Study of the compositional and melting characteristics of some Brazilian and Congolese tin slags

Daniel Mapa Clemente [1]*
Rafaela de Oliveira Teixeira Menezes [2]
Heitor Vieira Damaso [3]
Johne Jesus Mol Peixoto [3]
Carlos Antônio da Silva [3]

Abstract

Knowledge of the melting behavior of tin slags is essential to optimize the power input in the furnace during processing of cassiterite since it influences the energy required to melt the slag. Furthermore, the melting point of a slag depends on its composition, making it highly relevant. Considering these aspects, industrial tin slags from Brazil and DR Congo were analyzed by EDXRF and their melting temperatures were measured using a softening and melting furnace. The Brazilian slags presented a higher content of ZrO_2, as well as varying levels of Nb_2O_5, TiO_2, Al_2O_3, among others. This is related to contaminations of minerals in the cassiterite such as zirconite, ilmenite, and columbite. Most Brazilian samples melted below 1533K, contrasting with a previous study which indicated a range of 1603-1801K. The Congolese slags were not as reduced as those from Brazil and greater content of SnO_2 and Ta_2O_5 were measured. These Congolese slags melted on average at temperatures slightly above those from Brazil, which is mostly due to the greater SnO_2 content. Levels of different oxides were plotted against the measured melting temperatures and a preliminary prediction model was developed. This may assist smelters to estimate their slag's melting point, potentially leading to an optimization of energy consumption and Sn losses during processing of Brazilian or Congolese ores/slags.

Keywords: Tin; Melting temperature; Melting behavior; Tin slags.

1 Introduction

Sn is an important metal used in different applications such as lead-acid batteries, chemicals [1], solders, copper alloys, among others [1,2]. In addition, it demonstrates potential for use in new technologies, such as lithium-ion batteries [3,4] or new types of solar cells [5]. Despite its importance, an average of only 2 to 3 ppm of Sn is present in the earth's crust and its occurrence is limited to a few regions [2]. In its most recent report, the International Tin Association informs that resources and reserves of this element are mostly located in Russia, Australia, Peru, DR Congo, Brazil, China, Indonesia, Bolivia, and Egypt [6]. In this context, cassiterite is the only economically relevant ore of tin [2,7,8] and depending on its origin, it can be accompanied by other minerals such as quartz, albite, feldspar, muscovite and columbite [2].

The production of Sn alloy involves a step-wise reduction of cassiterite and during this process, at least two different slags are generated. A simplified flowchart of this production is shown in Figure 1. The first slag results from an addition of carbon below the stoichiometric requirement for the reduction of SnO_2 from the ore. This is performed to produce an alloy with high Sn content and low levels of Fe (Crude Sn), which requires further refining. Consequently, the first slag is still rich in SnO_2, as well as FeO. During the second smelting, which occurs under severe reduction conditions, both SnO_2 and FeO are greatly removed from this phase, leading to the formation of a FeSn alloy. This alloy, as well as filter dusts, are used as inputs in the first smelting step. At last, additional processing steps may be required if the slag still presents relevant levels of Sn [2,7,9].

Tin slags obtained through this process may have varying compositions, and examples considering different smelting steps and origins are available in Table 1. Those from Zulhan and Ryanta [10], as well as Wright [7], are examples of 1st and 2nd slags. Those from Clemente et al. [11] and Allain et al. [12] are included to highlight some compositional differences from slags originating from Brazil and DR Congo, which are countries relevant to the supply chain of Sn. Besides, that of Clemente et al. [11] is also an example of a slag processed in multiple steps. Slags from other countries

[1] *Laboratório de Pirometalurgia e Simulação, LAPSIM, Universidade Federal de Ouro Preto, UFOP, Ouro Preto, MG, Brasil.*
[2] *Departamento de Ciências Naturais, Universidade Federal de São João Del Rei, UFSJ, São João Del Rei, MG, Brasil.*
[3] *Departamento de Engenharia Metalúrgica e de Materiais, Universidade Federal de Ouro Preto, UFOP, Ouro Preto, MG, Brasil.*

**Corresponding author: daniel.clemente@aluno.ufop.edu.br*

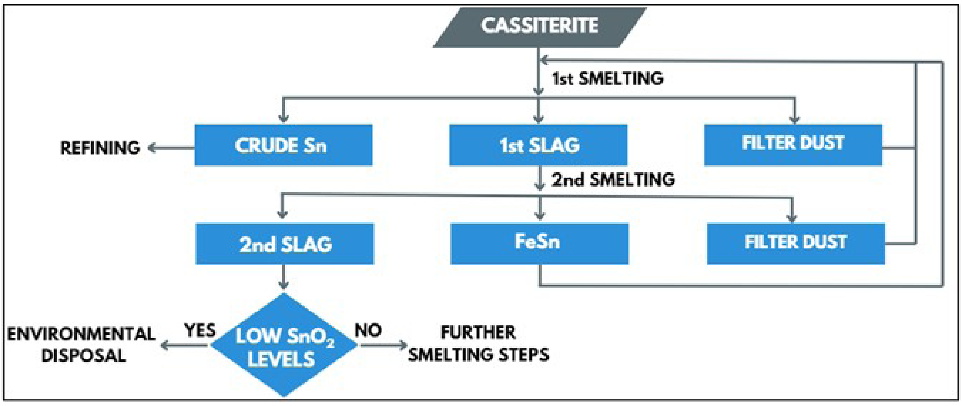

Figure 1. Classic flowchart of the production of Sn. Adapted from Graf [2], Wright [7], and Encinas [9].

