

CONVERSION OF TIN DIOXIDE DROSSES OBTAINED FROM SOLDERING SCRAP BY REDUCTION AND ALKALINE FUSION

Zoltán Harangi¹, Tamás Kékesi²

¹MSc student, ²Professor,

Inst. of Metallurgy and Foundry Engineering, University of Miskolc, Hungary;

kekesi@uni-miskolc.hu

ABSTRACT

Melting of the soldering scrap originating from the electronic industry also produces oxide dross, composed mainly of SnO_2 , which is resistant to the most commonly used lixiviants for hydrometallurgical treatment. We have investigated the possibility of converting the SnO_2 into a soluble form by carbothermic reduction and alkaline fusion using coke powder and NaOH , respectively. The experiments have been carried out in the 200 °C wide temperature ranges above 800 and 700 °C, respectively. The treated products were examined by scanning electron microscopy (SEM) in order to assess the processes of solubilization treatment. The reduced material was leached with boiling 6M HCl . The material resulting from the alkali fusion was leached with 40 °C distilled water until the crucible became clean. The obtained solutions were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). Under the optimized conditions, it was possible to reach a conversion rate of the originally insoluble tin of close to 90% by both methods. Applying the technology for solubilizing the SnO_2 component, the tin in the dross collected from the surface of the molten tin can be extracted by electrolytical methods and the environmental burden associated with the soldering waste handling can be eliminated, and this residue can be the source of further secondary tin.

1. INTRODUCTION

The soldering surface coating technologies applied in the electronic industry generate an oxidized and regularly skimmed by-product at the surface of the tin melt. It is visually presented in Fig. 1a. A novel technology has been devised for the separation of tin and the contained impurity or alloying elements from the soldering dross by electrorefining in aqueous solutions [1-2]. It requires the metal to be cast in the form of anodes after the dross had been partially melted. During this melting step a significant amount of secondary oxide dross is skimmed off the surface of the metal bath, as shown in Fig 1b. The aim of this research is to find a technology which can facilitate the recycling of the tin content in this oxide based heterogeneous waste material.



Fig. 1 Picture of the broken soldering waste material (a) , dross (arose from the melting of the metal in air) (b).

The main difficulty is the refractory character of the SnO_2 matrix. It is not soluble either in acids or bases [3]. The straightforward method is therefore preliminary reduction. The thermodynamic conditions of reducing SnO_2 can be seen in the diagram of Fig. 2.

