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Original Article

Separation behavior of arsenic and lead from antimony during vacuum distillation and zone refining

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ABSTRACT

When classifying impurities in commercial pure antimony (Sb, 99.8%), arsenic (As) and lead (Pb) should be brought to the forefront consideration. Due to the known difficulty of As removal through zone refining, it is meaningful to investigate its separation tendency through alternative methodologies such as vacuum distillation, promoted by the large difference of their vapor pressures. Here, a series of vacuum distillation trials with different process parameters were at first conducted with the aim of As removal. Pb, as an always accompanying impurity, seemed to be able to be significantly separated from Sb, so that its content in the refined phase could be reduced too, e.g. from 1200 ppm to less than 30 ppm. The reduction of As, however, is highly dependent on the distillation ratio of Sb and hence limited just to 450 ppm. The biggest obstacle here was the simultaneous evaporation of Sb and As when using high temperature and low pressure. In order to suppress the evaporation of As more intensely in vacuum distillation or selectively capture As in zone refining process, the additives – aluminum (Al) and zinc (Zn) – were studied and selected by using the respective phase diagrams as well as thermochemical Software FactSage and then individually added to Sb as alloying elements with the aim of intermetallic formation with As. The addition of Al led to a considerable reduction of As in vacuum distillation as well as while zone refining process. During vacuum distillation, 67% less As was obtained in the condensate in comparison to the trial without additive. Meanwhile, a huge As concentration gradient appeared in the residual Sb. During zone refining process, As concentration in the whole bar was considerably reduced from 456 ppm to below 150 ppm after only one zone pass, due to the enrichment of Al at the end of the bar in accompanying with As in form of an intermetallic compound. The addition of Zn, on the contrary, did not convince as an effective improvement in purification of Sb. In order to achieve a higher efficiency of As removal from Sb, the authors at the first priority suggest an addition of Al directly into the zone refining process. If specifically a vacuum distillation process is preferred, a multi-stage

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condenser, equipped with controlled temperatures, attendant with the addition of Al in the charge material, can deliver effective results as well.

1. Introduction

Ultra-high purity antimony (Sb, 99.999%) has a wide range of applications especially in semiconductors, either as tuning element or as main component in specific compounds such as InSb, GaSb and SbTe. Parallel to the increasing growth of semiconductor industries, the development of winning as well as the refining methodologies of Sb targeting on resource- and cost efficient routes is getting stronger attention. Principally, Sb is produced from stibnite ores (Sb_2S_3) through both pyro- as well as hydrometallurgical pathways [1]. The pyrometallurgical routes consist of roasting, oxide volatilization and then carbothermic reduction of Sb_2O_3 or – in the case of Sb-rich ores – directly metallothermic reduction of Sb_2S_3 to Sb using iron [1,2]. Hydrometallurgical routes are either based on an alkaline sulfide leaching followed by electrodeposition, or an acidic chloride leaching followed by hydrolysis. Independent from the winning methodologies, As and Pb stay the two main impurities in crude Sb, because As is fully miscible with Sb and Pb has a strong affinity for Sb. For example, crude 90% Sb produced through pyrometallurgical routes includes 0.2–0.3% As as well as 0.1–5 % Pb; while 98.5% pure Sb from hydrometallurgical methods contains 0.02–1% As [1]. Even at the purity level of 99.8%, Sb still contains significant concentrations of As (ca. 0.08 %) and Pb (ca. 0.12%). According to the state of the art, selective crystallization via zone refining is reported to be an effective technique to produce high purity metals by keeping the impurities in the liquid phase and separate them after final solidification by cutting the oversaturated area [3]. This technique can be conducted for any metal, in which the impurity solubility in liquid and solid is considerably different or better to say, the distribution coefficients (k) of the impurities are far from unity. However, As is severely difficult to be removed via zone refining, as its effective distribution coefficient is close to the unity (0.8 ± 0.1) [4]. Therefore and with the aim of achieving high- and ultra-high pure Sb, As has to be foremost reduced to an acceptable low level of content before applying zone refining. The commonly used methods for this purpose are distillation of $SbCl_3$ (dissolved in 6 M HCl) or direct vacuum distillation of Sb based on the big vapor difference between $SbCl_3$ and other chlorides or between Sb and other impurity elements [5]. Vacuum distillation has prominent advantages such as short workflow, low pollution risk and reasonable energy consumption, which can be applied not only in the production of high purity Sb but also recently in the manufacturing of porous antimony anode for Potassium-ion batteries (KIBs) [6]. During the production of high purity Sb, the presence of chlorines involves a complex environmentally-unfriendly process and high corrosivity to the equipment. Therefore, the removal of As (and Pb) through direct vacuum distillation of Sb would be a better preceding supportive to zone refining. However, a challenge remains, which is the separation of Sb and As, due to the their quite simultaneous evaporation characteristics [5]. It has been reported that they could be separated by using multi-level condensation setups, controlled by design and temperature [7] or by adding additives (e.g. Al) to suppress the evaporation of As through formation of non-volatile intermetallic compounds [8,9]. The usage of multi-level condensation setup involves a complex setup as well as complicated temperature control; it is hence not the focus in this work. The addition of metallic elements is a promising way due to its easy application and low cost. But zone refining is still required as the subsequent purification step, leading to at least two steps in view of the entire Sb purification process. For this reason, the investigations of this work focused on adding metallic additives directly into the charge of the zone refining process to improve As refining efficiency, hereby combining two steps into one. In this way, the As is expected to be removed along with formed solid intermetallic.

Due to the fact that the vacuum separation behavior of As and Pb at the level of common concentrations in commercial pure Sb is still not clear, this work firstly serves as a fundamental investigation in this area. Then, a detailed investigation on As removal with adding metallic additives during vacuum distillation will be conducted, as specific information are rarely available. The influence of metallic additives on the removal of As during zone refining process will be ascertained at the end. In both processes, the used metallic additives should have firstly a high affinity to form high temperature intermetallic compounds with As rather than with Sb, as well as they should be able to be removed easily via fractional crystallization or segregated by gravity. Based on these selection criteria, in this paper Al and Zn were selected as additive elements.