Table 1. Examples of slag compositions considering different origins and processing steps

Source	**Zulhan and Ryanta [10]***	**Wright [7]**	**Clemente et al. [11]**	**Allain et al. [12]**
Slag origin and type	**Indonesia - 1st slag**	**Many countries - 2nd slag**	**Brazil – multiple processing steps**	**DR Congo – processing steps were not informed**
SnO_2 (wt %)	13.3	0.11-1.12	0.5	0.7
FeO (wt %)	26.8	12	2	3.3
SiO_2 (wt %)	15.7	25	46	41.9
CaO (wt %)	4.9	22	15.8	11.6
ZrO_2 (wt %)	4.9	5.5	11.3	0.9
Nb_2O_5 + Ta_2O_5 (wt %)	NA	6	6.9 + 0.9	12.7
Al_2O_3 (wt %)	7.1	10	6.5	11.2
TiO_2 (wt %)	7.3	10	1.4	1.3
MgO (wt %)	0.4	6	1.4	NA
MnO (wt %)	0.4	0.01-0.1	NA	3.7
P_2O_5 (wt %)	1.7	2	NA	NA
ThO_2 (wt %)	0.3	1.3	NA	NA
Other oxides (wt %)	17.2**	0.01-1.0 (each)	7.1	12.7**

*Results were converted to oxides for better comparison; **Calculated by balance. NA – Non available.

such as China (which holds the largest reserves), Russia, Peru, among others are also of high relevance. However, it was noted that only a few studies focused on Brazilian and Congolese tin-slags, especially their properties.

From Table 1, it can be observed that the levels of SnO_2, as well as FeO, decrease from 1st to 2nd steps as expected according to the process described in Figure 1. Another interesting aspect is that these slags present different levels for certain components. For example, a comparison between those from Brazil and DR Congo reveals that the former has higher levels of ZrO_2, while the latter has a much greater content of Ta_2O_5 + Nb_2O_5. Furthermore, both exhibit lower values of TiO_2 compared to Zulhan and Ryanta [10], as well as Wright [7]. It can be inferred that compositional differences among these slags are related not only to the origin of the cassiterite but also to the ore beneficiation process (separation of impurities at the mine) and the smelting procedure.

According to Eisenhuttenleute [13], the physical and chemical properties of a slag are determined mainly by its structure. This means that its oxides can influence properties such as its viscosity and melting temperature. In this context, slags presented in Table 1 are highly complex and present relevant levels of at least SnO_2, FeO, SiO_2, CaO, ZrO_2, Nb_2O_5, Ta_2O_5, and TiO_2. Therefore, these oxides should be considered when estimating slag's properties. Concerning the melting temperature of tin slags, studies are scarce. Wright [7] estimated the melting temperatures of tin slags using a CaO.FeO.SiO_2 phase diagram but it should be noted this approach does not consider the influence of ZrO_2, Nb_2O_5, Ta_2O_5, as well as other oxides. It means that the higher the value of these contaminants, the more it diverges from this phase diagram and, therefore, the results are uncertain. Clemente et al. [11] calculated melting points for some Brazilian high ZrO_2 tin slags using FactSage 8.0, and obtained values ranging from 1693 to 1800K, which are higher than those indicated by Wright [7] for tin slags with lower ZrO_2 levels. It was inferred that greater content of ZrO_2 may be related to higher melting points. However, confirming this conclusion requires actual measurements of this property. Additionally, no studies were found regarding the melting temperature of Congolese slags.

Based on this information, this study's main objective was to measure the melting temperature of different industrial tin slags from Brazil and DR Congo and infer the influence of its components on this property, leading to the development of a preliminary prediction model for the melting temperature. Precise information on the melting temperature of tin slags can assist smelters working with Brazilian and Congolese cassiterites/tin slags to optimize the power input in the furnace since this property influences the energy required to melt the slag. Furthermore, reduced working temperatures could also diminish the volatilization of Sn, leading to lower losses during processing of these materials.

2 Materials and methods

2.1 Materials

A total of eleven industrial tin slag samples under 0.074 mm were received from a tin producer. Among these, seven originated from the processing of Brazilian cassiterite from the states of Amazonas (B-1 to B-5), Rondônia (B-6) and Pará (B-7). According to the producer, all Brazilian slags were processed in multiple steps using a 150 kVA single-phase electric arc furnace, in which limestone was added as a flux and charcoal was used as a reducer. The remaining four samples are of Congolese origin (C-1 to C-4) from the province of Haut-Lomami. According to the producer, these slags were processed in two smelting steps (second slags, as presented in Figure 1) also in a 150 kVA single-phase electric arc furnace.

2.2 Methods

2.2.1 Chemical analyses of slags

Chemical analyses were conducted using the EDXRF equipment Epsilon 3XL from the company Malvern Panalytical. For these analyses, the particle size of each sample was checked using a 0.074 mm sieve and, when necessary, further grinding was conducted. Following the manufacturer`s instructions, the material was carefully mixed with a binder (CeraWax Ceridust from the company Química Brasileira) in a proportion of 20 wt% and the mixture was pressed for 10s under a load of 20t. Analyses were conducted with helium atmosphere using the software Omnian, which quantifies the elements. Considering that this study only analyzed slag samples, it was chosen to present the results as oxides. A comparison of the composition of these Brazilian and Congolese slags was then performed and the origin of its components, which could influence the melting temperature, was also discussed.

2.2.2 Analysis of the stability and reduction of different oxides

In the production of Sn, contaminants that are not reduced tend to concentrate in the slag phase. For better comprehension of its composition, a thermodynamic evaluation using the standard free energy of formation (ΔGf) of different oxides was employed. Additionally, since carbon is added as a reducer in tin metallurgy [2,7,9], the formation of $CO_{(g)}$ was also included. ΔGf data for SnO_2 is from Barin [14], and for all other oxides, data from Chase [15] was used. Naturally, this approach is limited since it does not involve kinetic aspects and considers pure reactants and products [16]. Nonetheless, it shows the tendency for the reduction of these oxides. The possible reduction of Ta_2O_5 and Nb_2O_5 as well as the formation of TaC and NbC were also evaluated, with data for TaC and NbC being sourced from Barin [14].

2.2.3 Melting temperature measurements

The determination of melting temperatures of the different slags was performed at the LAPSIM at the Federal University of Ouro Preto (UFOP) using a softening and melting furnace from Ernst Leitz GmbH under air atmosphere. For the experiments, samples were pressed in a mold to form a cylinder with 3mm height and 3mm diameter using alcohol as a binder. These proportions followed DIN 51730:2007-09 [17].

