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学位論文題目	Phase Equilibrium and Thermodynamic Study of Antimony Smelting System (アンチモン製錬系の相平衡並びに熱力学的研究)
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論 文 内 容 要 旨

I INTRODUCTION

Antimony and its compounds have a wide range of industrial applications. There are more than 200 antimony-containing alloys of industrial significance, of which battery grids, bearing metals and type metals are the major alloys that consume large quantities of antimony. In the recent years, an approximate of 70% of primary antimony has been consumed annually for the manufacture of antimony trioxide which is widely employed in flame-retardant fabrics, enamel, pigment, glass, ceramics, etc.

Despite the wide applications of antimony, the extractive processes of antimony from its ores are still totally based only on pyrometallurgical methods. There are several processes already industrialized which may be summarized as follows:

- (1) Roasting and volatilization of antimony trisulfide (or stibnite ore) to produce condensed volatile antimony trioxide flue dusts.
- (2) Iron precipitation process where elemental iron is used to decompose the sulfide of antimony to make metallic antimony and iron sulfide matte.
- (3) Reduction of antimony oxides to metallic antimony. Antimony oxide ores either solely or

in combination with antimony trioxide brought out from the roasting and volatilization process may be treated by reduction smelting using carbon as reducing agent if metallic antimony is the desired product.

(4) Refining of antimony metal to minimize impurity elements such as sulfur, iron and tin.

These pyrometallurgical processes are still relying on ancient experiences and are more or less a state of the art practice. Fundamental researches on the pyrometallurgical methods for extraction of antimony appear to be insufficient, especially in the fields of thermodynamics, phase relations and distribution of impurity elements between different phases. As for this reason, the present study was carried out to provide basic information on antimony smelting systems. The main content is described in the order of chapters as follows:

II MEASUREMENTS OF SOME THERMODYNAMIC PROPERTIES OF ANTIMONY SULFIDE AND ITS COMPOUNDS

In this work, attempts have been made to determine activities of Sb_2S_3 in the $XS-Sb_2S_3$ mixtures ($X = Ag, Pb, Cu, Fe$) by transportation method. Due to the complexity of dissociation behavior of Sb_2S_3 , the terms volatility from pure substance (V_e), volatility from mixture (V_e, m), relative volatility (V_e, r), and α which is the summation of number of moles of the dissociated gas species of Sb_2S_3 and is related to activity (a) and V_e, r by $a = (V_e, r)^\alpha$, are proposed and discussed. By comparison to the reported activities of Sb_2S_3 in the $Ag_2S-Sb_2S_3$ system determined by a quantitative thermodynamic analysis method, it was found that the appropriate value of α should be 1.20. With this value of α in mind, activities in the $PbS-Sb_2S_3$, $Cu_2S-Sb_2S_3$ and $FeS-Sb_2S_3$ systems were determined. They were then converted to the mono-cationic valence expression. Finally, activity coefficients of PbS , FeS and Cu_2S at infinite dilute solution were obtained graphically by extrapolation. These are fundamental informations for the sulfidization refining of molten antimony when lead, copper and iron are eliminated by using antimony sulfide as refining slag.

III PHASE RELATIONS AND DISTRIBUTION OF MINOR ELEMENTS IN THE Fe-Sb-S AND Fe-Sb-S- Na_2S SYSTEMS AT 1473 K

Experiments on phase relations and distribution behaviors of tin, lead and arsenic in the $Fe-Sb-S$ and $Fe-Sb-S-Na_2S$ systems were carried out at 1473 K. The results from these fundamental studies can be applied directly to explain the various characteristics of iron precipitation smelting of stibnite (Sb_2S_3) ore, in which elemental iron such as steel scrap is used as reducing agent and Na_2S as fluxing material. The main results are summarized as follows:

(i) The phase relation in the $Fe-Sb-S$ system is characterized by a wide miscibility gap composed of high antimony metallic phase (crude antimony), containing small amounts of iron

and sulfur, and matte phase whose main constituent is FeS.

(ii) The addition of Na₂S to Fe-Sb-S system results in a much wider immiscible region between crude antimony and matte whose main constituent is a double sulfide of $m\text{FeS} \cdot n\text{Na}_2\text{S}$, and is very effective in increasing recovery of antimony into crude antimony.