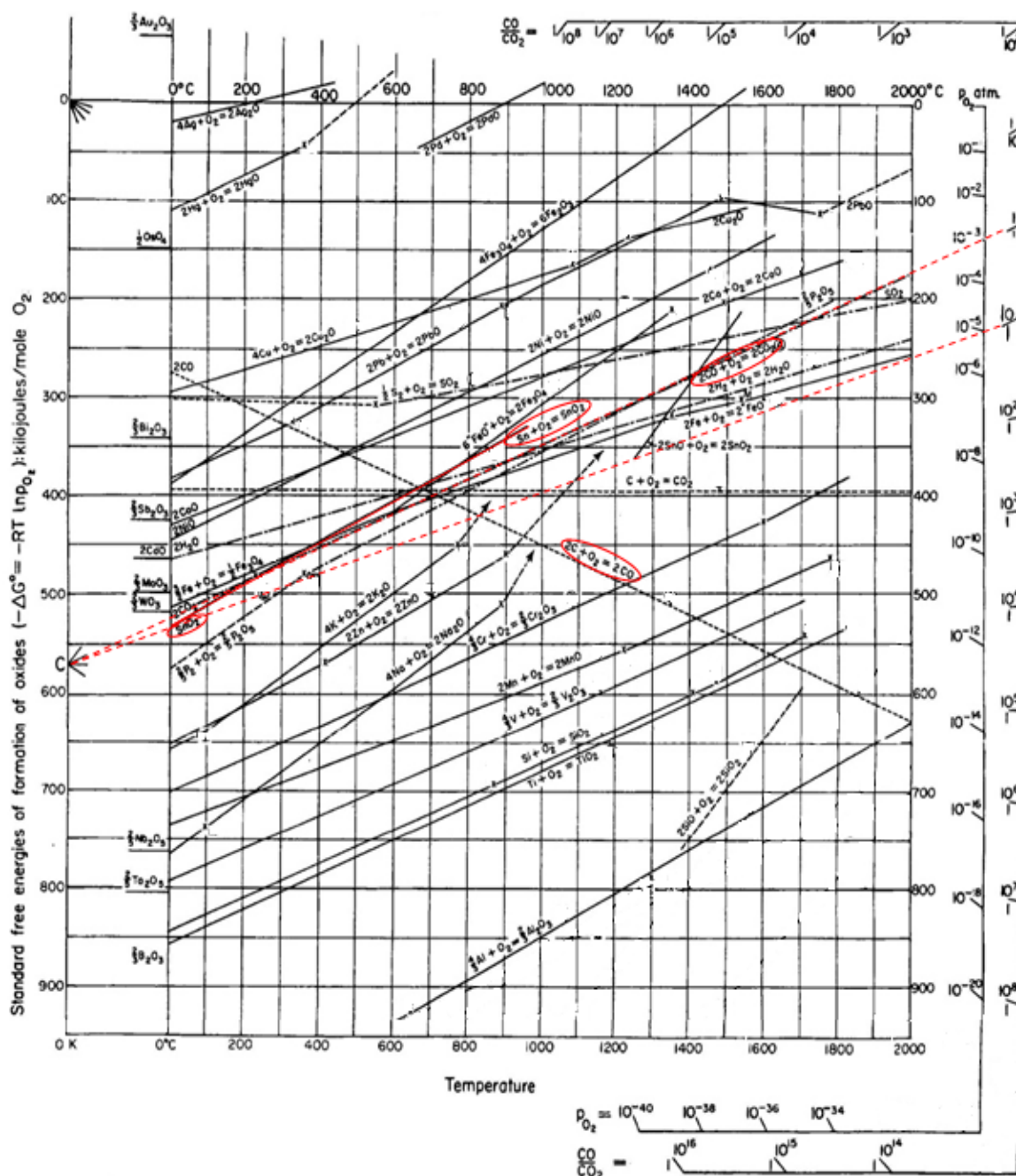


Fig. 2. The Gibbs free energy changes of oxidation reactions [4].

The reduction of SnO_2 by carbon in one step would be possible in standard states – with a relative partial pressure of CO_2 of unit value – above approximately 700 °C. The required reaction is however also possible by an indirect mechanism, with CO acting as the effective reducing reagent. Not only the kinetic but also the thermodynamic feasibility is more advantageous in this way. Even in a CO/CO_2 gas mixture of unit partial pressure ratio, the process is possible at temperatures above 400 °C, and if the partial pressure of

CO is increased to 10 times that of CO₂, the reaction should be possible at room temperature too.

Mitchell and Parker [5] reduced the stannic oxide with the use of anthracite and graphite powder. They have carried out derivatographic experiments and demonstrated that the reaction is practically possible in the temperature range of 800 to 1000 °C. The reaction rate was strongly dependent on the temperature. Whereas at 1000 °C the total conversion required only approximately 5 minutes, at 800 °C it took more than half an hour, as illustrated in Fig. 3. The recovery was found proportional to the used proportion of carbon in the 1 – 3 C/SnO₂ mol ratio range. The kinetic curves of Fig. 3 also show that the amount of carbon in moles consumed until the completion of the reduction process corresponded to the amount of the SnO₂.