Figure 2 shows a schematic representation of the experimental setup. The slag sample is placed on an alumina substrate, which is moved into the furnace chamber with the use of a sliding alumina tube. A type R thermocouple is positioned behind the sample, to best represent its temperature. The furnace is heated using a Kanthal A1 resistance, which is placed on the outer side of a fixed alumina cylinder. A second Type R thermocouple located at the center of the furnace chamber provides information to the furnace's PLC, which applies heating rates of 10K/min between 298-1073K and 5K/min until the furnace's limit of 1533K. As the temperature is increased, the shape of the cylinder changes. This is monitored using a digital camera linked to a computer (recording system), which allows to save photos. Tests that did not have its slag melted at the limit temperature of 1533K had to be interrupted and the melting point was registered as >1533K.

According to DIN 51730, as heating occurs, the shape of the sample changes, and different stages can be visually identified [17]. However, this standard was developed for fuel ashes. When determining the melting temperature of slags, one specific stage is normally considered as its melting temperature: the hemisphere temperature, at which the sample height reaches 50% of its initial value at room temperature [18-24]. This is known as the hemisphere method and a schematic representation is shown in Figure 3. The software ImageJ was used for measurements, and the highest observed point of the sample was considered for the

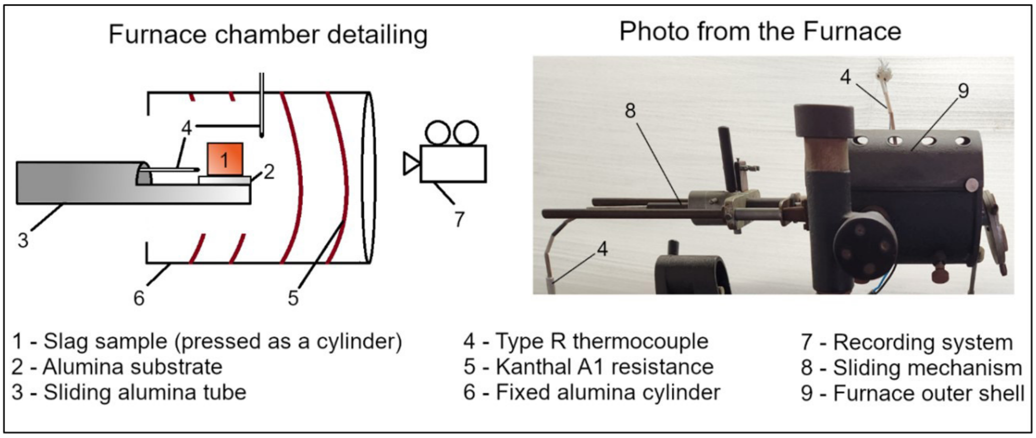

Figure 2. Schematic representation of the experimental setup for the Leitz softening and melting furnace.

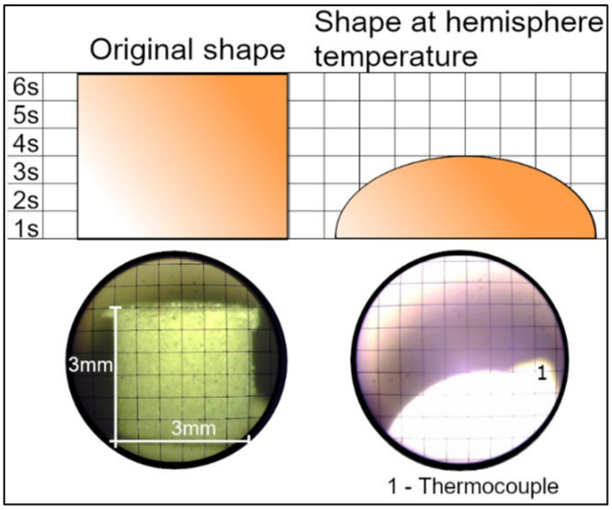

Figure 3. Adopted criteria according to the hemisphere method.

height evaluation. This was necessary due to the rounding of the cylinder`s upper surface, which is also evident in Figure 3. Additionally, due to the experimental setup, the thermocouple can be seen behind the sample when the temperature approximates the melting point, but only the height of the actual sample was considered.

Results were discussed based on the slags composition and origin. Finally, the influence of different components on the melting temperature was discussed and a preliminary prediction model was developed using the statistical software R.

3 Results and discussion

3.1 Composition of the studied slags and origin of some contaminants

The chemical analyses of the received Brazilian tin slags are available in Table 2. As can be seen, they have complex composition with many components present in relevant levels, such as SiO_2, CaO, ZrO_2, Al_2O_3, and Nb_2O_5. Besides, the content of FeO and SnO_2 is relatively low, but above some values from slags shown in Table 1. Thus, it can be inferred that there is still potential for the recovery of Sn from these sources.

According to Graf [2], elements such as Ti, Fe, Ta, Nb and Mn can be present in the tin ore. Additionally, deposits containing cassiterite can also present other ores, such as quartz, feldspar, magnetite, columbite, among others. If these are not effectively separated from the cassiterite during mineral beneficiation, their components can be concentrated in the slag phase.

For example, most Brazilian samples exhibit high levels of ZrO_2 and this coincides with slags studied by Clemente et al. [11], including that presented in Table 1. The source of Zr was identified as zirconite by Brocchi and Moura [25], normally contaminating Brazilian cassiterites. This is also aligned with a study from Silva and Price [26], which measured significant Zr levels in cassiterites from the state of Rondônia. Nonetheless, not all Brazilian slags have the same content of this impurity, and one example is sample B-7 (from cassiterite from the state of Pará), with only 3.6% ZrO_2.