2. Fundamental predictions and experimental procedure

2.1. Fundamentals

In order to predict the separation potential of different elements in an alloy during vacuum distillation, an index, so called separation coefficient (β) [10], which is a theoretical derivation of a non-ideal mixed i–j binary system, is to be considered. The β index is expressed as:

$$\beta_i = \gamma_i/\gamma_j * P_i^*/P_j^* \quad (1)$$

where, γ_i and γ_j are the activity coefficients of components i and j and P_i^* and P_j^* are the vapor pressure of these components respectively. A β_i bigger than unity means that the element i will be separated from the element j into the gaseous phase, while that would be vice-versa in the case of a β_i smaller than

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Table 1 – Vapor pressure of metallic elements [11] and separation coefficients of As and Pb in dilute Sb-As and Sb-Pb alloys.

Metal i	A	B	C	D	T/K
Sb	−6500	–	–	8.495	904–1860
Pb	−10130	−0.985	–	13.280	600–2013
As	−6160	–	–	11.945	873–1773

T (K)	P_{Sb}^* (Pa)	P_{Pb}^* (Pa)	P_{As}^* (Pa)	β (As) in Sb-As alloy	β (Pb) in Sb-Pb alloy
905	20.54	0.15	1.38×10^5	6718.60	0.01
950	44.97	0.49	2.89×10^5	6426.51	0.01
1000	98.85	1.58	6.10×10^5	6170.97	0.02
1050	201.62	4.58	11.9×10^5	5902.19	0.02
1100	385.40	12.02	22.13×10^5	5742.09	0.03
1150	696.35	28.94	38.77×10^5	5567.60	0.04

Table 2 – Gibbs energy of form of Al-Sb, Al-As, Zn-Sb and Zn-As intermetallic compounds (calculated by Factsage).

Intermetallic	ΔG (kJ/mol) at 1100 K	Melting/sublimation point (K)
AlSb	−25.2	1333
AlAs	−125.6	2013
SbZn	−15.2	822
Sb_3Zn_4	−29.7	834
Sb_2Zn_3	−21.7	837
As_2Zn	−89.0	1256
As_2Zn_3	−147.2	1378

one. In both cases, it results in segregation. However, when β_i is equal to one, no segregation between i and j takes place.

Vapor pressure of a metallic element is a function of temperature, Eq. (2), including some constant factors, as shown in Table 1. Based on the corresponding vapor pressure of each metallic element, the separation coefficients (β) of As as well as of Pb in Sb-base alloys at different temperatures can be calculated, whose results are also presented in Table 1. Here the activity coefficients for each component are assumed as unity because commercial pure Sb (~99.8%) can be regarded as an infinite dilute solution with Pb and As as the solutes. It shows that both As and Pb have significant tendencies to be separated from Sb but also different behavior due to the different levels of β, as discussed above. However, these β-indices are always far from unity, denoting that the temperature doesn't seem to be a critical parameter to increase the efficiency, but maybe in the kinetics aspects it is controlled e.g. by optimization of distillation setup or pressure.

$$\log P^* (Pa) = A/T + B \log T + CT + D \quad (2)$$

For purpose of verifying the selection of added elements Al and Zn, their individual binary phase diagrams with the impurity As as well as with the base metal Sb were initially studied, as presented in Fig. 1. The free Gibbs energies of Al-As- as well as Zn-As-intermetallics are much more negative than that of Sb (see Table 2), which indicates the higher possibility of formation of these compounds with As rather than with Sb. At the same time, the melting points of those intermetallic compounds are much higher than that of Sb. That implies that those As-compounds prefer to stay as residue in vacuum distillation process, leading to the separation of As from Sb. In addition, due to the extremely low distribution coefficient (k) of these two elements (k_{Al} = 0.06, k_{Zn} = 0.015 [4]), the subsequent removal of their unreacted residues in Sb-melt via fractional crystallization (e.g. by processing in a zone refining device) is quite easy. These characteristics of Al and Zn make them be appropriate selections to remove As by coming into the form of an intermetallic.

2.2. *Vacuum distillation process*

For experimental validation, an induction furnace with a maximum power of 40 kW and a frequency of 4 kHz was employed. In this furnace, a distillation setup, consisting of a pure graphite crucible (Φ = 12 cm, H = 12 cm), a pure graphite lid for the crucible (equipped with a baffle and an aperture) as well as a steel condenser with a collecting "bowl" at the bottom were installed as seen in Fig. 2. The temperatures of the molten charge and that of the vapor stream were measured continuously and online logged by type K thermocouples, using MCPS data processing software. The bowl-shaped collector at the bottom of the condenser is integrated to collect condensed metal, which may fall down from the upper cooling cover.

Commercial pure Sb (~99.8%, see chemical composition in Table 3) was applied for the experiments in this work. It can be seen that Pb and As are the main impurities with the amount of 1200 and 780 ppm respectively. For each experiment, 2.5 kg of Sb charge material was deployed. Pretests, which will not be addressed in this paper, showed that at temperatures lower than 1050 K the evaporated Sb blocked up the aperture and hindered any further distillation. It was most probably due to the cold area at the upper side of the crucible while using low distillation temperatures. This led to a sudden and undesired condensation of the vapor around the baffle and inside the aperture, blocking the pathway of vapor to the condenser. The lowest temperature to ensure a successful distillation in this special setup was identified to be 1050 K. The experimental plan was set with temperatures, all above 1050 K, as well as a variety of vacuum levels, whose details are represented in Table 4, as well as added values of alloying elements.

