STUDY OF FERROUS RESIDUE FROM THE BRAZILIAN TIN INDUSTRY AND PERSPECTIVES OF ITS RECOVERY

ESTUDO DE RESÍDUO FERROSO DA INDÚSTRIA BRASILEIRA DE ESTÂNHO E PERSPECTIVAS DE SUA RECUPERAÇÃO*

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Abstract

FeSn is a residue of the tin industry, which can be recirculated during processing of Cassiterite. A disadvantage of its recirculation is that it decreases furnace capacity, leading to lower tin production rates. Therefore, an optimization of the actual processing circuit can be related to the removal of FeSn from the system, which should be further processed in another equipment. As a first step toward a new processing route, characterization of alloys from different suppliers was performed through EDXRF, Metallography and SEM/EDX. Based on the results, a pre-treatment of the alloy and two possible recovery routes are suggested.

Keywords: Tin recovery, FeSn, Characterization, Residue.

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1 INTRODUCTION

In order to reduce environmental burdens and secure the supply chain, technological developments from all around the world are increasingly focusing on productivity and resource efficiency [1-4]. Thus, it is crucial to study the secondary products of the metal production, their impacts on the environment and possible new routes to economically recover the valuable metals remaining in the residues. Among metals, one that has particularly gained importance in recent years is tin (Sn). Besides its traditional use in solder, tinplate, chemicals, bronze and float glass [5], Sn has also high importance in the electronics and clean energy industry [6, 7] and has recently been pointed as the metal most impacted by new technologies [8]. Besides, prices are also being kept high in the market [9]. Brazil has the third largest global reserves of Sn (700 kt), just after China (1100 kt) and Indonesia (800 kt) [10, 11], which emphasizes the importance that should be given to the production of this metal in the country.

The production of Sn is performed in furnaces by reducing Sn concentrates or ores with carbon in temperatures ranging between 1150° and 1300°C [12, 13]. A flowchart of the process is presented in Figure 1.

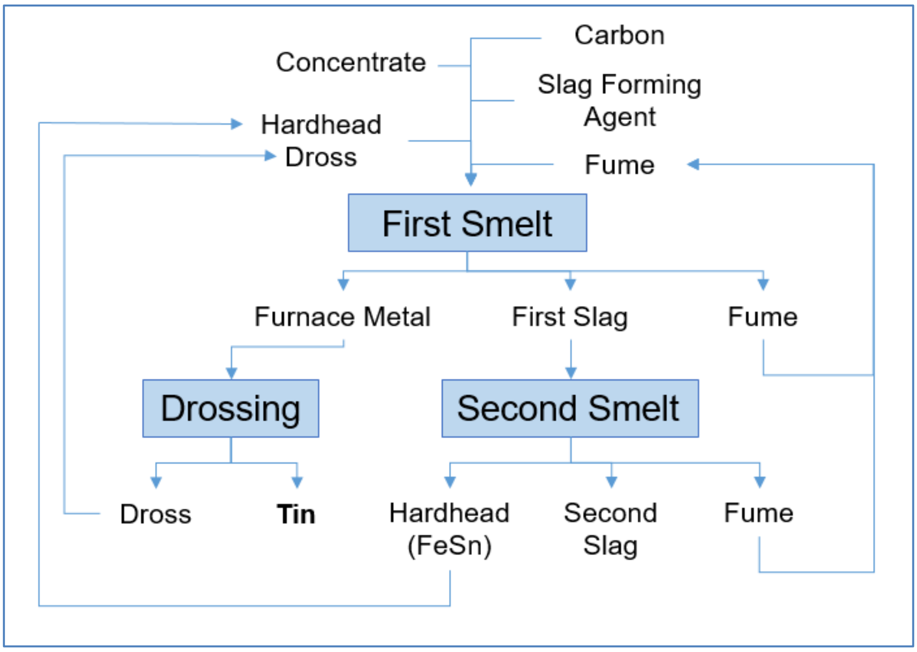

Figure 1. Traditional two-step process of Sn smelting [12]

Cassiterite, which is the main Sn ore, is also associated with iron-bearing minerals [12, 14] and once FeO and SnO_2 have similar values of standard free energies of formation [13], FeO tends to be reduced alongside with the SnO_2. To avoid contamination of Fe in the Furnace metal (a material containing mainly Sn), Fe should stay in the slag and Sn in the metal during and after a two (or more) stage process. This smelt occurs according through the equilibrium of the reversible reaction shown in equation 1, in which (s) indicates that the compound is in the slag and (m) in the metal [12]:

$$SnO_{(s)} + Fe_{(m)} \leftrightarrow Sn_{(m)} + FeO_{(s)} \qquad (1)$$

In each stage of the process, only part of the SnO is reduced, aiming to produce $Sn_{(m)}$ and $FeO_{(s)}$. Furnace metal and slag are tapped from the furnace and the latter is further processed in another stage in order to enhance the Sn yield. In the last stage, a very reducing atmosphere is required, so that both FeO and SnO are reduced and a FeSn alloy and a depleted slag are formed. This slag is extracted from the processing circuit and may be used for the recovery of other metals, such as Ta and Nb [15]. The Furnace metal is processed separately in order to remove impurities, so that a metallic tin with low contaminants is produced. The dross containing the oxides is also returned to the furnace.