Other impurities are specific to different minerals: for instance, sample B-7 presented a greater content of TiO_2 when compared to the others and this oxide can be linked to ilmenite. This mineral has been identified in cassiterites by authors such as Wright [7] and Dalimunthe et al. [27], reinforcing this inference. Additionally, Brazilian slags normally contain Ta_2O_5 and Nb_2O_5, which are related to occurrences of columbite together with tin ores [2,7]. In this case, this represents an opportunity for tin producers since many techniques for the recovery of Ta and Nb from slags are available in the literature [7,12,28,29]. At last, an interesting contamination was found in slag sample B-6 (originated from cassiterite from the state of Rondônia): it presented high levels of Al_2O_3 and MgO. This is a more complex case, as these components are also used in furnace refractories [7].

Table 2. Chemical analyses of the studied Brazilian tin slags

	MgO	Al_2O_3	SiO_2	CaO	TiO_2	MnO	FeO	ZrO_2	Nb_2O_5	SnO_2	Ta_2O_5	Others
B-1	1.5	6.7	46.2	15.8	1.3	0.7	1.9	11.1	6.9	0.7	0.8	6.4
B-2	1.4	5.2	35.8	30.3	1.0	0.6	4.7	8.0	6.3	0.9	0.7	5.1
B-3	1.3	5.4	39.0	24.6	1.2	0.7	4.9	9.4	7.4	1.9	0.8	3.4
B-4	0.4	6.3	42.4	24.8	1.2	0.6	1.6	9.1	5.7	1.3	0.7	5.9
B-5	1.2	5.7	40.6	25.2	1.2	0.7	3.7	9.6	7.4	1.0	0.8	2.9
B-6	3.0	29.1	38.0	7.8	2.5	0.6	3.4	7.4	2.4	3.1	0.6	2.1
B-7	0.3	7.1	36.9	16.3	9.1	0.6	7.1	3.6	3.9	5.9	1.6	7.6

Table 3. Chemical analyses of the studied Congolese tin slags

	MgO	Al_2O_3	SiO_2	CaO	TiO_2	MnO	FeO	ZrO_2	Nb_2O_5	SnO_2	Ta_2O_5	Others
C-1	0.4	6.2	25.9	30.3	3.9	0.6	5.0	5.9	2.0	10.6	4.2	5.0
C-2	0.2	5.1	20.7	21.6	3.7	0.5	7.9	3.5	1.7	24.9	3.8	6.4
C-3	0.3	6.7	25.0	26.9	3.6	0.6	4.8	4.1	1.6	17.5	3.8	5.1
C-4	0.2	4.3	17.9	22.6	2.5	0.5	6.0	3.3	1.7	33.6	3.5	3.9

Moreover, MgO can be present in limestone. Thus, the origin of these components is uncertain and could be related to refractories, fluxes, and/or ineffective separation of ores in the mine during the beneficiation process.

The chemical analyses of the Congolese tin slags are available in Table 3, and very high levels of SnO_2 were measured, which was at first not expected considering that these are 2nd slags. This fact does hamper the comparison between these Brazilian and Congolese slags, since after the reduction of SnO_2, other oxides would be concentrated in the slag. Nonetheless, it is interesting to note that they present relatively lower levels of Nb_2O_5, as well as ZrO_2 when compared to most of the Brazilian slags. However, the content of Ta_2O_5 is greater, indicating contamination by tantalite. The association of this mineral with cassiterite has been reported in the literature [30] and DR Congo is also a well-known source of tantalum ore [31]. Another aspect that differentiates these Congolese and Brazilian slags is the ratio (or basicity) %CaO/SiO_2. On average, Brazilian slags presented a basicity of 0.52, while the Congolese have a value of 1.4. CaO is not found in cassiterite at significant levels, but limestone is typically added as a flux during tin smelting [2,7]. Thus, it can be inferred that this difference is due to additions of limestone performed throughout the processing steps.

Once the origin of the main contaminants of the cassiterite has been discussed, it is also important to evaluate the concentration of their components in the slag during pyrometallurgical processing. A thermodynamic analysis considering the stability of the main oxides of the tin slag was performed and is shown in Figure 4. It is evident that oxides such as ZrO_2, SiO_2, CaO, MgO, TiO_2, Nb_2O_5, Ta_2O_5, and Al_2O_3 are more stable than SnO_2 and FeO. Consequently, these two latter oxides tend to be reduced before the others by carbon, forming Sn alloys (Crude Sn and FeSn).

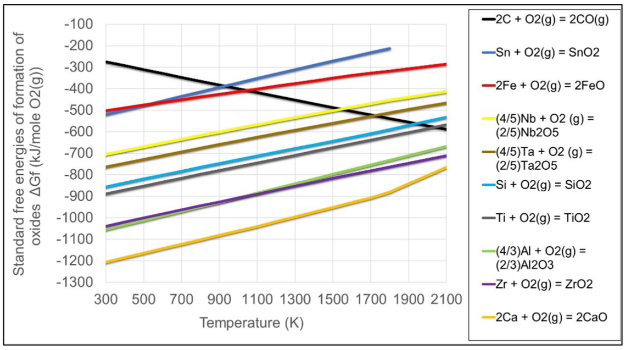

Figure 4. Ellingham diagram considering the most representative oxides in the studied tin slags

Considering the process presented in Figure 1, there is an excess of carbon in the 2nd step, as well as in subsequent processing steps. Theoretically, it would be possible to reduce other oxides during these stages, depending on processing conditions. However, the reduction of SiO_2 and TiO_2, as well as more stable oxides require very high temperatures. This is unlikely during tin production since an increase in temperature would tend to enhance the volatilization of Sn [32]. Thus, the economic viability of the process would be hampered.

Additionally, based on Figure 4, the reduction of Nb_2O_5 and Ta_2O_5 would also be possible around 1500K, which is compatible with some tapping temperatures measured by Clemente et al. [11] for high ZrO_2 tin slags, as well as with melting temperatures of tin slags inferred by Wright [7]. However, it is also important to note that Nb as well as Ta can form carbides during the reduction process [28]. A thermodynamic analysis considering the reduction of Nb_2O_5 and Ta_2O_5 was also conducted and confirmed that NbC and TaC are formed at lower temperatures when compared to the reduction to Ta and Nb. This evaluation is presented in Figure 5. Nonetheless, it is important to understand that with the reduction of Ta_2O_5 and Nb_2O_5, other oxides are further concentrated in the slag phase and can influence its properties.