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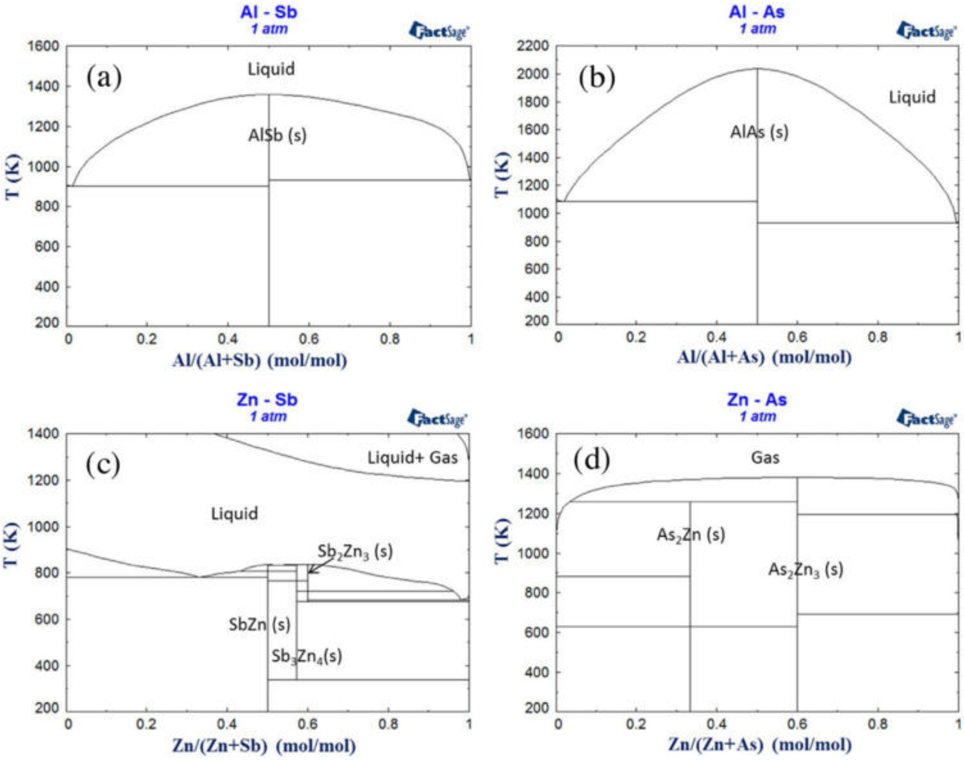

Fig. 1 – Binary phase diagrams of Al-Sb (a), Al-As (b), Zn-Sb (c) and Zn-As (d).

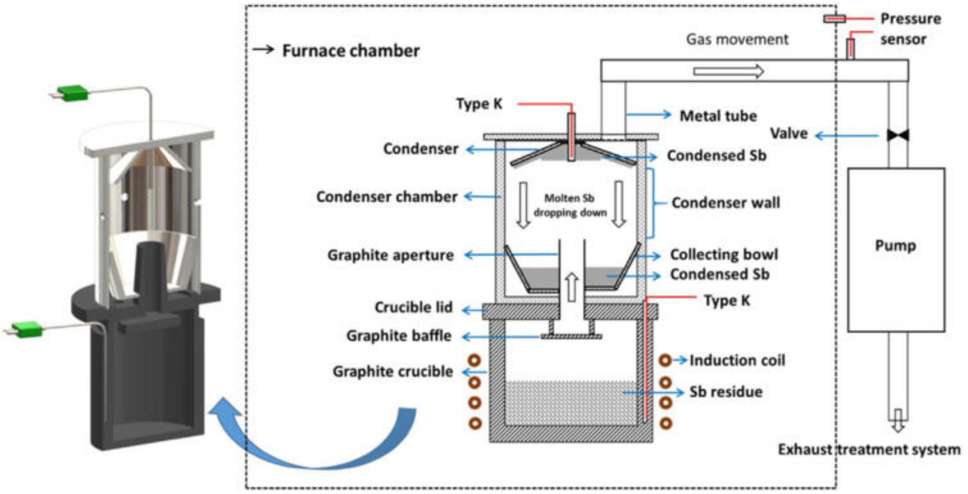

Fig. 2 – Distillation setup, illustrating all segments of melting, evaporation as well as condensation.

Table 3 – Main composition in commercial pure Sb.

Pb (ppm)	As (ppm)	Fe (ppm)	Cu (ppm)	Na (ppm)	S (ppm)
1200	780	80	32	21	16

Although the minimum content of Al and Zn, added to fully react with As to form the intermetallic compounds of Table 2, is – based on the stoichiometry – around 0,078% for each, in order to assure an accomplished formation of such intermetallic, a-bigger-than-stoichiometric amount of the additives is normally required. Especially for the case of Al, whose solubility is lower than Zn, it was decided to take even a more excess. In both cases in order to guarantee the homogeneity of the additional elements, these elements were added in the form of master alloys, containing higher values of each additive, by melting Sb and Al as well as Sb and Zn in a graphite crucible at 800 °C under Ar-atmosphere with an overpressure of 2 bar in an inductive furnace followed by casting them into a water-cooled copper mold.

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Table 4 – Experimental parameters of the conducted trials.

No. of trials	Additive	Temperature (K)	Residual pressure (Pa)	Time (min)
1	–	1050	200	15
2	–	1050	200	30
3	–	1050	50	30
4	–	1050	50	60
5	–	1100	40	60
6	–	1100	35	40
7	–	1100	20	30
8	–	1100	20	60
9	Al (1 wt. %)	1100	20	60
10	Zn (0.2 wt. %)	1100	20	60

2.3. *Zone refining process*

A horizontal zone refining equipment, working with one single induction heater was used in this work. A smaller quartz tube with two inert gas-outlets was inserted, as seen in Fig. 3, to control a Nitrogen flow. A high purity quartz boat crucible (L 60 cm × W 5 cm × H 2.5 cm) was used in the case of addition of Al, while a high purity graphite boat crucible with the same size was used for the addition of Zn, as quartz crucible would be easily damaged in the presence of Zn. The boat crucible was placed in the inner tube, with a small tiling angle (to avoid mass transfer during zone refining [12]).

The experimental parameters, applying in these series of trials, are represented in Table 5. The charge materials, i.e. Sb - 0.1 wt.% Al and Sb - 0.1 wt.% Zn alloys (preliminary produced with usage of the above mentioned master alloys in the inductive furnace), were put each in the form of block in the boat crucibles, and then the blocks were melted with a fast movement of the heater (avoiding crystallization along the crucible) to prepare the Sb bars for the followed zone refining process. Each bar was refined for two zone passes at a heater movement velocity of 1 mm/min. In addition, one experiment without any additives was conducted as a "reference" experiment. The entire operational process is illustrated in Fig. 4. All materials before and after zone refining were analyzed chemically by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). The samples before refining were taken from three different positions of the bar (left, middle and right); while the samples after refining were taken from the bottom every 5 cm along the bar (see Fig. 5). This sampling method assures the homogeneity of each bar before refining as well as avoids detecting intermetallic compounds at the top of the bar after refining.

