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# Effect of CaO/MgO Ratio on the Product Quality during Tin Smelting

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***Abstract –*** The existing tin smelting processes have the disadvantages of high smelting temperature, long smelting time and especially high tin losses. In this paper, the effect of basicity on the product quality during tin smelting was studied by monitoring the CaO/MgO ratio. It was found that the iron content in the metal product depends on the Fe/Sn ratio in the slag. A high tin metal product (98.52% Sn and 1.02% Fe) was obtained and a small loss of Sn went into the slag (<10%) at a reduction temperature of $1400^0$C and basicity of 1.2. The low Fe content in the Sn metal would make the subsequent tin refining easier. The Nb and Ta content in the slag increased to 4.96 and 5.06% respectively. The main phases in the slag were Ferrocolumbite, Niobium oxide and Tantalum oxide. The recovery was high for Sn in the metal and Nb/Ta in the slag.

***Keywords*****:** Cassiterite, Slag Basicity, Smelting, Nb-Ta.

## 1. Introduction

During the tin smelting, basicity plays a major role in the quality of the metal and slag. However, it can be controlled either by controlling the CaO/MgO ratio or the rate of reduction. The rate of reduction of stannic oxide with carbon was investigated by [1] where a direct comparison was made between the oxidation of coconut charcoal mix with CO-$CO_2$ and the reduction of $SO_2$ with coconut charcoal. It was found that cassiterite is reduced directly to Sn proceeding through the gaseous intermediates of CO and $CO_2$ and the overall rate of reduction is controlled by the oxidation of carbon $CO_2$. [2] have also investigated the condition of obtaining tin by the carbothermic reduction of cassiterite concentrate in the ionic melt. The results show that carbothermic reduction of cassiterite in the melt of the $NaCO_3$-$NaNO_3$ salt system with a ratio of 1:0.3 at a temperature range of 600-$950^0$C gave a higher degree of recovery of tin (95%) in the crude alloy. [3] investigated the impact of $NaCO_3$ content on the recovery of the metallic tin from cassiterite under a strong reducing atmosphere using pure chemical $SnO_2$ and $SiO_2$. It was found that $Na_2SiO_3$ effectively restrained the tin volatilization as SnO and the formation of hardly reductive SnO.$SiO_2$ during the reduction roasting process. This is due to the formation of $NaSiO_2$ and intermediate $Na_2SnO_3$ which is then reduced to metallic tin at higher temperature and under strong reducing atmosphere during the roasting process. The effect of roasting parameters and magnetite on the reduction of tin oxide ($SnO_2$) in the tin bearing iron concentrate was studied by [4]. The results show that magnetite significantly affect the tin volatilization and phase transformation of $SnO_2$ under CO-$CO_2$ atmosphere. Fe-Sn Spinel is easily formed during the reduction process at higher roasting temperatures and it has an adverse effect on the Sn volatilization ratio.

[5] studied the extraction kinetics of the tin metal and its mechanisms from Egyptian cassiterite concentrate using the alkaline molten salts as fluxing agents at a temperature of $850^0$C-$1000^0$C. It was found that the carbothermic reduction in the melt of $NaCO_3$-$NaNO_3$ salt system provides a yield of more than 95%. An investigation was made also by [6] on the effect of using a coal blend made up of anthracite (import) and Enugu coal (local) during the extraction of tin metal from the cassiterite deposit in the north-centre of Nigeria. The results revealed that with the increase in the Enugu coal in the blend, the recovery of tin metal decreased (71.90%). Then it was recommended that since the cost of production is the critical issue in the plants, so in order to make it work the smelting plant should use the Enugu coal between 5%-15% in their blends for the smelting of tin which will lead to the saving cost.

This paper presence a study on the effect of CaO/MgO ratio on the product quality during the tin smelting process by monitoring the Sn/Fe ratio in both the two products. Basicity was used to control the quality of the metal and the slag.

