

# Behaviour Comparison and Process Optimization of AI and Sb Zone Refining





## **Behaviour Comparison and Process Optimization**

## of Al and Sb Zone Refining

The Faculty of Georesources and Materials Engineering of the

**RWTH** Aachen University

submitted by

## Xiaoxin Zhang – M. Sc.

from Jiangxi, China

in respect of the academic degree of

## **Doctor of Engineering**

Supervisors: Univ. Prof. Dr.-Ing. Karl Bernhard Friedrich

Univ. Prof. Dr.-Ing. Andreas Bührig-Polaczek

Univ. Prof. Dr.-Ing. Daniela Zander

Aachen, 19.12.2019

Schriftenreihe des IME

Band 61

Xiaoxin Zhang

## Behaviour Comparison and Process Optimization of AI and Sb Zone Refining

Shaker Verlag Düren 2020

#### Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at http://dnb.d-nb.de.

Zugl.: D 82 (Diss. RWTH Aachen University, 2019)

Copyright Shaker Verlag 2020 All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of the publishers.

Printed in Germany.

ISBN 978-3-8440-7171-9 ISSN 1610-0727

Shaker Verlag GmbH • Am Langen Graben 15a • 52353 Düren Phone: 0049/2421/99011-0 • Telefax: 0049/2421/99011-9 Internet: www.shaker.de • e-mail: info@shaker.de

## Abstract

High purity Aluminum and Antimony (> 99.99 %) have nowadays found growing applications in high-tech areas, such as electronics, photovoltaic systems, optical elements, etc. Zone refining process is commonly used as the final purification step in the production of such high purity metals. Improving the refining efficiency as well as production yield and lowering the time consumption are always the research emphases in the field of metal purification via zone refining. Optimization of the relevant experimental factors is the major approach to meet the target, which has been extensively investigated since decades. Those factors mainly include zone length, heater movement velocity, number of passes, and initial concentration of the impurities. But most of optimized parameters are confined to some specific metals. A general rule for the optimum experimental parameters, which can be used in common, is still not clear. This work focused on zone length, considering its important role in the process, affecting not only the zone refining efficiency but also determining the time required to reach ultra distribution of impurities. The typical numerical simulation model proposed by Spim (called Spim model hereafter) has been applied to optimize this factor. An optimum zone length combination, by which the highest refining efficiency could be achieved in theory, was resulted through a series of comparison analysis by importing the model into the software Matlab. The optimized zone length combination is independent of the type of the impurities, which means it can be applied in any metals. Such zone length combination was then applied in zone refining process of Al and Sb, on one hand for verifying its effectiveness in two metallic systems with largely different physical properties, on the other hand for managing to produce high purity Al and Sb. Furthermore, a huge effort was made to reveal and deal with the specific problems appeared in the purification process of these two metals.

2N8-pure Aluminum with intended additives of Si and Fe (0.1 wt. % respectively) and commercial pure Sb (99.8 % Sb) were applied as initial materials. In the zone refining process of Al, an infrared camera was introduced to measure the real-time zone length and crystal growth rate. It has been the very first usage of such device in this process so far. It was found that those parameters were not stable as the heater moved forward with constant heating power and heater moving velocity, but both of them significantly affected the final impurity distribution. Unfortunately, the infrared camera could not be applied in the case of Antimony due to serious evaporation of Sb during the zone refining process. The application of the theoretically obtained optimized zone length combination in zone refining of Al brought

about a much higher refining efficiency compared with the usually used zone length combinations, which validated the simulation results. However, the result in case of the application of the optimized zone length in Sb was in opposition. It is presumably resulted from the unstable and high crystal growth rate, which is unavoidable for obtaining a long zone length under current system and setup. An alternate solution in terms of updating the equipment has been proposed in the text.

Another factor, i.e. initial concentration in the aspect of its influence in refining efficiency has been investigated as well in the case of Aluminum. Three different purity grades of Al (4N (product of three-layer electrolysis), 2N8 (commercial pure Al) and 1N7 (recycled from beverage cans)) were used as the initial materials. The result showed that the refining efficiency increased as the initial impurity concentration decreased. Aluminum with purity up to 5N5 was produced after five zone passes when using 4N pure Al as initial material. In the case of commercial pure Al and recycled Al, the refining efficiency achieved in the former system was slightly greater than that in the latter one. Nevertheless, for both cases less than 50 % of total impurities were reduced in the first half of the bar after five zone passes, which is unacceptable with a view to the aforementioned low production yield and high time-consumption for zone refining process. Therefore, it is suggested to only use already pure enough Al as the initial material to produce high purity Al.

In addition, extensive efforts have been exerted in this research to deal with a tough problem in zone refining of Sb – removal of Arsenic (As), one of the main impurities in commercial pure Sb, which is problematic to remove via crystallization process due to its high value (nearly one) of distribution coefficient (k). Overall three methodologies were proposed and tested, which are applying vacuum distillation process to separate As from Sb prior to execution of zone refining process, introducing gas flux to expel evaporated As during zone refining process, and adding metallic elements (Al and Zn) into Sb to form intermetallic with As in both vacuum distillation and zone refining processes. The results showed that the separation effect of As from Sb through simple vacuum distillation was unpromising. It actually depends on the mass of the distilled Sb because of a co-evaporation of Sb, which results that the high refining efficiency and low production yield have to be accepted at one time. The introduction of inert gas flux in zone refining process proved invalid as well due to the weak As evaporation at the low concentration level. However, the addition of Al significantly improved the refining efficiency of As in both vacuum distillation process as well as zone refining process, which could be regarded as a new effective solution to separate As from Sb. By contrast, addition of Zn did not make any obvious improvement compared with the case without additive.

This work provided a comprehensive understanding on the mechanism of zone refining process with particular focus on the purification improvement for the case studies of Al and Sb. Moreover, the results from this work can be extended in zone refining of other metals as well.

## Kurzfassung

Hochreines Aluminium und Antimon (> 99,99 %) finden heutzutage zunehmend Anwendung in Hightech-Bereichen wie Elektronik, Photovoltaik, optischen Elementen etc. Das Zonenraffinationsverfahren wird üblicherweise als letzter Reinigungsschritt bei der Herstellung hochreiner Metalle verwendet. Die Verbesserung der Raffinationseffizienz sowie der Produktionsausbeute und die Senkung des Zeitaufwands sind immer Forschungsschwerpunkte auf dem Gebiet der Metallreinigung durch Zonenraffination. Die Optimierung der relevanten experimentellen Parameter ist der Hauptansatz, um das seit Jahrzehnten intensiv untersuchte Ziel zu erreichen. Zu diesen Parametern gehören hauptsächlich die Zonenlänge, die Bewegungsgeschwindigkeit des Heizelements, die Anzahl der Durchgänge und die Anfangskonzentration der Verunreinigungen. Die meisten der bereits optimierten Parameter sind jedoch auf bestimmte Metalle beschränkt. Eine Regel für die optimalen experimentellen Parameter, die allgemein verwendet werden könnte, ist weiterhin unbekannt.