At last, it should be noted that the complexity of these slags hampers the use of ternary or even quaternary phase diagrams for the prediction of their melting point. Thus, actual measurements are crucial for a better understanding of processing conditions during tin smelting.

3.2 Melting temperature measurements

The melting temperatures of the studied slags were determined, and results were compiled in Table 4. As it can be seen, those of Brazilian origin have varying melting temperatures, which tend to be below 1533K. Additionally, on average, they have lower values than the studied slags from DR Congo. An exception is sample B-6, which did not completely melt considering the experimental conditions. However, the height of the cylinder almost reached the specified criteria, suggesting that this sample has a melting point above, but likely not far from 1533K. This is also shown in Figure 6, which compiles photos regarding three experiments performed with Brazilian slags, as well as three from DR Congo.

Some interesting aspects of the melting behavior of these slags were observed during the experiments. For example, an expansion of samples B-5 and C-1 took place before reaching their melting point. It is possible that a phase transition occurred, leading to the expansion of the samples. However, further studies are required to confirm this aspect and identify these phases. Additionally, in test C-3 the upper part of the cylinder was found to be serrated between 1273-1373K. This phenomenon has also been reported by Jiang et al. [33] and according to them, represents an additional uncertainty regarding the height of the sample. Although not clearly explained by these authors, this phenomenon does not impact the final measurement of the present research, since samples at 298K did not show this behavior.

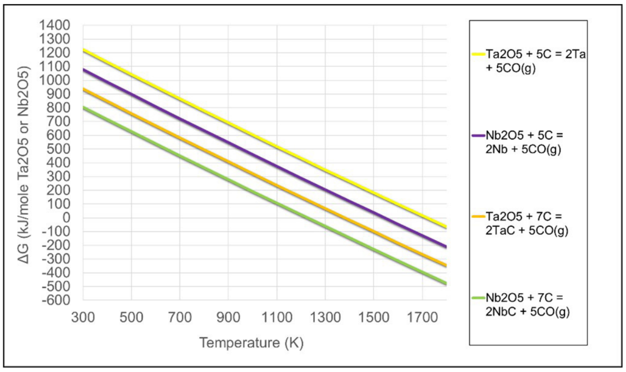

Figure 5. Change in the Gibbs free energy considering the reduction of Nb_2O_5 and Ta_2O_5 and the formation of Nb, Ta, as well as NbC and TaC.

As previously mentioned, the composition of the slag influences its properties, including the melting point [13]. In this context, Figure 7 compiles graphs showing the content of different oxides and the measured melting points for the Brazilian and Congolese tin slags. Results for tests B-6 and C-4 were not considered, as they could not be melted under the experimental conditions.

Since this research conducted only a few tests with complex industrial slags, it is understood that further studies are required to statistically determine the influence of each component on the melting temperature. Nonetheless, some first inferences were performed based on the slag's composition and experimental conditions. For example, Clemente et al. [11] used FactSage 8.0 to calculate melting points for some tin slags and inferred that significant levels of ZrO_2 would lead to high melting temperatures. The range obtained by these authors was 1693-1800 K for tin slags with ZrO_2 content varying from 6.8-11.3%. However, this significantly contrasts with the results from the present research, since it is indicated in Figure 7A that Brazilian slags with high ZrO_2 levels can melt below 1533K, depending on their composition. Besides, the slags with the highest levels of ZrO_2 presented the lowest melting points. A similar trend can be seen for Nb_2O_5 (Figure 7B), as well as SiO_2 (Figure 7C). For instance, Clemente et al. [11] found that Nb is present in the solid phase of high ZrO_2 tin slags as Nb_2O_5, that has a melting point of 1757 K [34]. No other complex components containing Nb were identified in the solid phase by these authors. Thus, according to this reasoning, the presence of Nb as Nb_2O_5 in the slag should have led to high melting temperatures, also contrasting with the results shown in Figure 7B.

No clear tendency was observed for the contents of CaO and TiO_2, for example, while for SnO_2 (Figure 7D), higher melting points were measured for increasing levels of this component. SnO_2 has a melting point of 1903 K [35], and it was also identified in the solid phase of high ZrO_2 tin slags by Clemente et al. [11]. Therefore, significant levels of this oxide may lead to increasing melting temperatures, and in this case, this could justify the difference between results from Brazilian and Congolese tin slags.

Table 4. Melting temperature measurements for all studied slags

Origin of the cassiterite	Brazil (State of Amazonas)					Brazil (State of Rondônia)	Brazil (State of Pará)	DR Congo			
Test ID	B-1	B-2	B-3	B-4	B-5	B-6	B-7	C-1	C-2	C-3	C-4
Melting temperature (K)	1399	1377	1373	1413	1359	>1533	1425	1464	1530	1533	>1533