(iii) The distribution ratios of tin, lead and arsenic between matte and crude antimony in the Fe-Sb-S system scatter at around unity. However, those of lead and arsenic decrease significantly with increasing Na₂S in the Fe-Sb-S-Na₂S system. As a result, it is clarified that the addition of Na₂S causes a severe problem in the removal of lead and arsenic from crude antimony.

IV DISTRIBUTION OF IMPURITIES SODA SLAGS AND MOLTEN ANTIMONY

Reduction smelting forming a soda base slag by the addition of sodium salt is applied to the extraction of antimony oxide ore or smelter recycles. To get a fundamental data on the reduction smelting of antimony, Na₂O-SiO₂ or FeO_n-Na₂O slag was equilibrated with metallic antimony containing small amounts of impurities such as iron, arsenic, tin, lead and copper at 1423 K. Dependences of the antimony solubility in slag and the distribution ratios of impurities on oxygen potential and slag composition were clarified. The results can be briefly stated as follows:

(i) The solubility of antimony in slag increases with the increasing of oxygen potential and the soda-ratio of $n_{\text{Na}_2\text{O}} / (n_{\text{Na}_2\text{O}} + n_{\text{SiO}_2})$. Activity coefficient of SbO_{1.5}(l) in the basic slag of high soda-ratio varies from 0.001 to 1 depending on oxygen potential.

(ii) The solubility of antimony in FeO₂-Na₂O system slag is about the same level of that of soda ratio 0.56–0.59 in the Na₂O-SiO₂ system slag.

(iii) It is evident that the actual dissolution of antimony in soda slags takes place chiefly in the form of trivalent cations.

(iv) Of all the impurity elements investigated, distribution ratios of iron show the highest values followed by those of arsenic, tin, lead and copper, respectively.

(v) As far as soda slags are concerned, high removability of iron and arsenic from liquid antimony can be achieved by control of oxygen potential and slag composition. Employment of low soda-ratio acidic slag is highly recommended if removal of iron is the prime objective, while, high soda-ratio basic slag seems to be most suitable when arsenic elimination is a must.

V PHASE RELATIONS AND DISTRIBUTION OF MINOR ELEMENTS BETWEEN Sb-S-O SLAGS AND LIQUID ANTIMONY

The Sb-S-O slag presents one rarest case where oxide and sulfide are continuously miscible in all proportions. It provides a unique opportunity to investigate the sulfidic and oxidic dissolu-

tion of minor elements as continuous functions of melt composition. For this reason, various series of experiments were carried out as a fundamental study for refining of liquid antimony by the application of Sb-S-O, as well as Sb-S-O- Na_2CO_3 , slags. Phase relations between liquid antimony and Sb-S-O melts were determined at 973 and 1173 K, and were basically expressed in a Sb-S-O ternary diagram. Distribution ratios of impurity elements between Sb-S-O or Sb-S-O- Na_2CO_3 system slags and molten antimony were also investigated. The relevant experimental results are summarized as follows:

(i) The content of antimony in the sulfide-rich slag phase was higher than that of the corresponding one in the Sb_2S_3 - Sb_2O_3 pseudobinary system, while those of the intermediate and oxide-rich slag phases were slightly smaller than the contents of the corresponding pseudobinary ones. Significant dissolution of sulfur in metallic phase was observed when antimony was equilibrated with sulfide-rich antimony slags.

(ii) Except for those of arsenic and iron, distribution ratios of lead, tin and copper increase with increasing concentration of Sb_2S_3 , indicating that these minor elements can be removed quite effectively by sulfidization. The best conditions for the removal of iron from liquid antimony would likely be the simultaneous combination of oxidization and sulfidization using antimony slags with around 70 mol% Sb_2O_3 . Arsenic will generally not respond to Sb-S-O slags. Low refining temperature such as 973 K is more preferable.

(iii) In case of arsenic removal, a high basicity and oxidizing slag, preparing from mixture of Na_2CO_3 and Sb_2O_3 , has been proved to be able to successfully eliminate arsenic from antimony. However, the addition of Na_2CO_3 to Sb-S-O slags gives negative effect to the elimination of lead, iron, tin and copper.