3. Results and discussion

The research is intended to thoroughly investigate the As and Pb separation behaviors during Sb vacuum distillation without and with the addition of metallic elements, as well as to explore a more efficient way to separate As from Sb in the production of high purity Sb, i.e. zone refining of Sb under the addition of metallic elements.

3.1. *Separation behavior of As and Pb from Sb in a direct vacuum distillation process*

Different mass fractions of Sb have been distilled from the crude alloy into the condenser depending on the applied temperature, vacuum level and dwelling time. The distilled Sb is silvery and lustrous, and the residue looks gray, as seen in Fig. 6. The most part of the distilled Sb was found in the condenser and comparatively only a minor part condensed on the wall or dropped into the collecting bowl. The concentration of As and Pb in the condenser and the residue respectively (chemically analyzed through ICP mass spectrometry) as well as the calculated mass ratios of distilled Sb in each trial are presented in Table 6. As expected, higher temperatures with lower residual pressure level and longer dwelling time lead to increased Sb-distillation.

The results of Pb consist well with the theoretical predictions (see Table 1). The concentrations of Pb in the condensed Sb for all experiments have been reduced to less than 30 ppm (best value <10 ppm) from original concentration of 1200 ppm, which means the crucible residue became richer in Pb, as shown in Table 6. Fig. 7 illustrates the increasing tendency of Pb-concentration in the residue parallel to the increasing of distilled Sb. The lower Pb content in the residue of trials No. 2, 3, 4 and 7 in comparison to the initial concentration could be due to the very slow solidification after shutting down the experimental power and as a consequence of an undesired segregation and heterogeneous distribution of Pb.

An interesting result of these trials has been detected in experiment No. 8, where Sb not only condensed as usual at the top of the condenser or found in the collecting bowl, but also deposited on the walls of the condenser (see Fig. 6, the upper right picture). Chemical analysis of these areas showed completely different concentrations of As. The Sb condensed on the walls of the condenser is significantly rich in As, in contrast to that condensed at the top or collected inside the bowl. This phenomenon is probably due to the high amount of evaporated Sb that leaves the crucible via aperture and arrives at the upper side of the condenser, having a huge heat energy and high temperature. That leads to a sudden and extreme increase of the temperature in this area, which could be even higher that the condensation temperature of As, forcing it to evaporate back in the gaseous phase and then condensed separately at regions with lower temperatures, for example

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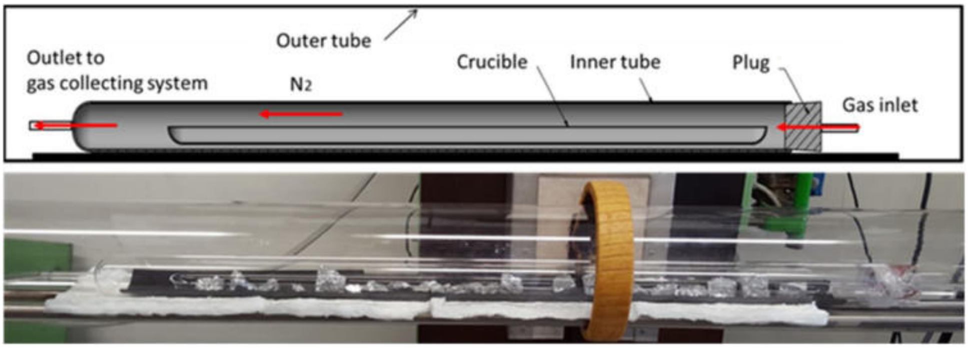

Fig. 3 – Setup of zone refining of Sb.

Table 5 – Experimental parameters of zone refining of Sb with additives of Al and Zn.

Experiments	No. of passes	Zone length	Crucible	Moving velocity	Gas flux
Sb without additive	2	0.25 L	Quartz (L 60 cm)	1 mm/min	N_2 (1 L/min)
Sb – 0.1 wt.% Al	2	0.25 L	Quartz (L 60 cm)		
Sb – 0.1 wt.% Zn	2	0.25 L	Graphite (L 60 cm)		

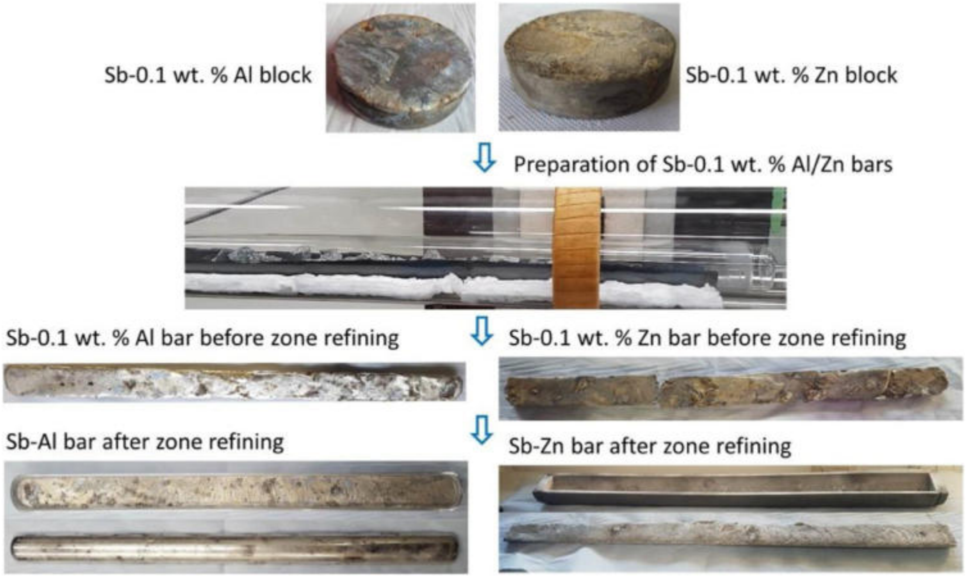

Fig. 4 – Sb - 0.1 wt.% Al and Sb - 0.1 wt.% Zn bars preparation and zone refining process.