According to the literature [12, 16], the FeSn alloy, also known as ‘hardhead’, has Sn amounts at least comparable to Fe amounts and the alloy is recirculated alongside with cassiterite. However, Clemente (2017) [17], showed the production of FeSn with much higher Fe and lower Sn contents, which can be a specific attribute from the Brazilian industry. As can be expected, recirculation leads to lower furnace capacity, something undesirable in a production process. Besides, an aggravate factor has recently appeared: due to very high graphite prices caused by the actual graphite market [18], the use of ‘paste’ electrodes in reduction furnaces for Sn production could be considered as an alternative due to its lower cost [12]. As the tubes containing the paste are made of iron sheet, more Fe is added indirectly to the melt, resulting also in a higher generation of FeSn alloy.

Considering these aspects, a logical solution is the removal of FeSn from the circuit. In this case, Sn recovery from the FeSn alloy has to be carried out in another process, as described by Wright (1982) [12]. According to the author [12], the addition of Si leads to the formation of a FeSnSi alloy, in which Sn is only slightly soluble for 25% Si. One disadvantage of such method is that a low grade FeSnSi is still produced and therefore, environmental aspects should also be taken into consideration. Another interesting factor is that data regarding this process in reduction furnaces are apparently inconsistent. Wright (1982) [12] stated that part of Si could be obtained from SiO_2 in an EAF under very reducing conditions. However, Clemente (2017) [17] conducted experiments regarding reduction of ferrous tin slags and concluded that part of the Si added to the charge oxidized in the furnace. Although many other aspects should be analyzed for a better conclusion, this inconsistence shows that the recovery of Sn from FeSn is not an ordinary process and demands further investigation.

In order to better comprehend the FeSn alloy and to propose study routes for the recovery of Sn from this alloy, a characterization of the material can be regarded as a first step. For this reason, methods including Energy Dispersive X-Ray Fluorescence (EDXRF), Light Microscopy, Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX) were used.

2 DEVELOPMENT

2.1 Materials and Methods

FeSn alloy from 5 different Brazilian smelters were available for this study. Considering that these FeSn alloy were sold to a single company, which allowed sampling of the alloy and provided the material for this work, it can be assumed that the original suppliers would no longer reprocess these FeSn alloy. In other words, these can be regarded as residues from the Sn production.

All FeSn alloy were sampled according to the standard D75/D75M [19]. For all elements except Sn, EDXRF analysis was conducted using an Epsilon 3X from the company Panalytical. A semi-quantitative approach was chosen, since it allows to scan the FeSn alloy regarding almost all elements. For the determination of Sn content in the FeSn alloy, titrimetric method was used to achieve more precise results.

To achieve metallographic images of the FeSn sample, a Light Microscope Leica DM 4000 M LED was used. The structure and element distribution were analyzed with a JEOL JSM-6300 Scanning Electron Microscope (SEM) and an Energy Dispersive X-Ray Spectroscopy (EDX) from Oxford Instruments.

2.2 Results and Discussion

2.2.1 Energy Dispersive X-ray Fluorescence (EDXRF)

Table 1 summarizes the composition of the residual FeSn alloy from 5 different smelters in Brazil. The data shows an overview of the ferrous residue production from Sn smelting process in the country.

Table 1. Composition of the FeSn alloy from different smelters in Brazil.

Supplier	Fe (%)	Sn (%)	Pb (%)	Al (%)	Si (%)	P (%)	Ca (%)	Nb (%)	Cr (%)	Mn (%)	W (%)	S (%)
1	52.60	26.40	0.20	0.98	6.32	1.03	2.96	0.26	0.34	0.29	2.07	0.07
2	59.40	9.90	0.00	0.50	6.65	4.35	3.40	0.21	0.73	0.43	4.51	0.00
3	65.99	4.95	0.00	0.09	11.11	4.87	0.00	0.51	0.06	0.13	2.87	0.00
4	66.90	14.87	0.15	0.20	3.88	1.36	0.54	1.57	0.22	0.27	1.62	0.00
5	80.80	15.64	0.39	0.09	0.46	0.42	0.00	0.99	0.00	0.03	0.76	0.00

As can be seen, there is a variety of contaminants in the FeSn alloy. Also, each element differs widely between the samples analyzed. In general, the alloy contains traces of contaminants such as Pb, S, Al, Nb, Cr and Mn, higher levels of contaminants such as W, P, Ca, and, of course, Sn, Si and Fe. Regarding this last element, compared to Wright [12] all samples have higher Fe contents and lower Sn contents, which are in accordance with Clemente (2017) [17] and indicate that these levels are characteristic of the Brazilian industry.

