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EXTRACTION OF TIN FROM OXIDIZED SOLDERING DROSS BY CARBOTHERMIC REDUCTION AND ACID LEACHING

ZOLTÁN HARANGI¹–TAMÁS KÉKESI²

The melting of soldering scrap originating from the electronic industry produces *inter alia* oxide dross, composed mainly of SnO₂, which is resistant to the lixiviants most commonly used for hydrometallurgical treatment. We have investigated the possibility of converting this SnO₂ into a soluble form by carbothermic reduction using coke powder in the 800–1000 °C temperature range. The raw material for the experiments was obtained by increasing the SnO₂ concentration in the dross skimmed from the tin bath by further oxidation at high temperature. The treated dross and the products were examined with scanning electron microscopy and X-ray powder diffraction (XRD). The efficiency of the treatment was determined by leaching the reduced material with boiling 6 mol dm⁻³ HCl solution. The obtained solutions were analyzed by atomic absorption to determine the dissolved portion of tin content. Under optimized conditions, it was possible to reach conversion rates higher than 90% of the originally insoluble tin-dioxide content.

Keywords: soldering waste, tin dioxide, carbothermic reduction, solubility

Introduction

The soldering and surface coating technologies applied in the electronic industry generate a layer of oxidized dross at the surface of the tin melt. It is removed periodically by skimming and it contains a large amount of entrapped metal. According to a novel process [1–2], the metallic component is separated by re-melting the primary dross and after skimming, the molten metal is cast into anodes for electrorefining. During this re-melting step a significant amount of secondary oxide dross is skimmed off the surface of the metal bath. The aim of this research is to find a method which can facilitate the recycling of tin from that oxide based heterogeneous waste material. However, the SnO₂ matrix is highly refractory [3]. It is rather difficult to dissolve either in acids or in bases [4]. This difficulty can be overcome by applying a preliminary reduction to achieve the conversion of SnO₂ into the soluble metallic or the lower state oxide forms. As it is shown in Fig. 1, the thermodynamic conditions would allow the reduction of SnO₂ by carbon in standard states (applying unit value relative partial pressure of CO₂) above approximately 700 °C. The required reaction is, however, more likely to occur through an indirect mechanism, with CO acting as the effective reducing reagent. Not only kinetic but also thermodynamic feasibility is more beneficial in this way. Even in a CO/CO₂ gas mixture of unit partial pressure ratio, the process is possible at temperatures above 400 °C. The reducing CO gas can be produced by the initial oxidation of the coke particles and the subsequent Boudouard-reaction. However, the latter step – as commonly known – requires

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temperatures higher than 800 °C. Besides thermodynamics, the kinetics of the reaction may require the application of even higher temperatures.

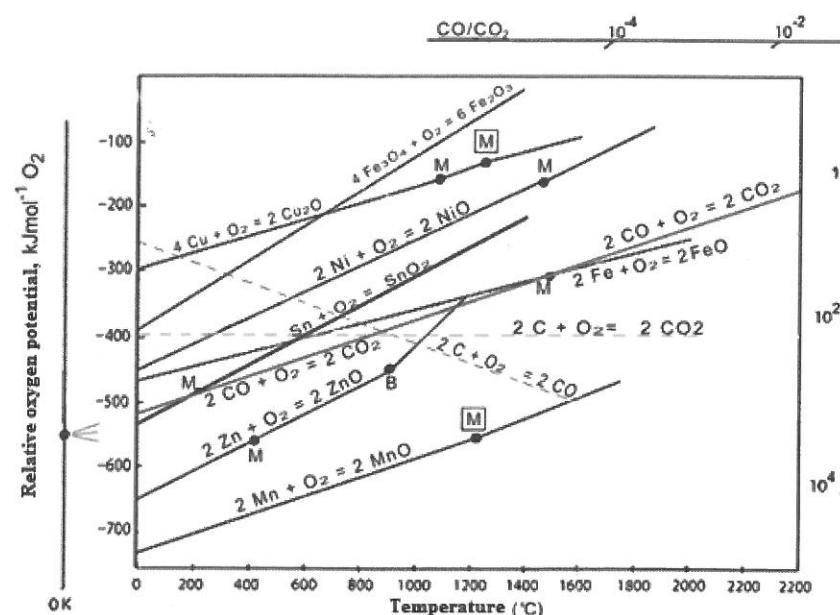
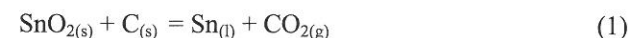
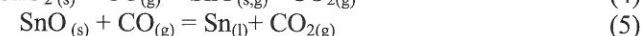