# 2. Experimental

## 2.1. Materials and Methodology

### 2.1.1. Materials

Cassiterite ore used in the present work was sourced from Kibara belt, in the Democratic Republic of Congo (DRC). The ore contains various rare earth metal mineralized Sn (Nb-Ta) pegmatites. The fluxes used was a CaO-bearing material (92.96%) and a MgO-bearing material (99.27%) supplied by Protea Chemicals, South Africa. A CO gas cylinder used for the reduction processes was sourced from AFROX, South Africa containing more than 99.97 vol %. The ore and the fluxes chemical composition was determined using X-ray fluorescence spectrometry (XRF) using a Rigaku ZSX primus 2 instrument with SQX analysis software. The mineral phases of the samples were obtained using a Rigaku ultimal V X-ray diffractometer (XRD) equipped with graphite monochromator in the diffracted beam and using CμKα radiation, PDXL analysis software. The scanning electron microscopy (SEM) TESCAN performing in nanospace at 15kv was used for the morphology analysis.

### 2.2.2. Methodology

The ore and the fluxes were crushed and milled to prepare it for the required analytical techniques for the characterisation. After the characterisation, they were mixed to reach the required basicity and the ratio CaO/MgO was therefore calculated. The basicity varied from 1.0 to 1.4. For homogenization purposes, the ore and the fluxes were milled together. A graphite crucible was used for the tests, placed in a silica crucible to prevent any spillages in case the graphite crucible defected. CO gas was blown in at a flowrate of 0.4 L/min in an alumina tube furnace. The heating rate was set at $8^{O}C$/ min and the set temperature was $1400^{o}C$ for all the experiments. The sample was kept at the working temperature for 1hour and the furnace was switched off and left to cool down to room temperature while the CO gas was only switched off when the temperature reached $600^{o}C$. This was to prevent any reaction between the graphite crucible and the unreacted oxides if present. The product was removed from the furnace, the metal separated from the slag and both analysed. A single experiment without any gas blown in was conducted to assess whether the graphite crucible was prone to react. It was found that the mass loss was around 0.01g. We therefore assumed that the crucible was not reacting. The basicity was calculated according to the equation 1:

$$Basicity = \frac{\mathrm{CaO + MgO}}{\mathrm{SiO2}} \tag{1}$$

The masses of the ore as well as those of the fluxes and the basicity used in this investigations are presented in Table 1 below.

Table 1: Feed Mass (g) and basicity.

| Tin Ore | CaO | MgO | Basicity |
|---|---|---|---|
| 30 | 1.5 | 1.22 | 1.0 |
| 30 | 1.5 | 1.78 | 1.2 |
| 30 | 1.5 | 2.05 | 1.3 |
| 30 | 1.5 | 2.33 | 1.4 |

# 3. Results and Discussion

## 3.1. Ore Characterization

The chemical composition of the ore is presented in Table 2.

Table 2: Chemical composition of the ore.

| Comp | MgO | Al2O3 | SiO2 | P2O5 | K2O | TiO2 | MnO | Fe2O3 | ZrO2 | Nb2O5 | SnO2 | La2O3 | CeO2 | Ta2O5 | WO3 | ThO2 | PbO |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| %wt mass | 0,13 | 3,19 | 5,93 | 0,4 | 0,29 | 1,33 | 0,25 | 7,41 | 1,56 | 0,62 | 76,01 | 0,31 | 0,8 | 0,81 | 0,21 | 0,04 | 0,02 |

From Table 2, it can be seen that tin oxide is the major compound followed by iron oxide in the ore. Some minor oxides present are Alumina, Silica, Titanium oxide, Niobium oxide and Tantalum oxide.

### 3.2. Smelting Results

The chemical composition of the metal product is presented in Table 3.

Table 3: Chemical composition of the metal product.

| Basicity | CaO/MgO | Fe | Sn | Fe/Sn ratio |
|---|---|---|---|---|
| 1 | 1.23 | 5.15 | 93.74 | 0.06 |
| 1.2 | 0.84 | 1.02 | 98.52 | 0.01 |
| 1.3 | 0.73 | 5.07 | 94.31 | 0.05 |
| 1.4 | 0.64 | 2.50 | 96.88 | 0.03 |

Results show that tin increases in the metal with the increase of CaO/MgO ratio as opposed to iron which deceases with CaO/MgO increase. However, it can be seen that although the trend of tin in the metal shows an increase, the best results are obtained at basicity 1.2. This implies that the increase in MgO has favoured tin recovery and that the best CaO/MgO ratio remained 0.84.

The trend is presented in Figure 1.