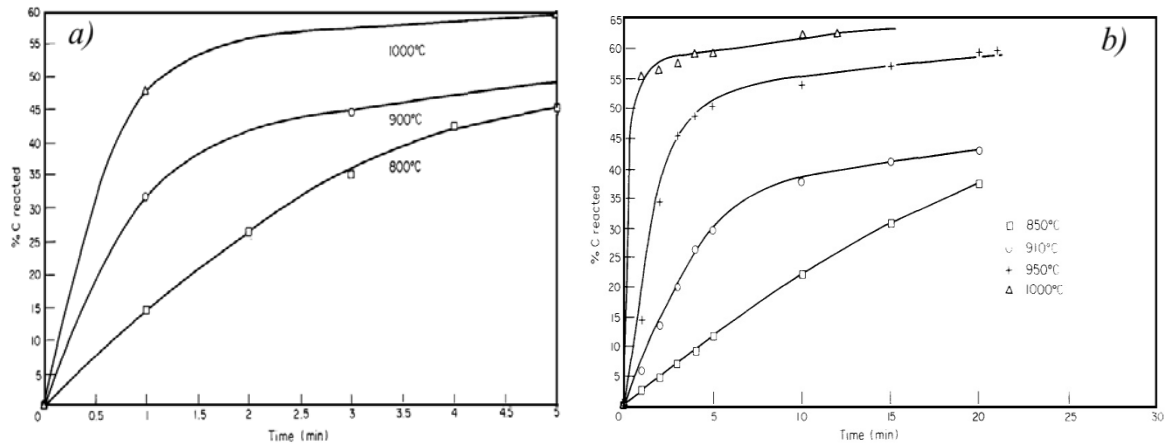
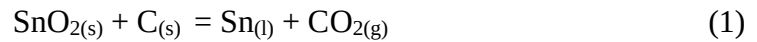
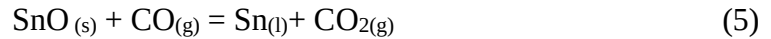
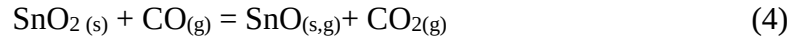


Fig. 3 Reduction with anthracite (a) and graphite (b) in a mole ratio of 2 to SnO₂[5].

Thus, the overall reaction can be expressed as:



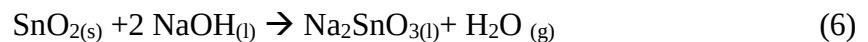
The mechanism should obviously depend on the generation of CO, as solid-solid reactions are very slow. The main steps of the reaction can be assumed as initially:



This assumed mechanism explains the strong change in the conversion rates observed in the cited experiments as the temperature is increased to 1000 °C.

According to the thermodynamic analysis, the reduction produces metallic tin. However it will be embedded in a dispersed form in the residual material of the reduction. Therefore, hydrometallurgical processing, implying hydrochloric acid leaching and subsequent extraction from the tin chloride solution by electrowinning [1,2] seems indispensable.

Bunnakkha and Jarupisithorn [6] tried to convert the SnO₂ into another type of compound, with the use of alkali fusion:



In their experiments, they examined the solubilization of hard-head obtained as a by-product from the pyro-metallurgical processing of cassiterite ores. They ground and fully oxidized the waste material, and after that they mixed it with different amounts of NaOH, followed by fusion at temperatures ranging from 500 to 700 °C. The resulting sodium-stannate was leached with distilled water at 60 °C for 1 hour. Tin can be extracted from the basic Na_2SnO_3 solution by electrowinning [7]. The advantage of the alkali fusion is its simplicity, however the use of NaOH implies a serious corroding effect and losses by evaporation. The reaction requires considerable excess of the reagent. With an oxide starting waste material that is grounded under 400 mesh and with the mixing of 750% excess NaOH at 700 °C and performing the fusion for 2 hours, approximately 95% metal recovery could be achieved after leaching with water.

2. EXPERIMENTAL MATERIALS AND PROCEDURE

Heating up the industrial soldering waste material over the liquidus temperature of the metal effected the separation of the contained metallic and non-metallic components according to their densities. The oxides produced a relatively dry secondary dross layer over the molten metal bath. After careful skimming, the removed secondary dross was oxidized at 700 °C in a crucible furnace, to convert the still remaining metallic portion into tin-dioxide. By the concentration of SnO_2 in the tested material, the examination could be more focused on the behavior of the oxide fraction of the dross generated in the melting operations. The oxidized material was ground and attrited in a ceramic mortar, then the brittle oxide particles were separated from the still remaining metal by passing through a 0.2 mm sieve. The main steps of the dross pre-treatment are shown in Fig. 4. The fine powder used as the raw material for the leaching tests was examined in different ways. The SEM image and the relevant energy dispersive X-ray spectrum (EDS) are shown in Fig. 5.

