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Metallurgy



Distribution of antimonium chalcogenides under conditions of vacuum thermal processing of mattes

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ABSTRACT

It was established based on the analysis of the results of published works and the results obtained by the authors that there is no information on the behavior and distribution of antimony chalcogenides - Sb_2S_3 , Sb_2Se_3 , Sb_2Te_3 , as well as double systems - $Sb_2S_3-Sb_2Se_3$, $Sb_2S_3-Sb_2Te_3$ and $Sb_2Se_3-Sb_2Te_3$ under the vacuum processing conditions for polymetallic mattes performed at 1100-1250 °C and a vacuum of 15 - 0.7 kPa. It was found based on the saturated vapor pressure values for monochalcogenides that the vapor pressure of free antimony sulfide will be 58.95 kPa at 1100 °C, i.e. the lower limit of the technological interval, which indicates its complete transfer to the vapor phase when the mattes are evacuated; the vapor pressure of free antimony selenide at 1100 °C exceeds the atmospheric pressure value (101.3 kPa), and Sb_2Se_3 would be completely extracted into the vapor phase in vacuum; the boiling point of liquid antimony telluride at atmospheric pressure corresponds to 971 °C, and it would be extracted into the vapor phase under the conditions of matte evacuation. The thermodynamic evaporation characteristics of antimony chalcogenides were found. It was concluded based on the location of the boundaries of the liquid and vapor phase coexistence fields that it is impossible to separate binary systems of antimony chalcogenides into separate compounds in the process of one evaporation cycle – condensation, in binary systems. Different effects of pressure reduction over melts were found. Lowering the pressure from atmospheric one to 0.7 kPa in $Sb_2S_3-Sb_2Se_3$ system did not change the position of the boundaries of the liquid and vapor fields (L + V) under the temperature; field width (L+V) decreases with decreasing pressure in $Sb_2S_3-Sb_2Te_3$ system; the field width first decreases with temperature, then increases in system $Sb_2Se_3-Sb_2Te_3$. At the same time, the position of the boiling curves of antimony chalcogenide solutions indicates the complete transfer of compounds into the vapor phase under the conditions of matte distillation processing (at 1100-1250 °C) at atmospheric pressure which is important for assessment of the distribution of antimony and rare metals - selenium and tellurium by processed products.

Keywords: antimony, sulfur, selenium, tellurium, chalcogenide, vapor pressure, vacuum, matte, thermodynamics, distribution.

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Introduction

Copper sulfides (Cu_2S) and iron (FeS) are the basis of polymetallic mattes of copper and lead plants forming an unstable complex - FeCu_2S_2 in melt. There are compounds of non-ferrous metals (PbS , ZnS), rare elements cadmium, antimony, indium, etc. in the form of sulfides, as well as selenium and tellurium, isomorphically replacing sulfur in sulfides in addition to the main components in the matte. Moreover, the largest amount in the matte after PbS and ZnS is represented by antimony chalcogenides.

Binary antimony sesquisulfide systems with Cu_2S and FeS as applied to the conditions of vacuum-thermal processing of sulfide melts are considered in detail in the monograph [1], the behavior of copper chalcogenides under the same conditions - in [2]. As a result, it was found that almost complete release of antimony sulfide into the condensate during distillation in a vacuum should be expected, and it was confirmed in the process of factory technological tests for the processing of mattes. The dissociation pressure of pure copper sulfide will fluctuate within 0.5-7 Pa, of copper selenide - 28-230 Pa, of copper telluride - 1.5-9 Pa in the process of distillation of volatiles at low pressure [2], performed, as a rule, at 1100-1250 °C. Therefore, copper sulfide and telluride completely, and copper selenide in the main degree will concentrate in the stillage residue.

The liquid-vapor equilibrium in the chalcocite-antimonite system at low pressures was studied in the study [3], and it was found that almost complete release of antimonite into the condensate should be expected during distillation in a vacuum, however, the pressure during the technological implementation of the matte distillation separation process should be at least 700 Pa in order to avoid Cu_2S build-up formation.