A precise origin and explanation for each contaminant is complex. For example, the presence of high contents of W in the sample from supplier 2 may be linked either to elevated levels of W in the ore and/or very high reducing condition in the furnace. The number of recirculation steps performed by a supplier in its original process may also influence the composition of the FeSn alloy: more elements may be oxidized or reduced according to the furnace’s temperature, reducing conditions and charge.

Nevertheless, with the restrictions commented above, some assumptions can be made based on the thermodynamic behavior of compounds. For instance, due to its high oxidation potential, the presence of Ca in some samples is likely to be due to small slag inclusions trapped in the alloy. Since tin slags are related to the CaO-SiO_2 system [12], it would mean that part of the percentage of Si in samples 1, 2 and 4 are actually from SiO_2 of the slag inclusion. Excluding these samples, the influence of Si in the Sn content can be inferred from samples 3 and 5.

As mentioned, the addition of Si leads to the formation of an FeSnSi alloy, in which Sn has a decreasing solubility until the composition reaches 25% Si. Therefore, it can be assumed that samples with high Si until this limit should contain less Sn. For example, the sample from supplier 5 contains 0,46% Si and 15,64% Sn, while the sample from supplier 3 contains 11,11% Si and 4,95% Sn. Both samples do not contain Ca and the results are partially according to the theory described by Wright (1982) [12]. A relevant difference is that the author [12] did not predict the influence of other elements such as W or P on the solubility of Sn in the alloy, which could interfere in the result. Another important consideration is that the addition of Si was not performed aiming the highest Sn yield in any FeSn alloy, since the highest Si in the alloy is still far from 25%. This apparent contradiction is likely due to economic issues regarding high costs of metallic Si. For example, huge quantities of Si should be added by supplier 3 in order to lower the Sn content from 4,95% to 3%, which is the best value report by Wright (1982) [12].

Note that the same tendency regarding Ca can be seen for Al and Cr. It could be inferred that these elements may also be partially in the form of oxides. This assumption is backed on the fact that these elements are used in refractories, which end on the slag phase during refractory wear.

As can be seen, the composition of the alloy is relatively complex and varies along the suppliers. The sample from supplier 5 is relatively pure, with low amounts of elements such as Si, P, Ca, Cr, Nb, Mn and W. This fact not only diminishes the influence other elements on the solubility of Si in the FeSnSi alloy, but also indicate the possibility of production of FeSn without significant contaminations. In theory, an uncontaminated alloy would be a material suitable for new applications, such as replacement of Sn in the foundry industry. For that reason, sections 2.2.2 and 2.2.3 focus on the further characterization of the sample from supplier 5, with the goal to better understand the material, to propose routes for new applications and to set comparison for materials produced using these new routes.

2.2.2 Metallography

Due to the high Fe content in the material from supplier 5, it is not interesting that it returns to the process, since it would generate an even higher recirculation in the following phases. However, the material differs from the others regarding contamination levels and this fact opens the possibility for new applications, as it will be explained in section 2.2.4.

The studied sample has also very low Si in its composition, as shown on Table 1. For that reason, the material is very ductile and hard to grind. Therefore, it was granulated in water as an alternative to achieve particles with a smaller size. This process originated globular structures, as shown in the Figures 2a and 2b.

The metallographic images 2a, 2b and 2c have increasingly higher magnifications, which allows an overview of the sample on the first two pictures and a more detailed image on the last (Figure 2c). As the images present, the globular structures consist of a lighter base and some darker phases. A SEM/EDX analysis was performed in order to achieve a better element distribution in this area, as section 2.2.3 discusses.