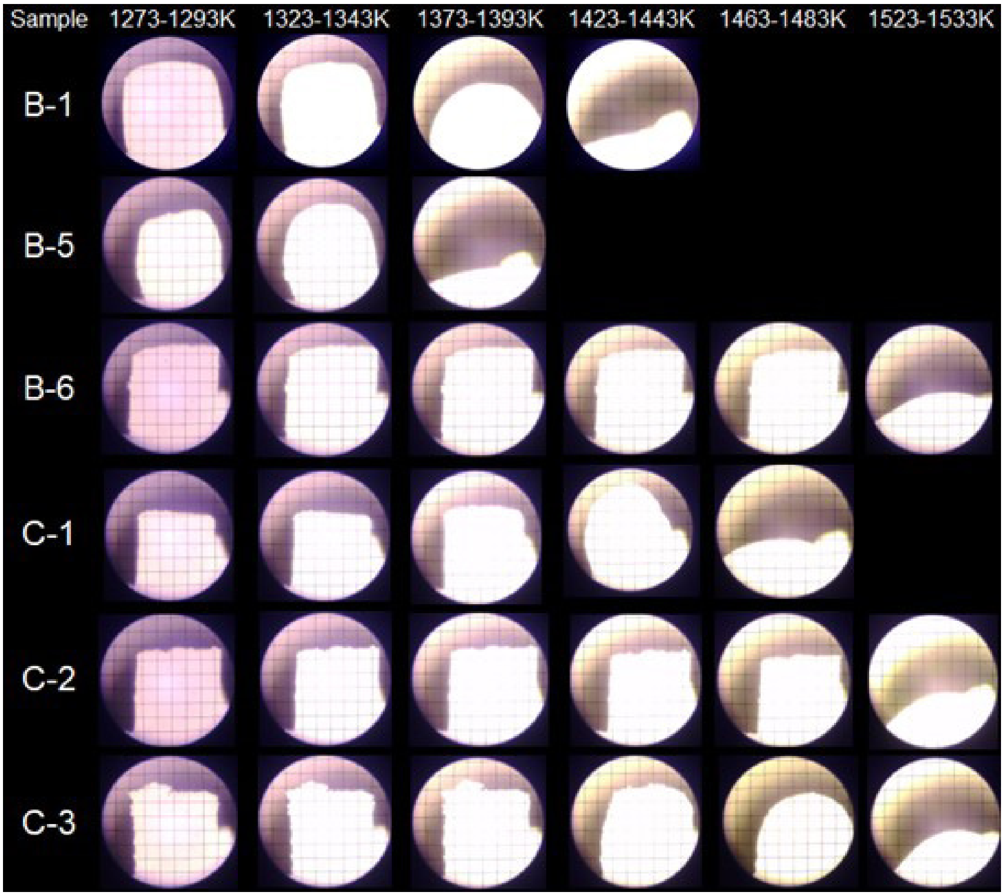

Figure 6. Melting temperature determination process of some studied tin slags.

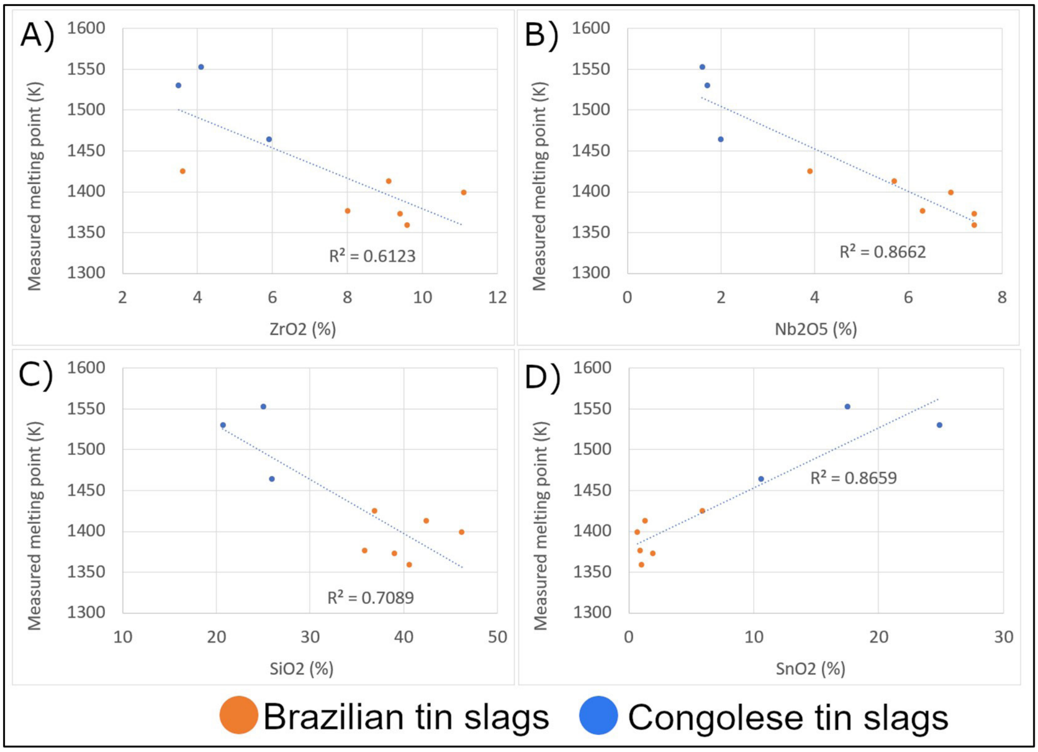

Figure 7. Melting temperatures and content of different oxides in the studied tin slags.

Finally, a multiple linear regression was performed using the statistical software R for a preliminary prediction of the melting temperature of these slags, and with a r^2 of 0.9824, Equation 1 was calculated. P-values for all variables in this equation were below 0.05.

$$T(K) = 1542.49 - 11.59\ \%\ ZrO_2 - 16.50\ \%\ FeO + 6.52\ \%\ SnO_2 \quad (1)$$

In sum, with the developed model, smelters working with Brazilian and Congolese slags with compositions similar to those studied in this research will be able to predict the temperature of their slags with a more accurate approach, based on statistical modelling. This information may be used in the energy balance for the processing of tin slags, resulting in an optimization of energy input. Furthermore, lower working temperatures may also lead to higher Sn yield, as a lower volatilization of Sn is expected [32].

4 Conclusions

This research has compared chemical compositions of Brazilian and Congolese tin slags and discussed the origin of their components. Then, the melting temperatures of different tin slags from these countries, which were not previously available in the literature, were measured. Inferences on the influence of different slag components on the melting temperature were performed and a preliminary prediction model was developed.

Regarding the origin of their components, most slags from cassiterites originating from three states in Brazil (Rondônia, Amazonas, and Pará) presented high levels of ZrO_2, which is associated with the significant presence of zirconite in the Brazilian tin ore.