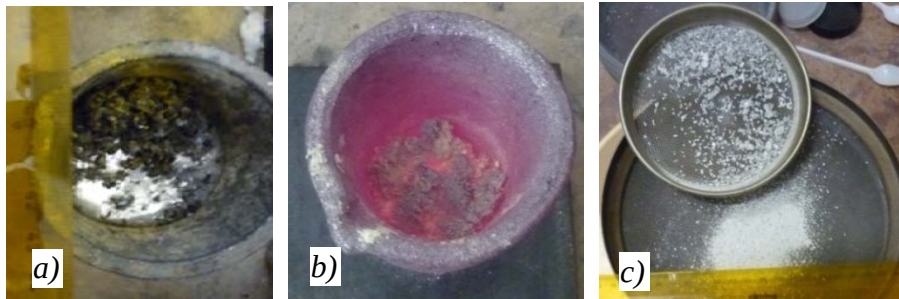


Fig. 4 Production of the SnO_2 raw material for testing (*a*– extracted metal and secondary dross, *b* – oxidation, *c* – fine oxide powder).

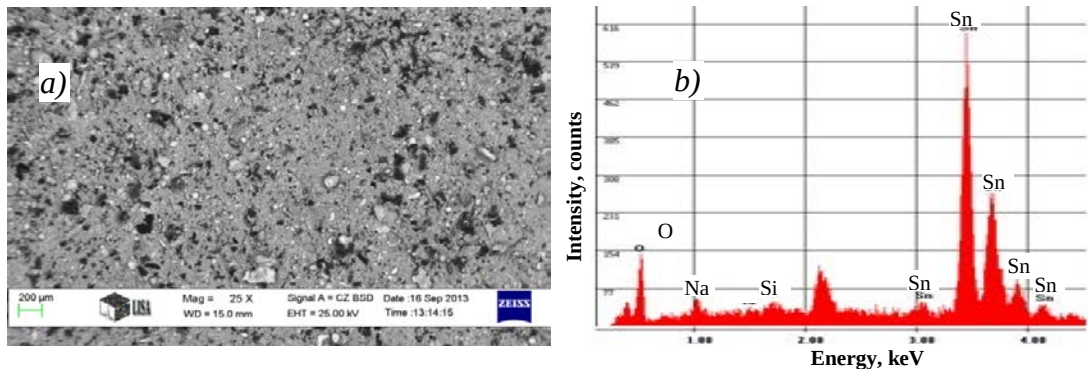


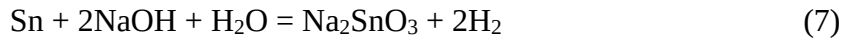
Fig. 5 The SEM image (*a*) and EDS spectrum (*b*) of the pre-treated SnO_2 powder.

The ICP-AES elemental analysis of the oxidized fine powder obtained from the pre-treatment applied to the tin dross is given in Table 1, where the composition of the metal bath obtained at the first step (Fig. 4a) in the pre-treating procedure is also included.

Table 1 The elemental analysis of the examined SnO₂ powder and the metal bath

Material	Concentration, %								
	Ag	As	Cu	Fe	Ni	Pb	Sb	Zn	Sn
Oxide powder	0,0101	0,0075	1,29	0,044	0,030	0,0190	0,0068	1,32	~71,6
Metal bath	0,0059	0,0025	1,72	0,022	0,012	0,0056	0,0030	0,0068	Balance (~98)

After all the pre-treatment, a minor amount of metallic tin can also be found in the oxidized and mechanically separated fine SnO₂ powder. This was determined by measuring the volume of the hydrogen gas it can evolve during dissolution in 6M NaOH:



The evolved hydrogen was collected in a gas burette connected to the reactor, and the volume was converted to standard conditions at room temperature for determining the equivalent mass of tin metal in the examined sample:

$$c_{\text{Sn}} = \left[\sum_i \left(V_i \frac{p_o - \rho g h_i - p_{\text{H}_2\text{O}}}{p_o} \right) \cdot \frac{298}{T} \cdot \frac{119}{2 \cdot 24 \cdot 1000} \right] \cdot \frac{100}{m_{\text{sample}}} \quad (8)$$

where c_{Sn} is the tin concentration in m-%, V_i is the partial volume of gas collected in one step, ρ is the density and $p_{\text{H}_2\text{O}}$ is the vapour pressure of the solution at T temperature at a height of h_i above the level in the reactor. The remaining metal concentration in the oxidised dross was X%. Although oxidation of tin in the secondary dross was incomplete, the remaining metallic fraction is very low, therefore the solubilization experiment can be carried out with high sensitivity. In practice, the remaining metal content causes no trouble; it will behave the same way as the metal obtained by the reduction of the dross.

For the reduction experiments, the starting material was the oxidized and finely ground dross powder. The sample was mixed with coke powder (87% C) to yield a stoichiometric excess of approximately 5 times in a ceramic mortar and the mixture was charged in a clay graphite crucible as seen in Fig 6.