(iv) When lead, iron, tin, copper and arsenic are all associated with liquid antimony, it is recommended that sulfidization using sulfide-rich Sb-S-O slags be conducted first to minimize lead, iron, tin and copper to the desired levels, followed by second refining stage where arsenic is removed by Na_2CO_3 - Sb_2O_3 slag.

VI AN IONIC MODEL FOR THE DISTRIBUTION OF MINOR ELEMENTS BETWEEN Sb-S-O SLAGS AND METALLIC ANTIMONY

The distributions of dilute mono-, di-, tri- and tetra-valent cationic elements between the Sb-S-O system slags and metallic antimony have been studied theoretically on the basis of the Flood-F ϕ rland-Grjotheim (FFG) model for ionic salts. The overall dissolution of a minor element in antimony slags may be regarded as consisting of two independent sulfidic and oxidic fractions, both of which have been mathematically defined based strictly on the FFG theory. The investigated minor elements are those commonly occurring in the commercial process for refining crude antimony; i.e., lead, arsenic, tin, copper and iron. The FFG theory predicts that

the dissolutions of both copper and lead in the slags are predominantly sulfidic, while, both oxidic and sulfidic dissolutions are nearly equally important for arsenic, iron and tin. The theory also rules that more than 98% of the total dissolved copper is cuprous, whereas both ferrous and ferric cations are almost equally responsible for iron dissolution. The distribution coefficients of both copper and arsenic can be predicted well by the FFG theory, and those of lead and iron satisfactorily well with some corrections due to short range orders of double sulfides or oxides in the slags.

VII THERMODYNAMIC CONSIDERATION OF ANTIMONY SMELTING

Various thermodynamic evaluations have been carried out to clarify the behaviors of several antimony smelting processes and to estimate optimum conditions. The results of the evaluation are summarized as follows:

(i) Roasting and volatilization of stibnite ore according to the reaction $Sb_2S_3 + 9/2O_2 = Sb_2O_3 + 3SO_2$ can be evaluated using sulfur-oxygen potential diagram. The possibility of local over temperature is proposed to explain why low temperature volatilization is possible in practical operations. In case of high temperature volatilization, such as at 1300 K, partial pressure of Sb_2O_3 becomes very high, but PbO vapor from the associated minerals may contaminate the condensed Sb_2O_3 product. To cope with this problem, it is suggested by thermodynamic evaluation that the roasting path should be selected in such a way that Sb_2S_3 be converted to metallic antimony first and then finally to Sb_2O_3 vapor. With this respect, the associated lead minerals such as PbS would also be converted to metallic lead and dissolved in much larger quantity of molten metallic antimony. As a result, activity of lead should be tremendously decreased that it is very difficult or impossible for metallic lead to be oxidized further to PbO, whose vapor pressure is much higher than that of metallic lead. Hence, the risk from lead contamination in Sb_2O_3 product is extremely minimized.

(ii) Reduction smelting of antimony oxides with less than 10% Sb loss can be realized, but arsenic, lead and copper are likely to concentrate in metallic phase, while iron and tin are distributed between slag and metal.

(iii) The optimum conditions for iron precipitation smelting of stibnite ore are around a_{Fe} of 0.08 with the least loss of Sb_2S_3 to matte, but almost all of the arsenic is introduced into metallic phase, iron and copper in matte phase, while tin and lead are partially distributed between the two phases.

(iv) Tin and arsenic in antimony can be removed by oxidization together with the application of strong basic soda fluxes. Iron and copper as well as lead may be minimized by sulfidization refining, although it is suggested by evaluation that removal of lead by chloridization is more promising.

VIII CONCLUDING REMARKS

The main results in this study may be summarized according to processes as follows:

(i) Roasting and volatilization process at high temperature such as at 1300 K, as well as a new roasting path to avoid contamination of PbO in the condensed Sb_2O_3 product, has been proposed and discussed theoretically in Chapter 7.

(ii) Iron precipitation process for the extraction of antimony from stibnite ore has been clearly explained in Chapter 3 by using Fe-Sb-S and Fe-Sb-S-Na phase diagrams obtained from experimental works.

(iii) Oxide reduction smelting for the extraction of antimony from antimony oxide ores or compounds has been experimentally investigated in Chapter 4. The results indicate that solubility of antimony in the slags increases with increasing oxygen potential and soda-ratio. Soda slag with soda-ratio around 0.5 is the most appropriate slag for this smelting process.

