

Article

Selective Recovery of Tin from Electronic Waste Materials Completed with Carbothermic Reduction of Tin (IV) Oxide with Sodium Sulfite

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Abstract: A new approach for the thermal reduction of tin dioxide (SnO_2) in the carbon/sodium sulfite (Na_2SO_3) system is demonstrated. The process of tin smelting was experimentally optimized by adjusting the smelting temperature and amounts of the chemical components used for the thermal reduction of SnO_2 . The numbers obtained are consistent with the thermodynamic characteristics of the system and molar fractions of reactants derived from the proposed mechanism of the SnO_2 thermal reduction process. They reveal that the maximum yield of tin is obtained if masses of C, Na_2SO_3 and SnO_2 are approximately in the ratio 1:2:3 and the temperature is set to 1050 °C. The key role in the suggested mechanism is the thermal decomposition of Na_2SO_3 . It was deduced from the available experimental data that the produced sulfur dioxide undergoes carbothermic reduction to carbonyl sulfide—an intermediate product involved in the bulk reduction of SnO_2 . Replacing sodium sulfite with sodium sulfate, sodium sulfide and even elemental sulfur practically terminated the production of metallic tin. The kinetic analysis was focused on the determination of the reaction orders for the two crucial reactants involved in the smelting process.

Keywords: tin; tin dioxide; carbothermic reduction; sodium sulfite; smelting



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1. Introduction

Tin is one of the most important metals commonly used in various industrial areas. It is the main component of low-melting alloys used as solders in the electronic industry. For the last two decades, the electronic industry has been the major consumer of this metal.

Cassiterite, a naturally occurring oxide of tin (SnO_2) containing about 79% tin, is the principal primary source of tin. It is the only natural mineral of tin from which extraction of tin is economically justified. The production of tin from its ore involves roasting and smelting processes [1]. In the first stage, the concentrates of cassiterite are roasted with specific reagents (including calcium chloride, calcium oxide and pyrite) to eliminate the sulfur at temperatures between 550 and 650 °C. The type of the roasting chemical depends on the type and amount of impurities. After the preparation (roasting) step, the material for smelting comprises tin dioxide and some impurities (mainly iron oxides). The smelting process carried out in either reverberatory, blast or electric furnaces is based on the reduction of tin dioxide by heating to 1300–1400 °C with carbon (in the form of anthracite coal or coke) and limestone (slag-producing agent) to produce tin and carbon dioxide [2]. The product of thermal reduction is then electrolytically refined and, as a result, up to 99.8% pure tin is obtained.

The tin-bearing natural sources will be exhausted in several years; therefore, currently, an increased effort is directed to the recovery of tin from tin-bearing secondary resources, including tin anode slime, tin slag, tin-bearing tailings and waste electronic and electrotechnical devices. A rapid growth in the amount of e-waste observed recently

makes this class of tin secondary sources of special importance. Many scientific papers deal with the methods for the extraction of tin from these materials. In general, the procedures proposed are based on the chemical leaching of metallic tin, followed by its hydrometallurgical or pyrometallurgical conversion back to its metallic form [3]. It is desired that leaching agents selectively extract tin from its alloys (which contain either lead or silver and bismuth and are usually deposited on copper substrates) to generate tin compounds in either ionic or oxide forms. In a large number of examples, the cheap and effective reagents for the preparation of a water-soluble tin compound involve solutions of either sodium hydroxide [4–6], hydrochloric acid [6–8] or iron (III) chloride [9]. A strong base reacts with metallic tin to produce well-soluble stannate, while acidic solutions of chlorides lead to the formation of chloride complexes of tin. Both stannate and tin chloride hydrolyze to the oxide form of tin or can be easily transformed into tin dioxide. By applying appropriate conditions, the soluble tin compounds can be electrolyzed. Alternatively, they can be quantitatively transformed into tin (IV) oxide and thermally reduced using various reducing agents. These include carbon/carbon monoxide [10], hydrogen [11], methane [12], carbon/molten $\text{Na}_2\text{CO}_3/\text{NaNO}_3$ [13] and Ar-balanced CH_4 (decomposed partially to H_2 and C) [14] systems. The optimal method for tin recovery is usually a combination of both hydrometallurgical and pyrometallurgical processes.