Diese Arbeit konzentrierte sich auf den Einfluss der Zonenlänge im Prozess auf die Effizienz der Zonenreinigung und auf die Bestimmung der Zeit, die erforderlich ist, um eine ultrahohe Raffination von Verunreinigungen zu erreichen. Das von Spim vorgeschlagene numerische Simulationsmodell (im Folgenden als Spim-Modell bezeichnet) wurde angewendet, um diesen Faktor zu optimieren. Durch eine Reihe von Vergleichsanalysen wurde durch den Import des Modells in die Software Matlab eine optimale Zonenlängenkombination errechnet, mit der theoretisch die höchste Raffinationseffizienz erzielt werden könnte. Die optimierte Zonenlängenkombination ist unabhängig von der Art der Verunreinigungen, das heißt, sie kann bei beliebigen Metallen angewendet werden. Eine solche Zonenlängenkombination wurde im Zonenraffinationsverfahren von Al und Sb angewendet, um einerseits ihre Wirksamkeit in den jeweiligen metallischen Systemen mit stark unterschiedlichen physikalischen Eigenschaften zu überprüfen und andererseits um hochreines Al und Sb herzustellen. Darüber hinaus wurden große Anstrengungen unternommen, um die spezifischen Probleme bei der Reinigung dieser beiden Metalle aufzudecken und zu lösen. Als Ausgangsmaterialien wurden 2N8-reines Aluminium mit Zusätzen von Si und Fe (jeweils 0,1 Gew.-%) und handelsüblichem reinem Sb (99,8 % Sb) verwendet. Bei der Zonenveredelung von Al wurde eine Infrarotkamera verwendet, um die Zonenlänge in Echtzeit und die Kristallwachstumsrate zu messen. Ein solches Gerät wurde damit zum ersten Mal für diesen Prozess verwendet. Es wurde festgestellt, dass diese Parameter nicht konstant sind, wenn sich der Heizer mit konstanter Heizleistung und Geschwindigkeit vorwärtsbewegt, dass aber beide Parameter die endgültige Verunreinigungsverteilung signifikant beeinflussen. Leider konnte die Infrarotkamera im Fall von Antimon aufgrund dessen starker Verdampfung während des Zonenraffinationsprozesses nicht angewendet werden.

Die Anwendung der theoretisch erhaltenen optimierten Zonenlängenkombination bei der Zonenveredelung von Al führt zu einer viel höheren Veredelungseffizienz im Vergleich zu den üblicherweise verwendeten Zonenlängenkombinationen, was die Simulationsergebnisse bestätigt. Das Ergebnis bei Anwendung der optimierten Zonenlänge bei Sb ist jedoch gegenläufig. Vermutlich ist dies auf die instabile und hohe Kristallwachstumsrate zurückzuführen, die für die Erzielung einer langen Zonenlänge mit dem gegenwärtigen System und Aufbau unvermeidbar ist. In der Arbeit wird eine alternative Lösung durch eine Veränderung des Versuchsaufbaus vorgeschlagen.

Ein weiterer Faktor, d. H. die anfängliche Konzentration hinsichtlich ihres Einflusses auf die Raffinationseffizienz, wurde ebenfalls im Fall von Aluminium untersucht. Als Ausgangsmaterialien wurden drei verschiedene Reinheitsgrade von Al (4N (Produkt der Dreischichtelektrolyse), 2N8 (handelsübliches reines Al) und 1N7 (recycelt aus Getränkedosen)) verwendet. Das Ergebnis zeigt, dass die Raffinationseffizienz ansteigt, wenn die anfängliche Verunreinigungskonzentration abnimmt. Bei Verwendung von 4N reinem Al als Ausgangsmaterial wurde nach fünf Zonendurchgängen Aluminium mit einer Reinheit von bis zu 5N5 hergestellt. Bei handelsüblichem reinem und bei recyceltem Al war die im ersteren System erzielte Raffinationseffizienz geringfügig höher als im letzteren. In beiden Fällen wurden jedoch nach fünf Zonendurchgängen weniger als 50 % der gesamten Verunreinigungen in der ersten Hälfte der Stange entfernt, was im Hinblick auf die oben erwähnte niedrige Produktionsausbeute und den hohen Zeitaufwand fiir den Zonenraffinationsprozess nicht akzeptabel ist. Es wird daher empfohlen, nur bereits ausreichend reines Al als Ausgangsmaterial zu verwenden, um mit diesem Verfahren hochreines Al herzustellen. Darüber hinaus wurden in dieser Forschungsarbeit Anstrengungen unternommen, um ein schwieriges Problem bei der Zonenveredelung von Sb zu lösen - die Entfernung von Arsen (As), einer der Hauptverunreinigungen in handelsüblichem reinem Sb, die aufgrund eines hohen Wertes des Verteilungskoeffizienten (k) von fast eins durch den Kristallisationsprozess schwierig zu entfernen ist. Insgesamt wurden drei Methoden getestet, die ein Vakuumdestillationsverfahren anwenden, um As von Sb vor der Durchführung des Zonenraffnationsprozesses abzutrennen. Dabei treibt ein Gasfluss verdampftes As während des Zonenraffnationsprozesses aus, und es werden metallische Elemente (Al und Zn) in Sb hinzuzugefügt, um intermetallisch mit As sowohl beim Vakuumdestillations- als auch beim Zonenraffnationsprozess zu reagieren. Die Ergebnisse zeigen, dass die Trennwirkung von As von Sb durch einfache Vakuumdestillation nicht vielversprechend ist. Tatsächlich hängt dies von der Masse des destillierten Sb ab, da Sb gemeinsam mit As verdampft, was dazu führt, dass eine hohe Raffinationseffizienz nur bei einer gleichzeitig niedrigen Produktionsausbeute erreicht werden kann. Die Einführung des Inertgasflusses in den Zonenraffinationsprozess erwies sich aufgrund der schwachen As-Verdampfung bei niedriger Konzentration ebenfalls als unwirksam. Die Zugabe von Al verbesserte jedoch die Raffinationseffizienz von As sowohl im Vakuumdestillationsverfahren als auch im Zonenraffinationsverfahren erheblich, was als neue wirksame Lösung zur Abtrennung von As aus Sb angesehen werden könnte. Im Gegensatz dazu zeigte die Zugabe von Zn keine offensichtliche Verbesserung im Vergleich zum Fall ohne Additiv.

Diese Arbeit liefert ein umfassendes Verständnis der Mechanismen des Zonenraffinationsprozesses mit besonderem Schwerpunkt auf der Verbesserung der Reinigung für die Fallstudien von Al und Sb. Darüber hinaus können die Ergebnisse dieser Arbeit auch auf die Zonenveredelung anderer Metalle ausgeweitet werden.

## **Table of Contents**

Ex	tended A	Abstract	XI
1	Introdu	uction	1
2	Backgr	round	3
	2.1 Hi	igh purity Aluminum	
	2.1.1	Definition of high purity Aluminum	
	2.1.2	Application of high purity Aluminum	4
	2.1.3	Production of high purity Aluminum	6
	2.1.3	3.1 Worldwide production distribution of high purity Al	6
	2.1.3	Production technology of high purity Al	7
	2.2 Hi	igh purity Antimony	
	2.2.1	Application of high purity Antimony	
	2.2.2	Production of high purity Antimony	
	2.2.2	2.1 Production distribution of commercial purity Sb	
	2.2.2	2.2 Production process of commercial pure Antimony	
	2.2.2	2.3 Production technology of high purity Antimony	
	2.3 In	ntroduction of zone refining	
	2.3.1	Zone refining mechanism	
	2.3.1	1.1 Basic equations in zone refining	
	2.3.1	1.2   Zone refining influencing factors	
	2.3.2	Variants of zone refining	
	2.3.3	Possibilities to improve zone refining efficiency	
	2.3.3	3.1 Optimizing experimental parameters	
	2.3.3	3.2 Cropping and connecting	
	2.3.3	3.3 Inclination of the charging bar	
	2.3.3	3.4 Application of an electric current for impurity transport	