Fig. 5 – Sampling sketch of Sb bar (side view) before and after zone refining.

the condenser inner wall. This result can give an idea for a successful separation of these two impurities by designing a multi-level condenser, in which the temperature of each level is individually selected and controlled.

The removal effect of As seems to be dependent on the mass ratio of co-distilled Sb, as illustrated in Fig. 8, showing an exponential relationship. The concentration of As in the Sb residue (Sb-product in this work) is easy to be reduced to about 450 ppm from initial composition of 780 ppm. The final purity ranges from 491 ppm at 1 wt.% of co-distilled Sb to 20 ppm at 72 wt.% accordingly. Such the reduction of the As-concentration in the Sb-product occurs simultaneously

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Fig. 6 – Condensed product as well as residue material after distillation trial No. 8 of Sb (C(As) of residue = 20 ppm, C(As) of condensed Sb in condenser and collecting bowl = 130 ppm, C(As) of condensed Sb on condenser wall = 1800 ppm).

Table 6 – Concentration of As and Pb in residue and condenser and the calculated mass ratio after vacuum distillation.

No. of trials	C(As) of residue (ppm)	C(As) of condensed Sb (ppm)	C(Pb) of residue (ppm)	C(Pb) of condensed Sb (ppm)	Ratio of distilled Sb (wt. %)
1	491	–	1300	–	1.20
2	450	–	900	–	2.59
3	350	2700	960	<10	7.09
4	330	4100	840	<10	8.76
5	103	1100	2300	<10	44.44
6	216	2200	1800	22	26.60
7	230	3300	1100	12	19.18
8	20	(130 or 1800)[a]	3900	33	71.73

[a] 130 ppm is the As concentration of condensed Sb in condenser and collecting bowl and 1800 ppm is the concentration of condensed Sb on the wall.

with the loss of Sb. This phenomenon leads to a contradiction between As-separation and Sb production yield. Furthermore, the condensed Sb is enriched with As with significantly higher concentrations than the initial one (see in Fig. 7), at least at lower temperatures. The concentration of As in the condensate decreases however, when Sb distillation mass rises, because the total concentration ratio of condensed Sb (%) is increasing.

Based on the state of the art where As-contaminated Sb is mostly refined in a long-chained process of vacuum distillation as chlorides and then oxidation of $SbCl_3$ to Sb_2O_3, as well as based on the results of the direct distillation investigations made in this paper, the removal of As seems to be the biggest challenge in ultra-refining of Sb. Therefore, in the next chapter the effectiveness of utilizing additives to arrest the As in the

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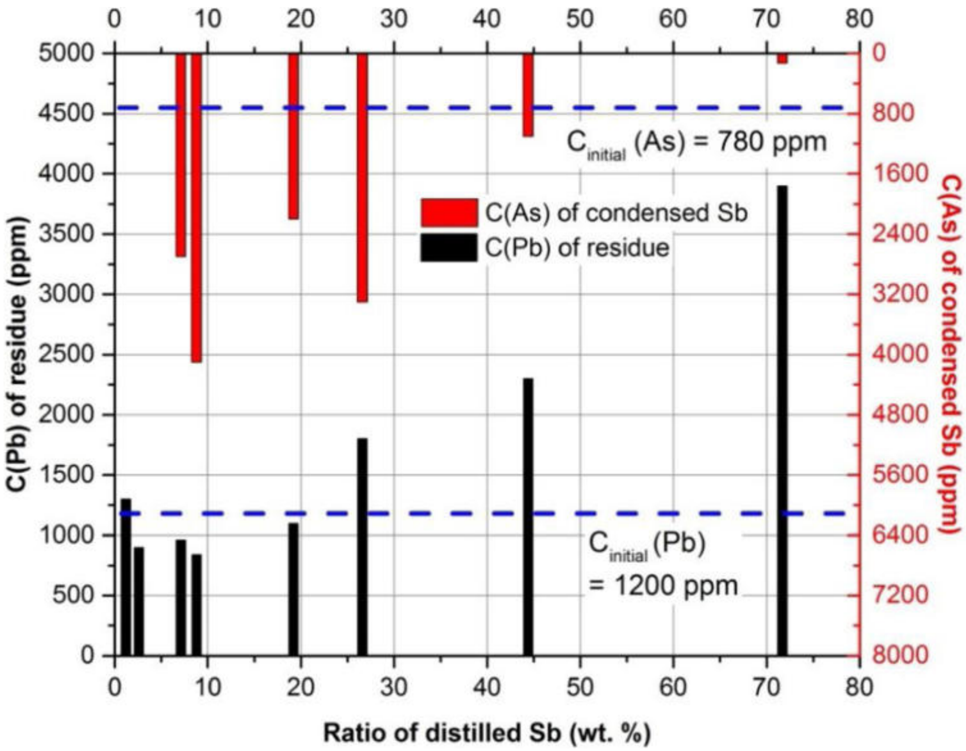

Fig. 7 – Correlation of Pb concentration in residue as well as As concentration in condensed Sb versus the mass ratio of distilled Sb (blue dotted lines represent initial concentrations of crude Sb).

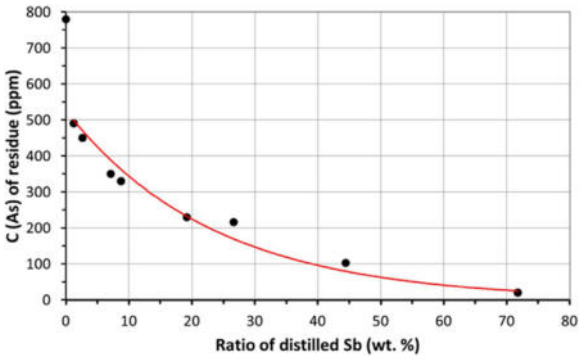

Fig. 8 – Correlation of As-concentration in the distillation residue with the mass ratio of distilled Sb.

residue to allow for a substantial selective Sb-distillation will be investigated.