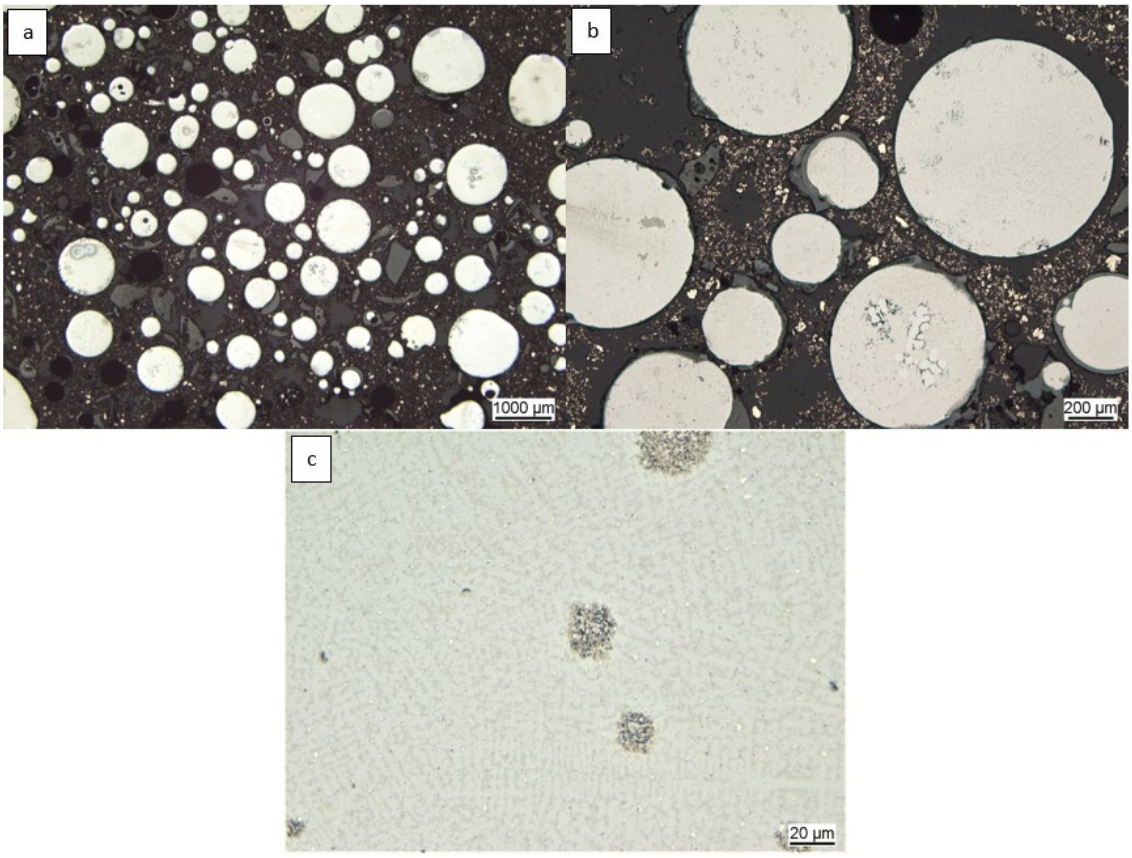

Figure 2. Metallography of FeSn Sample with different magnifications.

2.2.3 Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX) Analysis

With a Scanning Electron Microscope (SEM) and an Energy Dispersive X-Ray Spectroscopy (EDX), details of the sample were obtained, such as morphology and element distribution of a specific area. Figure 3 shows an overview of the sample with the globular structures, as previously saw in the light microscope (Figure 2). In Figure 4 the same sample is seen with a greater magnification, showing the selected points for a further EDX analysis. The results of this analysis are shown on Table 2 and on the spectrograms shown in Figure 5.

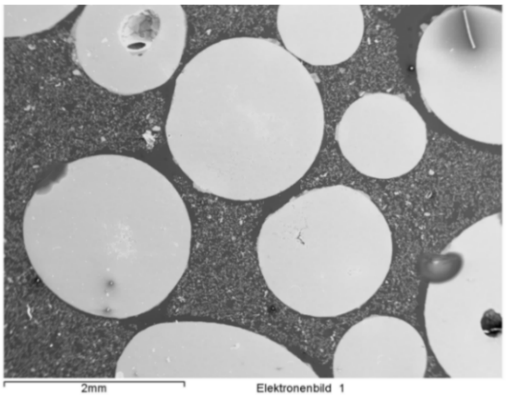

Figure 3. Overview image of the sample.

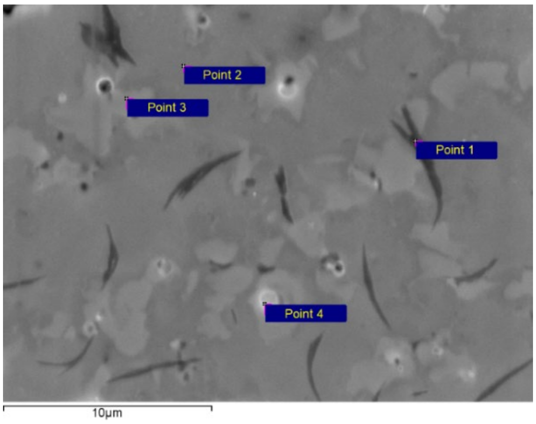

Figure 4. SEM (Scanning Electron Microscope in secondary electrons detection mode) image of the sample with focus on the globular structure and selected points used for the EDX analysis.

Table 2. Composition of points selected in Figure 4.