Other contaminations were also observed. For example, slag from cassiterite from Pará had a higher content of TiO_2, likely due to a greater contamination of ilmenite. Additionally, the slag originating from cassiterite from Rondônia had higher Al_2O_3 as well as MgO levels. In this case, it could be related to limited separation at the mine, the addition of fluxes, or even refractory erosion. All slags presented some level of Nb_2O_5, which is linked to occurrences of columbite together with cassiterite. A higher content of Ta_2O_5 was found in the Congolese slags, and this can be related to contamination of the cassiterite by tantalite. Furthermore, slag samples from DR Congo had higher levels of SnO_2, indicating that these were not as reduced as the Brazilian slags.

Most Brazilian samples melted in the range of 1359-1533K, significantly contrasting with the study of Clemente et al. [11], which presented much higher values, varying from 1693 to 1800K for similar slags. These results may have implications for the processing of Brazilian tin slags, as it is indicated that high ZrO_2 tin slags are liquid in temperatures lower than previously assumed. Thus, processing of these slags may be feasible under lower temperatures, such as those measured in this research.

Furthermore, the measured melting temperatures of Brazilian slags are, on average, below those from DR Congo. In general, it was observed that slags with greater levels of SnO_2 melted under higher temperatures, while those with increasing contents SiO_2, Nb_2O_5 and of ZrO_2, led to lower melting points. Interestingly, this last oxide presented in practice an effect opposite to that previously known.

A multiple regression model was developed for a preliminary prediction of the tin slag's melting point and a r^2 of 0.9824 was achieved. This information could potentially result in the optimization of power input in the furnace, as it enables a more precise calculation of the energy required to melt the slag. Besides, the volatilization of Sn may also be diminished if lower working temperatures are achieved. At last, it should be pointed out that this model, which was developed using Brazilian and Congolese tin slags, can possibly be enhanced, and expanded with more measurements with slags from other countries, including but not limited to China, Indonesia, and Peru.

Acknowledgements

The authors would like to acknowledge the support of Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG).

References

1 International Tin Association. Tracking tin use. 2020. [cited 2024 Jan 2]. Available at: https://www.internationaltin.org/how-is-tin-used

2 Graf GG. Tin, tin alloys, and tin compounds. In: Ullmann's encyclopedia of industrial chemistry. 6th ed. New York: Wiley-VCH; 2000. [cited 2024 Jan 2]. Available at: https://onlinelibrary.wiley.com/doi/epdf/10.1002/14356007.a27_049

3 Xu H, Li S, Zhang C, Chen X, Liu W, Zheng Y, et al. Roll-to-roll prelithiation of Sn foil anode suppresses gassing and enables stable full-cell cycling of lithium ion batteries. Energy & Environmental Science. 2019 [cited 2024 Jan 2];12(10):2991-3000. Available at: https://pubs.rsc.org/en/content/articlelanding/2019/ee/c9ee01404g

4 Wang G, Aubin M, Mehta A, Tian H, Chang J, Kushima A, et al. Stabilization of Sn anode through structural reconstruction of a Cu–Sn intermetallic coating layer. Advanced Materials. 2020 [cited 2024 Jan 2];32(42):2003684. Available at: https://onlinelibrary.wiley.com/doi/epdf/10.1002/adma.202003684

5 Xiao K, Lin R, Han Q, Hou Y, Qin Z, Nguyen HT, et al. All-perovskite tandem solar cells with 24.2% certified efficiency and area over 1 cm2 using surface-anchoring zwitterionic antioxidant. Nature Energy. 2020 [cited 2024 Jan 2];5(11):870-880. Available at: https://www.nature.com/articles/s41560-020-00705-5

6 International Tin Association. Global resources and reserves. 2020. [cited 2024 Jan 2]. Available at: https://www.internationaltin.org/wp-content/uploads/2020/02/Global-Resources-Reserves-2020-Update.pdf

7 Wright P. Extractive metallurgy of tin. 2nd ed. Amsterdam: Elsevier Scientific Publish Company; 1982.

8 Maia F, Veiga MM, Stocklin-Weinberg R, Marshall BG, Constanzo C, Hariojati N, et al. The need for technological improvements in Indonesia's artisanal cassiterite mining sector. The Extractive Industries and Society. 2019 [cited 2024 Jan 2];6(4):1292-1301. Available at: https://www.sciencedirect.com/science/article/abs/pii/S2214790X19301418

9 Encinas JEJ. Termodinámica de la fusión reductora de estaño. Revista Metalúrgica UTO. 2015 [cited 2024 Jan 2]:3-17.

10 Zulhan Z, Ryanta IG. Utilization of gypsum byproduct as fuming agent for tin smelting slag. Journal of Sustainable Metallurgy. 2018 [cited 2024 Jan 2];4:388-394. Available at: https://link.springer.com/article/10.1007/s40831-018-0185-1

11 Clemente DM, da Silva CA, Peixoto JJ, de Oliveira JR, de Souza RM. Investigation of the presence of metallic phases in brazilian tin-slags. Journal of Materials Research and Technology. 2023 [cited 2024 Jan 2];24:6861-6875. Available at: https://www.sciencedirect.com/science/article/pii/S2238785423009468

12 Allain E, Kanari N, Diot F, Yvon J. Development of a process for the concentration of the strategic tantalum and niobium oxides from tin slags. Minerals Engineering. [cited 2024 Jan 2];2019;134:97-103. Available at: https://www.sciencedirect.com/science/article/abs/pii/S0892687519300482

13 Eisenhüttenleute VD. Slag atlas. Dusseldorf: Verlag Stahleisen; 1995.

14 Barin I. Thermochemical data of pure substances. Weinheim: VCH Verlagsgesellschaft GmbH; 1995.

15 Chase MW, National Information Standards Organization (US). NIST-JANAF thermochemical tables. Washington: American Chemical Society; 1998.

16 Silva CA, Silva IA, Castro LFA, Tavares RP, Seshadri V. Termodinâmica metalúrgica. São Paulo: Blucher; 2018.

17 German Institute for Standardization. DIN 51730:2007-2009: Testing of Solid Fuels: Determination of Fusibility of Fuel Ash. Berlim: German Institute for Standardization; 2007.