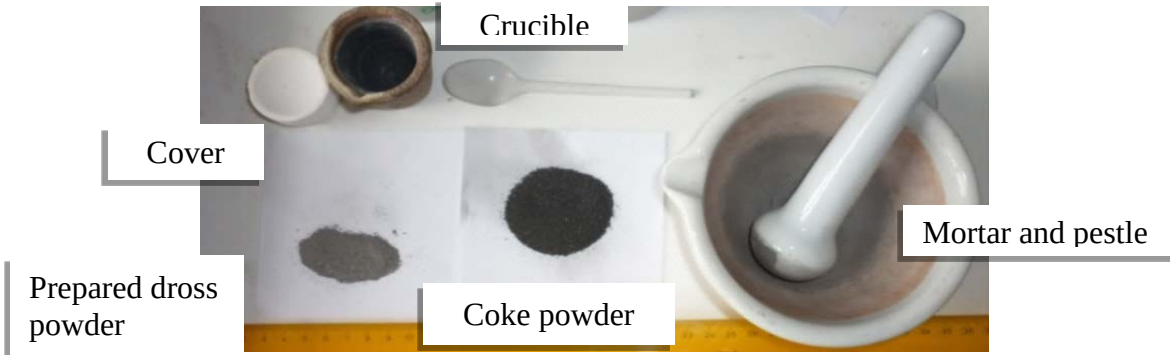


Fig 6. The utensils and materials used for the carbothermic reduction.

The carbothermic reduction of the SnO₂ dross was carried out in a Heraeus TIK 6.5/8 furnace, applying the temperature range suggested by the relevant literature [5]. The parameters are summed up in Table 2. The product of the carbothermic reduction was ground in a ceramic mortar and screened with a 0.45 mm sieve. The fine and coarse fractions were leached separately with 6M HCl at near boiling temperature. The solutions obtained were analysed for tin and some other significant elements by ICP-AES.

Table 2 Parameter settings of the carbothermic reduction experiments.

Sample weight, g	Reagent weight, g	Temperature, °C	Reduction time, min
5	4,63	800	30
			60
			120
		1000	30
			60
			120

For the alkaline fusion, nickel crucibles and covers were used, because they are resistant to the aggressive circumstances caused by the application of crystalline NaOH (97%) as the reagent. Its relative amount yielded approximately 7 times stoichiometric excess. The rest of the details were the same as in the case of the carbothermic reduction experiments. The main parameters of the alkaline fusion are shown in Table 3.

Table 3 Parameters applied in the alkaline fusion experiments.

Sample weight, g	Reagent weight, g	Temperature (°C)	Fusion time, min
2	7.5	700	30
			60
			120
		900	30
			60
			120

The fused product was leached with 500 ml distilled water at 40 °C. After leaching, the solutions were analyzed by ICP-AES, whereas the solid residue was examined by SEM and X-ray diffractometry.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The presence of metallic tin, produced by the carbothermic reduction, is outstanding in the electron micrographs. In Fig. 7a, the metal beads formed at 800 °C for 0.5 h reduction time are of only 1-5 µm diameter and almost uniformly dispersed. On the other hand, the higher temperature and longer time resulted in the generation of beads of larger diameters too. Fig. 7b shows that almost 50 µm diameters can arise as a result of merging the smaller droplets of tin during the longer time the material was kept at the higher temperature in the furnace. The EDS spectrum of the product indicates metallic tin and possibly silicate

material which may arise from the crucible or the ash content of the coke. The elemental analysis of the products obtained from the reduction is given in Table 4.