	P	Fe	Nb	Sn	Pb
Point 1	0,51	85,92	1,89	11,68	0,00
Point 2	0,00	91,85	0,77	7,38	0,00
Point 3	0,00	67,36	1,12	31,52	0,00
Point 4	0,00	16,26	1,17	77,78	4,79

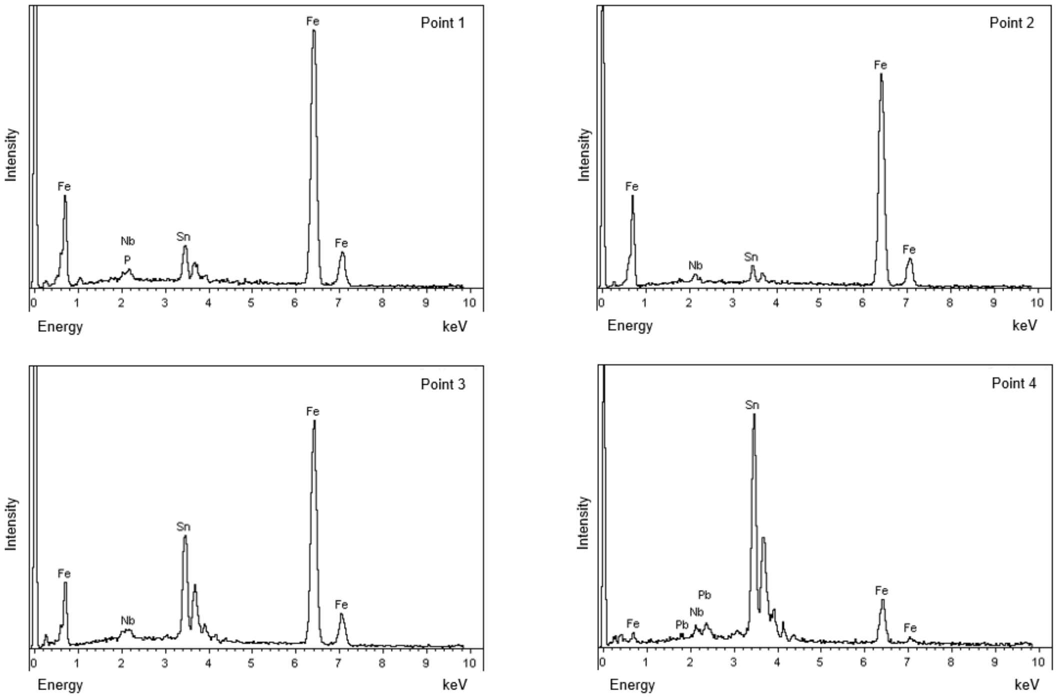

Figure 5. Spectrograms related to Figure 4 and Table 2.

The results shown in Figures 4 and 5 and Table 2 are important to understand the element distribution along the sample. The FeSn phase diagram, shown in Figure 6, provides a greater comprehension of these results.

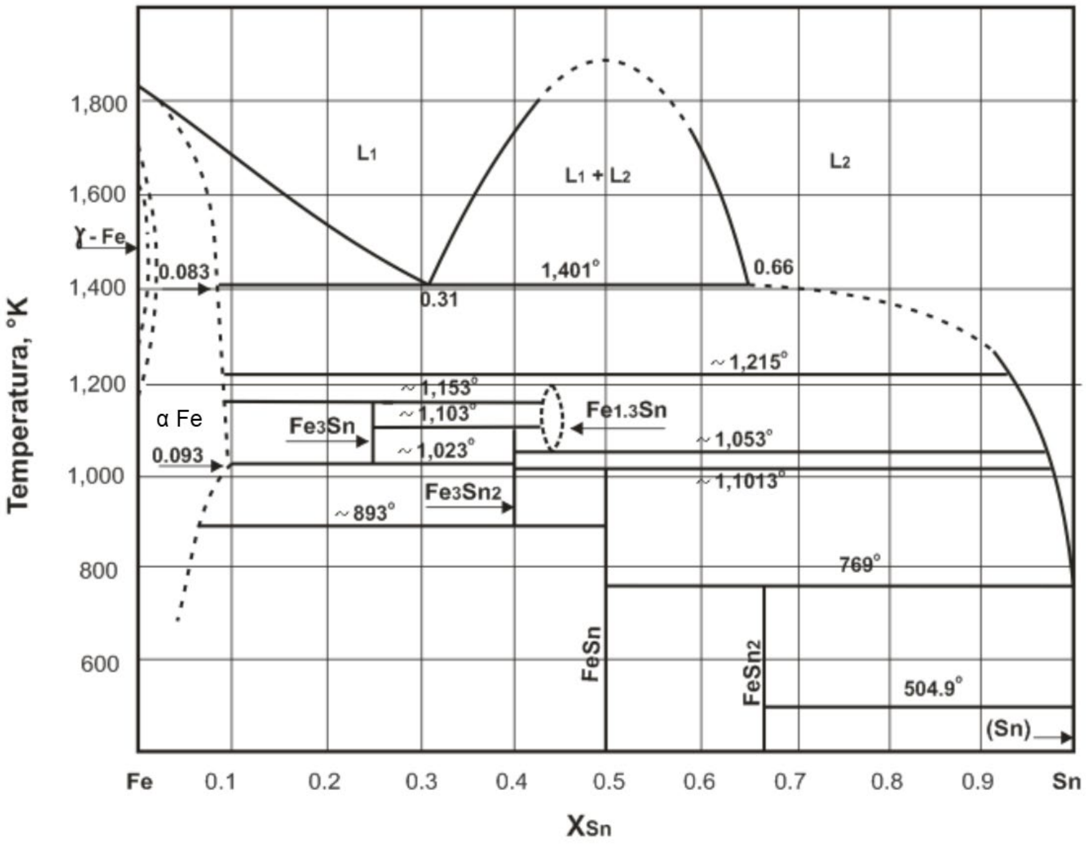

Figure 6. FeSn Phase Diagram. Adapted from Encinas [16].

