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THERMODYNAMIC ANALYSIS AND EXPERIMENTS ON VACUUM SEPARATION OF Sn-Sb ALLOY

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Abstract

In this study, the saturated vapor pressures of tin (Sn) and antimony (Sb), the separation coefficient β and the vapor-liquid phase equilibrium of Sn-Sb alloy were theoretically analyzed, which demonstrate that it is possible to separate Sn and Sb by vacuum distillation. The process parameters of vacuum distillation, including the distillation temperature, distillation time and alloy mass (thickness of raw materials) on the direct yield of Sn and the content of Sn in liquid phase were investigated by using single factor experiments. The preliminary results show that the direct yield and the content of Sn are 98.77 wt.% and 96.01% with the optimized distillation conditions of a distillation temperature of 1473 K, a distillation time for 45 min and a Sn-Sb alloy mass of 125 g (thickness of 8mm). The distillation parameters in the study provide effective and convenient conditions on separation of Sn-Sb alloy.

Introduction

As one of the earliest metals that human discovered and used, Sn is widely used and plays an indispensable key role in military industry and modern cutting-edge technology areas [1, 2]. Based on the unique physical and chemical properties, Sn and Sb were involved in a national strategy aiming at accelerating the cultivation and development of strategic emerging industries including the energy conservation and environmental protection, next generation information technology, biotechnology, new energy, new energy vehicles, high-end equipment manufacturing, and new materials industries [3]. However, the contradictions between the remaining productive life and demands of Sn and Sb resourses are becoming increasingly acute.

Large numbers of waste Sn-based alloys will be recycled from electroplates, solders and other various industries in China and elsewhere due to Sn was usually used to produce alloys with other metals, which will causes serious resources waste and environment pollution if the

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alloys cannot be recycled cleanly and efficiently. The common refining techniques to remove Sb from Sn-Sb alloy are pyrometallurgy and electrolytic method. There are some serious problems in conventional processs. The conventional process has some disadvantages such as procedure complex, lower direct rate of tin, bad state of operation, evident environment pollution [4-6]. Over past decades, vacuum distillation has been studied and successfully used in refining and recovery of various nonferrous crude metals and alloys by Kato [7], Gopala [8], Zhan [9], and Ali [10, 11] etc., and the area of its application is being extended rapidly.

The separation of Sn-Bi, Sn-Pb, Sn-Sb, Ag-Pb-Sb alloys by vacuum distillation has been studied in China and elsewhere for a long time, which has been described in numerous works [12-16]. The purpose of this study, therefore, was to obtain more obvious and optimum process parameters of Sn-Sb alloy during vacuum distillation, which will provide experience used for industrial production.

Theoretical analysis

Saturated vapor pressure

Crude metal can be separated from impurities by vacuum distillation due to the different properties of components contained when vaporizing and condensing. The basic principle for vacuum separation of crude metal is the difference in saturated vapor pressure of each element in a finite temperature. The saturated vapor pressure of pure components of these two alloys can be calculated from the following equation [17]

$$\lg P^* = AT^{-1} + B\lg T + CT + D \tag{1}$$

Where P^* represents the saturated vapor pressure of pure components; A, B, C and D are the evaporation constants of components of alloys, which were available in Ref. [17].

Separation coefficient

Dai [17] introduced the separation coefficient, viz. β, to determine whether two components can be separated from each other by vacuum distillation according to the composition difference between vapor phase and liquid phase. To estimate the feasibility of separation of alloys by vacuum distillation, the following equation from theoretical derivation for *i*–*j* binary alloy was derived, that is

$$\beta = (\gamma_i / \gamma_j) \cdot (P_i^* / P_j^*) \tag{2}$$

Where γ_i and γ_j are activity coefficient of *i* and *j* components; P_i^* and P_j^* are saturated vapor pressure of *i* and *j* in pure state, respectively. With a known value of β, the ratio of vapor densities of *i* and *j* can transform into

$$\frac{\rho_i}{\rho_j} = \beta \frac{\omega_i}{\omega_j} \tag{3}$$

Where ρ_i/ρ_j is the mass ratio of component *i* in the vapor phase to that of *j*, and ω_i/ω_j is the mass ratio of component *i* in the liquid phase to that of *j*, respectively. The separation of *i* and *j* could happen while $\beta > 1$ or $\beta < 1$, but it could not happen while $\beta = 1$.