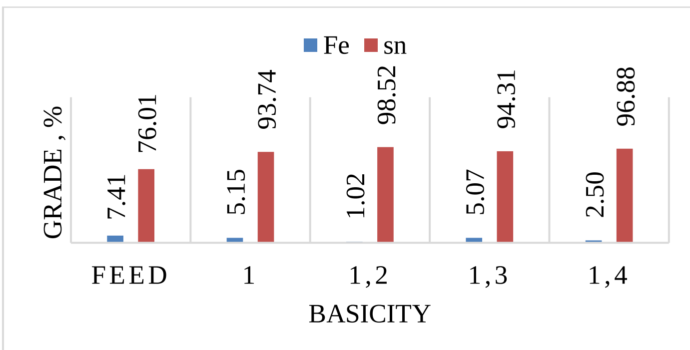



Fig. 1: Effect of smelting basicity on metal quality.

It is therefore important to mention that both the basicity and CaO/MgO ratio plays a vital role in tin recovery as illustrated in Table 3 and Figure 1. Also, the Fe/Sn ratio is inverse proportional to tin recovery.

The composition of the slag is presented in Table 4.

Table 4: Chemical composition of the slag.

| Basicity | Comp | MgO | Al2O3 | SiO2 | P2O5 | K2O | CaO | TiO2 | MnO | Fe2O3 | Y2O3 | ZrO2 | Nb2O5 | SnO2 | La2O3 | CeO2 | Ta2O5 | ThO2 | CaO/MgO |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | %wt mass | 7,06 | 3,68 | 9,35 | 0,50 | 0,20 | 22,80 | 4,45 | 2,52 | 1,35 | 0,20 | 13,46 | 5,02 | 17,92 | 1,25 | 2,68 | 5,54 | 0,22 | 1.5/1.22 |
| 1,2 | %wt mass | 9,70 | 3,38 | 8,62 | 0,32 | 0,11 | 21,14 | 4,94 | 1,18 | 1,50 | 0,22 | 13,69 | 4,96 | 20,46 | - | 2,85 | 5,06 | 0,22 | 1.5/1.78 |
| 1,3 | %wt mass | 7,38 | 3,58 | 9,07 | 0,47 | 0,35 | 21,73 | 4,59 | 1,44 | 1,54 | 0,23 | 13,80 | 5,27 | 20,39 | 1,39 | 2,61 | 5,25 | 0,23 | 1.5/2.05 |
| 1,4 | %wt mass | 9,56 | 3,71 | 9,82 | 0,70 | 0,21 | 20,97 | 4,77 | 3,00 | 1,50 | 0,21 | 11,16 | 4,43 | 22,36 | - | 2,63 | 4,76 | 0,20 | 1.5/2.33 |

The composition of the slag reveals that the lowest percentages of $Nb_2O_5$ and $Ta_2O_5$ are observed at basicity 1.4. Figure 2 reveals that the tin percentage is inverse proportional to both $Ta_2O_5$ and $Nb_2O_5$. It can also be observed that the MgO content in the slag is inverse proportional to $Ta_2O_5$ and $Nb_2O_5$.

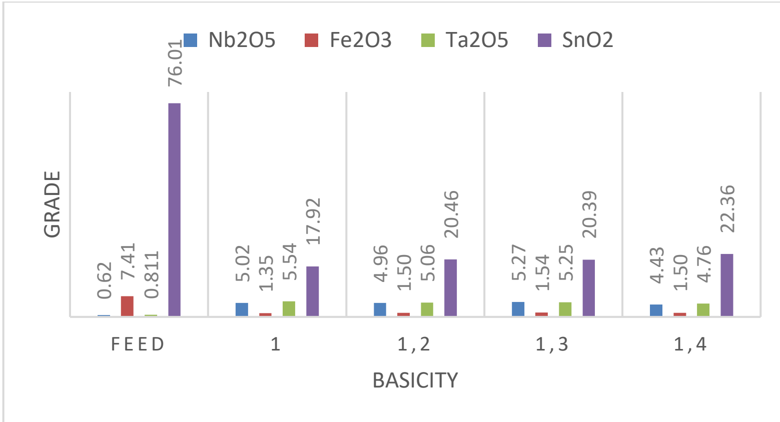


Fig. 2: The effect of basicity on the slag quality.

The mineralogical analysis of the concentrate sample using XRD in Figure 3 revealed that from the ROM spectrum, the ore is mainly composed of Cassiterite as the major mineral with low amounts of Sillimanite, Ferrotapiolite and Pyrochlore minerals scattered between the cassiterite crystals. It is clear that these slags have similar phases but at different amounts. Common phases include the major phases mainly Tantalum (ν) oxide, Niobium (ν) oxide, Ferrocolumbite, Fayalite and spinel.

