Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Purification of Tin by a New Method of Zone Refining

Y. Hoshino[a]; T. Utsunomiya[a]
[a] RESEARCH LABORATORY OF ENGINEERING MATERIALS TOKYO, INSTITUTE OF TECHNOLOGY 4259 NAGATSUTA, YOKOHAMA, JAPAN

To cite this Article Hoshino, Y. and Utsunomiya, T.(1980) 'Purification of Tin by a New Method of Zone Refining', Separation Science and Technology, 15: 8, 1521 — 1531
To link to this Article: DOI: 10.1080/01496398008055604
URL: http://dx.doi.org/10.1080/01496398008055604

SEPARATION SCIENCE AND TECHNOLOGY, 15(8), pp. 1521–1531, 1980

Purification of Tin by a New Method of Zone Refining

Y. HOSHINO and T. UTSUNOMIYA

RESEARCH LABORATORY OF ENGINEERING MATERIALS
TOKYO INSTITUTE OF TECHNOLOGY
4259 NAGATSUTA, MIDORI-KU, YOKOHAMA, JAPAN

Abstract

The purification of tin by a new method of zone refining is described. The method is characterized by alternating high-speed clockwise and anticlockwise rotations (0 to 3000 rpm) of the containing tube at short intervals (0.5 to 10 sec). The experimental parameters which affect the degree of purification were investigated in some detail. The concentration of major impurities was lowered by about two orders of magnitude by 20 zone passes under standard operating conditions.

INTRODUCTION

Numerous theoretical and experimental zone refining studies have been reported since Pfann made an application of the technique to germanium (*1*). In our laboratory an apparatus has been developed which reduces a time-consuming process to a minimum as proposed by Bollen (*2*). This apparatus is especially intended to purify substances which have melting points up to 1000°C. The purpose of the present paper is to investigate the effect of parameters on the purification of tin.

EXPERIMENTAL APPARATUS

In designing zone refining apparatus, it is necessary to obtain the required amount of material of specified purity with a minimum of time and expense. The parameters that have to be taken into account are (a) zone length l, (b) interzone spacing i, (c) number of zone pass n, (d) zone travel rate f, and (e) diffusion layer thickness δ. In this work $l = 3$ cm, $i = 5$ cm, $n = 1$ to 20, and $f = 0.23$ to 1.7 mm/min. The value of δ is a function of the properties of the liquid, the rotation velocity of the container, and the interval between alternating rotations.

Kirgintsev (*3*) and Iwano (*4*) suggested that the rotation of the container is one of the most effective methods of promoting the stirring effect.

A schematic diagram of the apparatus is shown in Fig. 1. The apparatus is composed of three main parts: (a) heaters and heater control units, (b) clockwise and anticlockwise rotation mechanism of the container up to 3000 rpm at intervals of 0.5 to 10 sec, and (c) heater driving unit. The mechanism of zone travel is simple. As an Archimedes' cam (L) rotates, a brass pole which is connected to the heaters goes up at a constant speed.

Five resistance heaters are placed around the container at 5 cm intervals. The zone heaters currently in use are helical coils of Nichrome wire bent into about 25 mm i.d. circular configuration. The heaters are controlled independently, and the power of the four upper heaters is somewhat less than that of the bottom heater which forms a new zone. In this work, however, only the bottom heater was used to see the effect of experimental parameters on the purification of tin. The container is cooled by compressed air streaming from sets of orifices (C) which protrude from the brass pole, further indicated as coolers. Heaters and coolers gradually move 5 cm upward and fall rapidly to the initial position, thus transferring each zone to the upper heater.

The container is a Pyrex glass tube of 8 mm o.d. placed vertically and

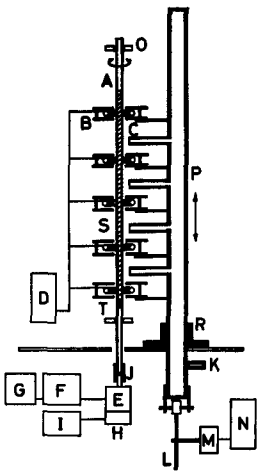

FIG. 1. Schematic diagram of the apparatus. (A) Pyrex glass tube, (B) heater, (C) orifice for air blast, (D) heater control unit, (E) dc motor, (F) timer switch, (G) dc source, (H) tachometer, (I) revolution counter, (J) coupling device, (K) compressed air inlet, (L) cam, (M) ac motor, (N) interrupter, (O) glass tube supporter, (P) brass pole, (R) supporter, (S) sample, (T) graphite stopper.

closed at its end by a high purity graphite rod inserted about 5 cm into the tube.