According to the phase diagram, at high temperatures there is parcial solubility of Sn in Fe in liquid state, which leads to the formation of two liquids. Considering the solidification of sample 5, a solid phase $\alpha(Fe)$ is formed. As can be seen, this phase is poor in Sn and explains partially Points 1 and 2 shown on Figure 4. Point 1 presents 85,92% of Fe and 11,68% of Sn. Point 2 is located in the matrix of the material, has a very high content of Fe (91,85%) and only 7,38% of Sn.

Also, enrichment of the liquid occurs consequentely, leading to the formation of phases with high Sn content, such as seen in Points 3 and 4. It could be inferred that these phases correspond to FeSn and $FeSn_2$. However, the exact determination of the solified phase is not possible, since the phase diagram considers equilibrium state and no contaminants. Point 3 presents a lower content of Fe (67%), a higher content of Sn (31,52%). Point 4 has an even lower Fe content of only 16,26% and much higher content of Sn (77,77%). Figure 4 shows that, in general, the lighter the area under SEM the higher is the Sn content.

For a further element distribution in this sample, an EDX mapping analysis took place, as shown on Figure 7. The element distribution inside the selected area shown in picture 7a can be seen on pictures b, c, d and e, for Fe, Sn, Nb and P, respectively, where the colorful areas would have a higher concentration of the concerned material.