Recently, we have developed and implemented a method for selective recovery of tin from e-waste materials by employing the leaching process with diluted nitric (V) acid [15]. Under the specified conditions, most metals from e-scrap are leached into the aqueous solution in the form of cations (Pb^{2+} , Cu^{2+} , Ag^+ , etc.). Tin, in turn, is transformed into a solid oxide phase, contaminated, to some extent, with lead oxides.

This paper presents a new approach for the final step in the tin recovery process. It utilizes a carbothermic reduction of tin dioxide with an addition of sodium sulfite (Na_2SO_3). The efficiency of the smelting process was studied as a function of temperature and the composition of the smelting mixture. Of special interest was the dependence of the amount of sulfites added to the system on the temperature at which tin dioxide is quantitatively reduced to metallic tin. Discussion on a possible mechanism of the SnO_2 thermal reduction is supported by the chemical, kinetic and thermodynamic analyses. The results allowed us to establish the optimal composition of the reaction mixture that can produce a maximum yield of tin in the smelting process. The possibility of Na_2SO_3 regeneration from SO_2 generated during the smelting process makes the whole process economically advantageous.

2. Results and Discussion

2.1. The Effect of Temperature and the Amount of Sodium Sulfite

The smelting process was examined under varying experimental conditions using fixed amounts of SnO_2 and charcoal. The effect of temperature and varying concentration of Na_2SO_3 on the efficiency of the thermal reduction of SnO_2 was investigated. It is worth noting that under the conditions employed for the experiments, no quantifiable amounts of metallic tin were obtained for the system, with no deliberately added sodium sulfite. The experimental results are presented in Figure 1 (in the 3D and 2D forms) where the percent yield of metallic tin is plotted against the temperature and the amount of Na_2SO_3 added to the thermally treated system. Each set of the results (represented by empty circles, grey squares, dark grey triangles and filled circles) corresponds to the selected temperature and represents a collection of averaged data obtained for melting crucibles made of different materials. The temperatures selected for the examination were set to 950, 1000, 1050 and 1140 °C, while the amount of sulfite ranged from 7.5 to 15.5 g. The experimental results clearly indicate that the best performance of the reduction process is achieved at 1050 °C for samples that comprise approximately 5 g of charcoal and not less than 10 g of Na_2SO_3 (i.e., 1/3 and 2/3 of the mass of tin dioxide in the sample, respectively). The quality of the smelting products was inspected using the elemental mapping mode of scanning electron microscopy. Two extreme sets of reduction conditions were selected for the comparison.

One (Figure 2A) was related to the conditions where the best performance of the process is achieved (i.e., at 1050 °C for the mixture composed of 15.0 g of SnO_2 , 10.1 g of Na_2SO_3 , 5.0 g of charcoal), while the other one (Figure 2B) represented the effect of the reduction under the unfavorable conditions (i.e., at 950 °C for the mixture composed of 15.0 g of SnO_2 , 5.2 g of Na_2SO_3 , and 5.5 g of charcoal). In the latter case, unreacted particles of sodium sulfite were clearly seen while the former case yielded a homogeneous metallic product covered with a very thin film of unreacted components. The differences observed may be due to the insufficient amount of carbon, which accelerates the Na_2SO_3 decomposition. Additionally, at lower temperatures, the reduction process involving sulfur-bearing species is not thermodynamically favorable. At this temperature, carbon is the only component that may reduce tin dioxide to the metallic phase.