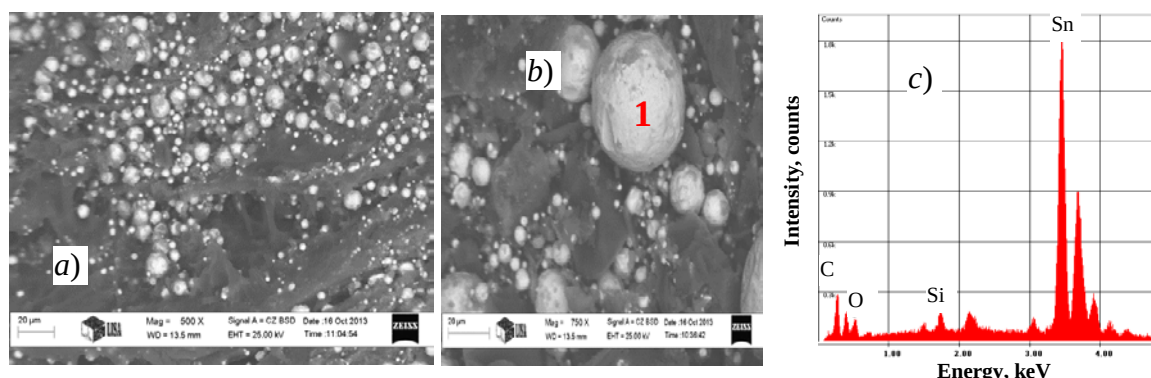


Fig 6 The SEM image of the product of the carbothermic reduction of tin dross at 800 °C, for 0.5 h (a), and at 1000 °C for 2 h (b), and the corresponding EDS spectrum (c).

Table 4 The analysis of products of carbothermic reductions

Reduction temp. / time, °C / h	Fraction		Concentration, %							
	Particle type	Mass, g	Sn	Mn	Al	Cu	Fe	Ni	Pb	Zn
1000 / 2	Fine	3.42	86.1	0.009	0.084	2.04	0.84	0.076	0.041	0.024
	Coarse	1.35	36.2	0.044	0.81	0.62	1.41	0.063	0.016	0.046
1000 / 1	Fine	3.71	84.7	0.008	0.084	2.08	0.85	0.079	0.041	0.032
	Coarse	1.27	31.3	0.067	0.87	0.45	1.85	0.11	0.017	0.062
1000 / 0.5	Fine	3.7	83.4	0.011	0.21	1.88	0.68	0.046	0.037	0.023
	Coarse	1.15	31.2	0.059	0.69	0.55	1.31	0.043	0.019	0.049
800 / 2	Fine	3.58	84.1	0.006	0.23	2.08	0.44	0.033	0.021	0.022
	Coarse	0.84	39.5	0.043	1.37	0.56	1.87	0.092	0.018	0.102
800 / 1	Fine	3.56	88.9	0.007	0.22	2.16	0.42	0.053	0.028	0.018
	Coarse	0.69	33.1	0.033	0.59	0.37	1.77	0.045	0.014	0.061
800 / 0.5	Fine	3.9	82.2	0.008	0.17	1.96	0.33	0.033	0.021	0.024
	Coarse	0.7	47.6	0.093	0.69	1.01	2.04	0.087	0.018	0.084

Most of the iron contamination – collected from the crucible and the mortars - appeared in the coarse fraction, while the copper content of the tin dross remained mostly in the fraction composed of the fine particles. As the applied conditions do not facilitate the coalescence of the reduced metallic tin, most of it remains in the fine powder fraction. The material also contains non-metallic particles and residual coke powder. The XRD examination indicated two major phases: the obtained metallic tin and the residual SnO₂. The partially reduced oxides (SnO·Sn₂O₃) could hardly be detected. The ratio of the metallic phases was increasing with the temperature and time of the reduction.

Leaching of the reduced products with 6M HCl effected the dissolution of the metallic tin by the reaction:



The presence of metallic tin was also indicated by the observed intensive gas evolution. The minor amount of any partially reduced tin oxide could also go into solution. Only little undissolved residue was observed remaining in the reactor, mostly corresponding to the silicate impurity entrapped in the material during the heating and grinding steps. The analysis results demonstrated the expected solubilisation of tin by the devised procedure. In order to assess the efficiency of the process, the extracted amount of tin was related to the analysed total tin content (71.6%) of the oxidised fine powder, used as the starting material for the reduction-leaching procedure. The recovery rates yielded by the reduction carried out with different operational parameters are given in Fig. 7.

