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Vaporization of zinc during thermal treatment of ZnO with tetrabromobisphenol A (TBBPA)

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ABSTRACT

In the present work we investigate the vaporization of zinc or its compounds during thermal treatment of ZnO with tetrabromobisphenol A. Samples of 2 g of ZnO:TBBPA (3.34:1) were isothermally heated in a laboratory-scale furnace at temperatures from 490 °C to 950 °C, and the solid, condensed and gaseous products formed were analyzed by X-ray diffraction analysis, electron probe microanalysis, inductively coupled plasma analysis, ion chromatography, and gas chromatography coupled with mass spectrometry. The results obtained indicate that the vaporization of $ZnBr_2$ formed strongly depends on heating time and temperature, yet is restrained by char, if formed with sufficient yield (above 15 wt%). Starting from 850 °C, this char commences carbothermic reduction of any remaining ZnO, which from then begins to evaporate as zinc metal vapor. Volatilization of zinc is completed at 950 °C.

The presence of 5 vol.% of oxygen has no significant effect on the vaporization of formed $ZnBr_2$, the carbothermic reduction or the volatilization of metallic zinc. Strongly oxidizing conditions (20 vol.% of oxygen), however, boost the oxidation of char and thus the vaporization of $ZnBr_2$, but prevent carbothermic reduction of any un-reacted ZnO by depleting this char.

1. Introduction

Electric arc furnace (EAF) dust, though classified by various government regulatory agencies as hazardous waste due to the presence of leachable zinc, cadmium, chromium and nickel compounds, is considered a valuable secondary raw material in the production of zinc [1–13]. On average it is approximately 20 wt% zinc [2], with a highest reported content of 35 wt% [3]. The worldwide generation of EAF dust represents a possible recovery of approximately 1.4 million tons of zinc [3]. Though numerous zinc recovery processes utilizing pyrometallurgical, hydrometallurgical or hybrid pyro-hydro techniques have been developed for these dusts, most never reached pilot plant stages and many investigations were stopped because of metallurgical and economic inefficiencies [4]. Only pyrometallurgical high temperature zinc oxide recovery processes have achieved commercial success [4], and this is mainly limited to variations of the Waelz rotary kiln process [4] and hearth furnace technology [5]. All recovery processes involve the reduction and volatilization of zinc metal from the dust by the carbothermic reduction method, which leaves an iron rich residue. These processes have low zinc yield, emit greenhouse gases and often generate valueless waste residues that present further disposal problems. Their main disadvantage is high energy consumption, since the Waelz process requires temperatures of 1200–1300 °C [3,12].

Recently, an alternative based on selective chlorination and evaporation of zinc with waste polyvinyl chloride (PVC) as chlorination agent was proposed [6–13]. Laboratory experiments revealed that this method has a promising yield of 96 wt% [12]. Unfortunately, initial study also indicated that the process might lead to an undesired volatilization of about 17 wt% of Fe in the form of $FeCl_3$ [12]. Additionally, in order to obtain high rates of zinc recovery a temperature of about 1000 °C is required to complete its volatilization [12], implying energy consumption only slightly lower than for the Waelz process. Therefore, for both environmental and technological reasons, further investigations on alternative recycling methods for zinc from EAF dusts are required.

In earlier studies we proposed another alternative method for pyrometallurgical recycling of EAF dust using plastic waste containing tetrabromobisphenol A (TBBPA) [14–16]. TBBPA is the most widely produced brominated flame retardant (BFR), used in more than 70% of the world's electronic and electric (E&E) appliances [17] as well as in many plastics, textiles and so forth. TBBPA easily decomposes during thermal processing, which generates large amounts of gaseous HBr [18–22] that acts as a brominating agent for the bromination–evaporation process.

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Potential advantages of the process are described in our previous papers [15,16]. In addition to the benefits discussed there, the lower boiling point of $ZnBr_2$ (650 °C) [23] compared to that of $ZnCl_2$ (732 °C) [23] suggests that the energy consumption could be lower than that of the chlorination–evaporation process. Vaporization of zinc oxide [24] during its treatment with carbon-based reducing agents [25–30], PVC [7,11,12], and another chlorination agents [4,8–10,13,31] is well known and described elsewhere. However, reports on the thermal evolution of zinc bromide are very scarce [32–34].

The mechanism and kinetics of bromination–evaporation was investigated using pure ZnO and TBBPA [16]. However, under dynamic conditions, at a heating rate of 10 °C/min only partial vaporization of formed $ZnBr_2$ was achieved at the boiling point of zinc bromide (650 °C) and the maximum yield did not exceed 45 wt% [15]; this indicated that evaporation of zinc bromide from the solid residue was restrained by an unknown factor.

