in three distinctive mechanisms, each of which dominates the structural depolymerization in each region of non-bridging oxygen number per tetrahedrally coordinated atom (NBO/T) [15]. In fact, both the *n* value in Q^n and NBO/T reflect the number of shared vertices of $[SiO_4]^{4-}$ basic structure units [16,17]. With the increase in polymerization degree of $[SiO_4]^{4-}$, the structural units gradually become larger and exist in the forms of rings, single chains, double chains, sheets, etc. Therefore, both the ability of structural units to jump potential barriers and the probability of creating "holes" in the liquid are decreased, thus leading to a high slag viscosity value.

Aluminosilicate melts consist of tetrahedral $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ units, while the $[AlO_4]^{5-}$ tetrahedron requires charge compensation due to its valence electron difference from that of $[SiO_4]^{4-}$. Zhang et al. suggested [18] that the priority for charge compensation is $Ca^{2+} > Mg^{2+}$. There are some obvious characteristics, such as the lubricant effect [19], the charge compensation effect for tetrahedrally coordinated aluminum [5], and the weak lubricant effect [20]. The local viscosity is maximum around the fayalite composition in the FeO-SiO₂ system [21], which reflects the influence mechanism of composition and structure on the viscosity of aluminosilicate slags. The lubricant effect and charge compensation effect also have a significant influence on the viscosity by changing the depolymerization degree. For silicate slags, the depolymerization degree depends on the O/Si ratio. For aluminosilicate slags, Al_2O_3 will exacerbate the depolymerization of the network structure as an alkaline oxide, while the polymerization of the network structure will be improved by the charge compensation effect when it acts as an acidic oxide. However, few studies have analyzed the effect of alumina on the slag viscosity.

In this work, the viscosity and conductivity of the slags formed in the smelting process of copper oxide concentrate with different ferrous oxide contents were measured. The relation between the viscosity and conductivity of slags was analyzed. On the basis of the above theory, the reasons for the change in slag viscosity and conductivity with composition and temperature were discussed. These results will be instructive in reducing the slag viscosity and operating temperature of the copper smelting process.

2. Experiment

2.1. Preparation of Slag Samples

The copper oxide concentrate used in the experiment was from the Koluwezi mining area in the Democratic Republic of Congo. It contains 20.92 wt.% copper, and the main mineral phases are quartz, malachite, and clinochlorite. The coke ratio is 5 wt.% and the carbon content in coke is more than 83 wt.%. The calcium oxide and ferrous oxalate used for slag preparation are analytically pure. The CaO/SiO_2 mass ratio was set to 0.4, and the FeO/SiO₂ mass ratio varied between 0.41 and 1.25. The mixture of copper oxide concentrate with 8 wt.% water content, slagging agent, and coke powder was granulated under 40 MPa pressure and then dried at 300 °C for 1 h. The dry material was put into a corundum crucible to reduce and melt with a sufficient reductive atmosphere in a muffle furnace at 1400 °C for 2 h. After the furnace was cooled, the crucible was taken out and broken to separate slag and crude copper. The slag samples were weighted and used for subsequent experiments. The compositions of smelting slags were determined by inductively coupled plasma-atomic emission spectrometry (ThermoFisher, ICAP PRO XP, Waltham, MA, USA). The NBO/T parameter, which represents the polymerization degree of melt, was calculated by Equation (2). And the NBO/S (nonbridging oxygen per silicon) can be calculated by Equations (3) and (4) by considering the Al_2O_3 as a basic oxide or not, respectively [22].

$$NBO/T = 2(X_{CaO} + X_{FeO} + X_{MgO} - X_{Al2O3})/(X_{SiO2} + 2X_{Al2O3})$$
(2)

$$NBO/S = (2X_{CaO} + 2X_{FeO} + 2X_{MgO} + 6X_{Al2O3})/X_{SiO2}$$
(3)

$$NBO/S = (2X_{CaO} + 2X_{FeO} + 2X_{MgO})/X_{SiO2}$$
(4)

where the X is the mole fraction of each oxide.