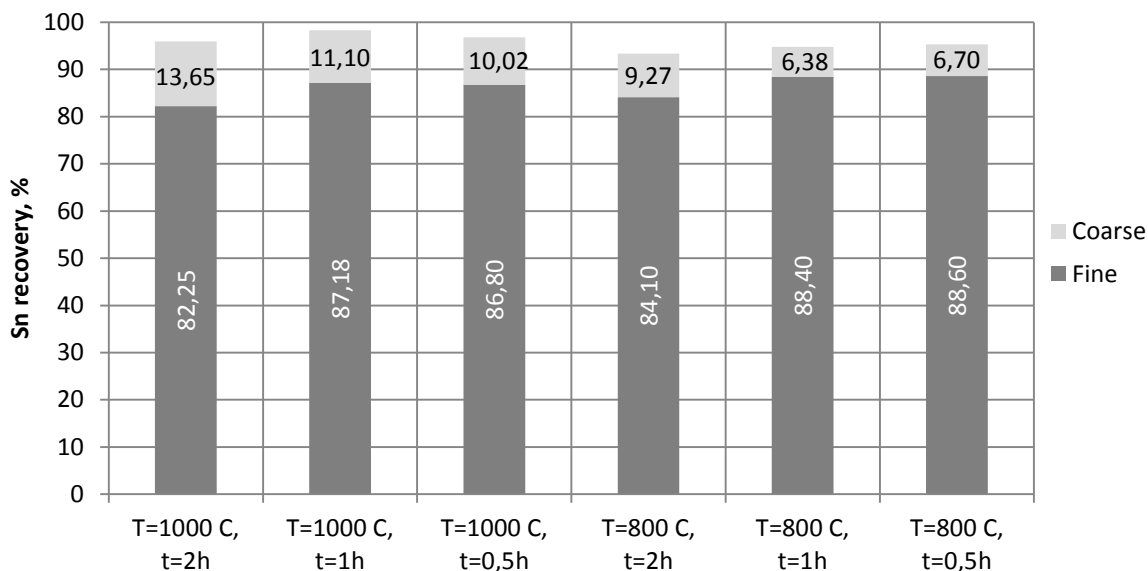


Fig. 7 Recoveries of tin in the fractions of the reduced material.

It is obvious that the shortest examined reduction time was enough, but the higher applied temperature was more efficient in converting the tin-dioxide into acid-soluble form. The conversion rates obtained with the materials pre-treated at the same temperature can be considered parallel results, as the reduction process reached its virtually full scale after the first 30 minutes. The differences are within the practical error margin. Further heating may have also resulted in losses caused unfavourable conversion or volatilization at the surface of the charge, where local re-oxidation may have happened. Considering the average levels of extraction figures, the solubilizing pre-treatment can convert the tin content of the SnO_2 dross to almost completely soluble form. The SnCl_2 – HCl solution thus obtained is suitable for electrolytical tin extraction [1,2].

At Fig 9a. can be seen the product of the fuse, and at Fig 9b. the EDS spectrum of the product.



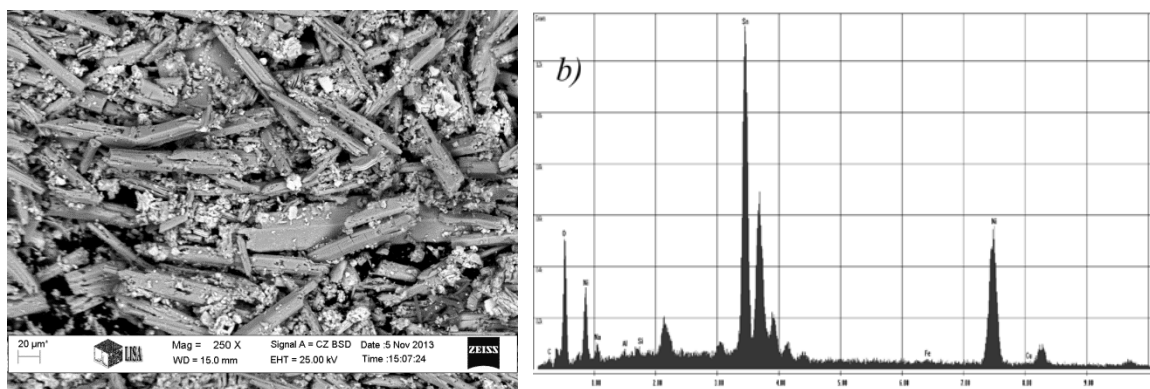


Fig. 9.

Produkt of the alkali fuse, SEM pic. (a), EDS spectrum (b)

At Table 4. can be seen the results of the analyzed alkali fused solutions. It showed 50-60% tin concentration.

Table 4.