Figure 1. The relative oxygen potential of the reactions

Mitchell and Parker [5] reduced pure stannic oxide with anthracite and graphite powder. They demonstrated that the reaction is practically possible in the temperature range of 800 to 1000 °C, yet the reaction rate was strongly dependent on temperature. At 1000 °C, the whole conversion process required only 5 minutes; at 800 °C it took more than half an hour. The rate of recovery was found proportional to the used proportion of carbon in the 1–3 C/SnO₂ mol ratio range, but the final carbon consumption corresponded to the overall reaction expressed as:



The main steps of the reaction can be assumed as:



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

According to the thermodynamic consideration, such a reduction has the potential to produce metallic tin. However, tin will be embedded in a dispersed form in the residual material. Therefore, hydrometallurgical processing – implying a hydrochloric acid leaching

and a subsequent extraction from the tin chloride solution by electrowinning [1, 2] – seems indispensable.

1. Experimental Materials and Procedure

By heating up the soldering waste material – the primary dross – over the liquidus temperature of the metal, the contained metallic and non-metallic components can be separated. After careful skimming, the removed secondary dross was oxidized at 700 °C in a crucible furnace to convert most of the still remaining metallic portion into tin-dioxide. The oxidized material was ground and attrited in a ceramic mortar, then the brittle oxide particles were separated from the residual metal by passing the powder through a 0.2 mm sieve. In this way, by increasing the concentration of SnO₂ in the tested material, we obtained results that more clearly reflected the behavior of the oxide fraction of the dross. The main steps of the dross pre-treatment are shown in Fig. 2. The fine powder used as the raw material for the leaching tests was examined in different ways. The scanning electron microscope (SEM) image and the relevant energy dispersive X-ray spectrum (EDS) are shown in Fig. 3.

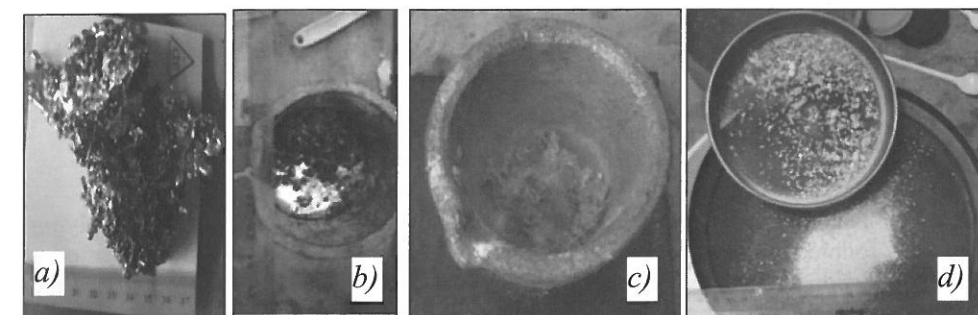


Figure 2. Pre-treatment of the soldering tin dross to produce the raw material for testing
a – raw dross, b – extracted metal and secondary dross, c – oxidation, d – fine oxide powder