After substituting activity coefficients γ_i and γ_j at different temperatures into Eq. (2), the separation coefficients can be easily calculated as shown in Fig 1., which indicates the content of Sb in gas is much higher than those in liquid. Therefore, Sb can be effectively concentrated in the gas phase by vacuum distillation.

Vapor-liquid phase equilibrium in vacuum distillation

For *i-j* alloy, the relationship between the mass fraction of *i* and *j* components in vapor and liquid phase can be respectively expressed as,

$$\omega_{i,g} + \omega_{j,g} = 1 \tag{4}$$

$$\omega_{i,l} + \omega_{j,l} = 1 \tag{5}$$

Where $\omega_{i,g}$, $\omega_{j,g}$ are mass fraction of *i* and *j* components in the vapor phase, respectively; $\omega_{i,l}$, $\omega_{j,l}$ are mass fraction of *i* and *j* components in the liquid phase, respectively.

When the two phases are in equilibrium, the mass fraction of component *i* in the vapor phase is related to the vapor densities of *i*, *j* components as follows [17].

$$\omega_{i,g} = \frac{\rho_i}{\rho_i + \rho_j} = \frac{1}{1 + (\rho_j / \rho_i)} \tag{6}$$

Substituting Eqs. (2) and (3) into Eq. (6), the mass fraction of component *i* in the vapor phase can be expressed as,

$$\omega_{i,g} = \left[1 + \left(\frac{\omega_{j,l}}{\omega_{i,l}} \right) \cdot \left(\frac{\gamma_j}{\gamma_i} \right) \cdot \left(\frac{P_j^*}{P_i^*} \right) \right]^{-1} \tag{7}$$

Where ω, γ, P^*, β are the mass fraction, activity coefficient, saturated vapor pressure, and separation coefficient, respectively. The relationship diagram of $\omega_{i,g}$–$\omega_{i,l}$ can be calculated by γ, P^* and a series of $\omega_{j,l}$ /$\omega_{i,l}$ at required temperatures, that is the vapor–liquid phase equilibrium diagram for *i*–*j* alloy system.

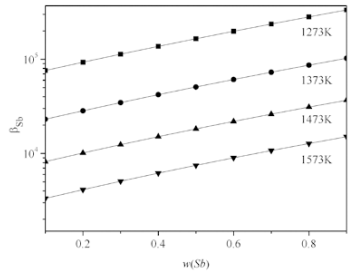

Fig 1. The separation coefficients of Sn-Sb alloy at different temperatures

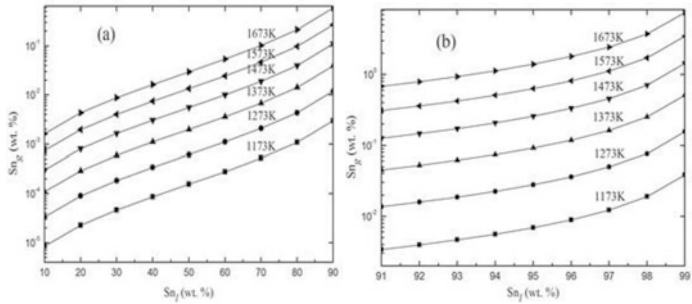

Fig 2. Vapor-liquid equilibrium diagram of Sn-Sb system (a) Sn_l=10-90 wt. %, (b) Sn_l=91-99 wt. %.

Based on Tao's the molecular interaction volume model (MIVM), a reliable and stable model in predicting thermodynamic properties of liquid alloys [18], the vapor-liquid equilibrium diagram of Sn-Sb system is shown in Fig 2. As it shows that the content of Sn in vapor phase, Sn(g), increases with increasing the distillation temperature and the content of Sn in liquid phase, Sn(l), which theoretically demonstrates the different content of Sn between Sn(g) and Sn(l) in a various range of distillation temperature.

Experimental

Raw materials

For all alloys (Sn 51.3 wt.%, Sb 48.7 wt.%), the tin (99.995 wt.%, YT Co., Ltd) and antimony (99.999 wt.%, YT Co., Ltd) were weighed out in the analytical balance, then arc melted under a high purity argon (99.999 wt.%, Messer®) atmosphere.

Equipment

The internal structure schematic diagram of the vacuum furnace used is shown in Fig.3. The vacuum system consists of mainly (1) Pit furnace, (2) Evaporator-Collector-Condenser set, (3) Retort-flange assembly, (4) Vacuum system using an oil pump, (5) Circulating water control system, and (6) Vacuum resistance furnace with two electrodes. A cylindrical crucible (ID × height = 60 × 100 mm) which consists of isostatic fine grain high density graphite (R-7340 of SGL Carbon, Germany) was used as the evaporator. The collector is a circular cold plate (surface area = 314 cm^2) made up of stainless steel.