	2.3.4	Numerical models to describe zone refining process	34
	2.3.5	Assessment of modelling versus experiment	38
	2.4 M	echanism of vacuum distillation	38
	2.5 H	igh purity analysis methods	41
3	Motiva	ation and Targets	43
4	Experi	mental and Modeling Investigations	45
	4.1 Ex	xperimental concept and workflow	45
	4.1.1	Experimental concept	45
	4.1.2	General workflow	46
	4.2 No	umerical simulation	49
	4.2.1	Zone length optimization through Spim model	49
	4.2.2	Refining efficiency comparison between using the optimum zone lengt	th and
	others	53	
	4.2.3	Chapter conclusion	54
	4.3 Zo	one refining of Aluminum	55
	4.3.1	Realization of the zone length measurement with the infrared camera.	56
	4.3.1	.1 IR camera temperature calibration	57
	4.3.1	.2 Zone length measurement through IR camera	57
	4.3.1	.3 Sectional summary	61
	4.3.2	Variation of the crystal growth rate and of the zone length during	; zone
	refinin	g of Aluminum	62
	4.3.2	2.1 Experimental procedure	62
	4.	3.2.1.1 Experimental design	62
	4	3.2.1.2 Data analysis	63
	4.3.2	2.2 Results and discussion	65
	4.	3.2.2.1 Characterization of zone refining process	65
	4.:	3.2.2.2 Dependency of zone length on power and heater movement velocity.	68
	4.	3.2.2.3 Crystal growth rate variation	70

4.3.2	.3 Sectional Summary	72
4.3.3	Influence of the zone length on the refining efficiency	.74
4.3.3	.1 Experimental process	74
4.3.3	.2 Results and discussion	76
4.3	3.3.2.1 Real zone length at each zone pass measured by IR camera	76
4.3	3.3.2.2 Zone refining efficiency under different zone length combinations	77
4.3.3	3 Sectional summary	78
4.3.4	Influence of initial concentration on refining efficiency	79
4.3.4	.1 Experimental process	.79
4.3.4	.2 Results and discussion	80
4.3	3.4.2.1 4N pure Aluminum	80
4.3	3.4.2.2 2N8 pure Aluminum	81
4.3	3.4.2.3 Recycled Aluminum	82
4.3.4	3 Sectional summary	84
		0.5
4.3.5	Chapter conclusion	85
4.3.5 4.4 Zo	Chapter conclusion ne refining of Antimony	85
4.3.5 4.4 Zo 4.4.1	Chapter conclusion ne refining of Antimony Separation behavior of As and Pb during vacuum distillation	85 87 88
4.3.5 4.4 Zo 4.4.1 4.4.1	Chapter conclusion ne refining of Antimony Separation behavior of As and Pb during vacuum distillation 1 Fundamental of vacuum distillation of Sb	. 85 . 87 . 88 . 89
4.3.5 4.4 Zo 4.4.1 4.4.1 4.4.1	Chapter conclusion ne refining of Antimony Separation behavior of As and Pb during vacuum distillation Fundamental of vacuum distillation of Sb	. 85 . 87 . 88 . 89 . 89
4.3.5 4.4 Zo 4.4.1 4.4.1 4.4.1 4.4.1	Chapter conclusion         ne refining of Antimony         Separation behavior of As and Pb during vacuum distillation         .1       Fundamental of vacuum distillation of Sb         .2       Experimental process         .3       Results and discussion	85 87 88 89 89 91
4.3.5 4.4 Zo 4.4.1 4.4.1 4.4.1 4.4.1 4.4.1 4.4.1	Chapter conclusion         ne refining of Antimony         Separation behavior of As and Pb during vacuum distillation         .1       Fundamental of vacuum distillation of Sb         .2       Experimental process         .3       Results and discussion         .4       Sectional summary	<ul> <li>85</li> <li>87</li> <li>88</li> <li>89</li> <li>89</li> <li>91</li> <li>94</li> </ul>
4.3.5 4.4 Zo 4.4.1 4.4.1 4.4.1 4.4.1 4.4.1 4.4.1 4.4.1 4.4.2	Chapter conclusion         ne refining of Antimony         Separation behavior of As and Pb during vacuum distillation         .1       Fundamental of vacuum distillation of Sb         .2       Experimental process         .3       Results and discussion         .4       Sectional summary         .1       Influence of the heater moving velocity on the refining efficiency	<ul> <li>85</li> <li>87</li> <li>88</li> <li>89</li> <li>91</li> <li>94</li> <li>of</li> </ul>
4.3.5 4.4 Zo 4.4.1 4.4.1 4.4.1 4.4.1 4.4.1 4.4.1 4.4.2 Antimo	Chapter conclusion         ne refining of Antimony         Separation behavior of As and Pb during vacuum distillation         .1       Fundamental of vacuum distillation of Sb         .2       Experimental process         .3       Results and discussion         .4       Sectional summary         .1       Influence of the heater moving velocity on the refining efficiency         ony zone refining	<ul> <li>85</li> <li>87</li> <li>88</li> <li>89</li> <li>91</li> <li>94</li> <li>of</li> <li>96</li> </ul>
4.3.5 4.4 Zo 4.4.1 4.4.1 4.4.1 4.4.1 4.4.1 4.4.1 4.4.2 Antimo 4.4.2	Chapter conclusion	<ul> <li>85</li> <li>87</li> <li>88</li> <li>89</li> <li>91</li> <li>94</li> <li>96</li> <li>96</li> <li>96</li> </ul>
4.3.5 4.4 Zo 4.4.1 4.4.1 4.4.1 4.4.1 4.4.1 4.4.1 4.4.2 Antimo 4.4.2 4.4	Chapter conclusion	<ul> <li>85</li> <li>87</li> <li>88</li> <li>89</li> <li>91</li> <li>94</li> <li>96</li> <li>96</li> <li>96</li> <li>96</li> <li>96</li> </ul>
4.3.5 4.4 Zo 4.4.1 4.4.1 4.4.1 4.4.1 4.4.1 4.4.1 4.4.1 4.4.2 Antimo 4.4.2 4.4 4.4	Chapter conclusion         ne refining of Antimony         Separation behavior of As and Pb during vacuum distillation         .1       Fundamental of vacuum distillation of Sb         .2       Experimental process         .3       Results and discussion         .4       Sectional summary         .1       Influence of the heater moving velocity on the refining efficiency         .1       Experimental process         .2       .1         Measurement of Arsenic evaporation         .2       .1.2         2       .1.2	<ul> <li>85</li> <li>87</li> <li>88</li> <li>89</li> <li>91</li> <li>94</li> <li>96</li> <li>96</li> <li>96</li> <li>96</li> <li>97</li> </ul>
4.3.5 4.4 Zo 4.4.1 4.4.1 4.4.1 4.4.1 4.4.1 4.4.1 4.4.2 Antimo 4.4.2 4.4 4.4 4.4	Chapter conclusion         ne refining of Antimony         Separation behavior of As and Pb during vacuum distillation         .1       Fundamental of vacuum distillation of Sb         .2       Experimental process         .3       Results and discussion         .4       Sectional summary         .1       Influence of the heater moving velocity on the refining efficiency         .1       Experimental process         .1       Experimental process         .1       Experimental process         .2       Influence of the heater moving velocity on the refining efficiency         .1       Experimental process         .1       Experimental process         .2       1.1         Measurement of Arsenic evaporation         .2       2.1.2         Zone refining of Sb under different heater moving velocities         .2       Results and discussion	<ul> <li>85</li> <li>87</li> <li>88</li> <li>89</li> <li>91</li> <li>94</li> <li>96</li> <li>96</li> <li>96</li> <li>96</li> <li>96</li> <li>97</li> <li>99</li> </ul>

	4.4.2.	2.2 Impurity reduction and effective distribution coefficients of impurities 100
	4.4.2.	2.3 Metallographic structure of Sb bar after zone refining 107
	4.4.2.3	Sectional summary108
	4.4.3 Ir	fluence of zone length on the refining efficiency of Antimony
	4.4.3.1	Experimental process
	4.4.3.2	Results and discussion110
	4.4.3.3	Sectional summary115
	4.4.4 In	nfluence of additives on As-removal during both vacuum distillation and
	zone refin	ing processes of Antimony
	4.4.4.1	Selection of additives117
	4.4.4.2	Experimental process119
	4.4.4.	2.1 Production of Sb-Al and Sb-Zn master alloys119
	4.4.4.	2.2 Vacuum distillation of Sb-Al and Sb Zn alloys 120
	4.4.4.	2.3 Zone refining of Sb-Al and Sb-Zn alloys
	4.4.4.3	Results and discussion
	4.4.4.	3.1 Vacuum distillation of Sb-Al and Sb Zn alloys 121
	4.4.4.	3.2 Zone refining of Sb-Al and Sb-Zn alloys 124
	4.4.4.4	Sectional summary128
	4.4.5 C	hapter conclusion
5	General A	ssessment
6	Outlook	
Ref	erence	
Арј	pendix	
Ack	knowledgen	nent