2. Experimental

2.1. Materials

Tetrabromobisphenol A (97.0%) was supplied by Aldrich Co. and ZnO (99.9%) by Wako Pure Chemical Industries. The average particle diameter of these chemicals was determined by laser diffraction and scattering (Microtrac MT 3300EX) as 2.6 and 63.1 μm for ZnO and TBBPA, respectively. These chemicals were manually mixed at a mass ratio of 3.34:1 (TBBPA:ZnO), and pressed into pellets of 0.5 g each. The ratio was determined from the stoichiometric ratio assuming that all bromine present in TBBPA was released and would react with zinc to form zinc bromide ($ZnBr_2$)

2.2. Furnace experiments

The experimental setup for the pyrolysis experiments is schematically presented in Fig. 1. The sample (approximately 2 g) was placed on an alumina combustion boat (width 12 × depth 9 × length 60 mm) located inside the cooler part (protruding beyond the furnace) of a quartz tube reactor heated by a small furnace. After the temperature of the furnace was stabilized at the desired temperature, the combustion boat with sample was moved inside the furnace, where it was isothermally treated in an Ar (purity = 99.9%) flow of 50 ml/min

The effect of heating time on formation and vaporization of $ZnBr_2$ was studied at 490 °C, 550 °C and 650 °C. At the two first temperatures the samples were heated for 10, 40 and 80 min, while at 650 °C – as vaporization of $ZnBr_2$ was immediate – heating time was limited to 10 min.

The further fate of any remaining zinc was studied by isothermal treatment of the sample at temperatures of 800 °C, 850 °C, 900 °C and 950 °C for 40 min.

After this treatment, the sample shut in the air-tight reactor, was rapidly cooled with compressed air, to prevent any secondary reactions. A quartz wool filter was placed inside the reaction tube, positioned where the temperature of the outgoing gases dropped to about 100 °C, to retain condensable phase evolved from the sample. A trap consisting of distilled water was used for inorganic gaseous products.

Additionally, the effect of oxidizing conditions (Ar + 5 vol.% Oxygen; and Ar + 20 vol.% Oxygen) on the vaporization of zinc was studied at selected temperatures (Table 1).

2.3. Sample characterization

The solid, condensed and gaseous phase products were characterized by an array of analytical methods as shown in Fig. 1. The solid residue was characterized by X-ray diffractometry (Rigaku, Rint 220) using Cu/K-alpha1 radiation (1.54059 A) and electron probe microanalysis (EPMA) (Jeol, JXA-8920).

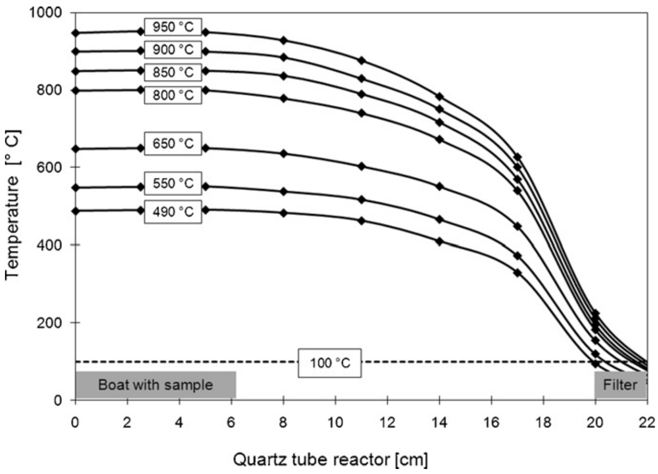

Fig. 1. Schematic presentation of the experimental set-up showing furnace and periphery, as well as an overview of the analytical procedures used (above). Temperature profile inside the quartz tube (below).

The total amount of zinc remaining in the residue was measured by inductively coupled plasma (ICP) using a PerkinElmer Optima 3300 SYS. Extraction with distilled water or 0.05 M HCl allowed to recover $ZnBr_2$ or ZnO, respectively. These solvents were selected based on the recoveries of pure $ZnBr_2$ (recovery 99 wt%) and ZnO (recovery 98 wt%) obtained during individual solubility tests. The recovery of ZnO from raw sample before thermal treatment was evaluated in triplicate, and the efficiency of the analytical method was 98.1 ± 1.0 wt%.

The inorganic compounds condensed on the quartz wool filter and inner walls of the reaction tube were analyzed by a combination of IC and ICP to determine their zinc content. Additionally, the condensed organic products from thermal decomposition of TBBPA were analyzed using GC–MS, i.e. a gas chromatograph (Rigaku, 6890N) coupled with a mass spectrometer (Jeol, JMS-AMSUN200S). The decomposition products in the chromatogram were identified by analysis of fragmentation patterns (MS) compared to the NIST spectral library. After each experiment, the trap of distilled water was analyzed by the IC/ICP technique.