(iv) Refining of molten antimony metal by Sb-S-O and Sb-S-O- Na_2CO_3 slags have been investigated experimentally in Chapter 5 and theoretically in Chapter 6. Type of refining slag recommended for the selective removal of each minor element from crude antimony produced in the iron precipitation and oxide reduction processes is summarized in Table 1. Here, metal, matte and slag refer to the phases in which minor elements are predominantly dissolved.

Table 1 Distribution behaviors of minor elements in antimony smelting processes and the proposed refining slag for selective removal of each minor element (m.e.).

minor element (m.e.)	concentration of m.e. in		Refining
	Iron precip. process	Oxide reduct. process	
As	metal	metal	$Na_2CO_3 + Sb_2O_3$
Pb	metal matte	metal	Sb_2S_3
Cu	matte	metal	Sb_2S_3
Fe	matte metal	slag	oxide-rich Sb-S-O slag
Sn	metal matte	slag metal	sulfide-rich Sb-S-O slag

審 査 結 果 の 要 旨

アンチモン (Sb) は工業材料として重要なレアメタルの1つであるが、その製精錬操業は経験に基づいており、理論的解析が十分なされているとは言い難い。本論文は、金属 Sb, マット, スラグなどの熱力学的性質、これら融体間の相関係あるいは随伴微量元素の分配などを実験によって明らかにし、さらに Pb, As などの有害成分を効率よく除去する工程の可能性を実験と理論の両面から確かめた結果をまとめたもので、全編8章よりなる。

第1章は緒論である。

第2章では Sb 硫化鉍の酸化揮発製錬や Sb の硫化精製などの基本系として重要な Sb_2S_3 と Cu_2S , PbS , Ag_2S , FeS との間の4種の硫化物2元系に対して、流動法を用いて活量の測定を行った結果について述べており、 Sb_2S_3 - FeS 系を除いてこれらの2元系融体の成分活量がラウール則からかなり大きい負の偏倚を示すことを見出した。このことはこれら有価成分がマットに安定に濃縮されることを示している。

第3章では Fe - Sb - S 系あるいは Fe - Sb - S - Na_2S 系溶融マットと金属 Sb との間の相平衡関係並びに微量成分の分配を実験的に定め、 Na_2S の添加は金属相とマットの相互分離を助長する一方、Pb や As の分配係数を低下させるので不純物除去の点から問題があることを明らかにした。これらの知見は鉄還元置換法による Sb 硫化鉍処理の基礎として重要である。

第4章では Na_2O - SiO_2 系あるいは Na_2O - Fe_2O_3 系スラグと金属 Sb 間における Sb 並びに微量成分の分配係数と気相の酸素分圧並びにスラグ組成の間の関係を実験により求め、これに基づいて金属 Sb の回収と不純物のスラグへの除去の両面から最適条件を検討している。これらは反射炉による Sb_2O_3 の還元溶錬の基礎として重要である。

第5章は Sb - S - O 系スラグと金属 Sb 間の相平衡関係と微量成分の分配について調べた結果を述べている。その結果、Fe は Sb_2O_3 濃度の高いスラグ中に、Pb, Cu, Sn は Sb_2S_3 濃度の高いスラグ中に、また As は Na_2CO_3 を添加したスラグ中にそれぞれ濃縮されることを見出している。これらは Sb の乾式精製プロセスの基礎として重要な知見である。

第6章はイオンモデルを用いた統計熱力学的手法に基づき、第5章で得られた実験結果の理論解析を行った結果について述べている。

第7章は金属-イオン-酸素系の相反応平衡図を作成し、これに基づいて Sb 鉍石中の Sb_2S_3 および随伴硫化物の酸化反応について検討している。これは Sb 硫化鉍の酸化焙焼の基礎として有用である。

第8章は結論である。

以上要するに本論文は、Sb の製精錬に係わる融体相の熱力学的性質や相平衡関係、微量成分の分配挙動などを明らかにするとともに、それらの結果に基づいて酸化焙焼法、鉄還元置換法、反射炉還元法、スラグ化精製法など各種 Sb 乾式製精錬工程について実験的、理論的に検討したもので、金属工学の発展に寄与するところが少なくない。

よって、本論文は工学博士の学位論文として合格と認める。