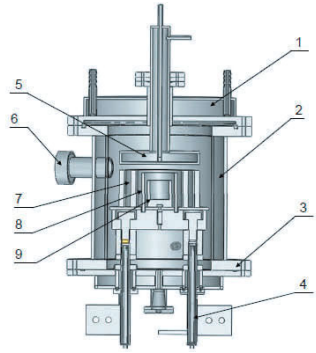

Fig 3. Internal structure schematic diagram of the vacuum furnace. 1. furnace lid; 2. furnace body; 3. furnace bottom; 4. electrode; 5. cold plate; 6. observation door; 7. heat holding cover; 8. heating unit; 9. graphite evaporator.

Experiments design

Learning from industrial practice, the major effects on this study include distillation temperature, distillation time, alloy mass (thickness of raw materials) and vacuum degree. With a stable equipment of 5 Pa below, however, the vacuum degree causes little effect. Therefore, the vacuum distillation was carried out for Sn-Sb alloy at the distillation temperature range of 1173-1673 K, distillation time range of 15-65 min and alloy mass range of 85g (4mm)–185g (14mm).

The temperature error of ± 3 K and the alloy mass error of ± 0.3 g were found due to

device limitation and operating error.

After each distillation experiment, the component content in the residual and volatile were analyzed by ICP-AES combined with chemical analysis method. The content of Sn in liquid phase (the component content in the residual) and the direct yield of Sn were taken as evaluation indexes. And the direct yield of Sn was defined as following equation,

$$\text{The direct yield of Sn} = (m_0 \times x)(m_1 \times y) \quad (8)$$

Where m_0 and m_1 are the raw materials and the mass of residuals, respectively; x and y are the content of Sn in liquid phase and the content of Sn in raw materials, respectively.

Results and discussion

Effect of distillation temperature

The vacuum distillation was carried out at the distillation temperature range of 1173 - 1673 K with a gradient of 100 K, distillation time of 35 min, and alloy mass of 125 g (8 mm). The relationship between components contents of products and temperature is shown in Fig 4..

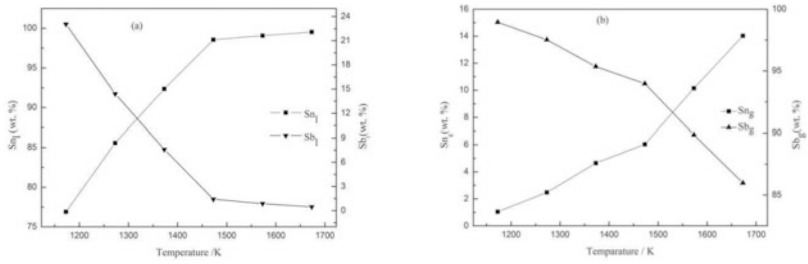

Fig 4. Effect of temperature on the component of (a) residue, (b) volatile

It can be seen from Fig 4. that the content of Sn and Sb in residue were76.89 wt. % and 23.05%, while in vapor phase, they were 1.05 wt. % and 98.95 wt. % at 1173 K. Owing to a quicker growth rate of the statured vapor pressure of Sb with the increasing temperature, the volatilizing quantity of Sb increases constantly, leading the concentrating of Sn in liquid phase. However, the growth rate of Sn in residue slows down when the distillation temperature is higher than 1473 K. This phenomenon shows that part of Sn is wasted under a higher distillation temperature.

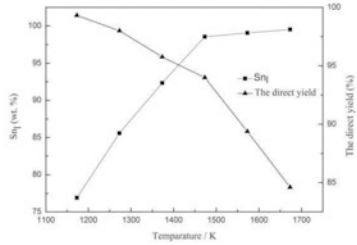

Fig 5. Effect of temperature on the the content of Sn in liquid phase and the direct yield of Sn

As can be seen in Fig 5., the direct yield of Sn decreases with the increase of distillation temperature while the content of Sn in liquid keeps raising until at 1473 K which shows the turning point for a quicker decreasing rate of the direct yield of Sn. The proper distillation temperature in this study presents to 1473 K.

Effect of distillation time

Based on the proper distillation temperature of 1473 K, the following experiments aim to investigate optimum distillation time of vacuum separation of Sn-Sb alloy. The results at conditions of distillation time range of 15 - 65 min with a gradient of 10 minutes and alloy mass of 125 g (8 mm) were shown at Table 1..