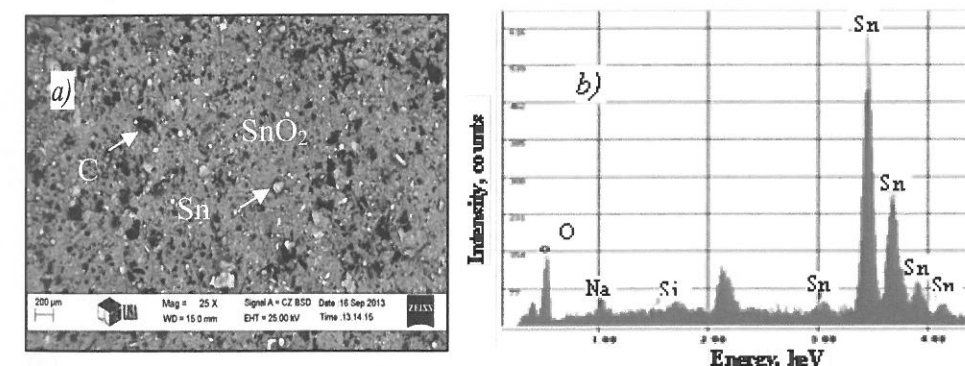


Figure 3. The SEM image (a) and EDS spectrum (b) of the pre-treated SnO₂ powder

According to both the SEM and EDX examinations, the oxidized fine powder obtained from the pre-treatment of the tin dross contained mainly tin and oxygen. The phase composition of the material was examined by X-ray diffraction (XRD), the result is given in the diffractogram of Fig. 4.

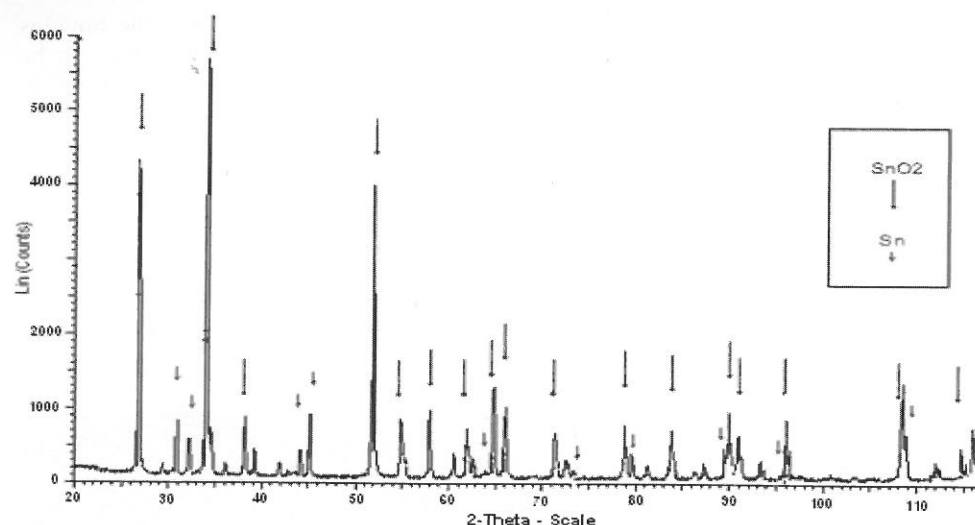


Figure 4. X-ray diffraction pattern of the treated tin dross

The elemental analysis regarding the metal content was carried out by applying inductively coupled plasma atomic emission spectrometry (ICP-AES) method after a complete digestion procedure. The results are given in Table 1, which also includes the composition of the metal bath obtained at the first step (Fig. 2b) in the pre-treating procedure.