3.2. *Influence of additives on reducing As-evaporation in a vacuum distillation process*

As is ultimately soluble in Sb, no matter in liquid or solid state, with a distribution coefficient of almost unity, disabling its separation by becoming a heterogeneous form, precipitation or crystallization. The almost similar evaporation behavior of As to the Sb makes it even a problematic impurity during a vacuum distillation too, as was shown in the previous chapter. Thus it was tried to strongly decrease the activity of As by adding intermetallic forming elements with As, insoluble in Sb melts. The process parameters for the trial with 1 % Al as additive (trial No. 9) was the same as for the “reference” trial No. 8. However, a significant drop of distilled Sb (19.22 wt.%) takes place compared to the trial No. 8 according to Table 7. This is assumed to be due to the formation of an interface layer on the surface of melt and hence suppressing the evaporation of Sb. This assumption is supported by the surface structure of the solidified crucible residue, as represented in Fig. 9. The density of Al-As intermetallic (3.8 g/cm^3) is considerably lower than that of the base metal Sb, leading to a gravity separation of these two phases and pushing the intermetallic phase to the surface. Comparing the chemical composition at the top and bottom of the crucible residue (see Table 7 and Fig. 9), a significant difference between the concentration of Al and As in these two positions is being observed. The concentration level of these two elements at the top of the residue is much higher than at the bottom, confirming again the theory mentioned above. This, beside the high melting temperatures of these intermetallic compounds (> 1500 °C, see Table 2) is the reason of the formation of a solid layer on the surface, hindering Sb-distillation. In that case, stronger vacuum levels and/or higher temperatures would be required for more efficient distillation. Nevertheless, the mass of distilled Sb in trial No. 9 was coincidentally almost the same with that of trial No. 7, which was performed with half of the evaporation time, as compared in Table 7. It shows that the amount of As has been reduced in the condensed Sb product to almost one third just by adding Al, which proves the positive effect of Al as additive and such the hypothesis of the current research. However, the absolute value of As concentration in condensed Sb is still as high as

Table 7 – Comparison between vacuum distillations of Sb doped with Al and without additive under condition of 1000 K and 20 Pa.

Sb - 1 wt.% Al	60 min, trial No. 9 Concentration (ppm)	Pure Sb without Al	60 min, trial No. 8 Concentration (ppm)	30 min, trial No. 7 Concentration (ppm)
Ratio of distilled Sb (wt. %)	19.22 %	Ratio of distilled Sb (wt. %)	71.73 %	19.18 %
As in top of residue	1800	As in residue	20	230
As in bottom of residue	69			
As in condensed Sb	1100	As in condensed Sb	130 or 1800	3300
Pb in residue	1550	Pb in residue	3900	1100
Pb in condensed Sb	39	Pb in condensed Sb	33	12
Al in top of residue	3530			
Al in bottom of residue	940			
Al in condensed Sb	< 10			

Fig. 9 – Comparison of appearance of residues after vacuum distillation between Sb - 1 wt.% Al (trial No. 9) and Sb without additive (trial No. 8).

1100 ppm and obviously far away from the requirement of 5 N pure Sb (C(As) <1.5 ppm).

The experiment No. 10 was conducted, using Zn as additive. It however did not show the same efficiency as Al for the purpose of As-fixation. As shown in Table 8, the quantitative results of distilled material as well as the concentration of impurities As and Pb after the trials with or without Zn did not have tremendous differences. That could be due to its huge evaporation of Zn and the limited reaction time between Zn and As, preventing intermetallic compound formation.

3.3. *Influence of additives on separation of As in zone refining process*

The additive of Al in Sb vacuum distillation showed an effective influence on suppressing the evaporation of As, as presented in the last chapter, while the effect of Zn was not observed. However, a subsequent zone refining process is usually required as the final purification step to further reduce the impurities and remove the probably co-evaporated additive elements for producing high purity Sb. The task in this chapter is to verify the feasibility of effectively removing As by directly adding additives into zone refining process, allowing to obtain a shorter process chain.

3.3.1. *Zone refining of Sb-Al alloy*

The concentration of As, Pb as well as Al in the initial Sb block (as stated before, produced with usage of master alloys in an inductive furnace) is almost homogeneous, as seen in Table 9. However, a big difference of the As concentration between the top and the bottom of the prepared bar appears already before zone refining. That is contributed to the formation of an Al-As intermetallic compound, having the lower density than that of Sb and hence accumulating at the surface of the bar. Besides, it was ascertained through chemical analysis that As and Al are

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Table 8 – Comparison between vacuum distillations of Sb with Zn additive (trial No. 10) and without additive (trial No. 8).

Sb - 0.2 wt.% Zn (trail No. 10)	Concentration (ppm)	Pure Sb (trial No. 8)	Concentration (ppm)
Ratio of distilled Sb (wt.%)	74.48%	Ratio of distilled Sb (wt. %)	71.73%
As in residue	28	As in residue	20
As in condensed Sb	1200	As in condensed Sb	130 or 1800
Pb in residue	4400	Pb in residue	3900
Pb in condensed Sb	<10	Pb in condensed Sb	33
Zn in residue	<10		
Zn in condensed Sb	1.18%[a]		

[a] The high value of Zn concentration could be due to its heterogeneous distribution caused by precipitation from Sb.

Table 9 – Compositions of the Sb - 0.1 wt.% Al block and bar before zone refining.

	Position	As ppm	Pb ppm	Al ppm
Sb - 0.1 wt.% Al block	Top	409	1200	1000
	Bottom - 1	328	1100	800
	Bottom - 2	632	1000	800
	Average	*456*	*1100*	*867*
Sb - 0.1 wt.% Al bar before zone refining	Top-1	262	1600	1100
	Top-2	1500	1200	2100
	Top-3	1100	900	1400
	Top - average	954	1233	1533
	Bottom - 1	290	1700	1500
	Bottom - 2	206	1100	700
	Bottom - average	248	1400	1100

homogenously distributed over the length of the bar neither at the top nor at the bottom before zone refining.