The removal of non-ferrous metal impurities from copper matte was studied by the authors in [4] where it was found that the antimony content was below 0.1 % after vacuum treatment at 1200 °C and a pressure of 60 Pa.

The authors [[5], [6], [7], [8], [9], [10]] conducted studies to determine the oxide solubility of copper, lead, arsenic and antimony from copper-lead mattes into slag. The results obtained can be used to predict the loss of valuable components with slag, and to develop optimal solutions to reduce the total loss of metals during processing.

The teams of authors [[11], [12]] studied the decomposition of jamsonite ($\text{Pb}_4\text{FeSb}_6\text{S}_{14}$), and the optimal temperatures equal to 650 and 900 °C were established for the separation of antimony and lead sulfides. Up to 98 % Sb_2S_3 with a purity of 99.17 % and up to 99.5 % PbS with a content of 98.7 % of the main compound was obtained.

The extraction of non-ferrous metals from secondary raw materials by vacuum sulfiding at 1050 °C was studied in [13], and a new method intended to remove impurities from secondary copper raw materials was proposed.

The authors of [14] found that when copper mattes are evacuated at 1250 °C and a pressure of 130 Pa, up to 92 % of antimony in the form of sulfide can be extracted into the vapor phase and, accordingly, into the condensate.

To date, a modified volumetric model of the molecular interaction of the components in a PbS - Sb_2S_3 binary system was developed and used consistent with experimental data. It can be used for the technological separation and purification of sulfides [15].

Despite a significant number of studies for the Sb_2S_3 isolation from sulfide melts, there are no studies on the behavior of other antimony chalcogenides and their binary systems which form a continuous series of solid solutions [16] under the conditions of vacuum thermal processing of mattes.

In this regard, the behavior of antimony monochalcogenides and binary systems of antimony chalcogenides is of great interest at high temperatures and low pressure, with the construction of vapor-liquid equilibrium fields for binary systems to consider which enable to judge the distribution of elements, as well as the possibility of their concentration in a separate middling product.

Distribution of antimony monochalcogenides

Judgment on the behavior and distribution of antimony chalcogenides is based on the saturation vapor pressure of each of them.

Vapor pressure over antimony sulfide. A significant number of studies, including [[17], [18], [19], [20], [21], [22], [23], [24], [25], [26]], and summarized in monographs [[27], [28], [29]], are devoted to determination of the magnitude of the pressure and composition of vapor over antimony sesquisulfide. Such attention to the thermodynamic studies of Sb_2S_3 is due to the semiconductor properties of the compound and the very complex

composition of the vapor phase. When the composition of vapor over liquid antimony trisulfide is studied, it was established [[17], [21], [22]] that SbS , S_2 , Sb_2S_2 , Sb_2S_3 , Sb_2S_4 , Sb_3S_2 , Sb_3S_3 , Sb_3S_4 , Sb_4S_3 , Sb_4S_4 , Sb_4S_5 molecules and other fragment ions were present in it.

Due to the complex composition of the vapor phase, when the boiling points of alloys were calculated, the saturation vapor pressure of antimony sulfide found by the boiling point method was used [[23], [24], [30]]. This method does not require knowledge of the molecular weight of the vapor, and the corresponding dependences: $\ln p_{Sb_2S_3(l)} [Pa] = 23,889 - 17718 \cdot T^{-1}$, while the thermodynamic functions of evaporation: $\Delta H_{Sb_2S_3(l)}^{vap} = 147,31 \text{ kJ/mol}$, $\Delta S_{Sb_2S_3(l)}^{vap} = 102,79 \text{ J/(mol K)}$.

The vapor pressure of free antimony sulfide at 1100 °C, i.e. at the lower boundary of the technological interval, will be 58.95 kPa indicating its complete transfer to the vapor phase when the matte is evacuated at a rarefaction of 15 - 0.7 kPa.