Table 1
Elemental analysis of the examined SnO_2 powder and the metal bath

Material	Concentration, mass percent						
	Ag	Cu	Fe	Ni	Pb	Zn	Sn
Oxidized dross	0.0101	1.29	0.044	0.030	0.0190	1.32	71.6
Metal bath	0.0059	1.72	0.022	0.012	0.0056	0.0068	~98

A minor amount of metallic tin was still found in the oxidized and mechanically separated fine SnO_2 powder. This was determined from the measured volume of the hydrogen gas that evolved during the dissolution of tin in hot 6 mol dm^{-3} HCl solution:



The released hydrogen was collected in a gas burette connected to the reactor, and the volume was converted to standard conditions at room temperature so as to determine the concentration of the metallic tin in a sample of mass m_{sample} (g):

$$c_{\text{Sn}} = \left[\sum_i \left(V_i \frac{p_o - \rho g h_i - p_{\text{H}_2\text{O}}}{p_o} \right) \cdot \frac{298}{T} \cdot \frac{119}{2 \cdot 24 \cdot 1000} \right] \cdot \frac{100}{m_{\text{sample}}} \quad (7)$$

where c_{Sn} is the tin concentration in mass percent, V_i is the partial volume of the gas collected (cm^3), ρ is the density of the solution (kg m^{-3}) and $p_{\text{H}_2\text{O}}$ is the vapour pressure of the solution (Pa) at a height of h_i (m) above the level of the solution in the reactor. The temperature of the system is T (K). Performing this analysis with the necessary repetitions, the remaining metal concentration in the oxidised dross was found to be 16 mass %. In actual practice, however, the metal content of the dross would be definitely higher, which nonetheless causes no difference in the suitability of the hydrometallurgical processing route. The original metal content will behave the same way as the metal obtained by the reduction of the dross.

In order to determine the kinetically efficient range of the intended reaction, preliminary investigations were also carried out by derivatography. The pre-treated oxide based pulverized raw material was charged in the corundum crucible of the C-MOM type derivatograph either directly or mixed with coke. Controlled heating was carried out in contact with air. The results are given in Fig. 5.

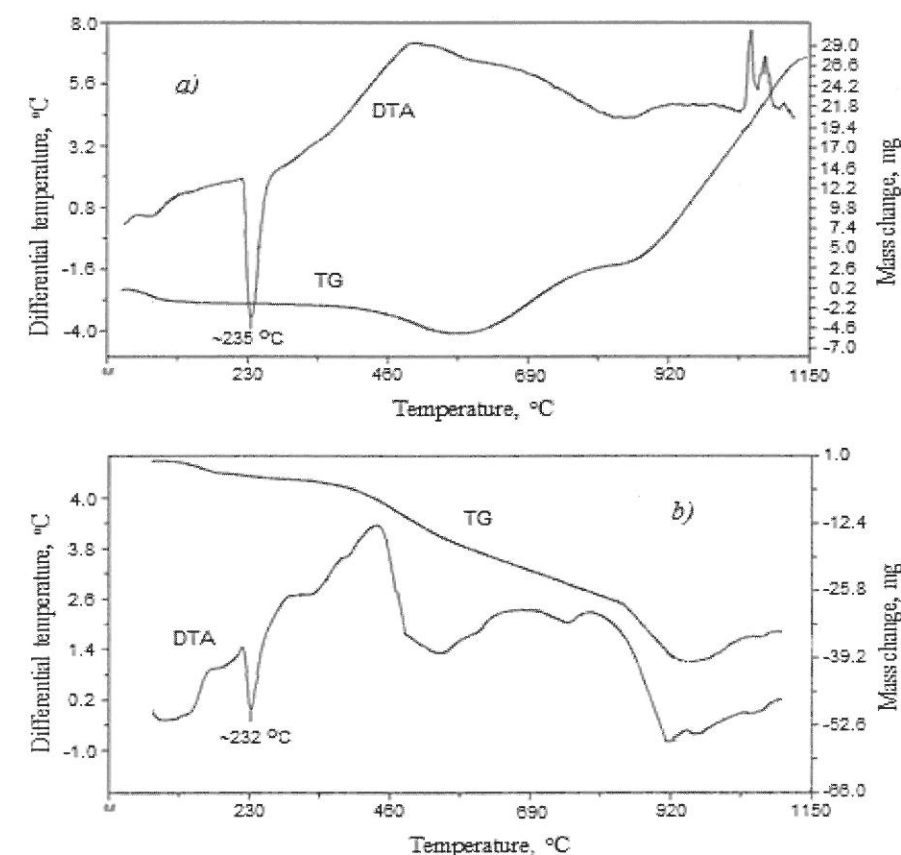


Figure 5. Derivatograms of pre-treated dross (a) and that of the dross-carbon mixture (b)