Another feature of this apparatus is the direction of zone travel. Zones moving from the bottom to the top guarantee a good contact of liquid and solid at the freezing interface, and this satisfies the essential conditions for obtaining a smooth interface. Of course, the upward zone movement necessitates special precautions for preventing breakage of the containers during zoning. Many attempts have been made to prevente the breakage of containers (*5*). The details of the apparatus are reported elsewhere (*6*).

STARTING MATERIALS

Three tin mixtures were used in this work.

(a) $\geqslant$99.99% pure tin shot from Wako Pure Chemical Ind. Used for multipass experiments.
(b) Sn + 1 wt-% Pb. Pb was added because (1) it is the most common impurity contained in commercially available tin and (2) it is relatively easily determined by flameless atomic absorption spectrophotometry (AAS). This composition was used to obtain the optimum or standard operating conditions.
(c) 1000 ppm Pb, Fe, Cu, Cd, and Bi added. Used to investigate the behavior of impurities which commonly exist in tin.

PREPARATION OF SAMPLES

At first 500 g of the starting material tin shot was etched in dilute HCl to remove oxide film, washed with deionized water, and then rinsed with ethanol. The dried material was melted in a high-purity graphite crucible of 40 mm i.d. and 100 mm depth in vacuum. During this process the oxide which was included in the bulk of the tin shot formed a thin layer on the melted surface. A desired amount of melted tin was sucked up in a glass tube of 6 mm o.d. in a nitrogen atmosphere. The solidified tin was then transferred to a larger glass tube and sealed at about 0.1 Pa. Although a small amount of oxide was taken in the sample, the oxide layer was easily collected on the top of the tin bar by melting the whole sample. This did not affect the results of the experiments.

Armington (*7*) stated that the oxide could act as a precipitating medium for impurities in the tin, and that several elements are present in a higher concentration in the oxide layers than in the bulk of the tin. However, in this work, zoning without the removal of the oxide film of the starting tin shot gave a scattered impurity distribution.

ANALYSIS OF THE ZONE REFINED TIN

The determination of impurities was conducted in the following manner. Approximately 100 mg of filings was taken from near the starting point of zoning (about 2 to 3 mm) in the determination of the effective distribution coefficient and every 5 mm in the determination of impurity distribution in multipass experiments. The sample was dissolved in 10 mL of 10% tartaric acid, 2 mL of HCl, and 1 mL of HNO_3, as directed by Varian Techtron (*8*). Then the solution was diluted with 0.1 *N* HNO_3 to 100 mL. The impurities in the sample were determined by graphite furnace AAS.