## **Extended Abstract**

High purity metals (4N (i.e. 99.99 %) or above) are intensively demanded in high-tech industrial fields, as in these areas even low concentrations of impurities could completely deactivate the desirable functions. The production of high purity metals is very challenging and the production process always needs to be optimized with a view to obtain better balance between the final purity, the yield and the cost. Zone refining is a proven effective methodology since the early 1950s to produce high purity metals. However, the refining efficiency and final purity are practically dependent on many factors, including effective distribution coefficient (keff, i.e. real distribution coefficient of one impurity in the practical process), zone length, movement velocity of the freezing interface (crystal growth rate), number of the zone passes and the type and concentration of the impurities. The optimization of those factors to improve the refining efficiency is generally centered on the subject that applying various zone length, appropriate initial purity and convection in the molten zone to achieve as high refining efficiency as possible, and at the same time to enable applying high movement velocity of freezing interface and low number of zone passes. In addition, the structure design and performance of the equipment, the characteristic of the operated metal as well as the selection of the crucible play an important role in the refining process too. The complexity and specificity of zone refining make it imperative to optimize the investigations by combining experiment with numerical modeling or simulation. Two metals – Aluminum and Antimony - are the focus of investigation in this study.

#### Background

#### • Production of high purity Aluminum

The basic production process of high purity Al is shown in Figure I. Primary Al with purity of 99.5-99.8 % is first produced by Hall–Héroult process. 3-layer Electrolysis and Segregation are the main technologies in the production of high purity Al, although they work on different mechanisms. 3-layer Electrolysis is based on the electronegativity difference between Al and its impurities. Segregation utilizes the solubility difference of impurities between in molten as well as solid Al. As the technologies constantly develop, each of them would now be individually capable of producing 4N+ purity of Al. However, to achieve higher purity (5N+) a combination of them is needed. For example, Hydro company initially applies 3-layer

Electrolysis to get 4N-Al by using commercial pure Al as raw material, and later Segregation technology to achieve the purity of 5N-6N. [21]



#### Figure I Production process of high purity Al [27]

Segregation is a kind of generic term of crystallization purification technology, which is based on the difference between impurity solubility in liquid and solid state of the matrix. It can normally be classified in different ways as reported in publications. But typically it can be divided into three categories, i.e. fractional crystallization, unidirectional crystallization and zone refining, according to their specific equipment design and operation. Zone refining shares the same purification mechanism with fractional crystallization and unidirectional crystallization. But the furnace design and working process are different. It works by moving one or more molten zone (heated by heating coils) along a metallic from one side to another, as presented in Figure II. As a result, the impurities will be collected at the end or beginning of the bar, depending on the distribution coefficient (less or more than unity). It is usually used as the final purification step to produce ultra-pure Aluminum. But its yield is very low due to the time consumption and the size of the charge.



Figure II One exemplary draft of zone refining process

Overall, among the above mentioned three ways, fractional crystallization is the most competitive industrial segregation technology to produce 4N-5N pure Al in terms of refining efficiency and yield. Currently, the production for one fractional crystallization furnace is 1.2-1.5 t/d and the energy consumption is around 3000 kW·h/t. For producing higher pure Al such as 5N5+, zone refining process has to be put into action.

#### • Production of high purity Antimony

The possible technologies and relevant processes to produce high purity Sb can be concluded in the flowchart of Figure III.



Figure III Flowchart of possible production processes of high purity Sb (note: \* the purity of "high purity Sb" and their contained impurity types vary with the selection of the pathways)

As Arsenic atom is inherently adhesive to Antimony atom, Sb ingot or Sb<sub>2</sub>O<sub>3</sub> usually will be first transformed into SbCl<sub>3</sub> with the aim to separate As from Sb through vacuum distillation. That is contributed to the low as well as different boiling points of SbCl<sub>3</sub> and AsCl<sub>3</sub>, It is reported that 99.99-99.999 % of As can be removed during this process (pathway 2). [40] After that, three different pathways have been tried out by different researchers, as presented in Figure III. In comparison with those processes, which are mostly complex with high cost and high corrosion risks to the equipment, a clean and low cost technology – purifying Sb metal directly through vacuum distillation, has been envisaged as an alternative way to produce high purity Sb (pathway 15/16). In 1960s, Ivanov [47] and Min [48] obtained 5N pure Sb by repeated vacuum distillation, but in rather low yield. It was found that adding 1-2 % Al during distillation was remarkably helpful to reduce As content in the condensate and to achieve 4N pure Sb. [49] Applying multiple layer design of condenser in vacuum distillation to allow vapors to be selectively condensed on different layers (depending on the property of the compositions and the temperature of each layer) could be a good way to improve the final purity of products and shorten the process time. It proves effective in the work [46], but a lot

of issues are still not clear, such as appropriate setup design, operation parameters and upscaling of the production, etc. After vacuum distillation, zone refining is commonly used to further improve the purity of Sb (pathway 15/17/7). However, As is a problematic element due to its high distribution coefficient (close to unity). Therefore, As must be separated prior to zone refining. The concept of combining vacuum distillation and zone refining has been hence put forward since 1950s, and it was reported that 4N-5N pure Sb was obtained by this way in 1967. [50] Afterwards, few works have been done on this area, which may be due to the small market requirement at that time. The information on optimized operation parameters, appeared phenomenon, refining efficiency, etc., is still nearly blank, except for some simple reports [42,51].

#### • Numerical models to describe zone refining process

Th optimization of experimental parameters is of limited general use, as they are strongly dependent on individual system characteristics. For this reason, many numerical models have been developed to predict the solute distribution or to optimize experimental parameters as well as to give guidance for empirical trials.

The most typical iterative model was proposed by Spim, et al [8], which was concentrated on simulating distribution activity of impurity elements at any stage for multi-pass zone refining process. In this model, the solute concentration profiles for each pass of a molten zone have been quantified by considering four different regions along the sample (see Figure IV), Region 1: surface (X = 0); Region 2: intermediate ( $0 < X \le 1-Z$ ); Region 3: normal freezing (1-Z < X < 1) and Region 4: end of the sample (X = 1).



### Figure IV Sketch of four regions considered in Spim model

All of the above equation can be concluded as following:

$$C_{S(X)}^{n} = \begin{cases} k_{i} \left(\frac{dx}{Z}\right) \left(\sum_{q=0}^{M-1} C_{S(q \ dx)}^{n-1}\right), & X = 0\\ \\ C_{S(X-dx)}^{n} + \frac{k_{i} dx}{Z} \left(C_{S(X+Z-dx)}^{n-1} - C_{S(X-dx)}^{n}\right), & 0 < X < 1 - Z\\ \left[1 + \left(\frac{1-k_{i}}{1-X}\right) dX\right] C_{S(X-dx)}^{n}, & 1 - Z \le X < 1\\ \\ \frac{1}{dX} C_{0} - \left(\sum_{X=0}^{X-1-dX} C_{S(X)}^{n}\right), & X = 1 \end{cases}$$
Equation I

This simulation model can be used to research on the effects of zone length and distribution coefficient k on the refining efficiency, including the ultimate impurity concentration distribution as well as the minimum zone passes necessitated to reach the final purity level.