The obtained derivatograms implied the presence of metallic tin through a sharp negative DTA-peak at $\sim 230^\circ\text{C}$. As can be seen in Fig. 5a, after the initial drying, there was no noticeable variation in the mass (shown by the TG curve) of the oxidised raw material until approx. 600°C was reached. Subsequently to that, the mass increased slightly at first, then (above approx. 900°C) more rapidly, showing the gradual formation of tin dioxide. When the raw material was mixed with carbon, as shown in Fig. 5b, the mass slightly but continuously decreased until approx. 400°C due to the formation of sub-oxides from the initial reduction steps. The effect of oxygen removal may be coupled with the evaporation of volatile species. At higher temperatures, especially in the $800\text{--}1000^\circ\text{C}$ range, the weight loss indicating the reduction process intensified. The derivatogram of the mixed material showed less heat effect on the DTA differential temperature curve at the melting point of the metal. This results from the dilution of the dross in the sample by the added carbon. However, the mass loss caused by the reduction process (Fig. 5b – TG) even slightly exceeded the mass increase resulting from the oxidation of the unmixed starting material (Fig. 5a – TG), indicating that the molar amount of the oxide was higher than that of the metal in the dross. It can also be seen in Fig. 5b that the carbon content of the mixture got consumed by the reduction process and the unavoidable aerial oxidation by the time the 920°C was reached. After this point, the oxidation of the reduced metal could take place.

The experimental carbothermic reduction of the pre-treated secondary dross was carried out in a Heraeus TIK 6.5/8 furnace, applying the temperature range suggested by the relevant literature [5] and by the preliminary test results (i.e. derivatography). The starting material was the oxidized and finely ground dross mixed with coke powder (87% C) in a ceramic mortar (in a way to yield a stoichiometric excess of carbon approximately 10 times). The mixture was charged in a clay graphite crucible. The parameters are summarized in Table 2.

Parameter setting of the carbothermic reduction experiments

Sample mass, g	Reagent mass, g	Temperature, $^\circ\text{C}$	Reduction time, min
5	4.63	800	30
			60
			120
		1000	30
			60
			120

The product of the carbothermic reduction was ground and screened with a 0.45 mm sieve. The fine and coarse fractions were leached separately in $6\text{ mol dm}^{-3}\text{ HCl}$ solution close to boiling temperature. The obtained solutions were analysed for tin and for some other significant elements by ICP-AES.

2. Experimental Results and Discussion

The carbothermic reduction of the pre-treated tin dross under milder and stronger conditions produced the material illustrated by Fig. 7. The presence of metallic tin is prominent in the electron micrographs. In Fig. 7a, the metal beads formed at 800°C in 0.5 h reduction time are only $1\text{--}5\text{ }\mu\text{m}$ in diameter and almost uniformly dispersed. On the other

hand, higher temperature and longer residence time resulted in metal beads with larger diameters. Fig. 7b shows that when the material is kept for a longer time at the higher temperature, the dispersion of the reduced metal remains principally the same, but almost $50\text{ }\mu\text{m}$ diameters might as well arise due to the merging of smaller tin droplets. Besides the dominance of tin, the EDS spectrum of the product indicates the presence of a possibly silicate material which may derive from the ash content of the coke and to a lesser extent from the crucible. The macrophotograph in Fig. 7d demonstrates that the metal content is very dispersed though still recognizable to the bare eye and the material crumbles easily.