EFFECTIVENESS OF ALTERNATING ROTATION

Figure 2 shows the effectiveness of stirring when a mixture of naphthalene

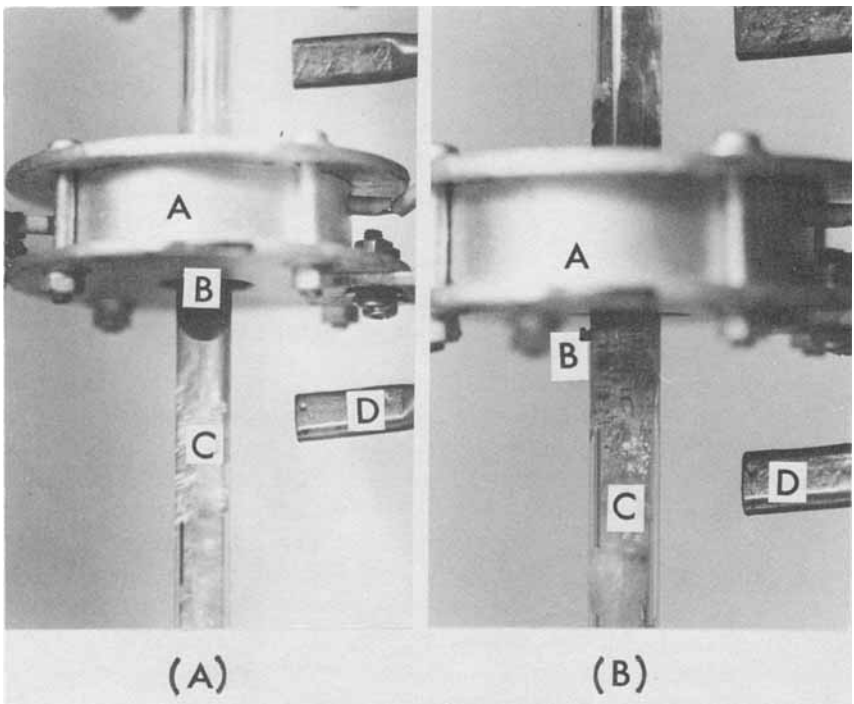

FIG. 2. A: Stirring by alternating rotation with rotation velocity = 1000 rpm and alternating period = 1 sec. B: Stirring by free convection. Effectiveness of stirring in zone refining. Sample: naphthalene-sudan red (100 ppm). Zone travel rate: 0.2 mm/min. (A) Heater, (B) region concentrated in Sudan Red, (C) purified naphthalene, (D) orifice for air blast.

and Sudan Red (impurity) was zoned as an example. It is apparent from the figure that the melt region concentrated in the impurity forms a clear ellipsoid of gyration. The transparent part is purified solid naphthalene. By transferring the melt to the upper heater, the impurity can be collected to the upper end. In the present case, although it is uncertain whether a clear solid–liquid interface in Fig. 2 (A) forms or not, we suppose a similar situation was realized because the degree of purification was far greater in alternating rotation than in free convection as described below.

RESULTS AND DISCUSSION

The degree of purification can be increased by stirring the melt. This is well understood from Burton, Prim, and Slichter's equation (*9*):

$$\frac{k_0}{k} = k_0 + (1 - k_0) \exp [-f\delta/D] \tag{1}$$

where k and k_0 are the effective and equilibrium distribution coefficients, respectively, f is the zone travel rate, δ is the diffusion layer thickness which decreases as stirring is increased, and D is the diffusion coefficient of the solute in the melt. When f decreases to zero, k approaches k_0.

OPTIMIZATION OF OPERATING CONDITIONS

The following experiments were performed to evaluate the influence of some of experimental parameters on the degree of purification. The degree of purification was characterized by the effective distribution coefficient k which was obtained in the following manner. The mean concentration of impurity in the charge is C_0. As the zone begins its advance, the initial concentration to freeze, at $x/L = 0$, is kC_0. Thus k is approximately obtained by taking the ratio of the concentration of the initially purified charge to that of the original charge. In this alternating rotation method, no constitutional supercooling nor striations in the purified tin bar were observed because of constant mechanical stimuli and the air blast.

Effect of Rotation Velocity and Alternating Period of Rotation

Although we were unable to observe the state of fluid flow of the melt, it is obvious that there is a time lag for the fluid flow of the melt as it follows the rotation of the solid body because the degree of purification decreased to near a rest value when the melt rotated synchronously with the glass tube. Therefore the stirring effect is believed to be affected

markedly by both the difference of rotation velocity of the solid body and the melt, and its time of duration. Yoshida (*10*) reported that the stirring effect depended greatly on the maximum rotation velocity of the container and the time duration of angular acceleration. It is reasonable to assume that the stirring effect increases as the rotation velocity of the container increases. However, Fig. 3 shows that the stirring effect diminishes above 500 rpm.

According to Burton (*8*) and Wilcox (*11*), δ is a function of the kinematic viscosity of a sample ν, the angular velocity of a rotating solid ω, and D:

$$\delta = 1.6D^{1/3}\nu^{1/6}\omega^{-1/2} \tag{2}$$

When Eq. (2) is substituted in Eq. (1), we obtain

$$\log\left(\frac{1-k}{k}\right) = C_1 - C_2\omega^{-1/2} \tag{3}$$

where $C_1 = \log(1 - k_0/k_0)$ and $C_2 = 1.6D^{-2/3}\nu^{1/6}$. These are constant if the zone travel rate and the substance are determined.

Yoshida confirmed that Eq. (2) is applicable even in the alternating rotation method if ω is corrected by taking into account the maximum rotation velocity and its time of duration. However, the relation between $\log(1 - k/k)$ and $(\omega_{\text{corrected}})^{-1/2}$ deviated from a straight line in the present work. Mechanical turbulence, such as vibration or deflection of the glass tube during rotation, affected k.