### **Motivation and targets**

This work is dedicated to address the following issues:

- 1. Apply a numerical model (Spim model) to derive a theoretical generally applicable optimum zone length. The obtained optimum zone length will be applied in both Sb as well as Al zone refining experiments.
- 2. Detect and reveal the zone length variation in one single pass during zone refining process and investigate its probable influence on the refining efficiency.
- 3. Investigate the influence of initial concentration of the impurities (the purities of the initial materials are in different levels) on the refining efficiency during zone refining process.
- 4. Ascertain the separation behaviors of As and Pb, the two main impurities in commercial pure Sb, during vacuum distillation of Sb.
- 5. Systematically investigate the process of Sb zone refining. The separation of As and Pb will be put into focus.
- Propose a new methodology to improve the removal efficiency of As from Sb both in vacuum distillation and zone refining processes, e.g. adding metallic elements into the charge.

### Experimental and modeling investigations

The general experimental process of the whole work is summarized in Figure V.



Figure V General experimental process of the whole work

#### • Numerical simulation

The Spim model was applied to predict the impurity concentration distribution profiles by considering the parameters of distribution coefficient (k), zone length (Z) and zone passes (n) due to its high reliability and simplicity. The application process is firstly to import the model into Matlab, which means the Equation I is to be expressed in the form of program code. The impurity distribution was then to be automatically predicted by running Matlab with assigning the desired values of k, Z and n. Zone length can be varied at each pass and the impurity reduction varies accordingly as the zone length changes. Figure VI shows an exemplary relation of the impurity reduction versus zone length when the ratio and k both are equal to 0.5. It can be seen that the highest impurity reduction at the first pass is obtained when the zone length is equal to the length of the whole bar, i.e. when an unidirectional solidification appears, similar to the report of [82]. Moreover, it clearly shows that the optimum zone length in each pass decrease as the zone passes increases, whose results are listed in Table I.



Figure VI Influence of the zone length variation in the impurity reduction in each pass when the ratio = 0.5 and k = 0.5; the calculation of impurity reduction in each pass is based on the acquisition of the optimum zone length (at which maximum impurity reduction appears) in the last zone pass.

Table I The optimum zone length at each pass for 50 passes of zone refining in the case of k = 0.5 and ratio = 0.5

Zone passes	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Optimum Z (×L)	0.95	0.34	0.22	0.19	0.17	0.15	0.14	0.13	0.12	0.11	0.1	0.1	0.1	0.09	0.09
Zone passes	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Optimum Z (×L)	0.08	0.08	0.08	0.08	0.07	0.07	0.07	0.07	0.07	0.06	0.06	0.06	0.06	0.06	0.06
Zone passes	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Optimum Z (×L)	0.06	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.04	0.04	0.04
Zone passes	46	47	48	49	50										
Optimum Z (×L)	0.04	0.04	0.04	0.04	0.04										

Considering the slight difference between the optimum zone length in the case of impurities with different k, as well as for the better operability in regulation of the zone length in practical production process, the optimum zone length in the first 20 passes is suggested to be adapted (based on the results in Table I). The results are presented in Table II, and shown to be independent from the impurities.

Table II Suggested practical zone length in 20 passes of zone refining for all impurities

Zone passes	1	2	3	4	5	6	7	8	9	10
Optimum Z (×L)	1	0.35	0.2	0.15	0.15	0.15	0.1	0.1	0.1	0.1
Zone passes	11	12	13	14	15	16	17	18	19	20
Optimum Z (×L)	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05

#### • Zone refining of Aluminum

An industrial-scale horizontal zone melting refining equipment equipped with one single inductive heater (heating coil with width of 5 cm) was utilized in this work, as seen in Figure VII. It consists of one movable heater unit, one big quartz tube, vacuum system, one infrared camera, a water cooling system and two control panels (intern and extern). The detailed specification of the equipment has been presented in Table III. The quartz tube chamber can be pumped to be less than 1 mbar, meanwhile Ar or N<sub>2</sub> are available as protective atmosphere. The infrared camera was mounted on the heater unit and moves along with the induction coil for detecting the temperature (650-1000 °C) of the charge during the process. This camera has a wide-angle lens of 4.8mm (horizontal field of view (HFOV) of 72.5) and a pixel resolution of 1280 × 1024. It measures the infrared radiation in the spectral range between 0.78 and 1.1  $\mu$ m, which allows the capture of the radiation passing through the quartz tube of the equipment.



Figure VII Zone refining device, equipped with an infrared camera

Table III Specification of zone refining equipment

Heater	Max power	Max frequency	Velocity	Vacuum	Quartz tube size
Induction coil	45 kw	10 kHz	0.01-1.99 mm/min	< 1  mbar	$\Phi$ 17× L180 cm

One graphite crucible (ash content < 200 ppm from CTG GmbH & Co KG) was used for Al as heating resource due to the weak inductive coupling between Aluminum and the electromagnetic field. The shape and size of the crucible are illustrated in Figure VIII.



#### Figure VIII Sketch of graphite crucible for zone refining of Al

#### (1) Realization of the zone length measurement with the infrared camera

During the running of the experiment, the camera was positioned with an inclination of  $45^{\circ}$  from the molten zone surface and a height of 400 mm respectively from the crucible region directly below the induction heating coil (see Figure IX). The heating coil was located in the middle of the crucible and remains stable. The charged Al bar was melted under a 400-mbar Argon-atmosphere, applying a power of 11 kW.

	Specification	DSLR Camera	IR Camera
	Supplier	Canon	Infratec
View angle: 45,3" h: 100 mm	Model	D600 with the lens EF-S 18–55mm	PIR uc SWIR HD
	View angle	45.3°	72.5°
	Heigth from object [mm]	500	400
	Inclination angle	45°	45°
	Sensor size (horizontal) – [mm]	14.9	7.04
	Max. horizontal resolution [pixels]	3456	1278
	Focal distance [mm]	18	4.8

Figure IX Position of IR and DSLR camera to detect the zone length (left) and their technical details (right)

To calculate the exact interface positions, the temperature values along the bar were exported to form a plot of temperature against the distance in pixel, as shown in Figure X. The region with temperature higher than 660 °C could be defined as the molten zone, when talking about pure aluminum. Meanwhile, the temperature gradient  $(\Delta T/\delta x)$  in the molten zone was derived as well.



Figure X Relation between thermographic image (a) and its corresponding temperature distribution profile in the molten zone along the Al bar (b)

Because of the special position of the cameras in terms of inclination and distance point of view leads to a perspective observation of the zone length, the transformation between pixel and mm was conducted essentially based on the geometrical illustration presented in Figure XI. With the help of Matlab, the zone length or positions of interfaces can be continuously detected when the IR camera is applied in the entire process. That means the zone length variation and moving velocities of interfaces can be also detected online through the application of the IR camera.





# (2) Variation of the crystal growth rate and of the zone length during zone refining of Aluminum

The position of the molten zone and the variation of the zone length are closely correlated with the freezing interface movement (crystal growth) and the dissolving capacity of impurities in the molten zone. It is simultaneously affected by many experimental conditions, like heating power, zone movement velocity, crucible size and material, charging material as well as the way of cooling. All of these lead to the challenge of the regulation of zone length. The application of a thermographic analysis system, as presented in last section, can deliver a variety of new information to ease the complexities in the measurement of zone length.

#### Experimental procedure

As generally zone refining process demands a very low velocity in order to allow an effective segregation of impurities, the movement velocities of heater were adjusted here as 1.2 mm/min as well as 0.8 mm/min. Due to an additional heating generated through the graphite (susceptor) mass at the end edges of the crucible, the starting position of the heater was set in the trials here at 20 cm after the edge. That assured a similar and stable heating effect all along the investigated area. The experiments with velocity of 0.8 mm/min ended at the moment the melting interface of the molten zone arrived at the end of the crucible. While the experiments of velocity of 1.2 mm/min were running over that moment and finished until the heater was located at the end of the crucible in order to additionally investigate the variation of zone length and crystal growth rate in the end section (unidirectional crystallization region). The sketch of the refining process is illustrated in Figure XII, where one pass was conducted for each experiment under 400 mbar Argon atmosphere. The 2N8 Aluminum, initially doped with 0.1 wt. % Fe as well as 0.1 wt. % Si was used as the initial material.