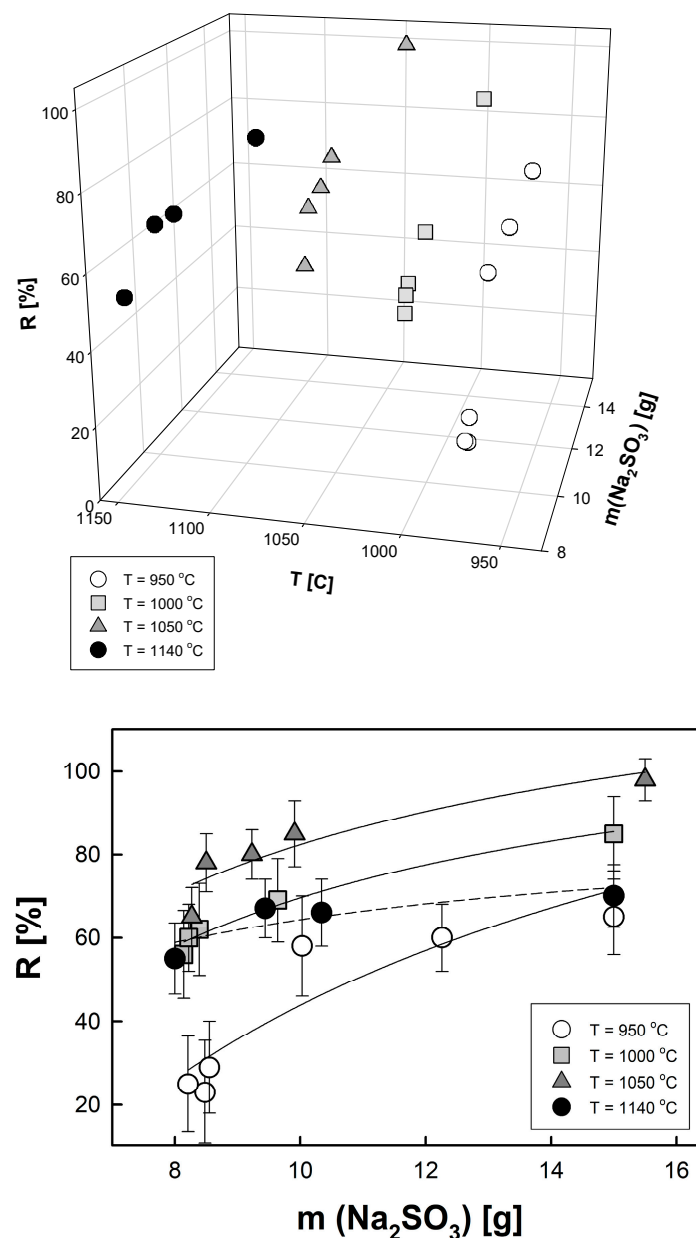


Figure 1. Percent yield of tin versus temperature and mass of sodium sulfite added to the system. Amount of charcoal: ~5 g. Each set of results corresponds to the selected temperature and represents a collection of averaged data obtained for melting crucibles made of different materials. Error bars represent expanded uncertainties of the determined quantities (i.e., their 95% confidence intervals).