2.2. Determination of Slag Viscosity

The slag viscosity was measured on a self-developed RTW-10 melt physical property tester (Northeast University, Boston, MA, USA) by a rotating cylinder method. The specifications of the apparatus and crucible were the same as the reference [23]. The pre-melted sample (150 g) was put inside a molybdenum crucible and heated in a rotatory viscometer. The highly purified Ar atmosphere (0.35 L/min) was continuously used to prevent the oxidation of the spindle and slag during the test process. After the desired temperature was reached and maintained for more than 30 min, the slag melt was homogenized. The molybdenum spindle was connected to the viscometer through an alumina shaft, then immersed into the liquid slag 10 mm above the crucible base and rotated at a fixed speed of 200 r/min. The viscosity was measured at different temperatures, with a temperature step of 30 °C during the temperature-dropping process.

2.3. Determination of Slag Conductivity

The electrical conductivities of slag melts were determined with the contact compensation method by measuring the alternating current resistance of a melt in an alundum crucible in an Ar atmosphere using an electrochemical comprehensive tester (Versa STAT 3F, AMETEK SI, Berwyn, PA, USA). The measuring cell consisted of two electrodes of a molybdenum wire enclosed in two channels of a single alundum rod. The distance between the measuring electrodes and their immersion depth in the melt was 20 mm. The melt temperature range was 1290–1410 °C, and measurements were performed upon steplike cooling of the melt at a step of 30 °C.

3. Results and Discussion

3.1. Chemical Composition of Slag Samples

The compositions of the obtained smelting slags under different FeO/SiO_2 burden ratios are shown in Table 1. The reducing atmosphere in the slag production process

basically maintains the iron in the slag in the Fe/FeO equilibrium state, so it can be considered that no Fe₂O₃ exists in the slag. The copper contents in the slags vary from 0.13 to 0.42 wt.%, and the equivalent molar fraction of Cu₂O is between 0.001 and 0.002. Therefore, the influence of Fe₂O₃ and copper on slag viscosity and conductivity can be ignored due to its low content, indicating that the slag belongs to the typical CaO-FeO-MgO-Al₂O₃-SiO₂ system. Table 2 shows the measurement results of slag viscosity and conductivity. It can be found that the viscosity and conductivity gradually decrease with the increase in the FeO/SiO₂ ratio but increase sharply at 0.79 and 0.87, which may result from the structural change of the slags. In addition, according to the measured melting temperature of slags, except for the flow temperature of the Z6 slag, which is close to 1290 °C, the other melting temperatures are lower than the test temperature (1290~1410 °C). Therefore, the slags will not crystallize and are suitable for Newtonian fluid type.

| Slag | FeO/SiO ₂ - | | Cu | | | | |
|------|------------------------|------|-------|-----------|-------|------------------|--------|
| | | CaO | MgO | Al_2O_3 | FeO | SiO ₂ | (wt.%) |
| Z1 | 0.41 | 0.22 | 0.13 | 0.050 | 0.050 | 0.55 | 0.23 |
| Z2 | 0.56 | 0.23 | 0.13 | 0.050 | 0.068 | 0.52 | 0.39 |
| Z3 | 0.71 | 0.22 | 0.13 | 0.055 | 0.097 | 0.50 | 0.27 |
| Z4 | 0.79 | 0.21 | 0.12 | 0.066 | 0.16 | 0.45 | 0.13 |
| Z5 | 0.87 | 0.19 | 0.11 | 0.050 | 0.20 | 0.45 | 0.24 |
| Z6 | 1.10 | 0.16 | 0.088 | 0.069 | 0.30 | 0.38 | 0.23 |
| Z7 | 1.17 | 0.15 | 0.085 | 0.059 | 0.32 | 0.39 | 0.42 |

Table 1. The composition of slag samples at different FeO/SiO₂ burden ratios.