3. Results and discussion

Thermal decomposition of TBBPA and char formation in presence of ZnO, and parameters affecting the efficiency of the ZnO bromination reaction have been comprehensively discussed in earlier reports [15,16]. The new materials discussed in this paper relate to the vaporization of the $ZnBr_2$ and zinc metal formed and to the parameters controlling these vaporization processes.

3.1. Effect of heating time on vaporization of Zn

Vaporization of $ZnBr_2$, formed during thermal treatment of TBBPA with ZnO (3.34:1) at 490 °C and 550 °C strongly depends on heating time (Fig. 2, Tables 1 and 2). At 490 °C during the first 10 min of thermal treatment (Table 2) just 9 wt% of $ZnBr_2$ evaporates; the yield rises significantly, however, i.e. to 34 wt% and 55 wt% after further heating for 40 min and 80 min, respectively (Fig. 2, Table 2). Even then, almost half of the zinc bromide formed still remains in the solid residue (Tables 1 and 2). Taking into account that Zn bromination rate was 53 wt% at these conditions, only 29 wt% of initial amount of zinc present in mixture with

Table 1
Main data obtained from experiments on isothermal treatment of TBBPA:ZnO (3.34:1) at various conditions. The initial weight of sample was 2000 mg, with an initial zinc content of 363 mg.

	Temp °C	Time min	Solid residue mg	Zn ($ZnBr_2$) (SR) mg	Zn (Total) (V) mg	Zn ($ZnBr_2$) (V) mg	Zn (metallic) (V) mg	Zn loss mg	Br (inorg.) (T) mg	Br (inorg.) (SR) mg	Char mg
Argon	490	10	1162	196	20	20	0	22	368	306	621
		40	946	136	69	69	0	31	436	217	496
		80	761	86	105	105	0	47	483	165	370
	550	10	963	144	60	60	0	39	511	290	468
		40	568	34	171	171	0	27	492	51	303
		80	449	5	192	192	0	34	530	2	227
	650	10	433	6	209	208	0	30	619	<1	234
	800	40	424	2	197	197	0	35	675	0	209
	850	40	399	2	200	192	8	52	666	0	188
	900	40	313	2	257	216	41	60	699	0	172
	950	40	249	0	308	241	67	55	732	4	170
5% Oxygen	490	40	903	130	66	66	0	46	477	257	428
	550	40	509	31	165	165	0	46	528	57	233
		80	358	3	176	176	0	50	463	4	115
	650	10	419	3	185	185	0	47	503	1	189
	800	40	389	1	196	196	0	32	720	0	172
	950	40	204	0	300	240	60	63	714	0	116
20% Oxygen	490	40	563	76	114	114	0	47	480	144	191
		80	201	2	166	166	0	63	444	6	30
	550	40	262	3	181	181	0	58	487	6	101
		80	158	0	205	205	0	34	522	0	0

(SR) – solid residue; (V) – vaporized; (T) – total.

TBBPA was successfully separated (Table 2). The reason of such limited vaporization of $ZnBr_2$ is most certainly low vapor pressure of this compound at this temperature (Table 2). Since evaporation rises with heating time some additional kinetic factors still affect volatilization.

The same time-dependent factor probably controls the process at 550 °C. At this temperature, the yield of vaporization increases from 29 wt% to 84 wt% and even 98 wt% after 10, 40 and 80 min of heating, respectively (Table 2, Fig. 2). These rates are much higher than those obtained at 490 °C. It is worth reminding here that the vaporization of $ZnBr_2$ studied in dynamic conditions with constant heating rate of 10 °C/min achieved only 6 wt% ± 1, at 550 °C [15].

This effect of time on $ZnBr_2$ vaporization is reduced at 650 °C: at this temperature vapor pressure causes intensive vaporization (yield of 97 wt%) within the first 10 min of heating (Table 2, Fig. 2). Time may still affect the yield within even shorter heating times, as the vaporization measured under dynamic conditions was significantly lower, not exceeding 45 wt% ± 1 [15]. However, precise investigations are not possible with this experimental setup, since after moving inside the furnace the sample requires about 10 min of heating to attain the desired temperature.