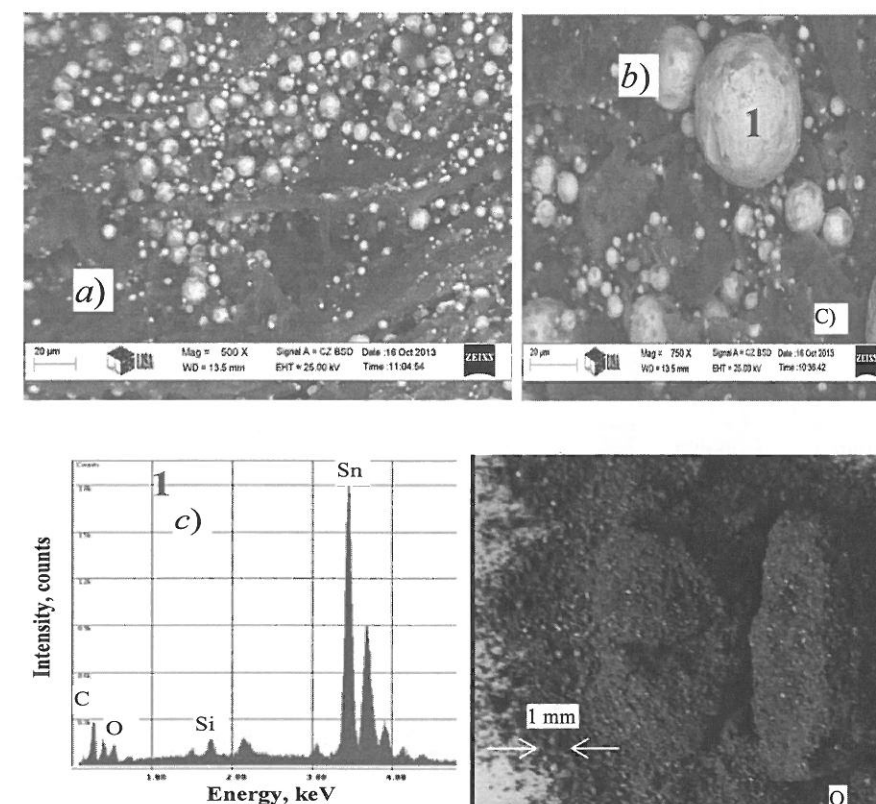


Figure 7. SEM images of the products of carbothermic reduction at 800°C for 0.5 h (a), and at 1000°C for 2 h (b), together with the corresponding EDS spectrum (c) and the macrophotograph of the fine material obtained

The XRD spectrum in Fig. 8 proves that the major phase in the reduced material is Sn, although some tin sub-oxides and a minor amount of SnO_2 can also be detected. The ratio of the metallic phases was found to be increasing with the temperature and time of the reduction. The results of the elemental analysis of the products obtained during the reduction process are given in Table 3.