| Slag | 1290 °C | | 1320 °C | | 1350 °C | | 1380 °C | | 1410 °C | |
|------|---------|------|---------|------|---------|------|---------|------|---------|------|
| | κ | η | κ | η | κ | η | κ | η | κ | η |
| Z1 | 11.96 | 3.22 | 15.09 | 2.45 | 19.48 | 1.81 | 23.79 | 1.37 | 28.67 | 1.15 |
| Z2 | 7.94 | 3.49 | 10.35 | 2.41 | 12.99 | 1.72 | 16.61 | 1.29 | 19.76 | 1.02 |
| Z3 | 6.72 | 4.03 | 8.63 | 2.64 | 10.66 | 1.73 | 13.04 | 1.04 | 16.43 | 0.71 |
| Z4 | 9.65 | 4.49 | 12.43 | 3.04 | 15.52 | 2.35 | 18.87 | 1.49 | 22.92 | 1.04 |
| Z5 | 12.94 | 2.51 | 17.02 | 1.73 | 22.57 | 1.22 | 28.48 | 0.93 | 35.55 | 0.67 |
| Z6 | 5.33 | 3.28 | 7.42 | 2.01 | 9.14 | 1.56 | 12.54 | 1.22 | 16.08 | 0.69 |
| Z7 | 5.89 | 2.68 | 7.81 | 2.17 | 7.79 | 1.67 | 8.53 | 1.57 | 11.29 | 1.28 |

Table 2. Measured viscosity (Pa·s) and conductivity (S/m) of slags at different temperatures (°C).

3.2. Effect of NBO/T and Temperature on Viscosity

Based on Equations (2)–(4) and Table 1, the NBO/T and NBO/Si values can be obtained and shown in Table 3. In general, the increase in NBO/T implies depolymerization of the melt structural units, which will result in the decrease in slag viscosity. However, this feature cannot be found in Figure 1. It demonstrates a very complicated relationship between viscosity and NBO/T of slags. Moreover, the viscosity change of the same slag sample is more different at different temperatures. At 1290 °C, the viscosity of the slag increases first with the increase in the NBO/T value. When NBO/T is greater than 1.45, the viscosity value decreases rapidly and then stabilizes. The viscosity change of the slag follows a similar pattern, despite the increase in temperature. However, because high temperature is beneficial for reducing the slag viscosity, the fluctuation of the viscosity value with NBO/T is obviously weakened.

| Slag | Basicity | Basicity | NBO/Si | NBO/Si | |
|------|--|--|--|--|-------|
| | (Al ₂ O ₃ Ignored) | (Al ₂ O ₃ as Base) | (Al ₂ O ₃ as Base) | (Al ₂ O ₃ Ignored) | NBO/1 |
| Z1 | 0.74 | 1.01 | 2.03 | 1.48 | 1.09 |
| Z2 | 0.81 | 1.10 | 2.20 | 1.63 | 1.21 |
| Z3 | 0.90 | 1.23 | 2.46 | 1.80 | 1.29 |
| Z4 | 1.09 | 1.53 | 3.06 | 2.18 | 1.45 |
| Z5 | 1.10 | 1.43 | 2.86 | 2.20 | 1.62 |
| Z6 | 1.42 | 1.96 | 3.92 | 2.84 | 1.83 |
| Z7 | 1.41 | 1.87 | 3.74 | 2.83 | 1.94 |

Table 3. Calculated O/Si, NBO/Si, and NBO/T values of different slags (mol).



Figure 1. Effect of NBO/T and temperature on slag viscosity.