Figure XII Sketch of zone refining process for investigation of variation of zone length and crystal growth rate

#### Results

Figure XIII illustrates the positions of melting as well as freezing interface during the continuous movement of the heater along the aluminum bar. The zone length (difference of positons of these two interfaces) shows that without changing the heating power the zone length is quite big at both ends and relatively stable at smaller values in the middle of the bar. Furthermore, it can be seen from Figure XIII that in the case of zone refining of aluminum,

the heater is always located in the middle of the molten zone. That is contributed to the low Prandtl number of Aluminum (low ratio of viscosity to the thermal conductivity), preferentially resulting in symmetrical molten zones [13].



Figure XIII Positions of the melting interface, freezing interface and heater against of time for the experiment with 11 kW - 1.2 mm/min, showing that the freezing- and melting interfaces moved nonlinearly

**Dependency of zone length on power and heater movement velocity:** The relationship of the zone length with the position of the heater as well as the position of the freezing interface at different power and velocities are represented Figure XIV. In general, the zone length varies even when the power and moving velocity of heater remain constant. The variation tendency is firstly decreasing and then increasing for all power and heater movement velocity combinations. The percentage difference of zone length between maximum and minimum can be depressed by increasing the power. Lowering the heater movement velocity delays the freezing interface position where the zone length becomes minimal.



## Figure XIV Zone length variation versus the position of the freezing interface for the heater movement velocity of 1.2 mm/min (a) and the heater movement velocity of 0.8 mm/min (b)

**Crystal growth rate variation:** It was found that that the crystal growth rate is not equal to the heater movement velocity, but fluctuates around the heater movement velocity. The fluctuation of impurity concentration profile after refinement mainly results from the variation of crystal growth rate.

#### (3) Influence of the zone length on the refining efficiency

An initial material – 2N8 pure Al including 0.1 wt. % Fe and 0.1 wt. % Si – was applied. Five zone passes were conducted for Spim's optimized zone length and constant zone length with usage of a one meter long graphite crucible. However, three zone passes were conducted for the optimized zone length in this work with usage of a 60 cm long graphite crucible due to the limitation of the minimal zone length the equipment could achieve. All experiments were conducted under 450 mbar Ar atmosphere with a heater moving velocity of 1.2 mm/min and the processes were recorded with the IR camera.

*Results:* this work-suggested zone length combination has highest refining efficiency and the refining efficiency after three passes with this zone length combination is at the same level of that achieved after five passes with other two zone length combinations, as presented in Figure XV.



Figure XV Comparison of Fe-removal efficiency between different zone length combinations after zone refining with three (a) and five passes (b)

#### (4) Influence of initial concentration on refining efficiency

Three-layer electrolysis pure (4N), - commercial pure (2N8)- and recycled Al (1N7) were first melted in an inductive furnace and then casted into Al bars (c.a. 1.3 kg) to be used as the charge in zone refining process. The choice of expected zone length is based on both the

theoretical optimized zone length suggested in this work as well as the experimental conditions. All experiments were conducted at rate of 1.2 mm/min for five passes.

*Results:* A 5N5-pure Al could be produced after five zone passes when using 4N-purity level of Al as initial material. In comparison between the commercial pure Al and the recycled one, the former refining efficiency is slightly bigger than the latter. But for both cases, less than 50 % reduction of total impurities could be achieved in the first half of the bar after five zone passes. It can be concluded that the refining efficiency of Al increases when the initial purity increases. It is suggested to use zone refining process to only produce high purity Al with high added economic value, at the same time using already pure enough Al as the initial material.

#### • Zone refining of Antimony

A commercial pure Antimony with a purity of 99.8 % was used as raw material in this work, whose chemical composition is presented in Table IV. An alternative way – i.e. vacuum distillation of Sb – was firstly investigated with the aim of reducing Pb and As content before deploying of zone refining. The As-poor product of vacuum distillation was then charged into zone refining process. A self-designed setup, providing N<sub>2</sub> gas flux as protective atmosphere, was used in this process. The As evaporation behavior under gas flux (or in another word, the possibility of As separation from Sb by introducing gas flux) was investigated as the first step during zone refining. As the next step, the experiments were conducted with the optimum zone length derived from numerical simulations. At the end, an innovative way to remove As through addition of some selected additives to form intermetallic compounds with As was tried in both vacuum distillation and zone refining processes.

Impurity	As	Pb	Bi	Cu	Fe	Na	Ni	Se	Те	Zn	S
Concentration	780	1200	< 10	32	80	21	< 10	< 10	< 10	< 10	16

Table IV Composition of initial commercial pure Sb (2N8) analyzed by ICP-OES (ppm)

The setup deployed for Antimony trials was a bit more complicated than that for Aluminum. It contained an inner small quartz tube with two outlets. The quartz crucible ((IOTA high purity, from TQS GmbH), L 60 cm  $\times \Phi$  6 cm) and the charge material were to be located in the inner tube, while the inner tube was placed in the outer quartz tube with a tiling angle (see Figure XVI). The application of the inner tube was not only for introducing N<sub>2</sub> gas flow as protective atmosphere, but also for protecting the outer tube from polluting by evaporated Sb, which would in favor avoid the difficulty in cleaning the outer tube. In addition, the gas flow is expected to carry away the evaporated Arsenic as well.



Figure XVI Setup of zone refining of Sb

#### (1) Separation behavior of As and Pb during vacuum distillation

The setup designed for the Antimony vacuum distillation consisted of a graphite crucible ( $\Phi$  12 cm, H 12 cm), a steel-made condenser, a collecting bowl located on the bottom of the condenser as well as a graphite aperture between them for transporting the evaporated Sb from the crucible into the condenser, as illustrated in Figure XVII.





For each experiment, 2.5 kg of Antimony charge material was deployed. Different temperatures as well as a variety of vacuum levels were selected for the trials in this work, whose details are represented in Table V.

No. of Experiment	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

Table V Experimental parameters of the conducted trials

**Results:** Different mass ratios of Antimony were distilled into condenser depending on the applied temperature, vacuum level and dwelling time. The most of the distilled Sb was condensed in the condenser and comparatively only a minor amount of that was condensed on the wall or dropped into the collecting bowl. The concentration of Arsenic and Lead in the condenser and the residue respectively as well as the calculated mass ratio of distilled Sb in each trial are presented in **Table VI**. As expected, higher temperatures with lower residual pressure level and longer dwelling time lead to an increased Sb-distillation.

No. of Experiment	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)*	3900	33	71.73 %

Table VI Concentration of As and Pb in residue and condenser after vacuum distillation and the calculated mass ratio  $% \left( {{\left[ {{{\rm{C}}} \right]}_{{\rm{C}}}} \right)$ 

Note: \* 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.

The results of Pb consisted well with the theoretical predictions. The concentration of Pb in the condensed Sb was reduced for all experiments to less than 30 ppm from the original concentration of 1200 ppm. The removal effect of Arsenic seems to be dependent on the mass ratio of unwanted co-distilled Sb, as illustrated in Figure XVIII, in an exponential relationship. The concentration of As in the Sb-product (crucible residue) is easy to be reduced to about 450 ppm from the initial composition of 780 ppm. As the increase of distilled Sb, it ranges from 491 ppm with 1.2 wt. % of co-distilled Sb to 20 ppm with 71.7 wt. % accordingly. The

reduction of the As-concentration in the Sb-product occurs simultaneously with the loss of Sb. This phenomenon leads to a contradiction between effective As-separation and higher production yield.