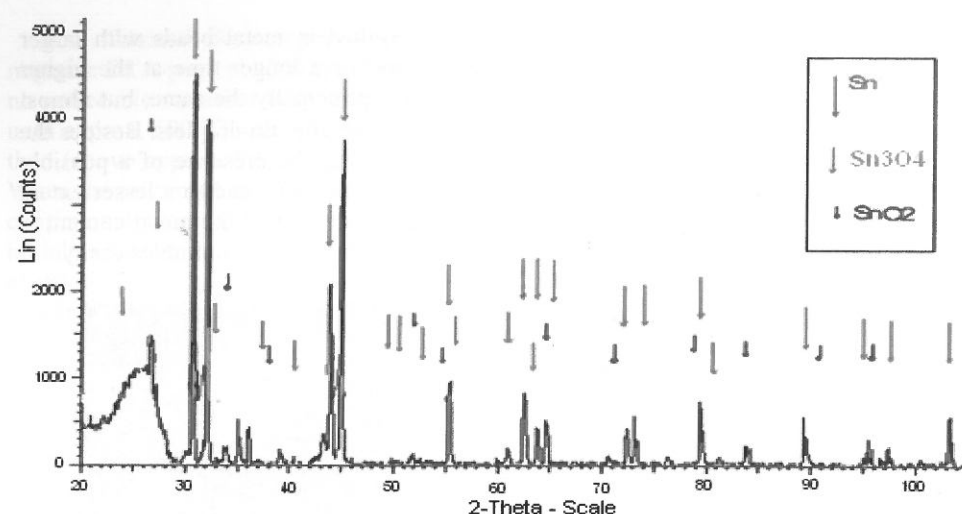


Figure 8. XRD spectrum of the material obtained from the carbothermic reduction of the pre-treated tin dross (1000 °C, 2h)

The analysis of the products from carbothermic reductions

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

Most of the iron and aluminium contamination – collected from the coke, 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. This may indicate that the coarse fraction is mostly attributable to the original metal content of the pre-treated tin dross, whereas the reduced metal can be found principally in the fine particles. Since the

applied conditions do not facilitate the coalescence of the reduced metallic tin, most of it remains in the fine powder fraction.

The leaching of the reduced products with hot 6 mol dm⁻³ HCl solution resulted in the dissolution of the metallic tin according to reaction (6). The presence of metallic tin was also detectable from the observed intensive gas evolution. Any partially reduced tin suboxide also transfers into solution. Only little undissolved residue was observed to remain in the reactor, mostly corresponding to the residual SnO₂ content and the silicate impurity entrapped in the material during the heating and grinding steps. The ICP-AES analytical results demonstrated the expected solubilisation of tin by the devised reduction procedure. In order to assess the overall efficiency of the process, the extracted amount of tin was compared to the analysed total tin content (71.6%) of the pre-treated dross in the form of the oxidised fine powder (Fig. 3d), expressed in Table 1. Efficiency is the ratio of the tin content obtained in the solution to that in the starting material used for the reduction-leaching procedure. The recoveries yielded by reduction carried out with different parameters are given in Fig. 9.

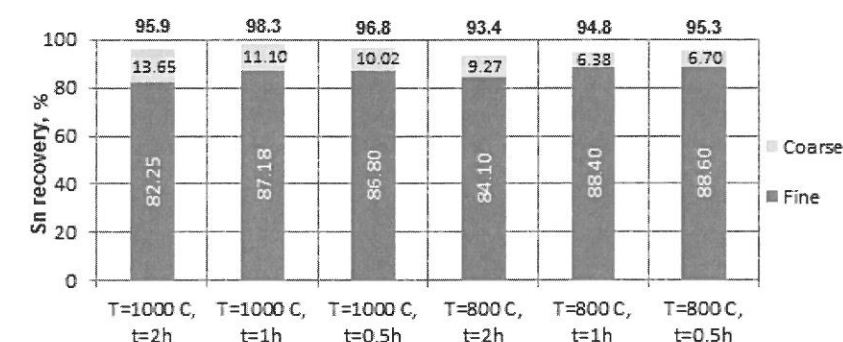


Figure 9. Recoveries of tin in the fine and coarse fractions of the reduced material.

Since the starting material of the reduction-leaching procedure also contained 16% metallic tin, conversion efficiency has to be expressed with reference to the remaining amount of oxidised tin, corresponding to 55.6% of the starting mass. Conversion efficiencies are accordingly given in Table 4.

Table 4

Tin recovery from the dross by 6M HCl leaching after different reducing steps

Reduction Temp., °C / time, h	1000/2	1000/1	1000/0.5	800/2	800/1	800/0.5
Sn conversion, %	94.7	97.8	95.9	91.5	93.3	93.9
Average Sn conversion, %	96.1			92.9		

The shortest testing time (0.5 h) was practically sufficient for reduction. At 800 °C, increasing time resulted in slightly but continually decreasing recovery. This tendency recurred with respect to the shortest and longest times also at 1000 °C. Prolonged heating resulted in losses caused by unfavourable re-oxidation locally at the surface of the charge, where the reducing effect was weak and volatile monoxide or inert dioxide could arise by

partial reduction or re-oxidation. Increased temperature, however, could raise the efficiency of reduction. The conversion rates obtained at the same temperature for different times can be considered practically parallel results within the error margin, since the reduction process virtually reached its full scale after the first 30 minutes.