For simplicity, the viscosity changes of Z1, Z2, and Z3 samples were further analyzed based on slag basicity. Without considering Al_2O_3 , the basicities of these three samples are 0.74, 0.81, and 0.90, respectively (Table 3), indicating all of them are acidic slags. If the Al_2O_3 in the slag is taken as basic oxide, the basicity of the Z1, Z2, and Z3 samples will increase to 1.01, 1.10, and 1.23, respectively. The corresponding NBO/Si values of the Z1, Z2, and Z3 slags also increase to 2.03, 2.20, and 2.46. Hence, their basicity becomes gradually stronger, and the added Al_2O_3 can act as a network-forming agent together with SiO₂. Therefore, the polymerization degree of aluminosilicate melt increases gradually, which will result in an increase in viscosity. This variation feature can be verified by the viscosity change at 1290 °C. However, when Al_2O_3 acts as a network former, the polymerization strength of the structural units becomes weaker. With the increase in temperature, the polymerization degree of aluminosilicate will reduce, resulting in a decrease in slag viscosity.

Notably, the Z4 slag has a maximum viscosity value over the whole temperature range since more Al_2O_3 is available to act as a network-forming agent. The viscosity value becomes weaker with the increase in temperature due to the weak polymerization strength of $[AlO]_4^{5-}$. When Al_2O_3 is considered to act as a network former, the NBO/T value of the Z4 slag is 1.45. The structural units are still limited to the highly polymerized mica-like sheet and amphibole-like double chain. In addition, the NBO/T values of the Z1, Z2, Z3, and Z4 slags are in the range of 1.09~1.45. Hence, the number of shared vertices of SiO_4^{4-} and $[AlO]_4^{5-}$ is between 2.91 and 2.51, and the structural units correspond to the transition region of sheet mica and amphibole. However, the Z5 slag has an NBO/T value of 1.62 (slightly higher than 1.5), indicating the formation of a structural unit intermediate between amphibole (double chain) and pyroxene (single chain). The sharp decrease in polymerization degree resulted in the lowest viscosity value for the Z5 slag at each temperature. The

NBO/T value of the Z6 slag increases to 1.83, and its polymerization degree and viscosity should be lower than that of Z5. However, the Al_2O_3 mole fraction of slag Z6 reaches 0.069, which is higher than that of the Z5 slag, thus resulting in more $[AlO]_4^{5-}$ to improve the polymerization of structural units. Therefore, the viscosity of Z6 slag slightly increases even at higher NBO/T values. Similarly, the Z7 slag has a molar fraction of 0.059 for Al_2O_3 , resulting in an increase in viscosity.

3.3. Effect of NBO/T and Temperature on Conductivity

Figure 2 shows that the conductivity values of the Z1, Z2, and Z3 slags drop gradually with the increase in NBO/T. These results imply that the increase in network former and the polymerization degree of structural units leads to a gradual increase in the binding of conductive cations, which in turn results in a decrease in conductivity. The Z4 slag contains enough Al_2O_3 to act as a network former. However, the intervention of excess $[AlO]_4^{5-}$ will lead to a reduction in the bonding strength of the structural units, thus reducing its binding ability to the cations. Meanwhile, the increase in NBO/T will also improve the polymerization of structural units, which will make cation migration more difficult. These two effects contribute to the slight increase in conductivity.



Figure 2. Effect of NBO/T and temperature on slag conductivity.

As for the Z5 slag, the structural units have passed through the transition region of infinite sheet clays and into the amphibole and pyroxene chains because of its NBO/T = 1.62. As a result, the binding between the slag structural units and conductive cations would be significantly reduced, and its conductivity would increase rapidly. However, the Z6 slag has a significantly higher Al_2O_3 content than the Z5 slag and needs more calcium ions for charge compensation. The increase in NBO/T comes mainly from the increase in FeO content, but both FeO and SiO₂ have a strong tendency to form fayalite, resulting in a reduction in free cations that can migrate and conduct electricity, thus reducing the conductivity.