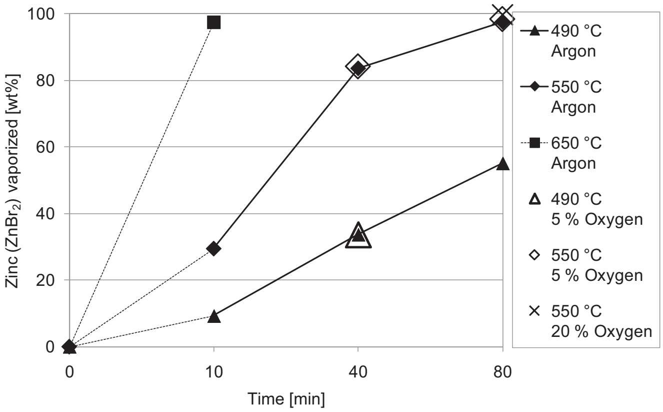

Fig. 2. Effect of time on vaporization of zinc bromide during the isothermal treatment of TBBPA:ZnO (3.34:1) at selected temperatures.

At the isothermal conditions used in these new tests the time-dependent vaporization of $ZnBr_2$ seems to results from restraining effects exerted by cross-linked high molecular weight compounds ('char') formed during thermal decomposition of TBBPA. As previously reported [16] ZnO boosts the formation of this complex residue, which delays vaporization of phenol and its derivatives, including bromophenols and dibromophenols from the solid residue. Some dibromophenols could be identified in solid residue collected after 10 min of thermal treatment of TBBPA with ZnO at 490 °C (not shown here). The vaporization of $ZnBr_2$ is highly anti-correlated with the yield of the formed char (correlation coefficient = −1.0) (Table 2), calculated from the weight differences of the sample before and after thermal treatment (excluding the inorganic phase present in the sample) (Table 1). For example, at 490 °C the amount of $ZnBr_2$ vaporized (from 9 wt% to 55 wt%) rose with declining amounts of char (from 30 wt% to 19 wt%) and with extended time of heating (from 10 to 80 min) (Table 2).

A similar relation was observed at 550 °C (Table 2). At this temperature, a further decomposition of char (amount declining from 21 to 15 wt%) resulted in much higher yields of $ZnBr_2$ vapor (rising from 29 wt% to 98 wt%). At its boiling point of 650 °C [35] vaporization of bromide (Table 2) is fast (<10 min) and attains a high-yield (97 wt%). Thus, char inhibits vaporization of $ZnBr_2$ from solid residue and rising levels of char oxidation are directly responsible for time-control in $ZnBr_2$ vaporization. The limiting effect of char on $ZnBr_2$ vaporization decreased as its degradation increased, and it became marginal once the char content was reduced to 15 wt% or less. This suggests the limiting effect should be considered as char bounding, which involves physical confinement of isolated particles of formed $ZnBr_2$ in small closed pores of the residue.

3.2. *Effect of temperature on vaporization of Zn*

Volatilization of Zn was studied by isothermal treatment of the sample from 490 °C to 950 °C for 40 min (Tables 1 and 2, Fig. 3). As expected, the results show strong effects of temperature on the volatilization of Zn: the yield of $ZnBr_2$ rises together with vapor pressure, whereas the restrictive effect of char decreases with its oxidation. Further heating of the sample to 800, 850,

Table 2
Bromination and vaporization of zinc during isothermal treatment of TBBPA and ZnO at various conditions, expressed as percentages of the original amount provided.

	Temp.	Time	Released Br/Br bounded to Zn for Br released	Brominated Zn for total Zn	Vapor pressure[a] of $ZnBr_2$	Vaporized Zn ($ZnBr_2$) for brominated Zn/total Zn	Vaporized Zn (metallic) for remaining/total Zn	Vaporized Zn (total) for total Zn	Zn loss	Char
	°C	min	wt%	wt%	Pa	wt%		wt%	wt%	wt%
Argon	490	10	41/100	59	3422	9/5	0/0	5	6	30
		40	48/100	57		34/19	0/0	19	9	25
		80	53/100	53		55/29	0/0	29	13	19
	550	10	56/100	56	12,944	29/17	0/0	17	11	21
		40	54/100	56		84/47	0/0	47	7	18
		80	59/95	54		98/53	0/0	53	9	15
	650	10	53/100	59	75,517	97/57	0/0	57	8	15
	800	40	75/80	55	507,208	99/54	0/0	54	10	14
	850	40	74/79	53	830,506	99/53	4/2	55	14	12
	900	40	77/83	60	1,287,451	99/59	27/11	71	16	11
	950	40	81/86	67	1,903,222	100/66	53/18	85	15	11
5% Oxygen	490	40	53/100	54	3422	34/18	0/0	18	13	19
	550	40	58/96	54	12,944	84/45	0/0	45	13	13
		80	51/98	49		98/8	0/0	48	14	7
	650	10	56/96	52	75,517	99/51	0/0	51	13	12
	800	40	80/74	54	507,208	99/54	0/0	54	9	11
	950	40	79/87	66	1,903,222	100/66	50/17	83	17	8
20% Oxygen	490	40	53/99	52	3422	60/31	0/0	31	13	8
		80	49/97	46		99/46	0/0	46	17	2
	550	40	54/97	51	12,944	98/50	0/0	50	16	6
		80	58/98	56		100/56	0/0	56	9	0