The composition of these impurities along the bar after zone refining has been outlined in Table 10, showing a significant reduction in As concentration compared to the initial composition (Table 9). The As content decreases from the beginning to the end of the bar, which will be explained below. Arsenic has been reduced to below 150 ppm for the whole bar after only one pass and even to below 100 ppm in the second half of the bar after two passes. The concentrations at the end of the bar after first and second passes are both as low as 50 ppm. In addition, as expected, Pb and Al contents both are intensely accumulated at the end of the bar, showing a signification purification effect in zone refining process. A very low concentration for them (around 50 ppm) has been achieved only after two passes in the front area of the bar.

Fig. 10(a) illustrates the As distribution profiles in the crystallized phase via zone refining in comparison to the trail without addition of Al. It obviously confirms the increased refining efficiency achieved by the additive. Moreover, it is interesting to see that the As concentration decreases from the beginning to the end along the bar, which is converse to the normal concentration distribution of those impurities with distribution coefficient ($k < 1$) after zone refining. Considering the opposite concentration variation tendencies of As and Al (see Fig. 10(b)) as well as the huge difference between the results of zone refining with or without Al-additive, the efficient reduction of As and its abnormal distribution can be explained as following (see Fig. 11). Aluminum additive reacts with As to form the AlAs intermetallic phase. AlAs has a very high melting temperature of around 1740 °C and a density of about 3.8 g/cm^3, both enable to separate them efficiently from a molten Sb substrate. That results in low concentrations of As at the bottom of the bar, leading to its accumulation at the top. Simultaneously, Al is expelled to the end of the bar during zone refining due to its $k \ll 1$, leading to a significant concentration gradient along the bar (low Al content at the beginning and higher at the end). More AlAs will be hence formed at the end of the bar than at the beginning considering the higher reaction chance between atoms of Al and As. That means more As will be captured to go up to the surface at the end of the bar, leaving less amount of As at the bottom. This tendency is more remarkable as more zone passes are conducted, as seen in Fig. 10(b). Zone refining of Sb-Zn alloy

Table 11 show the composition of the Sb - 0.1 wt.% Zn block and the prepared Sb-Zn bar before zone refining. The compositions in Sb-Zn alloy are more homogeneous than the above mentioned Sb-Al alloy. The initial concentration of As, Pb and Zn is assigned with the average of their concentration in the block and bar.

Table 12 lists the impurity concentration along the bar after zone refining. As expected, Zn was highly accumulated at the end of the bar. But the refining efficiency of As is still low, showing not significant improvement compared to that without addition of additive (similar to the vacuum distillation process), as seen in Fig. 12. The reason could be that As-Zn intermetallic was practically not formed during the process; or the formed As-Zn intermetallic is neither concentrated through zone refining process, nor selectively aggregated like AlAs intermetallic compound due to its high density, which needs further study.

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Table 10 – Concentration of impurities along the Sb - 0.1 wt.% Al bar at the bottom after zone refining (ppm).

Position (cm)		2	7	12	17	22	27	32	37	42	47	52	57
1st pass	As	142	139	110	115	102	115	145	107	120	90	124	53
	Pb	385	800	241	390	332	479	890	1000	1300	1600	2700	2450
	Al	292	404	183	300	257	369	541	581	705	888	2200	5500
2nd pass	As	294	246	195	170	141	121	109	94	65	67	63	52
	Pb	41	47	56	76	168	214	368	410	1600	1600	4000	25800
	Al	57	51	60	85	146	184	290	318	929	1200	2500	5000

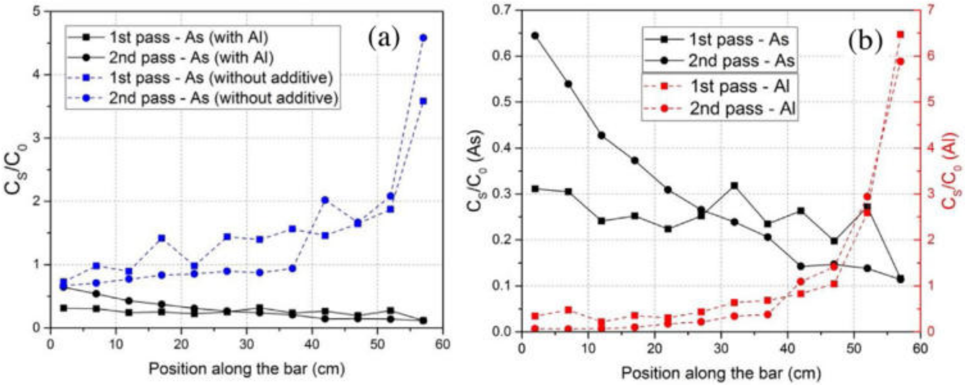
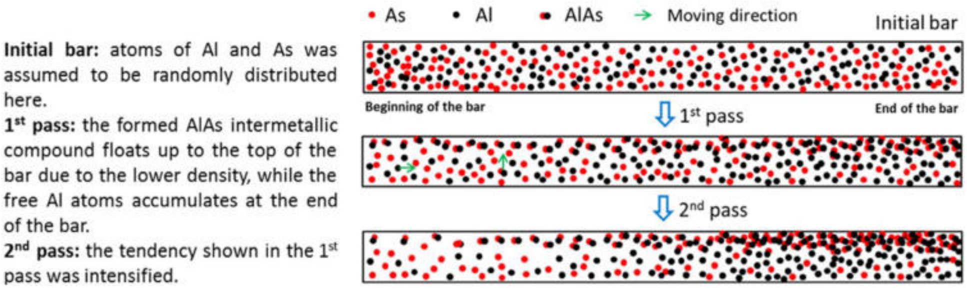


Fig. 10 – Comparison of As concentration distribution along the bar bottom between the trials with and without Al-additive (a) and comparison of As and Al concentration distribution after two passes (b) (C_0 the initial impurity concentration (in Sb - 0.1 wt.% Al block); C_S the impurity concentration in the refined crystallized Sb).



Initial bar: atoms of Al and As was assumed to be randomly distributed here.

1st pass: the formed AlAs intermetallic compound floats up to the top of the bar due to the lower density, while the free Al atoms accumulates at the end of the bar.

2nd pass: the tendency shown in the 1st pass was intensified.