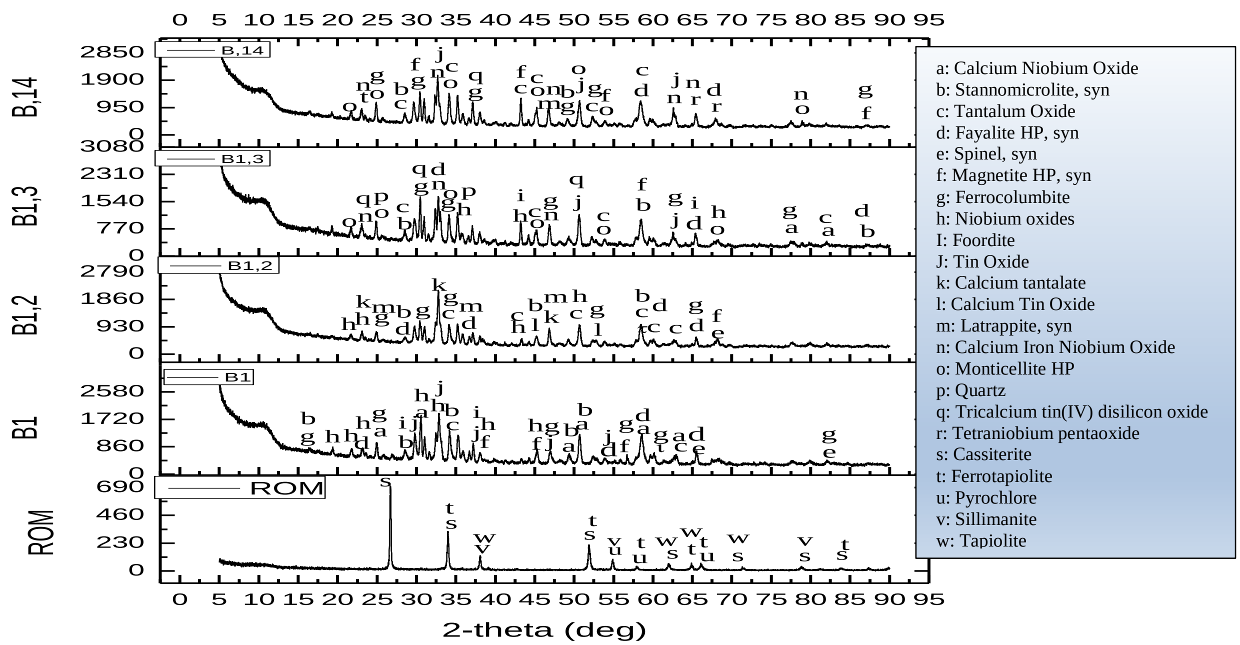
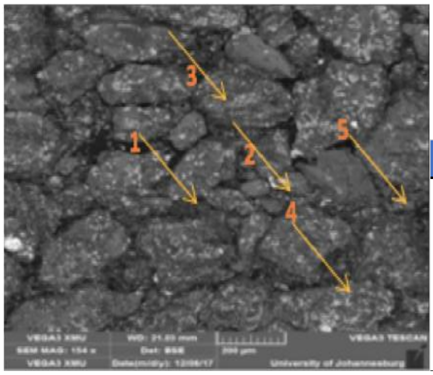


Fig. 3: XRD patterns of ROM and the Slag at different basicities.

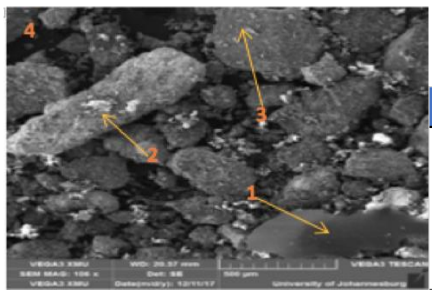
The morphologies shown in Figures 4-7 below have been obtained using SEM technique. From the SEM analysis, chemical composition of phases have been identified at different basicities and CaO/MgO ratios. At basicity of 1, the surface morphology of the slag in Figure 4 shows different phase that were formed at different points. A number of phases and their contents show the presence of Calcium Niobium oxide, Tantalum oxide, Niobium oxide, Fayalite and Ferrocolumbite with some other phases.