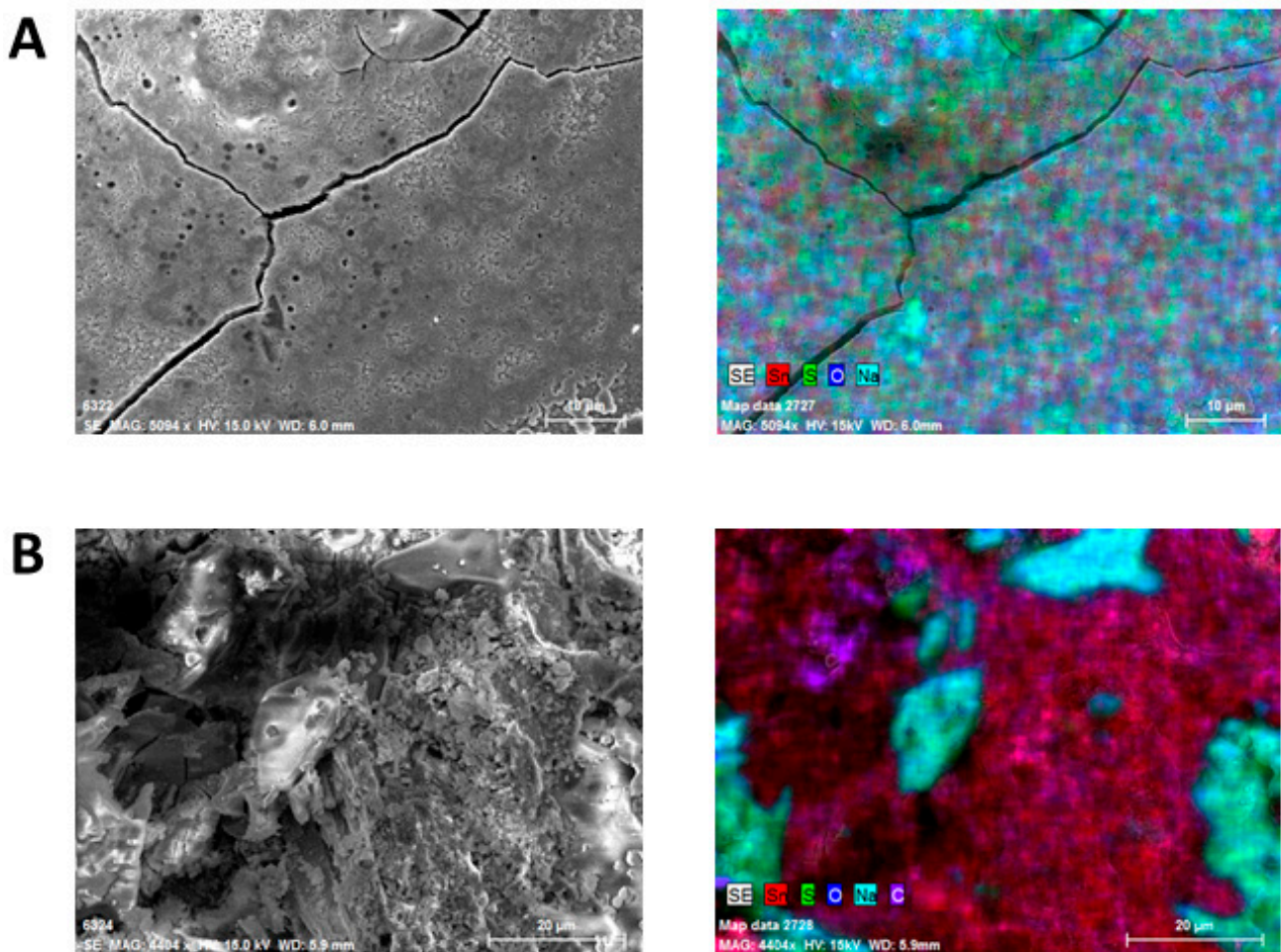


Figure 2. SEM images and elemental mapping of surfaces of tin samples obtained for the systems composed of 15.0 g of SnO_2 , 10.1 g of Na_2SO_3 , 5.0 g of charcoal at 1050 °C (A) and 15.0 g of SnO_2 , 5.2 g of Na_2SO_3 , 5.5 g of charcoal at 950 °C (B).

2.2. Kinetic Studies

To validate the observations, a more detailed kinetic analysis was performed for the process at 1050 °C. The partial orders of the reaction with respect to sodium sulfite and carbon were determined via the unweighted linear regression analysis of the dependencies between logarithms of the normalized average reaction rates and logarithms of normalized molarities of either sodium sulfite or carbon (Figure 3). The average reaction rate is directly proportional to $R/\Delta t$, where Δt is the duration of the smelting process at the given temperature. The numerical results obtained are as follows: 0.81 ± 0.32 for sodium sulfite and -1.05 ± 0.82 for carbon. The numbers after the $\pm$ sign represent expanded uncertainties (with a coverage factor of 2) of the determined kinetic parameters. The negative partial order of the reaction indicates that the concentration of that species inversely controls the overall reaction rate and suggests a complex mechanism of the reduction process. The mechanism may involve a reaction step that proceeds at the phase boundaries limited by the adsorption/desorption rates. It is also possible that one of the final products of the reduction process is involved in another step of the reaction mechanism.

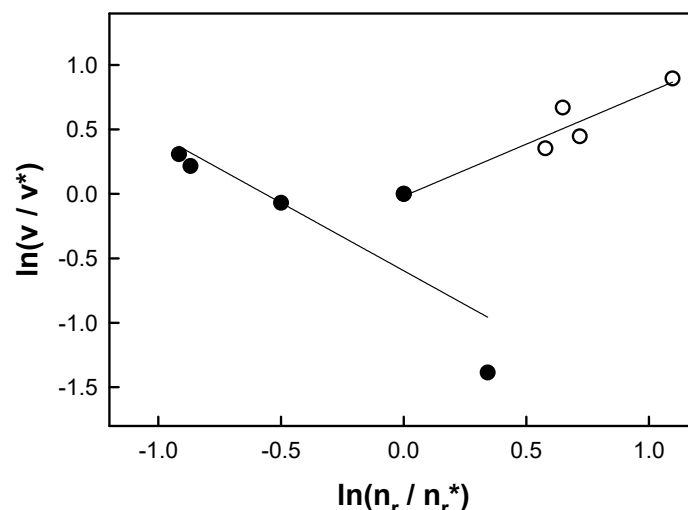
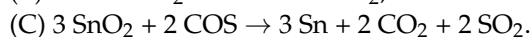
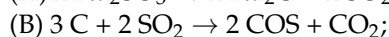
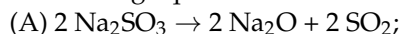