The effect of an alternating period of rotation on k is presented in Fig. 4. The alternating period was varied from 0.5 to 10 sec. The degree of

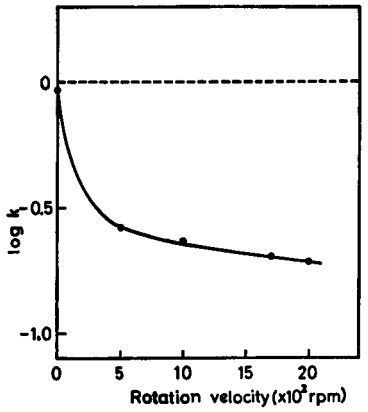

FIG. 3. Effect of rotation velocity on the effective distribution coefficient. Zone travel rate = 0.23 mm/min. Alternating period = 1 sec.

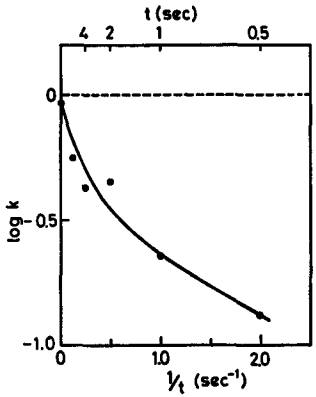

FIG. 4. Effect of alternating period on the effective distribution coefficient. Rotation velocity = 1000 rpm. Zone travel rate = 0.23 mm/min.

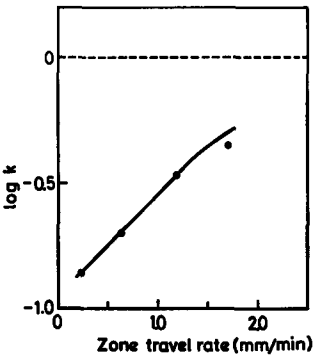

FIG. 5. Effect of zone travel rate on the effective distribution coefficient. Rotation velocity = 1000 rpm. Alternating period = 1 sec.

purification increased as the alternating period decreased. It is important that the direction of rotation of the glass tube be alternated before the melt reaches solid body rotation.

Effect of the Zone Travel Rate

The effect of the zone travel rate on k is presented in Fig. 5. The effective distribution coefficient decreased almost linearly as the zone travel rate decreased. By rearranging Eq. (1):

$$\ln\left(\frac{1-k}{k}\right) = \ln\left(\frac{1-k_0}{k_0}\right) - f\delta/D, \qquad \text{for } k < 1 \tag{4}$$

Therefore the values of k_0 and δ/D can be obtained by measuring k in the charge purified at different zone travel rates with identical stirring conditions and by plotting $\ln(1 - k/k)$ against the zone travel rate f. The result is shown in Fig. 6. By using the method of least squares, the value of δ/D was obtained as 1.1 and the equilibrium distribution coefficient k_0 as determined from extrapolation of the zone travel rate to zero was 0.11. This value is in good agreement with that from the phase diagram (*12*).

OPTIMUM AND STANDARD OPERATING CONDITIONS

From the above discussion, the best degree of purification is achieved when a high rotation velocity, a short alternating period of rotation of the container, and a slow zone travel rate are applied. Therefore, the following conditions are recommended as optimal in this work:

rotation velocity	2000 rpm
alternating period	0.5 sec
zone travel rate	0.23 mm/min

However, taking into account the mechanical stability of the apparatus and the zone refining efficiency which, of course, is a function of the degree of purification and the time required for purification, the following conditions are suitable for routine work (standard operating conditions):

rotation velocity	1000 rpm
alternating period	1 sec
zone travel rate	0.83 mm/min

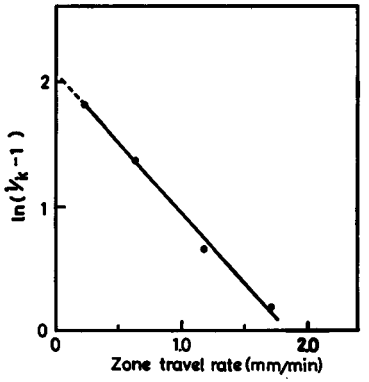

FIG. 6. Determination of the equilibrium distribution coefficient of lead in tin.

EFFECTIVE AND EQUILIBRIUM DISTRIBUTION COEFFICIENT

Table 1 gives a summary of measurements of the effective distribution coefficient for some impurities obtained under standard operating conditions. The equilibrium distribution coefficient estimated roughly from phase diagrams and the effective distribution coefficient reported by Armington (*7*) and Pfann (*13*) are compared with experimental data. The values obtained in this work indicate that these are in good agreement with the trend of Pfann's results and are also in good agreement with the equilibrium distribution coefficient.