Figure XVIII Correlation of As-concentration in the residue with the mass ratio of distilled Sb

# (2) Influence of the heater moving velocity on the refining efficiency of Antimony zone refining

The Sb residues produced from vacuum distillation under low temperature and high pressure, with composition as listed in Table VII, were applied as the initial materials. The three major impurities in initial Sb – Pb, As and Fe – were selected as the reference elements to evaluate the refining efficiencies under different moving velocities. The As evaporation behavior under different holding times and gas fluxes was firstly investigated. Then there different levels of moving velocities (2, 1 and 0.5 mm/min) were tested during zone refining process. Moreover, the Spim model as well as the BPS model were respectively used to fit the experimental date for deriving the  $k_{eff}$  and to obtain the important factors of values of  $\delta/D$  and  $k_0$ .

Table VII Initial materials for investigating the influence of heater moving velocities on refining efficiency

No. of material	As	Pb	Bi	Cu	Fe	Na	Ni	Se	Te	Zn	S
а	430	1100	< 10	27	84	18	15	13	< 10	13	64
b	670	1100	10	30	82	< 10	17	14	< 10	14	67
с	380	1100	< 10	27	60	16	11	12	< 10	< 10	64
d	480	1200	< 10	22	75	13	< 10	11	< 10	< 10	83
e	840	1300	14	44	86	< 10	18	< 10	< 10	11	71

#### Experimental process

**Measurement of Arsenic evaporation:** A pure ceramic block was placed in the quartz crucible to form a 15 cm long section. This form of setup was to focus the heater power on a

limited area to increase the temperature and provide the As-evaporation (see Figure XIX). Material of No. a and b with different initial As concentration (see Table VII) were used to investigate the dependence of the evaporation rate on melting time as well as the effect of initial concentration on the evaporation behavior. The influence of gas flux in As evaporation was also determined on the material of No. a. The outgoing gas was led into an exhaust treatment system of the institute for environmental protection. The detailed experimental parameters are listed in Table VIII.



Figure XIX Sketch for measurement of As evaporation (a) and a photo during running of experiment (b) Table VIII Experimental parameters for measurement of As evaporation

No. of experiments	Material	Time (min)				Flux ra	ate (1 L/m	in, N <sub>2</sub> )
1	а	60	120	240	360		1	
2	b	60	120	240	360		1	
3	a		120			0.1	1	5

Zone refining of Sb under different heater moving velocities: Antimony blocks with a weight of around 1.5 kg were charged in the quartz crucible for preparing a Sb bar. The experiments were conducted under three different moving rates of the heater under 1 L/min  $N_2$  gas flux and each experiment ran for two zone passes. The materials of No. c, d and e in Table VII were used in this series of experiments. All experimental parameters were outlined in Table IX.

Table IX Experimental parameters of zone refining

No. of experiments	Material	Zone length (cm)	Moving rate (mm/min)	Number of pass
4	с	15 (0.25 L)	2	2
5	d	15 (0.25 L)	1	2
6	e	15 (0.25 L)	0.5	2

#### Results

**Evaporation of Arsenic:** Figure XX (left), show that for the initial concentration of 670 ppm, the As concentration reduces slightly as the melting time increases. Moreover, the As cannot be removed considerably when its concentration is 430 ppm or lower. Besides, the low reduction of As under different gas flux rates is illustrated in Figure XX (right). The effects of gas flux rate on the As reduction seem to be negligible, which means the separation of As depends on As evaporation from the Sb-surface instead of mass transport by the gas flux. All the above results demonstrate the difficulty in evaporation of As from Sb when As is diluted in Sb. The lower the As concentration in Sb is, the less the extent of the reduction is.



Figure XX As concentration of molten Sb versus melting time at flux rate of 1 L/min (left) and versus flux rate (right) in As evaporation measurement

**Effective distribution coefficients of impurities:** The  $k_{eff}$  of impurities are obtained by fitting the experimental concentration profiles with the simulated profiles based on the Spim model. The reuslts for Pb, As and Fe at each heater moving rates were summarized Table X. It can be seen that the sequence of difficulty in removal from Sb via zone refining is that Pb < Fe < As.

Impurity	Moving rate of heater (mm/min)	k <sub>eff</sub>	$\ln\left(rac{1-k_{eff}}{k_{eff}} ight)$
	2	0.15	1.73
Pb	1	0.10	2.20
	0.5	0.08	2.44
	2	0.80	-1.39
As	1	0.75	-1.10
	0.5	0.50	0.00
	2	0.30	0.85
Fe	1	0.20	1.39
	0.5	< 0.12	> 1.99

Table X Summary of keff of Pb, As and Pb at each heater moving rate

The effective distribution coefficient ( $k_{eff}$ ) is a function of equilibrium distribution coefficient ( $k_0$ ), movement velocity of molten zone (f, i.e. heater moving rate) and ratio of thickness of diffusion boundary layer to the diffusion coefficient ( $\delta/D$ ), as interpreted in BPS model. But it can be transformed into another form as following:

$$\ln\left(\frac{1-k_{eff}}{k_{eff}}\right) = \ln\left(\frac{1-k_0}{k_0}\right) - f\delta/D$$
 Equation II

As seen from the above equation, the item of  $\ln \ln \left(\frac{1-k_{eff}}{k_{eff}}\right)$  has a linear relationship with the heater moving rate. The values of  $\delta/D$  and  $k_0$  can be obtained by the slop and intercept. The calculated  $\delta/D$  and  $k_0$  were presented in Table XI. It shows that the obtained  $k_0$  are consistent with the one shown in the reference [115] or calculated from Factsage, which verifies the effectiveness of the deployed process.

Impurity	$\delta/D$	$\ln\left(\frac{1-k_0}{k_0}\right)$	$k_0$	<i>k</i> <sub>0</sub> in reference [115]	k <sub>0</sub> from Factsage
Pb	0.47	2.67	0.06	0.06	0.05
As	0.17	0.93	0.72	0.64	0.66
Fe	0.73	2.26	0.09	0.03	<< 0.01

Table XI  $\delta \!\!\!/ D$  and  $k_0$  for Pb, As and Fe

#### (3) Influence of zone length on the refining efficiency of Antimony

The refining efficiency of Arsenic and Lead as main impurities was taken as focus of comparison between the refining efficiencies at different zone lengths. Figure XXI shows that the refining efficiency of As in the case of optimized zone length is higher than the constant one after five passes, while it is opposite in the case of Pb. The reduction percentage of As after 3<sup>rd</sup> pass for optimized zone length is higher than that after 5<sup>th</sup> pass of zone refining with a

constant zone length, as seen in Figure XXI (a). For the impurity of Pb, the concentration in two thirds of the bar with the constant zone length was reduced below detection limit after 5 zone passes. In comparison, only in one third of the bar is the Pb concentration reduced below the limit with the optimized zone length. The results of Pb is more convincing than that As in this case due to its non-volatility, which means the constant zone length led to a higher refining efficiency in comparison to the optimized one, which was contrary to the theoretical predictions. The contradiction is presumably due to the high real crystal growth rate, generated in the applied equipment when using an optimized zone length. This negative effect extinguished the beneficial effect of optimum zone length, as the real crystal growth rate essentially determines the impurity redistribution



Figure XXI Comparison of refining efficiencies of As (a) and Pb (b) in the case of constant- as well as optimized zone length

#### (4) Influence of additives on As-removal during both vacuum distillation and zone

#### refining processes of Antimony

Arsenic removal is the biggest challenge in Sb purification through either vacuum distillation or zone refining, as mentioned before. Arsenic is always co-evaporated with Sb during vacuum distillation, resulting in low removal efficiency. Regarding to zone refining, no practical method at present is able to significantly improve the As removal efficiency. One of the general suggested solutions is the additives, added to the charge while remelting to form non-volatile intermetallic compounds with Arsenic and to suppress its evaporation e.g. during distillation of Sb. In that case, not only lead but also Arsenic (in the form of intermetallic) would remain in the residue, while Antimony is removed by distillation. The derived As-poor product after vacuum distillation would be then charged into zone refining for further purifications. There is also another possibility to add those additives directly to the charge during zone refining. In the case of success, that would shorten the refining process, as the distillation setup can be then deleted. The appropriate additives should have firstly a high affinity to form an intermetallic with Arsenic rather than with Antimony. It should also be easily removed via fractional crystallization (e.g. zone melting process). Based on these two selection criteria, Aluminum and Zinc were selected here as additive elements through Factsage and free Gibbs energies of As-intermetallic.