3.4. Relationship between Conductivity and Viscosity

Several studies illustrated the relationship between conductivity and viscosity of various electrolytes [24], based on Walden's rule [25]. This empirical rule indicated that the product of viscosity and equivalent ionic conductance at infinite dilution in electrolyte solution is constant. In oxide melts, however, there is little evidence that Walden's rule is valid. The prediction of conductivity based on melt viscosity cannot be reliably done, but a strong correlation between these two properties is evident in some melts but not in all [24]. The general rule is that there is a linear relationship between the logarithm of conductivity and viscosity, but the slope and its corresponding influence degree are different for diverse systems. Even for the same CaO-MgO-Al₂O₃-SiO₂ system, the deviation reaches 30.7% for the data of Winterhager [26] and 6.3% for the data of Sarkar [27], respectively. For the CaO-MgO-FeO-Al₂O₃-SiO₂ system, Wanli Li et al. [28] obtained the relation $ln\eta = 1.89 - 1.14ln\kappa$ with a mean deviation of 14.92%.

Figure 3a shows the good linear fitting result between the logarithm of conductivity and viscosity for each slag. The results in Table 4 show that both viscosity and conductivity can be well described by the Arrhenius law (Equations (5) and (6)). Meanwhile, as temperature increases, the slag viscosity decreases while its conductivity increases. Therefore, the temperature dependence of the conductivity is opposite to that of the viscosity.

$$\ln \kappa = A_{\kappa} - E_{\kappa} / RT \tag{5}$$

$$ln\eta + nln\kappa = C + \Delta E / RT \tag{6}$$

where $C = A_{\eta} + nA_{\kappa}$, $\Delta E = (E_{\eta} - nE_{\kappa})$. For a specific system, if there exists a constant "n" that always fulfills the condition of $E_{\eta} = nE_{\kappa}$ regardless of composition, the logarithm of the viscosity will be the linear function of the logarithm of the conductivity. Therefore, it is theoretically possible to build a linear function between them. The linear relationship between the logarithm of viscosity and conductivity can be described with Equation (7).

$$ln\eta = \mathbf{C} - n\ln\kappa\tag{7}$$



Figure 3. (a) Logarithm relation between viscosity and conductivity and (b) the linear fitting slope of CaO-MgO-FeO-Al₂O₃-SiO₂ systems at different NBO/T values.

| Table 4. Logarithm relation between viscosi | y and conductivity | and the related | parameters. |
|---|--------------------|-----------------|-------------|
|---|--------------------|-----------------|-------------|

| Slag | Equation | R ² | E_{η} | E_{κ} | A_η | A_κ |
|------|-----------------------------------|-----------------------|------------|--------------|----------|------------|
| Z1 | $ln\eta = 4.133 - 1.195 ln\kappa$ | 0.997 | 186.35 | 156.23 | -13.60 | 14.84 |
| Z2 | $ln\eta = 4.071 - 1.366 ln\kappa$ | 0.998 | 227.18 | 166.41 | 16.22 | -8.89 |
| Z3 | $ln\eta = 5.284 - 2.018 ln\kappa$ | 0.994 | 320.22 | 158.94 | -23.21 | 14.12 |
| Z4 | $ln\eta = 5.372 - 1.688 ln\kappa$ | 0.985 | 261.97 | 155.32 | -18.55 | 14.17 |
| Z5 | $ln\eta = 4.168 - 1.274 ln\kappa$ | 0.997 | 234.03 | 184.18 | -17.15 | 16.73 |
| Z6 | $ln\eta = 3.371 - 1.313 ln\kappa$ | 0.966 | 261.38 | 198.91 | -18.96 | 17.01 |
| Z7 | $ln\eta = 3.095 - 1.184 ln\kappa$ | 0.892 | 130.14 | 110.36 | -9.08 | 10.29 |

The values of E_{η} and A_{η} can be calculated based on Equation (1) and the data in Table 2. Therefore, the E_{κ} and A_{κ} values can be obtained and summarized in Table 4. It can be seen from Figure 3b that the linear fitting slope of CaO-MgO-FeO-Al₂O₃-SiO₂ systems is highly dependent on the NBO/T value of slag. The above data show that the viscosity and conductivity of slag depend on the depolymerization and ion transport behaviors

of the aggregated structural units, respectively. The gradually increasing fitting slope indicates that at NBO/T less than 1.29, the structural transition of the slag leads to a more pronounced negative correlation between viscosity and conductivity. This phenomenon has been weakened when NBO/T further increases, suggesting that increasing the FeO component enhances the depolymerization of slag and thus decreases its viscosity.