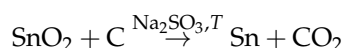
Figure 3. Logarithmic dependencies of normalized reaction rates and normalized numbers of moles of reactants examined: sodium sulfite (empty circles) and charcoal (filled circles). The rates and numbers of moles were related to the selected points that correspond to the following compositions of the system: 15.60 g of SnO₂, 5.00 g of charcoal and 5.18 g of sodium sulfite (empty circles), and 15.06 g of SnO₂, 10.90 g of charcoal and 10.00 g of sodium sulfite (filled circles). Smelting temperature: 1050 °C.

2.3. The Proposed Mechanism of the Smelting Process

All the information obtained from the kinetic studies and the qualitative chemical analysis (Section 3.4) allowed us to establish a possible mechanism for the thermal reduction of SnO₂ with Na₂SO₃. The mechanism can be summarized by three key reactions represented by the following equations:

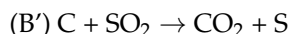


The smelting process can be thus represented by the following reaction scheme:



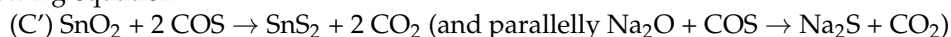
First of all, the molar fractions of the crucial reagents (SnO₂: C: Na₂SO₃ = 1 mole: 1 mole: 2/3 mole, i.e., 150.7 g: 12 g: 84.0 g) confirm roughly the empirically determined mass ratio of the reactants (i.e., 150 g: (0.6 × 50 g): 100 g, where the number 0.6 corresponds to the fraction of carbon in charcoal) that generates the maximum percent yield of tin for temperatures ranging from 950 to 1140 °C. Secondly, it suggests the presence of an intermediate sulfide product—carbonyl sulfide (COS)—in the reaction pathway that may speed up the reduction of tin dioxide. Depending on the temperature and proportions of the reactants used, it may act as a reducing agent (more effectively than carbon) or decompose to produce another effective reducing agent—CO. COS is a product of the carbothermic reduction of SO₂. The latter substance can be easily produced by the thermal decomposition of sodium sulfite, which occurs above 500 °C [16]. This property justifies the application of sodium sulfite and excludes other sulfur-bearing compounds. Additional experiments performed with other sulfur-bearing additives (sodium sulfate, sodium sulfide and even elemental sulfur) supported this conclusion. Replacing sodium sulfite with the above-mentioned alternative additives practically terminated the production of metallic tin (the percent yield of tin was close to 0).

At temperatures above 700 °C, SO₂ undergoes carbothermic reduction to produce carbonyl sulfide. The formation of the latter substance can be catalyzed by some portion of SnO₂ as shown by Han et al. [17]. This stage of the process can be affected to some extent by another reaction path:



However, at the boiling point of sulfur, the reaction B' also leads to the formation of carbonyl sulfide [18]. At higher temperatures (above 650 °C), the rate of COS decomposition increases leading to the formation of CO and elemental sulfur [19].

In step (C), involving COS, SnO₂ is reduced to metallic tin by either COS or CO. At this stage, SnO₂ may also be partially transformed to SnS₂ by COS [17], which will lower, to some extent, the reaction yield. An alternative reaction path can be represented by the following equation:



The proposed mechanism and the experimental conditions employed for the studies were also characterized thermodynamically. The expression for the standard free enthalpy for the reduction process is summarized by the net chemical reaction ($\text{SnO}_2(\text{s}) + \text{C}(\text{s}) + (2/3) \text{Na}_2\text{SO}_3(\text{s}) \rightarrow \text{Sn}(\text{s}) + \text{CO}_2(\text{g}) + (2/3) \text{SO}_2(\text{g}) + (2/3) \text{Na}_2\text{O}(\text{s})$), which is as follows:

$$\Delta G^\circ = 444 - 0.328 T \text{ [kJ]} \quad (1)$$

where T is the smelting temperature.