[a] The vapor pressures of $ZnBr_2$ were calculated according to equation given in Ref. [39].

and 900 °C raises the yield of vaporization of $ZnBr_2$ to 99 wt% (Tables 1 and 2, Fig. 3). At these temperatures, char is limited to less than 11 wt% (Table 2). Complete vaporization of $ZnBr_2$ was achieved at 950 °C (Figs. 3 and 4, Tables 1 and 2). At this temperature, neither EPMA (Fig. 4) nor X-ray shows any remaining zinc in solid residue (Fig. 5).

The data obtained can be roughly compared to those on the volatilization of zinc chloride as reported by other authors. Lee and Song [12] measured vaporization of $ZnCl_2$ during 1 hour of thermal treatment of EAF dust (with 27.4 wt% of ZnO) with PVC (2.33:1) in a laboratory furnace and yields of 7, 12, 30, 57, 76 and 98 wt% at 500, 600, 700, 800, 900, and 1000 °C, respectively [12]. Zhang et al. [7] reported vaporization yield of formed $ZnCl_2$ of 74 wt% ± 16 and 84 wt% ± 12 of its the initial amount, during TG–MS investigations on volatilization of ZnO during heating with PVC (at weight ratio of 1:2 and 1:3.33).

X-ray diffraction patterns and EPMA of solid residue obtained at 950 °C (Figs. 4 and 5) reveal of absence of any zinc, even un-reacted ZnO that about one-third of its initial amount should remain in the residue (Table 2). To explain this deficiency one must investigate the behavior of zinc from 850 °C upwards. From this point, the total amount of zinc vaporized from solid residue becomes higher than that evaporated in form of bromide. The “excess” zinc is insoluble in water and well soluble in weak hydrochloric acid. Taking into account, that the ZnO remaining in solid residue is very stable at this temperature range [35] and that its diffusion is not expected at these conditions, its carbothermic reduction by carbonaceous char followed by its vaporization in metallic form must be considered. This is basically as in the Waelz process.

Since neither X-ray diffraction nor electron probe microanalysis indicate the presence of metallic zinc in solid residues, prompt evolution of zinc takes place soon after its formation; it is controlled by the yield of carbothermic reduction, and both processes depend on temperature (Table 2, Fig. 3). At 850 °C about 4 wt% of the ZnO still remaining in solid residue undergoes carbothermic reduction and evaporates. An increase in temperature by 50 °C intensifies these processes, resulting in vaporization of 27 wt% of residual Zn. At 950 °C, at least 53 wt% of remaining zinc oxide undergoes carbothermic reduction and then leaves the solid residue as vapors of elementary zinc. In fact, this number may be even higher, but unavoidable analytical losses (Table 2) do not allow more precise determination. Nevertheless, at 950 °C, all zinc present in the initial sample, vaporized in bromide (at least 66 wt% of the original amount) and at least 18 wt% elementary zinc forms (Table 2, Figs. 3–5).

Mechanism of the carbothemic reduction of ZnO is well recognized [25–30]. There are many reactions involved in the reduction of ZnO, however, the main reactions can be expressed as:

$$ZnO(s) + C(s)(char) = Zn(g) + CO(g) \quad (1)$$

$$ZnO(s) + CO(g) = Zn(g) + CO_2(g) \quad (2)$$

$$CO_2(g) + C(s) = 2CO(g) \quad (3)$$

The effectiveness of carbothermic reduction is reported to depend on many parameters: the molar ration of C/ZnO, the density of the sample, the particle size of carbon and zinc oxide, temperature and time of reaction, rate of gas flow [25], and presence of different additives [29,30]. After 40 min of thermal treatment at 900 °C it may vary from a few percent [29] through around 30 wt% [25] to almost 40 wt% [30]. Thus, by comparing reported values to these obtained in this study, we may conclude that char seems to be a quite effective reducing agent for ZnO, at least at the conditions applied here. This reveals the ability of TBBPA of being an effective reducing agent at temperatures above 850 °C, additional to brominate ZnO at lower temperature. Similar behavior was also reported for PVC [36].

3.3. *Effect of oxidizing conditions on vaporization of Zn*

The effect of oxidizing conditions on zinc vaporization was investigated at different oxygen concentrations, i.e. 5 vol.% of oxygen (typical value inside an industrial rotary kiln, used for WEEE treatment), and 20 vol.% of oxygen (quasi-atmospheric level).