| | | Elem | Mg K | Al K | Si K | Ca K | Ti K | Mn K | Fe K | Zr L | Nb L | Sn L | Ta M | W M | minerals phases |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 502 x | 1 | Wt% | 3.37 | 1.24 | 0 | 27.60 | 13.52 | 0 | 0.18 | 15.85 | 8.93 | 0.91 | 21.23 | 0 | Calcium Niobium Oxide,Stannomicrolite, Tantalum Oxide, Niobium Oxide |
| | 2 | Wt% | 0.60 | 0.20 | 0 | 0.05 | 0 | 0 | 82.91 | 0 | 0 | 7.67 | 1.51 | 7.06 | Stannomicrolite, Tantalum Oxide, magnetite, Tin Oxide |
| | 3 | Wt% | 2.64 | 0.97 | 1.64 | 0 | 0 | 0 | 0.18 | 0 | 0.13 | 93.93 | 0.52 | 0 | Spinel, Fayalite, Foordite, Ferrocolumbite |
| | 4 | Wt% | 12.29 | 4.52 | 10.49 | 13.18 | 2.07 | 0 | 0.63 | 4.12 | 2.15 | 50.06 | 0.48 | 0 | Spinel, Calcium Niobium Oxide, Foordite, |
| | 5 | Wt% | 3.50 | 1.03 | 2.90 | 4.43 | 0.47 | 0 | 0.11 | 1.57 | 0.61 | 84.91 | 0.48 | 0 | Tin Oxide, Ferrocolumbite, Stannomicrolite |

Fig. 4: SEM and EDS of Slag at basicity of 1.

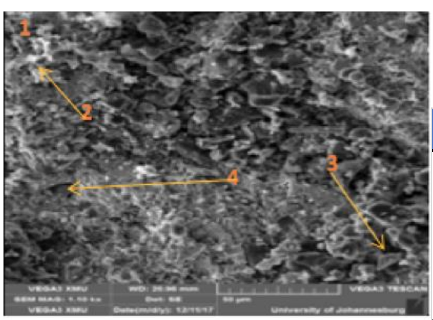
The phases that formed in the slag at a basicity of 1.2 are shown in Figure 5. It can be noticed that phases are similar to those obtained at basicity of 1. However, the combination of the data revealed in the morphological analysis and the chemical composition of the slag show that Nb and Ta oxides are embedded in specific phases.



| | | Elem | Mg K | Al K | Si K | Ca K | Ti K | Fe K | Zr L | Nb L | Sn L | Ta M | W M | minerals phases |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 106x | 1 | Wt% | 17.13 | 9.17 | 21.67 | 25.83 | 3.17 | 0.90 | 11.98 | 3.98 | 3.98 | 0.77 | 1.43 | Spinel, Latrappite,Calcium Tin Oxide, Niobium Oxide |
| | 2 | Wt% | 16.60 | 5.41 | 12.74 | 10.42 | 1.43 | 0.36 | 5.76 | 1.98 | 43.99 | 0.98 | 0.33 | Calcium Tin Oxide, calcium tantalate, Stannomicrolite, Niobium Oxide |
| | 3 | Wt% | 22.81 | 17.50 | 0 | 13.01 | 1.64 | 0.54 | 4.00 | 1.30 | 1.10 | 27.77 | 10.34 | Tantalum Oxide, Ferrocolumbite, calcium tantalate,Calcium Tin Oxide |
| | 4 | Wt% | 19.26 | 8.19 | 16.37 | 19.28 | 2.32 | 1.05 | 8.71 | 3.08 | 19.24 | 0.60 | 1.90 | Magnetite, Latrappite, Niobium Oxide, Fayalite, Spinel |

Fig. 5: SEM/EDS of the Slag at basicity of 1.2.