The expression for ΔG° was derived using the tabulated values of the standard molar enthalpies of formation (in kJ/mol) and standard molar entropies (in J/mol/K) of the reactants of Equation (1), i.e., −577.6 and 49, 0 and 5.7, −1100.8 and 145.9, 0 and 51.2, −393.5 and 213.6, −296.8 and 248.2 and −414.2 and 75.1 for SnO₂(s), C(s), Na₂SO₃(s), Sn(s), CO₂(g), SO₂(g) and Na₂O(s), respectively.

According to Equation (1), at temperatures higher than 1080 °C, the value of ΔG° is negative, and the reaction may proceed in the indicated direction.

2.4. The Effect of the Presence of Lead

The interfering effect of lead or copper is related to the fact that lead and copper (e.g., present in the oxide forms) react preferably with sulfur-bearing fluxes (carbonyl sulfide, elemental sulfur) at higher temperatures, producing lead or copper sulfides. These reactions would consume a significant part of the reducing agent and result in the decrease or even termination of the tin smelting process. The results of experiments performed for SnO₂ and PbO₂ mixed at various mass ratios, presented in Figure 4, led to the conclusion that the use of the method results in an acceptable yield of tin (more than 70%) if the level of lead impurities does not exceed 5%.

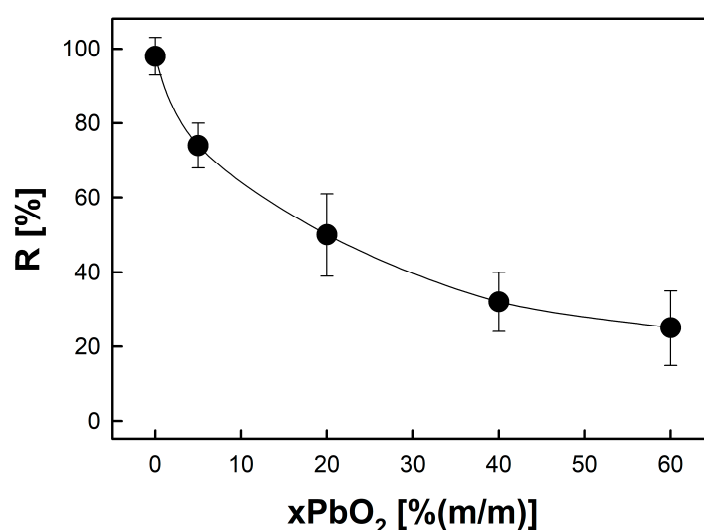


Figure 4. Percent yield of tin versus mass fraction of PbO₂ in the SnO₂/PbO₂ mixture. Masses of mixture of tin/lead oxides, charcoal and sodium sulfite: 15, 5 and 10 g, respectively. Smelting temperature: 1050 °C. Error bars represent expanded uncertainties of the determined quantities (i.e., their 95% confidence intervals).

3. Materials and Methods

3.1. Chemicals

Tin oxide (IV) (98%, SnO_2), charcoal (containing approximately 60% of carbon), sodium sulfate (IV) (99.8%, Na_2SO_3), lead (II) nitrate (V) (99.9%, $\text{Pb}(\text{NO}_3)_2$) and sodium hydroxide (99%, NaOH) were purchased from Keramos (Poland) and Sigma-Aldrich (Poland).

3.2. Instrumentation

The smelting process was conducted in a laboratory electric furnace (Argenta, Poland).

An X-ray Fluorescence Spectrometer (XRF) (model S1 Titan, Bruker, Billerica, MA, USA) was used for the determination of the chemical composition of the solid materials.

An Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (NexION 300D, PerkinElmer, Poland) was used for the validation of the results produced by the XRF method.

The inspection of the surfaces of the smelting products was performed using a scanning electron microscope, model LEO 435VP.