3.5. SEM Analysis of Z3 Slag

Because the Z3 slag has low viscosity at high temperatures and does not need to add too much iron ore ingredient, it is a suitable slag type for site application. Therefore, the Z3 slag sample was further analyzed by SEM analysis, as shown in Figure 4. The element content at point 1 (Figure 4a,b) shows the presence of the pyroxene phase with a single-chain structure, although the pyroxene phase may form when NBO/T is between 1.5 and 2.0. However, the NBO/T of the Z3 slag is only 1.29, which means that the structural unit will be between the sheet (mica) and the double chain (amphibole). Moreover, the NBO/Si of Z3 will reach up to 2.46 when Al₂O₃ is considered a basic oxide. Therefore, a large fraction of Al₂O₃ must be used as a basic oxide to satisfy the requirement for the formation of pyroxene. The general chemical formula of pyroxene group minerals is $W_{1-p}(X, Y)_{1+p}Z_2O_6$, where W represents Ca^{2+} and Na^+ , X represents Mg^{2+} and Fe^{2+} , Y represents smaller Fe^{3+} , Al^{3+} and Ti^{3+} , and Z represents Si^{4+} and Al^{3+} [27]. It can be inferred that a large part of Al^{3+} will enter the pyroxene phase as a six-coordinated form represented by Y, while other Al^{3+} will become the network former of the pyroxene chain as a four-coordinated form represented by Z.



Figure 4. (a) SEM of Z3 slag, (b–d) EDS patterns at three points, and (e) the corresponding elemental composition.

The elemental composition in point 2 (Figure 4a,c) corresponds to the fayalite phase. The results show that a small amount of Ca^{2+} and Mg^{2+} ions are mixed in the fayalite, which is an orthosilicate formed at NBO/T = 4. Therefore, the presence of fayalite in the Z3 slag indicates that ferrous oxide and silicon dioxide have a strong tendency to form orthosilicate. The basicity of Z3 was only 0.9 when Al_2O_3 was ignored, hence the formation

of fayalite, which will allow more Al^{3+} to form pyroxene with a six-coordinated structure. As a result, the polymerization degree and viscosity of the melt will be reduced. It is in accordance with the viscosity change feature in Figure 1. The composition of point 3 (Figure 4a,d) is a copper-bearing Fe alloy with a particle size of 25 to 30 µm, which belongs to metal droplets that can be separated from the slag. It can be seen that the slag is mainly composed of pyroxene and fayalite phases (Figure 4e). There are three main reasons for the certain deviation from the designed fayalite slag type. First, in order to reduce the added dosage for the desired forsterite slag type, the original basic components of the concentrate, alumina, and silica, were designed as metasilicate components. At the same time, the added amount of iron oxide was reduced. The formation of fayalite is incomplete because the slag composition could not achieve the alkalinity required for complete protosilicate. Moreover, the partial reduction of the added ferrous oxide reduces the basicity of the slag and makes the pyroxene mineral the main phase of the slag.

4. Conclusions

Seven slag samples were prepared by reductive smelting of copper oxide concentrate under the different ferrous oxide contents. The viscosity and conductivity data of these slag samples were measured and discussed based on the change of structural units of the aluminosilicate melts. The results indicate that even if the slag composition is acidic, there is a strong tendency to form protosilicates. The formation of fayalite would allow more Al^{3+} to form pyroxene with a six-coordinated structure. $[AlO]_4^{5-}$ as a network former will reduce the bonding strength of the structural units, thus reducing its viscosity at high temperatures. In the experimental range, the viscosity of each slag sample has a good linear logarithm relationship with its conductivity. However, there is no uniform linear equation for the CaO-MgO-FeO-Al₂O₃-SiO₂ system with a wide range of composition variation.

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