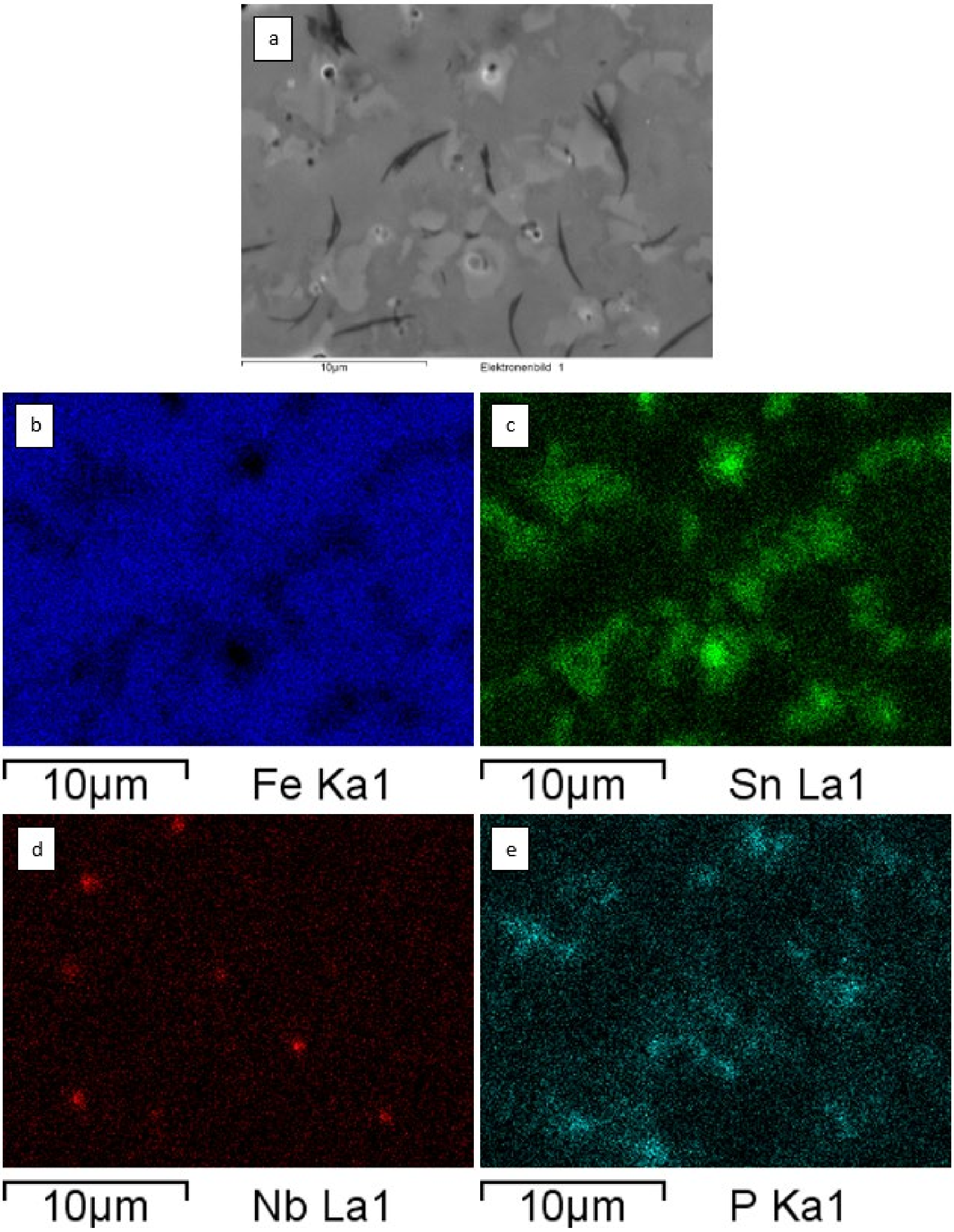

Figure 7. EDX mapping analysis of the previous sample.

To further relate the distribution of the different elements, some relations were made between the Figures 7 b-e, as shown on Figures 8 a-b.

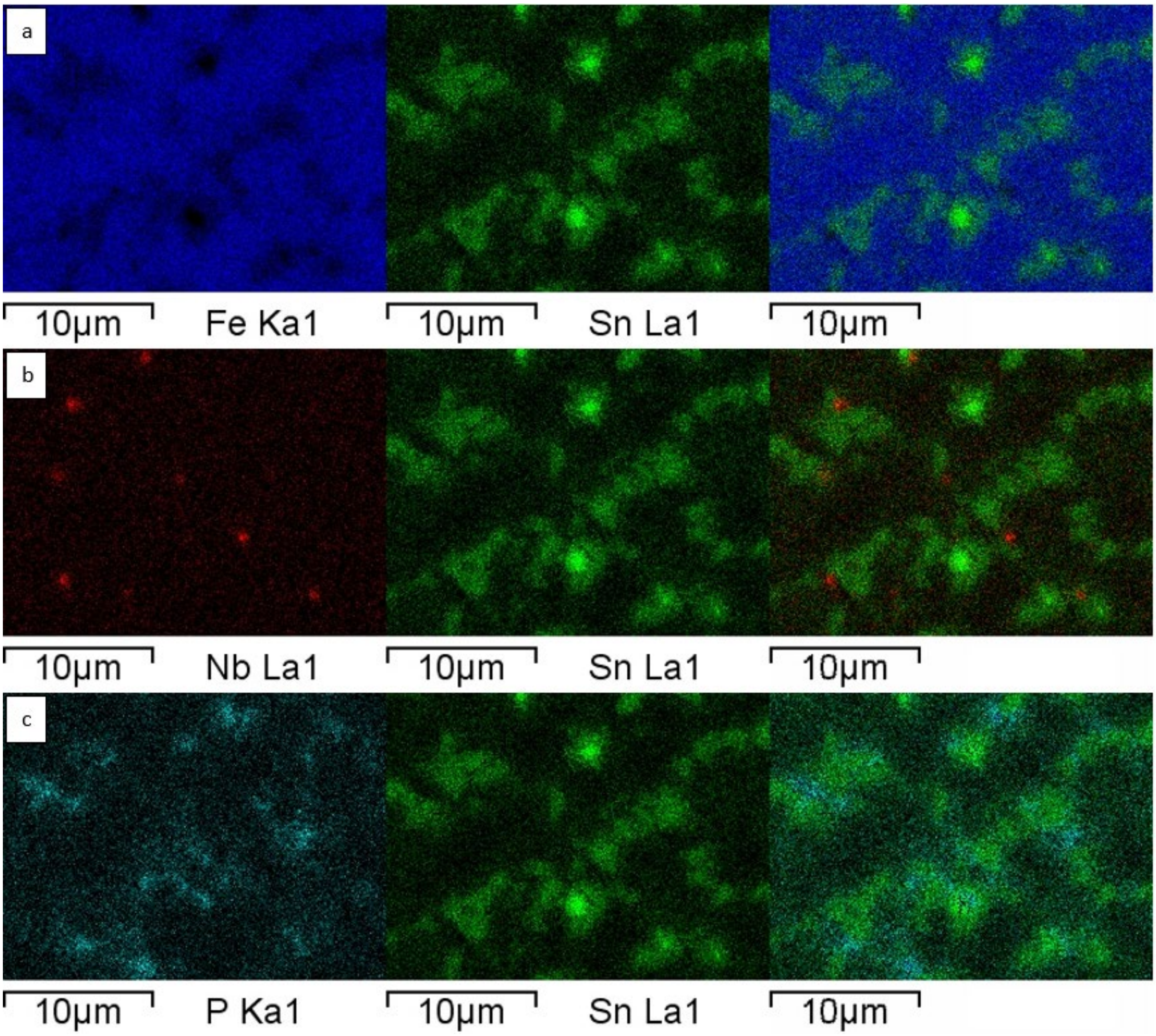

Figure 8. Relation between mapping analysis of different elements.