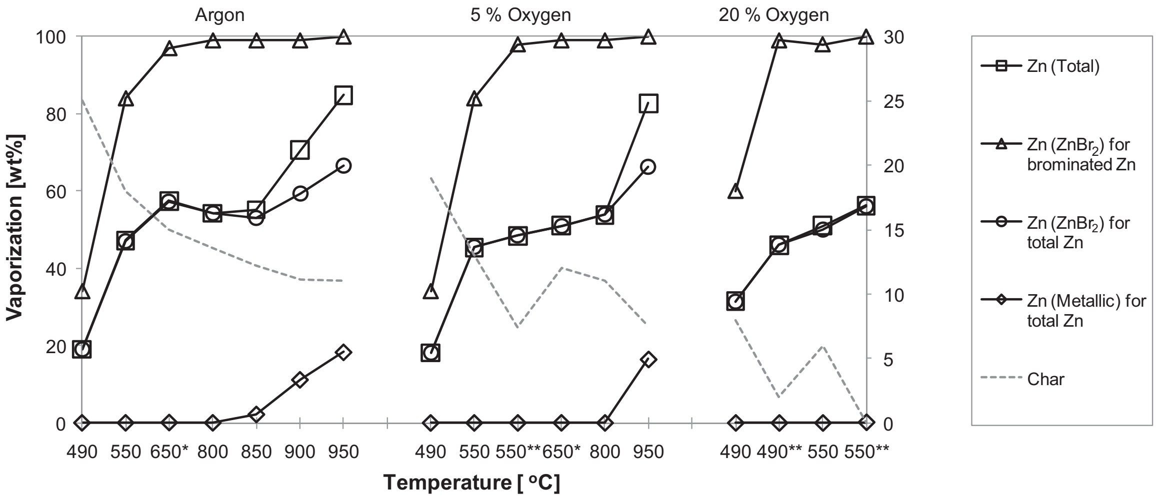

Fig. 3. Effect of temperature on vaporization of zinc under inert and oxidizing conditions during thermal treatment of TBBPA:ZnO (3.34:1) for 40 min. The temperatures marked by asterisks indicate different times of thermal treatment: single asterisk – 10 min; double asterisks – 80 min.

The presence of 5 vol.% of oxygen had no significant effect on the vaporization of $ZnBr_2$ (Table 2, Fig. 3). This observation agreed with some previous reports indicating no relevant differences in either the measured yield of zinc bromination [16] and chlorination [10] or in the thermal stability and decomposition of flame retardant [21,37,38] under slightly oxidizing conditions. The absence of any effect on $ZnBr_2$ vaporization is, however, a bit surprising in this study, because the presence of 5 vol.% oxygen fosters degradation of char by 3–8 wt% (Table 2), whereas char oxidation showed close consistency with zinc vaporization yield at inert atmosphere (see Section 3.1 for details). Moreover, these conditions seem not to prevent the carbothermic reduction of ZnO, even though they slightly weaken the intensity of the process (Table 2, Fig. 3) as manifested by trace amounts of ZnO remaining in solid residue (Table 2).

The presence of an oxygen volume fraction of 20% (Fig. 3, Table 2) on the contrary provided further confirmation of the limiting effects of char on $ZnBr_2$ vaporization. For example, when only a small amount (8 wt%) of char remained after thermal treatment at 490 °C for 40 min under strong oxidizing conditions, there was high vaporization of $ZnBr_2$ (60 wt%). In contrast, in an inert atmosphere in the presence of abundant char (25 wt%), vaporization was approximately halved to 34 wt% (Table 2, Fig. 3). Successive processing of the sample for another 40 min under strongly oxidizing conditions resulted in further oxidation of up to 2 wt% of the remaining char, and was accompanied by 99 wt% vaporization of the formed $ZnBr_2$ (Table 2, Fig. 3). These conditions resulted in even greater enhancement at 550 °C, and the char completely disappeared after 80 min of thermal treatment (Table 2, Fig. 6), resulting in 100 wt% vaporization of $ZnBr_2$ (Table 2, Fig. 3). To obtain the same vaporization efficiency in inert conditions required a temperature of almost 400 °C higher (Table 2, Fig. 3).