Table 1. Effect of Distillation Time on the Separation of Sn-Sb Alloy

Distillation time/ min	Alloy mass/ g	Residue			Volatile			The direct yield/ %
		Sn wt. %	Sb wt. %	Mass/ g	Sn wt. %	Sb wt. %	Mass/ g	
15	125.25	97.13	2.85	62.74	5.29	94.71	62.5	99.31
25	125.11	97.69	2.27	61.83	5.96	94.04	63.27	98.00
35	124.89	98.44	1.53	61.13	6.10	93.90	63.76	95.76
45	124.96	98.79	1.15	60.88	6.18	93.82	64.08	93.99
55	124.88	98.35	1.64	60.83	6.62	93.38	64.05	89.38
65	125.04	98.83	1.15	60.54	6.69	93.31	64.5	84.61

The content of tin in the vapor phase increased with the increase of distillation time resulting in continuous decreasing of the direct yield of Sn. The content of Sn in liquid phase increased to 98.44 wt. % at the distillation time of 35 min. However, there was not obvious change for Sn in the residue after extending the distillation time to 65 minutes. The content of tin in the liquid phase was 98.44 wt pct, while extending distillation time at a gradient of 10 minutes, it had a range of ± 0.4 wt. %. Based on the fact of the ceaseless volatility of Sn in liquid phase, there is no need to set a longer distillation time.

Effect of alloy mass

According to the recommended parameters in this study, the distillation time and temperature were selected at 1473 K and 35minutes. The results under conditions of alloy mass range of 85g-185g with a gradient of 20 g were shown in Fig 6..

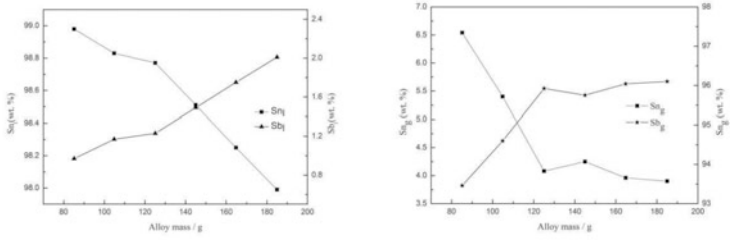

Fig 6. Effect of alloy mass on the component of (a) residue, (b) volatile

It can be seen from Fig 6. (a) that the content of tin in the liquid phase sostenuto decreased with the increase of alloy mass, especially, it declined rapidly after the mass at 125 g. Fig 6. (b) shows that the content of Sn in the vapor phase decreased slowly when the alloy mass was 125 g. It delicates that the alloy mass has little effect on the volatilizing of Sn and Sb. However, the production of vacuum distillation will decrease with the increase of alloy mass (thickness of raw materials).

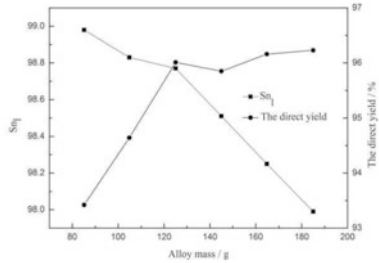

Fig 7. Effect of alloy mass on the the content of Sn in liquid phase and the direct yield of Sn

After increasing to a peak at alloy mass of 125 g (thickness of 8 mm), as can be seen in Fig 7., the direct yield of Sn decreased with the incremental alloy mass , which shows a turning point for obtaining the Sn production. And the content of Sn in liquid phase reached a stable level when the raw materials of 125 g. It demonstrates that the optimal treatment amount for vacuum distillation of Sn-Sb alloy is 125 g (thickness of 8 mm).

Conclusions

The results validate the probability of the separation of Sn-Sb alloy by vacuum distillation. After the vacuum processing, the content of Sb in Sn-Sb alloy and the direct yield of Sn can attain levels of 2 wt. % below and 95 % above, respectively. The distillation parameters, such as distillation temperature, feeding materials (thickness of 8mm) and distillation time, have effect on the direct yield of Sn and the content of Sn in both liquid and vapor phases. In this study, optimized distillation parameters of a distillation temperature of 1473 K, a distillation time for 45 min and a Sn-Sb alloy mass of 125 g (thickness of 8mm) were obtained, which provide referential experience for the distillation separation of Sn-Sb alloys in cleaning industry production.

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