Conclusions

The oxide content of the dross obtained from the melting of soldering scrap is resistant to common known acids and bases. However conversion of the SnO_2 to acid soluble form by carbothermic reduction has proved practically viable. Experiments have been carried out to examine the feasibility and the characteristics of this method using coke powder as the reducing agent for various durations of heating at different temperatures in a feasible range determined by preliminary derivatography. Examination of the product by direct SEM, EDS XRD techniques pointed at the formation of metallic tin and some sub-oxides. The converted material was leached with hot 6 mol dm^{-3} HCl solution. ICP-AES analysis of the pre-treated fine oxidized powder starting material and the obtained solutions was used to express the recovery and conversion rates. With carbothermic reduction it was possible to convert the oxidized tin of the dross into acid soluble form with an efficiency of 93–96% depending on the conditions applied. The optimum parameters of reduction with coke powder were found to be 1000°C temperature and 0.5 hour duration. The effect of increased reduction time is negligible because unfavorable re-oxidation and evaporation may also occur at the surface. Decreasing the temperature to 800°C slightly reduces process efficiency (by $\sim 3\%$) of reductions carried out in the 0.5–2 h time range. Metallic tin was formed as finely dispersed particles, amenable to hydrometallurgical extraction. Although carbothermic reduction with cheap coke powder is efficient in converting the SnO_2 content of the tin dross into soluble form, but the subsequent leaching of the metal requires the use of boiling 6 mol dm^{-3} HCl solution in a closed system.

Acknowledgement

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COMPUTER SIMULATION OF THE HEATING PROCESS OF FUSED CAST REFRACTORY BLOCKS

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After the solidification process of fused cast refractories – used for glass melting furnaces – the sprue is cut off with a cutting machine in wet operation. Then, the cavity is sealed with refractory concrete. The aim of our research was to determine the most important parameters (e.g. gas permeability) for the safe application of the refractory concrete used for the sealing of the solidification hole. In order to validate the permeability test results, test blocks were made from fused cast alumina-zirconia-silicate (AZS) material equipped with pressure and temperature sensors. The investigations revealed that the gas permeability of the sealing material allows the steam (evolving from the moisture contained by the concrete and from the water trapped in the shrinkage cavity) – which can cause damage to the refractory block – to flow out safely during the first heat-up of the fused cast blocks.

In order to better understand the heating process and the temperature field inside the refractory blocks a numerical model was created with ANSYS FLUENT software. More articles revealed that the accuracy of the results depends largely on the choice of material properties [1][2]. The differences between the temperature values calculated by the computer model and those measured with thermocouples during the tests are within the acceptable limits of industrial practice. Based on the experiences we constructed a model of a real-size AZS block built into a glass furnace with insulation layers. In the case of the industrial block we can declare: the gauge pressure in the cavity is not likely to cause damage to the refractory blocks by itself.

Keywords: fused cast refractory, shrinkage cavity, refractory concrete, gas permeability, simulation

Introduction

A fused cast refractory block is usually built-in so that it contains the shrinkage cavity, which is formed during solidification. It has the same properties and durability yet lower costs than the block that has no porosity or cavity.

Two glass melting furnaces built of these types of blocks had problems during the first heat-up operation. When the furnace temperature reached about 350°C , one brick was damaged and broke out of the lining of both equipment. It was claimed that the steam coming from the moisture content of the concrete or from the water trapped in the shrinkage cavity caused the damage. In our previous paper we reported on the gas permeability and thermogravimetry tests of the refractory concrete. The aim of the research was to determine the following parameters:

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