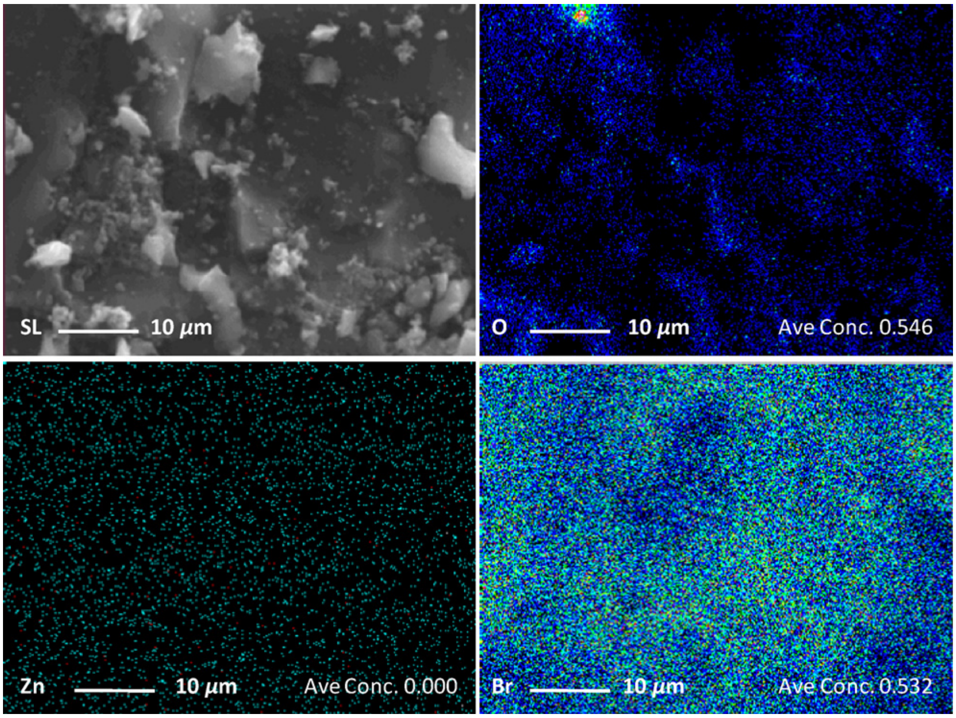

Fig. 4. Electron probe microanalysis of solid residue obtained after the 40 min thermal treatment of TBBPA:ZnO (3.34:1) at 950 °C in Argon atmosphere.

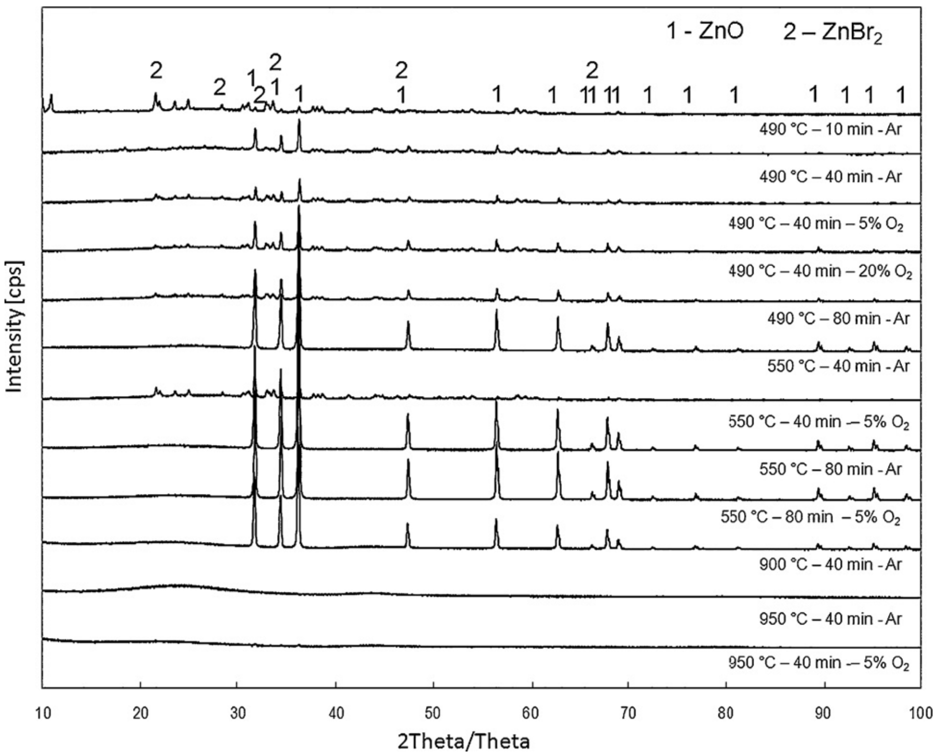

Fig. 5. XRD patterns of the residues from isothermal treatment of TBBPA:ZnO (3.34:1) at various conditions. The lowermost pattern (950 °C–40 min–5% Oxygen) indicates presence of trace amounts of ZnO in solid residue, but the peaks are not visible at scale of this figure.