3.3. Smelting Process

In general, the smelting process was examined on batches containing approximately 15 g of tin dioxide, 5 g of charcoal and varying content of sodium sulfite. Kinetic studies were performed for two sets of samples containing approximately 15 g of tin dioxide and either a fixed amount of charcoal (5 g) and varying content of sodium sulfite (ranging from 5.2 to 15.6 g) or a fixed amount of sodium sulfite (10 g) and varying content of charcoal (ranging from 4 to 15.5 g). All reactants were mixed thoroughly in a crucible and ground into fine powder. The electric furnace with a maximum temperature of 1150 °C was preheated to the desired temperature. Then, the content of the crucible was transferred to a melting pot, which was then inserted into the furnace. The smelting process was carried out for 25–30 min with access to air. After completing the reduction reaction for each run, the pot was removed, liquid metal was poured out and the slag was collected. The obtained metallic tin and slag were weighed and analyzed. The smelting process was examined in graphite, stainless steel and fireclay crucibles. Each run was repeated 3–5 times.

3.4. Chemical Analysis

To determine qualitatively the products of the reduction process, the reaction solid residue and gaseous products were chemically tested.

The XRF analysis of the solid residue revealed the presence of tin, sodium and sulfur. This implied the presence of unreacted tin compounds, sodium oxide/carbonate, small amounts of sulfides and elemental sulfur in the residue. The speciation process was performed via qualitative chemical analysis using selective precipitation. The residue was dissolved in ultrapure water and the resulting suspension was filtered. The filtrate pH was significantly greater than 7. The basic character of the solution confirmed the presence of sodium oxide and probably sodium carbonate. The resulting solution was then treated with lead (II) nitrate (V). The formation of black precipitate suggested the presence of sulfide anions. The presence of sulfides in the smelting residue implied the formation of sulfide by-products during the smelting process.

The gaseous products of the smelting process were directed to an aqueous solution of sodium hydroxide and the resulting solution was treated with lead (II) nitrate (V). The formation of a white precipitate suggested the presence of sulfite and carbonate anions—the products of the neutralization of SO_2 and CO_2 by the strong base.

The allotropic form of the metallic product was determined from the examination of its density. The obtained value, 7.1 g/cm³, confirmed that SnO_2 was reduced to crystalline β -Sn.

3.5. Experimental Data Analysis

The obtained metallic tin and the slag were analyzed chemically using a handheld XRF spectrometer (S1 Titan, Bruker) using the tin alloy calibration mode. Based on the XRF measurement results, the grade of tin metal and the composition of the slag were

determined. The efficiency of the smelting process was quantified by the percent yield of tin given by the following formula:

$$R = 100 \times m_{Sn} \times P_{Sn} / (0.788 \times m_{SnO_2} \times P_{SnO_2}) \quad (2)$$

where R is the percent yield of tin metal, m_{Sn} and P_{Sn} are the mass and purity of tin metal produced, respectively, m_{SnO_2} and P_{SnO_2} are the mass and purity of tin dioxide in the charge, respectively, and 0.788 is the fraction of tin in tin dioxide.

4. Conclusions

The thermodynamic characteristics (in the form of the temperature dependence of the standard free enthalpy) of the reduction process validate the optimum smelting temperature determined experimentally. It confirms that SnO_2 in the C/ Na_2SO_3 system can be converted to metallic tin at a temperature greater than 1080 °C. The significant increase in temperature above the equilibrium level leads to a drop in the percent yield of tin, probably due to the more effective release of the gaseous intermediate products from the system.

The smelting process was tested in crucibles made of various materials: graphite, stainless steel and fireclay. Although we have not observed any relation between the efficiency of SnO_2 reduction and the type of the crucible material, it is worth noting that the porous structure of the graphite material was easily penetrated by gaseous products, leading to the intensification of its corrosion.

The data on the experimental conditions and the tin recovery levels extracted from the related works in the literature, along with the details from our work, are summarized in Table 1.

Table 1. The experimental systems employed for the thermal reduction of SnO_2 .

Reducing Agent (Temperature [°C])	Tin Recovery [%]	Reference
C graphite/CO (1000)	100	10
H ₂ (1300)	100	11
CH ₄ (1473)	100	12
C charcoal/ Na_2CO_3 - $NaNO_3$ (1000)	95	13
Ar-balanced CH ₄ (1000)	80	14
C charcoal/ Na_2SO_3 (1050)	98	This work

Among the limitations of the method developed, one may list the concurrent reactions involving possible contaminants of tin dioxide. This is especially vital for tin dioxide obtained from the secondary sources of tin (mainly e-scrap materials) containing lead additives. The method produces an acceptable yield of tin (more than 70%) if the level of lead impurities does not exceed 5%.

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Conflicts of Interest: The authors declare no conflicts of interest.

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