MULTIPASS EXPERIMENTS

The effect of the number of zone passes on the degree of purification is presented in Fig. 7. It is obvious that the degree of purification increases as the number of zone passes increases. If theoretical purification were to be achieved, it would be expected that the initial concentration of impurities would decrease at a rate of k^n, where n is the number of zone passes. However, in general, theoretical purification cannot be achieved by various kinds of mechanical and thermal turbulence.

In addition to single pass zoning, several multipass experiments were performed to see if the apparatus works well. The tin in this case was subjected to more than 10 zone passes. Figure 8 shows the distribution

TABLE 1

Comparison of Equilibrium Distribution Coefficients with Effective Distribution Coefficients

Element	k_0, Ref. *12*	k		
		This study[a]	Ref. *7*	Ref. *13*
As	~0.1			
Bi	0.2		4.5	
Cd	0.3	0.5		
Cu	~0.1	0.12	1.1~2	<1
Fe	~0.1		2.5~3.3	<1
In			1.7~2.3	
Ni			<0.6	
Pb	0.08	0.4	2~3	<1
Sb	1.6			
Zn	0.1			

[a]Operating conditions: rotation velocity = 500 rpm, alternating period = 1 sec, zone travel rate = 0.23 mm/min, zone length = 3 cm, interzone spacing = 5 cm.

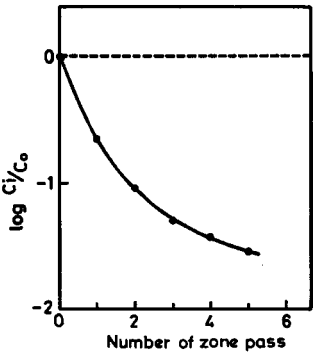

FIG. 7. Effect of number of zone pass on the degree of purification. C_i in the vertical axis indicates the concentration of impurity in the initially purified charge.

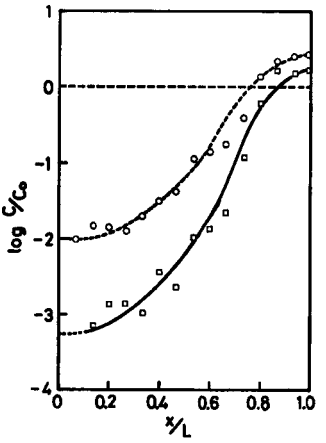

FIG. 8. Impurity distribution after 20 zone passes. Initial concentration of impurities = 1000 ppm. Rotation velocity = 1000 rpm. Alternating period = = 1 sec. Zone travel rate = 0.23 mm/min. (○) Pb. (□) Cu.

of impurities when Sample 3 was used. The major impurities (Pb, Cu, and Cd) show a 100-fold decrease as a result of 20 zone passes. Similar behavior has been observed for undoped Sn, although analysis at low concentrations may not be too reliable. The time required for purification is ~10 hr under standard operating conditions.

REFERENCES

1. W. G. Pfann, *Trans. AIME, 194*, 961 (1952).
2. N. J. G. Bollen, M. J. Van Essen, and W. M. Smit, *Anal. Chim. Acta, 38*, 279 (1967).
3. A. N. Kirgintsev and E. G. Avrakumov, *Sov. Phys. Solid State, 10*, 375 (1965).

4. T. Iwano, T. Yokota, and T. Oosawa, *Nippon Kagaku Kaishi*, p. 1783 (1972).
5. G. Oneal, Jr., *Rev. Sci. Instrum.*, *34*, 1150 (1963).
6. T. Utsunomiya, T. Yasukawa, and Y. Hoshino, *Rep. Res. Lab. Eng. Mater.*, *1*, 120 (1976).
7. A. F. Armington and G. H. Moates, *Ultrapurification of Semiconductor Materials, Proceedings of a Conference*, Boston, Massachusetts, 1961, p. 502.
8. Varian Techtron, *Analytical Methods for Flame Spectroscopy*, 1972.
9. J. A. Burton, R. C. Prim, and W. P. Slichter, *J. Chem. Phys.*, *21*, 1987 (1953).
10. T. Yoshida, H. Kobayashi, and K. Ueno, *Jpn. Analyst*, *23*, 769 (1974).
11. M. Zief and W. R. Wilcox, *Fractional Solidification*, Vol. 1, Dekker, New York, 1967.
12. M. Hansen, *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
13. M. Tanenbaum, A. J. Goss, and W. G. Pfann, *Trans. AIME*, *200*, 762 (1954).

Received by editor March 7, 1980