18 Wang H, Zhang T, Zhu H, Li G, Yan Y, Wang J. Effect of B2O3 on melting temperature, viscosity and desulfurization capacity of CaO–based refining flux. ISIJ International. 2011 [cited 2024 Jan 2];51(5):702-706. Available at: https://www.jstage.jst.go.jp/article/isijinternational/51/5/51_5_702/_pdf

19 Li J, Wang SJ, Xia YJ, Kong H. Study on dephosphorisation of hot metal pretreatment with Al2O3 to replace CaF2 in slag. Ironmaking & Steelmaking. [cited 2024 Jan 2];2015;42(1):70-73. http://doi.org/10.1515/htmp-2020-0090.

20 Jiang YJ, Deng YC, Bu WG. Pyrometallurgical extraction of valuable elements in Ni-metal hydride battery electrode materials. Metallurgical and Materials Transactions. B, Process Metallurgy and Materials Processing Science. 2015 [cited 2024 Jan 2];46:2153-2157. Available at: https://link.springer.com/article/10.1007/s11663-015-0362-6

21 Diao J, Qiao Y, Liu X, Zhang X, Qiu X, Xie B. Slag formation path during dephosphorization process in a converter. International Journal of Minerals Metallurgy and Materials. [cited 2024 Jan 2];2015;22:1260-1265. Available at: https://link.springer.com/article/10.1007/s12613-015-1193-9

22 Zhao J, Zhao Z, Cui Y, Shi R, Tang W, Li X, et al. New slag for nickel matte smelting process and subsequent Fe extraction. Metallurgical and Materials Transactions. B, Process Metallurgy and Materials Processing Science. 2018 ;49:304-310. http://doi.org/10.1007/S11663-017-1145-Z.

23 Cai Z, Song B, Yang Z, Li L. Effects of CeO2 on melting temperature, viscosity, and structure of CaF2-bearing and B2O3-containing mold fluxes for casting rare earth alloy heavy rail steels. ISIJ International. 2019 [cited 2024 Jan 2];59(7):1242-1249. Available at: https://www.jstage.jst.go.jp/article/isijinternational/advpub/0/advpub_ISIJINT-2018-760/_pdf

24 Zhao Z, Zhao J, Tan Z, Qu B, Lu L, Cui Y. Effect of the heating rate and premelting process on the melting point and volatilization of a fluorine-containing slag. Scientific Reports. 2020 [cited 2024 Jan 2];10(1):11254. Available at: https://www.nature.com/articles/s41598-020-68210-z

25 Brocchi EA, Moura FJ. Chlorination methods applied to recover refractory metals from tin slags. Minerals Engineering. 2008 [cited 2024 Jan 2];21(2):150-156. Available at: https://www.sciencedirect.com/science/article/abs/pii/S0892687507002270

26 Silva E Fo, Price RF. Development of the Mamore tin smelter, Brazil. In: Mining Latin America/Minería Latinoamericana. Dordrecht: Springer; 1986. p. 347-359.

27 Dalimunthe DY, Aldila H, Nuryadin A. Optimization on the purification of cassiterite from low-grade cassiterite concentrate. IOP Conference Series: Earth and Environmental Science. 2020 [cited 2024 Jan 2];599(1):012002. Available at: https://iopscience.iop.org/article/10.1088/1755-1315/599/1/012002

28 Mudzanapabwe NT, Chinyamakobvu OS, Simbi DJ. In situ carbothermic reduction of a ferro-columbite concentrate in the recovery of Nb and Ta as metal matrix composite from tin smelting slag waste dump. Materials & Design. 2004 [cited 2024 Jan 2];25(4):297-302. Available at: https://www.sciencedirect.com/science/article/abs/pii/S0261306903002310

29 De Oliveira JM, Anes IA, Coleti JL, Espinosa DC, de Carvalho MS, Tenório JA. Niobium and tantalum recovery from the primary source and from tin slag, an industrial challenge: a review. Canadian Journal of Chemical Engineering. 2023 [cited 2024 Jan 2];101(4):1743-1761. Available at: https://onlinelibrary.wiley.com/doi/abs/10.1002/cjce.24621

30 Köck W, Paschen PJ. Tantalum: processing, properties and applications. JOM. [cited 2024 Jan 2];1989;41:33-39. Available at: https://link.springer.com/article/10.1007/BF03220360

31 USGS. Mineral Commodity summaries 2023. Tantalum 2023 [cited 2024 Jan 2]. Available at: https://pubs.usgs.gov/periodicals/mcs2023/mcs2023-tantalum.pdf

32 Yu Y, Li L, Sang XL. Removing tin from tin-bearing iron concentrates with sulfidation roasting using high sulfur coal. ISIJ International. 2016 [cited 2024 Jan 2];56(1):57-62. Available at: https://www.jstage.jst.go.jp/article/isijinternational/56/1/56_ISIJINT-2015-428/_html/-char/en

33 Jiang W, Tian L, Hao S, Bo H, Ma T. A new method for evaluating the melting performance of the slag. Ironmaking & Steelmaking. 2023 [cited 2024 Jan 2];50(7):1-7. Available at: https://www.tandfonline.com/doi/full/10.1080/03019233.2023.2165520

34 Hidde J, Guguschev C, Klimm D. Thermal analysis and crystal growth of doped Nb2O5. Journal of Crystal Growth. [cited 2024 Jan 2];2019;509:60-65. Available at: https://www.sciencedirect.com/science/article/abs/pii/S002202481830647X

35 Chen Z, Xu Z, Zhao H. Flame spray pyrolysis synthesis and H2S sensing properties of CuO-doped SnO2 nanoparticles. Proceedings of the Combustion Institute. 2021 [cited 2024 Jan 2];38(4):6743-6751. Available at: https://www.sciencedirect.com/science/article/abs/pii/S1540748920304089

Received; 10 Jan. 2024
Accepted: 10 Apr. 2024