The Sn is located in the lighter areas in Figure 7a and, as previously stated, these correspond to areas with lower concentration of Fe. Nb seems to be located in the dark round areas shown on Figure 7a, often close to areas with higher amounts of Sn, as shown on Figure 8b.

Figure 8c shows a relation between the P and the Sn concentrations. As can be seen, P contents are related to higher concentrations of Sn. Further studies are needed to better understand the relation between these elements and to remove the P impurities from the material.

The SEM results allowed deeper understanding of the material. This is crucial for the selection of a forthcoming more adequate route to recover the alloy and for further comparisons of future results.

2.2.4 Proposed study routes for enhancement of Sn recovery

Enhancements of the actual processing route or new processing routes should focus on the removal of FeSn from the processing cycle, as it would increase furnace capacity and diminish Sn losses. Another interesting consideration is that, since it cannot be guaranteed that a supplier always buys cassiterite with the same composition, a direct relation between FeSn characteristics and a specific supplier cannot be met. Therefore, any method regarding recovery of Sn from FeSn alloy should aim for a wide range of FeSn composition.

As explained, the characterization focused on better comprehending the FeSn available in Brazil so that new routes could be researched. Many contaminants were identified such as P and S, which also have to be taken into account when developing a new method regarding the recovery of Sn. One specific sample (number 5) showed a much lower contaminant level when compared with the others, which indicates that it is possible to produce a "clean" FeSn and even opens the possibility to pretreat existent FeSn alloy in order to obtain lower contaminant levels. With this possibility in mind, a new Sn recovery route would be to research and develop a pre-treatment process for the alloy in general, in which contaminants such as P, W and S are removed. The SEM analysis identified for example that P contents are related to Sn levels. The reasons behind this fact and techniques to lower these contaminant contents are critical for further development concerning Sn recovery from FeSn alloy.

By lowering the contaminants, two possible recovery routes could be further studied: firstly, the addition of Si could be optimized. No studies have been found regarding the influence of contaminants on the solubility of Sn in the FeSnSi alloy. It could be possible that the presence of elements such as W or Pb diminishes the solubility of Sn in the FeSnSi alloy. Therefore, by pre-treating the alloy, there would be more accuracy for the addition of Si considering the theory described by Wright [12] and lower Sn levels could be reached. Further studies regarding the addition of Si should focus on the oxidation/reduction behavior of Si/SiO_2 in the EAF, since it affects the economy of the process. Other furnaces should also be studied, aiming higher efficiency for the process. For instance, GARCIA (2009) [20] reported the usage of Induction furnaces for the addition of Si in the FeSn alloy. However, production or technical data were not presented, which is crucial for the process choice. Also, no studies have been found regarding the influence of the temperature on the solubility of the alloy, which in an important aspect.

Another possibility would use the pre-treated alloy as a replacement for Sn in the foundry industry. Since some contaminants can be very harmful for these applications, a wide study regarding restrictions for the usage of FeSn in these industries has to be performed. A possible advantage of using FeSn instead of metallic Sn is a higher melting point of the alloy, which would lead to the melting of the alloy at the bottom of the furnace. Therefore, a higher yield of Sn is expected.

5 CONCLUSION

With the objective of proposing new study routes for the recovery of Sn from FeSn alloy, characterization of this by-product from different suppliers was conducted using EDXRF, Metallography and SEM/EDX.

With the EDXRF, it has been found that the FeSn alloy sampled were not processed aiming the highest possible Sn yield. This fact is likely due to an economic balance of the operation, since high quantities of metallic Si should be added in order to enhance the Sn yield by a small fraction. Also, contaminants such as P, W and S were found in the alloy. These could also influence the solubility of Sn in the metal and prevent higher Sn yield. Interestingly, a FeSn sample with low contaminant levels has also been found (sample 5), which would diminish these effects. This sample indicates the possibility of producing a FeSn alloy with lower contamination levels. However, since the majority of samples analyzed contain much higher contaminant levels, it has been pointed that it is critical to research a pre-treatment process, capable of removing contaminants from FeSn alloys in general.

Considering a pre-treated alloy, the addition of Si could be further improved through a deeper understanding of the influence of temperature and processing conditions on the solubility of Sn in the alloy. Also, FeSn could be studied as a replacement for Sn in foundries. Therefore, a wide study regarding tolerance levels for contaminants in these industries has still to be performed.

Also, a SEM/EDX analysis was conducted in sample 5 aiming to reveal details of this material with low contamination levels and in order to generate results for comparison with future pre-treated alloys. The analysis presented the chemical composition found in the sample and the element distribution of the alloy. The material has a matrix with high concentrations of Fe, while some areas have a higher concentration of Sn. Using EDX mapping, it has been found that areas with high Sn contents tend to have also high P contents. The reasons for this behavior is still to be investigated in further studies.

The EDXRF, Metallography and SEM/EDX allowed a deeper understanding of the ferrous residue from the Brazilian tin industry, which is crucial to guide the selection of an adequate process for its recovery route.

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