#### **Experimental process**

**Vacuum distillation of Sb-Al and Sb Zn alloys:** The amounts of Al and Zn elements adding to the commercial pure Sb were 1 wt. % and 0.2 wt. % respectively, using the prepared master alloys. The content of these two additives were beyond the required amounts to completely transform As (around 800 ppm) into As contained intermetallic compounds based on the stoichiometric number of intermetallic. More Al was added to the Sb than Zn in consideration of the probable up-floating for Al, resulting in shorter reaction time, due to its much lower density (2.4 g/cm<sup>3</sup> at m.p.) compared to Sb (6.5 g/cm<sup>3</sup> at m.p.). This phenomenon was not expected to happen for Zn as its density (6.6 g/cm<sup>3</sup> at m.p.) is close to Sb. The experiments were conducted at 1100 k and 20 Pa for 60 min.

Zone refining of Sb-Al and Sb-Zn alloys: Sb - 0.1 wt. % Al and Sb - 0.1 wt. % Zn alloy blocks were firstly produced using the above obtained master alloys. The block of Sb-Al alloy was then broken down into pieces for charging in a quartz crucible. Due to the harmfulness of zinc on quartz, a graphite crucible was used for melting Sb-Zn alloy. The Sb-Al and Sb-Zn bars were formed by meting the pieces in zone refining equipment. The produced bar was then refined at the heater moving velocity of 1 mm/min under N<sub>2</sub> gas flux for two zone passes, using the zone length of 0.25 L.

#### Results

**Vacuum distillation of Sb-Al and Sb Zn alloys:** A significant drop of distilled Sb (19.2 wt. %) took place with the addition of Al, compared to the experiment without additive (71.7 wt. %), as seen in Table XII. This was assumed to be due to the formation of a layer on the surface of melt and hence suppressing the evaporation of Antimony. In this case, stronger vacuum levels and/or higher temperatures would be required for more efficient distillation. The As concentration in residue of Al-added experiment was still higher than that without additive. That is because of the co-evaporation of As accompanied with the massive evaporation of Sb in the latter case. Nevertheless, the mass of distilled Sb with Al after 60 min

was coincidentally almost the same with that of the experiment without additive after 30 min (see Table XII). It shows that the amount of Arsenic in the condensed Antimony was reduced 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 concentration value of this impurity was still as high as 1100 ppm and obviously far away from the requirement of 5N pure Sb (C(As) < 1.5 ppm).

Table XII	Comparison	between	vacuum	distillations	of Sb	doped	with	Al and	without	additive	under
condition o	of 1000 K and	20 Pa									
-											

Sb - 1 wt. % Al (60 min)	Concentration (ppm)	Pure Sb without Al* (60 min)	Concentration (ppm)	Pure Sb without Al* (30min)	Concentration (ppm)	
Ratio of distilled Sb (wt. %)	19.22 %	Ratio of distilled Sb (wt. %)	71.73 %	Ratio of distilled Sb (wt. %)	19.18 %	
As in top of residue	1800	As in residue	20	As in residue	220	
As in bottom of residue	69	As in residue	20	As in residue	230	
As in condensed Sb	1100	As in condensed Sb	130 or 1800	As in condensed Sb	3300	
Pb in residue	1550	Pb in residue	3900	Pb in residue	1100	
Pb in condensed Sb	39	Pb in condensed Sb	33	Pb in condensed Sb	12	
Al in top of residue	3530					
Al in bottom of residue	940					
Al in condensed Sb	< 10					

The last vacuum distillation trial was conducted using Zinc as additive

Zone refining of Sb-Al alloy: Figure XXII(a) obviously confirms the much higher refining efficiency achieved by the additive. Moreover, it is interesting to see that the As concentration decreased from the beginning to the end along the bar, which is converse to the expected As concentration distribution after zone refining as its distribution coefficient (k) is below one. Al was efficiently reduced at the beginning of the bar and was enriched in the end, as predicted according its small k (much lower than one). Considering the opposite concentration variation tendencies of As and Al (see Figure XXII(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. Aluminum additive reacted with Arsenic to form AlAs intermetallic. The so called Aluminum Arsenide has a very high melting temperature of around 1740 °C as well as a density of about 3.81 g/cm<sup>3</sup>, both enabling this process separate them efficiently from a molten Antimony substrate. That resulted in low concentrations of As at the bottom of the bar, due to its accumulation at the top. Simultaneously, Aluminum was 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 were hence formed at the end of the bar than at the beginning because of the higher reaction chance between Al and As atoms. That means more As was captured to go up to the surface at the end of the bar, leaving less amount of As at the bottom. This tendency was more remarkable as more zone passes are conducted, as seen in Figure XXII(b).



Figure XXII Comparison of As concentration distributions along the bar between the trials with and without Al-additive (a) and comparison of As and Al concentration distribution along the bar after two passes (b)

**Zone refining of Sb-Zn alloy:** The addition of Zn did not effectively improve the removal of As during zone refining process, the same as during vacuum distillation process.

#### Conclusion

The know-how to improve its refining efficiency is always the core part of the investigations in this area. The optimization of zone length as a considered fundamental parameter deserves special interests due to its huge potential in improving the refining efficiency and shortening the time required to reach the purification limit. In this work, numerical simulation based on Spim model was used to predict the optimum zone length. Al and Sb were selected as the research objects to verify the effectiveness of the results due to their important applications in high purity level in current industry as well as notable difference in their physical properties. In the case of zone refining of Al, the zone length and the crystal growth rate were successfully measured through application of an infrared camera. The influence of initial impurity concentrations on the refining efficiency were investigated too; In the refining process of Sb, vacuum distillation, with and without addition of metallic elements, was surveyed mainly to remove Arsenic. The findings from those efforts will help to improve the refining efficiency of these two metals besides the usage of optimized zone length in the future. The main conclusions from this work can be concluded as following:

- 1. The optimum zone length combination was derived through a numerical simulation based on Spim model, which is theoretically independent of the impurities.
- 2. Application of an infrared camera was shown to be a good way to characterize the whole zone refining process. It enables the measurement of the real-time zone length, crystal growth rate, etc., allowing an innovative view to interpret the purification results.
- 3. The parameters of the zone length and the crystal growth during zone refining of Al were not stable, when using constant power and heater moving velocity. Instead, they varied with a tendency of being decreased as well as increased afterwards.
- 4. The efficiency of zone refining increases when applying higher initial purity of Al. Although a significant purification can take place in zone refining of low purity of Al too, it is not worthy to use this technique in this case due to the low production yield and high time-consumption.
- 5. Vacuum distillation is an effective way to separate Pb from Sb. But the separation efficiency of As from Sb is limited. It actually depends on the mass of the distilled Sb, which results to the point that when aiming high refining efficiency, the production yield should be low.
- 6. One of the main impurities, Lead can be efficiently removed during zone refining process of commercial pure Sb, which is contrary to the other main impurity, As. A purity level of 3N8 or 3N9 Sb can be easily produced after five passes of zone refining.

Addition of metallic Al into Sb to form intermetallic compound with As can considerably improve the separation efficiency of As from Sb both in vacuum distillation and zone refining processes. Especially, the latter case is more attractive as it simplifies the traditional two-steps, i.e. vacuum distillation followed by zone refining, and reduces it into one step (only zone refining).