The oxidizing conditions had minimal impact on the efficiency of ZnO bromination. The bromination rates appeared to decrease by 5–7 wt% in oxidizing conditions when compared to those obtained in an inert atmosphere (Table 2, Fig. 3). However, this overlapped with losses in the mass balance of zinc, which were 4–9 wt% more in oxidizing than in inert treatment (Table 2). Comparison of the results of two experimental runs with identical losses of zinc after 80 min of heating at 550 °C unequivocally indicated that the oxidizing conditions had no impact on efficiency of zinc bromination (Table 2). This may result from the fact that bromination of diffused particles of ZnO occurs in dense molten TBBPA, which may restrict contact between the reaction zone and

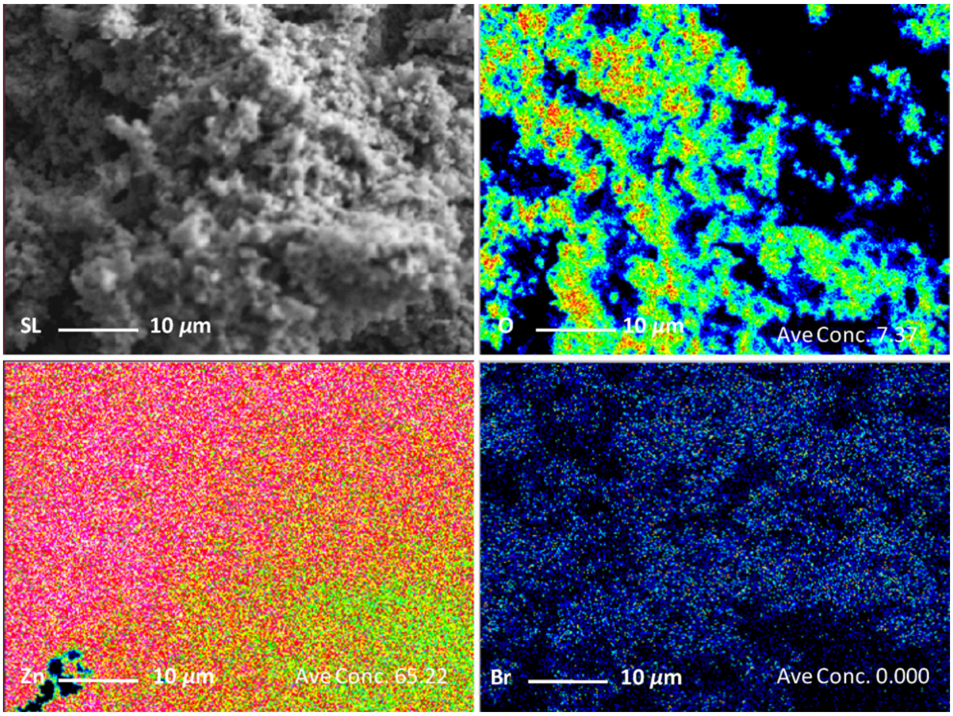

Fig. 6. Electron probe microanalysis of solid residue obtained after the 80 min thermal treatment of TBBPA:ZnO (3.34:1) at 550 °C in oxidizing atmosphere (Argon + 20% Oxygen).

outer oxidizing atmosphere. For the same reason, formation of oxide-bromide complex compounds (ZnOBr) was not observed in this study or a previous one on the bromination reaction [16].

The coupling of bromination of ZnO, degradation of char, and vaporization of $ZnBr_2$ observed in this study for pure chemicals may be important for practical applications. However, first the mechanism needs to be confirmed with real EAFD samples rather than pure chemicals. Earlier results have indicated that the bromination rate is strongly dependent on the amount of HBr available near particles of ZnO, and altering the proportions of the components in the initial mixture may modify the rate [15]. In summary, all these results suggest that complete bromination-vaporization of zinc is feasible at temperatures much lower than those currently applied in pyrometallurgical recovery of zinc [4,12]. However, this requires confirmation in further experiments with real samples.

4. Conclusions

Isothermal treatment of TBBPA with ZnO at selected temperatures indicates that the effectiveness of vaporization of formed $ZnBr_2$ is strongly dependent on heating time. This dependency seems to be directly related to the containment effect of the formed char, which decreases with an increase in char degradation and is almost negligible when its concentration drops to 15 wt% and lower. Thus, almost complete (97–98 wt%) diffusion of $ZnBr_2$ requires 80 min of heating at 550 °C or just 10 min at 650 °C.

With effect from 850 °C, the char serves as source of carbon for carbothermic reduction of remaining un-reacted ZnO, which evaporates from solid residue in metallic form. Complete evaporation of both forms can be obtained at 950 °C.

The presence of 5 vol.% of oxygen had no significant effect on vaporization of formed $ZnBr_2$. The strong oxidizing conditions (20 vol.% of oxygen), however, boost its vaporization together with amplifying influence on char degradation.

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