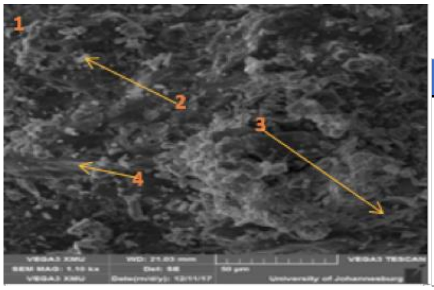
The Figure 6 shows the phases that were formed at basicity of 1.3. As mentioned earlier, there is similarity in phases that are present in the slag. Amongst major phases were Monticellite, Calcium Iron Niobium oxide and Tricalcium together with some other phases such as quartz.



| | | Elem | Mg K | Al K | Si K | Ca K | Ti K | Fe K | Zr L | Nb L | Sn L | Ce L | Ta M | W M | minerals phases |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 103x | 1 | Wt% | 21.64 | 7.04 | 17.65 | 21.65 | 2.97 | 1.16 | 10.09 | 3.45 | 14.34 | 0 | 0 | 0 | Calcium Iron Niobium Oxide, Monticellite, Tricalcium tin(IV) disilicon oxide, niobium oxide |
| | 2 | Wt% | 19.64 | 6.94 | 19.37 | 26.45 | 3.33 | 0.77 | 13.21 | 4.95 | 3.29 | 0 | 1.69 | 0.37 | Tantalum Oxide, Stannomicrolite, niobium oxide, Ferrocolumbite, Quartz |
| | 3 | Wt% | 9.34 | 1.84 | 5.25 | 4.51 | 0.57 | 0.97 | 3.50 | 1.13 | 70.23 | 0 | 1.92 | 0.75 | Magnetite, Foordite, Tin Oxide, Ferrocolumbite, Monticellite |
| | 4 | Wt% | 8.40 | 1.87 | 5.18 | 3.90 | 0.76 | 0.92 | 3.04 | 1.17 | 73.43 | 0 | 1.11 | 0.22 | Tantalum Oxide, Stannomicrolite, niobium oxide, Ferrocolumbite, Quartz |

Fig. 6: SEM/EDS of Slag at a basicity of 1.3.

From the EDS, we can see that Figure 7 shows that some new phases reappeared again such as Tetraniobium pentaoxide, Latroppite together with some other major phases as Monticellite, Calcium iron niobium oxide and Tantalum oxide. The similarity stated earlier is here again confirmed.




| | | Elem | Mg K | Al K | Si K | Ca K | Ti K | Fe K | Zr L | Nb L | Sn L | Ta M | W M | minerals phases |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 109 x | 1 | Wt% | 25.23 | 8.13 | 18.79 | 23.31 | 2.81 | 0.91 | 9.11 | 3.79 | 7.91 | 0 | 0 | Monticellite, Latrappite, Tetraniobium pentaoxide, Calcium Iron Niobium Oxide, Magnetite |
| | 2 | Wt% | 27.20 | 6.88 | 17.87 | 27.17 | 3.13 | 0.54 | 6.80 | 0 | 7.76 | 1.72 | 0.93 | Stannomicrolite, Tantalum Oxide, Tin Oxide, Fayalite, Monticellite |
| | 3 | Wt% | 25.56 | 9.83 | 17.76 | 20.30 | 2.53 | 0.64 | 7.91 | 2.80 | 11.26 | 0.87 | 0.55 | Ferrocolumbite, Tetraniobium pentaoxide, Latrappite, Monticellite, Tin Oxide |
| | 4 | Wt% | 31.04 | 1.34 | 31.22 | 28.83 | 0.58 | 0.29 | 2.24 | 0.73 | 3.73 | 0 | 0 | Monticellite, Latrappite, Tetraniobium pentaoxide, Calcium Iron Niobium Oxide |
| | 5 | Wt% | 23.77 | 7.37 | 19.45 | 24.61 | 2.52 | 0.36 | 15.18 | 4.12 | 1.75 | 0.86 | 0 | Ferrocolumbite, Tetraniobium pentaoxide, Latrappite, Monticellite, Tin Oxide |

Fig. 7: SEM/EDS of Slag at basicity 1.4.

## 4. Conclusion

The results showed that with increase of CaO/MgO ratio during tin smelting, tin grade increases in the metal and the Fe grade decreased. However, it can be seen that although the trend of tin in the metal shows an increase, the best results are obtained at basicity 1.2. The morphologies have shown some similarities at all the basicities. A number of phases and their contents show the presence of Calcium Niobium oxide, Tantalum oxide, Niobium oxide, Fayalite, Monticellite, Niobium oxide, Tantalum oxide, quartz, Latrappite, tetraniobium pentaoxide, Stannomicrolite and Ferrocolumbite. A further investigation on the quantification of phases that formed in the slag during the smelting process at different basicities would reveal the correlation between CaO/MgO ratio and the phases.

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