Fig. 11 – Schematic diagram of As removal during zone refining of Sb with Al additive.

Table 11 – Compositions of the Sb - 0.1 wt.% Zn block and bar before zone refining.

	Position	As ppm	Pb ppm	Zn ppm
Sb - 0.1 wt.% Zn block	Top	1100	1000	1500
	Bottom	1100	1000	1100
	Average	*1100*	*1000*	*1300*
Sb - 0.1 wt. % Zn bar before zone refining	Top	910	1300	2100
	Bottom - 1	900	1100	950
	Bottom - 2	1000	1600	1600
	Bottom - 3	900	1200	1200
	Average	928	1300	1463
	Initial concentration (Average of concentrations in the block and bar)	1014	1150	1382

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Table 12 – Concentration of impurities along the Sb - 0.1 wt.% Zn bar after zone refining (ppm).

Position (cm)		2	7	12	17	22	27	32	37	42	47	52	57
1st pass	As	740	750	800	870	930	760	750	790	880	960	1200	1800
	Pb	203	195	306	598	845	265	218	460	742	1400	4000	10700
	Zn	200	125	213	229	406	157	125	253	338	1400	4000	9600
2nd pass	As	580	630	670	690	730	730	750	860	1500	1400	–	–
	Pb	46	57	68	69	95	102	130	191	3700	2800	–	–
	Zn	100	112	104	72	66	116	113	140	2000	1500	–	–

Note: - the samples were missing by accident.

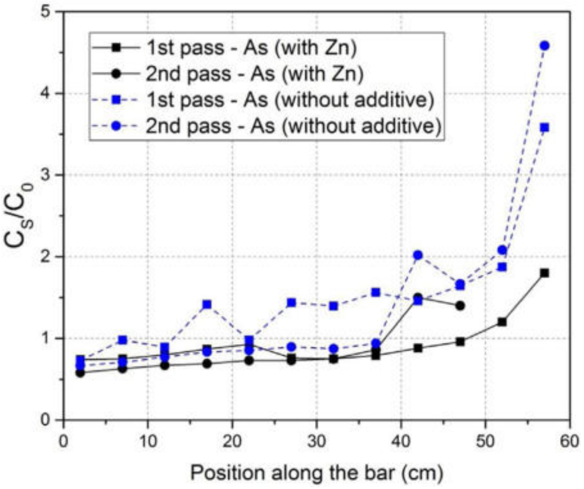

Fig. 12 – A comparison between As concentration distribution along the bar (bottom samples) with and without addition of Zn, both after two passes of zone refining.

4. Conclusion

Due to the huge difference between the vapor pressures (e.g. Pb: 12.02 Pa, Sb: 385.40 Pa, As: 22.13 × 10^5 Pa at 1100 K), theoretical interpretations indicate the removal potential of As and Pb from Sb – the two most common impurities in Sb – through vacuum distillation. The practical experiments on commercial pure Sb (i.e. 99.8%, including 780 ppm of As and 1200 ppm of Pb) shows that removal of Pb is in accordance with the theoretical predictions. The Pb content could be reduced to less than 30 ppm in the condensed Sb-product. The situation of As however was different. It could be reduced from 780 ppm to 450 ppm in the residual Sb product even at low temperatures and high pressures (e.g. at 1050 K with pressure of 200 Pa), but its concentration was still too high for the further purification by zone refining. If more reduction of As by using higher temperatures and/or lower pressures is desired, a lower Sb-yield (residue as the product without consideration of Pb impurity here) – e.g. As content can be reduced to 20 ppm with a Sb-yield of 30 wt.% – has to be accepted because of a co-evaporation of Sb. That means, a favorable separation of Sb and As via simple vacuum distillation seems not to be realizable, if not some alternative methodologies are considered.

One promising alternative is the addition of elements, which – at least theoretically and based on phase diagrams – are able to form intermetallic compounds with As and therefore avoid its co-evaporation. This task can lead to remove As by capturing it in the form of intermetallic compounds, which can shorten the purification process time from two steps (vacuum distillation followed by zone refining) into one (only zone refining). Following this hypothesis the addition of selected elements – in this case Al as well as Zn – was practiced during zone refining. The results indicated that the addition of Al significantly improves the refining efficiency of As in both vacuum distillation as well as zone refining process:

- During vacuum distillation process, the experiment with 1 wt.% Al addition proved the effectiveness in the suppression of As evaporation, as the concentration of As in the condensed Sb-product was much lower than that without additive. However, Al can highly hinder the evaporation of Sb as it covers the molten surface. In this case only 20 % of Sb could be distilled into the condenser. As in the residue was analyzed with a great concentration gradient from the top to the bottom of the crucible, confirming the formation of light and high temperature AlAs-intermetallic at the top of the melt.
- During zone refining process, As concentration in the whole bar was considerably reduced from 456 ppm to below 150 ppm (and as low as 50 ppm at the end of the bar) after only one zone pass by adding 0.1 wt.% Al into the Sb, which is contributed to the floating of formed AlAs intermetallic. Moreover, opposite to the normal As distribution, the As concentration in the case of addition of Al decreases along the bar because of the enrichment of Al in the end. The As concentration in the end of the bar after one passes is much lower than that achieved after two passes without additive, proving a very satisfying result with focus on a time-saving process.

In the case of addition Zn, no obvious improvements from the one without additive could be observed. In short, this work first revealed the removal behavior of the impurities of As and Pb from Sb during both vacuum distillation and zone refining processes and then provided an effective methodology to increase the removal efficiency of As. These findings not only have substantial values in the production of high purity Sb, but has also potential to improve the recovery of lead, antimony and/or other valuable metals from lead-rich secondary materials. Nevertheless, to this topic the further research on optimizing the process parameters or finding other possible effective metallic additives could be conducted in the near future.

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Author contributions

Bernd Friedrich was the principal investigator and final proof reader. Xiaoxin Zhang and Semiramis Friedrich conceived and designed the experiments. Xiaoxin Zhang and Semiramis Friedrich analyzed the data. Xiaoxin Zhang and Semiramis Friedrich wrote and edited the manuscript.

Conflict of interest

The authors declare no conflicts of interest.

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