The solved materials, during leaching the alkali fused samples into dist. water (mg/2g)

	Solved weight, mg							
Fuse temp...-time, °C-h	Sn	Ag	Al	Bi	Cu	Fe	Zn	Ni
900-2	948,85	1,40	1,63	0,31	0,16	0,10	0,21	0,05
900-1	1189,50	0,59	1,78	0,28	0,08	0,09	0,07	<0,003
900-0,5	990,30	0,48	1,91	0,29	0,14	0,05	0,13	0,00
700-2	1119,85	1,41	3,66	0,29	0,43	0,10	0,33	0,01
700-1	1258,55	0,64	3,07	0,33	0,09	0,03	0,13	0,03
700-0,5	1044,15	1,71	4,55	0,32	0,14	0,25	0,72	0,02

At Fig 10. it can be seen the results of the 2g samples of the alkaline fusion. It is surprising that the higher temp. had not increased the efficiency of the fuse, moreover it decrease it in a mild way. The best fuse time was 1 hour. Those experienced phenomena could occur due to the instability of the Na_2SnO_3 at high temperature and with the connect of air [8], and due to the high steam-pressure of the NaOH [9]. If we see the dross as a source of pure SnO_2 , then the metal recovery could be between 60 – 79 %. But if we use the tin concentration of dross, which one was added by the analytical measurement, (71,6 %), then the metal recovery could be between 66 – 88 %. These results are less with 10 -20 % than the results which we got from the carbothermic reduction experiments.

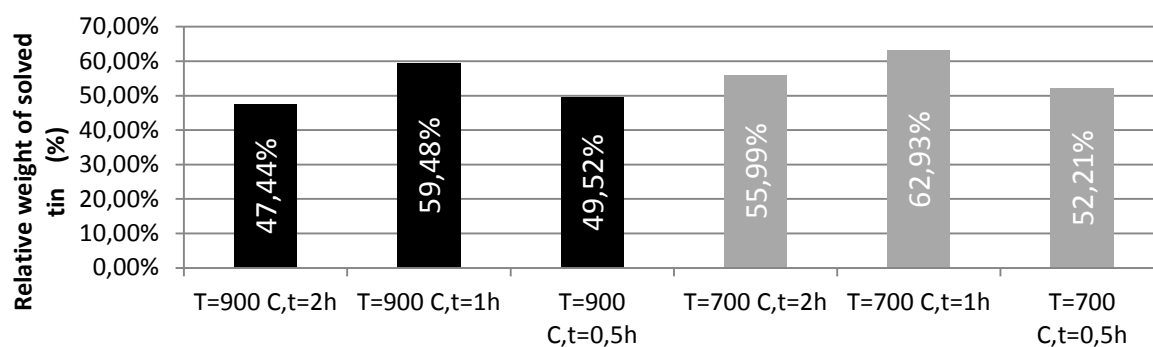


Fig 10.

The summa solved tin, compared to the 2g starting weight.

4. CONCLUSIONS

The dross which arose from the melting of the soldering waste scrap is a very resistant material. It is resistant against the most common known acids and bases. Our main task were to find any kind of technologies which can convert this material into something that can be reused in the main soldering waste scrap recycling system. We had founded two methods in the literature which can solve the problem, the carbothermic reduction and the high temp. alkaline fusion. We had made experiments with the two method, and after it the products had been analyzed by SEM and ICP-AES.

The results of the carbothermic reactions showed that the reduction could convert the tin of the dross into metallic tin, and/or into stannous oxide (Red. temp: 1000 °C, red. time 2 hour). If we decrease the temperature with 200 °C or the time with 1,5 h, than it occur a 10% decrease in the metal recovery. If we compare the metal recovery, the productivity and the cost, the technology could be a very good method for the recovery of the drosses. The metallic tin mostly arose in a fine powder, due to it a hydrometallurgical way is the best choice to extract it.

The results of the alkali fuse was also promising with the outcome of the SEM and ICP-AES measurements it could be seen that the SnO₂ based starting material could be converted mostly into Na₂SnO₃, which can be solved into water. The analytical results of the ICP-AES measurements showed that the metal recovery was between (60 - 80 %).

In the end the price of the two reagents can be compared. The carbothermic reduction needs coke powder, strong HCl, and a lot of time. The alkali fuse needs a lot of NaOH (which is also expensive), but it is fast, and it can be solved into water, on the other hand the media is very aggressive during the fuse.

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