Vapor pressure over antimony selenide. A number of researchers were involved in physicochemical studies of liquid alloys. The authors of [31] measured the kinematic viscosity and density of melts in the composition range of 40 mol. % Sb_2Se_3 + 60 atm. % Se – 20 mol. % Sb_2Se_3 + 80 atm. % Sb from melting temperature to 1100-1200 °C.

The crystallization kinetics of glassy alloys was studied in [32] using differential scanning calorimetry at different heating rates. $Se_{100-x}Sb_x$ ($2 \leq x \leq 10$), the activation energy of the crystallization process, the order parameter, the rate constant, the frequency factor was determined, and it was found that chalcogenide glasses with a higher crystallization rate, have lower thermal stability.

The authors of [33] studied the behavior of antimony sesquiselenide during sublimation in vacuum and established the congruent character of evaporation.

Mass spectrometric determination of vapor composition over Sb_2Se_3 established [[34], [21]] the predominant presence of $SbSe$ molecules, half less - Sb_2Se_2 , triple less – Sb_2Se_3 and so on in the descending order: Sb_3Se , Sb_4Se_4 , Sb_4Se_3 , Sb_3Se_3 , Sb_3Se_2 , Se_2 , Sb_2Se_4 and very few Sb_2Se_4 .

The vapor pressure of antimony sesquiselenide using radioisotopes in the temperature range from 491 to 687 K (218–414 °C) was determined in studies [[35], [36]]. The temperature dependence of the vapor pressure corresponded to the expression:

$$\lg p[\text{mm Hg}] = 8,7906 - 6432,3 \cdot T^{-1}.$$

Vapor pressure over liquid antimony selenide in the temperature range of 550–868 °C (823–1201 K) was determined by a static method using a quartz membrane manometer in the study [20]. The results of the determinations are described by the equation: $\lg p[\text{mm Hg}] = (8,4130 \pm 0,0328) - (7220,4 \pm 250) \cdot T^{-1}$.

Later, the authors of [[37], [38]] determined the vapor pressures and activities of selenium and antimony at 994 K (721 °C) by the isopiestic method over the entire concentration range of the system.

The equation of the dependence of vapor pressure on temperature recommended in [39] was used by us to calculate the boundaries of the liquid-vapor phase transition, and it was transformed by us to the form: $\ln p_{Sb_2Se_3(l)} [Pa] = 23,908 - 16498 \cdot T^{-1}$.

Hence the enthalpy and entropy of liquid Sb_2Se_3 vaporization: $\Delta H_{Sb_2Se_3(l)}^{vap} = 137,17 \text{ kJ/mol}$,

$$\Delta S_{Sb_2Se_3(l)}^{vap} = 102,95 \text{ J/(mol K)}.$$

The vapor pressure of free antimony selenide at 1100 °C, the lower boundary of the technological range, exceeds atmospheric pressure (101.3 kPa), and Sb_2Se_3 will be completely extracted into the vapor phase in a vacuum.

Vapor pressure over antimony telluride. The number of works devoted to thermodynamic studies of antimony sesquitelluride is not so large in comparison with sulfide and selenide. The physical and chemical properties of the antimony - tellurium and Sb_2Te_3 system were studied by the authors of [[19], [20], [25], [29], [39], [40], [41], [42], [43]]. When the composition of the vapor was studied by the mass spectrometric method, the existence of the following molecules was established [[11], [29]]: Sb_4 , Sb_2 , $SbTe$, Sb_2Te_2 , Te_2 . However, the authors of [41] noted that the “degree of incongruence” is very low during the sublimation of antimony sesquitelluride in vacuum at 770–830 K.

Sb_2Te_3 steam pressure values found by different methods differ from each other. In this regard, the dependence of the vapor pressure of antimony telluride obtained based on measurements by the torsion-effusion method in the latest work [26] were used by us and converted to the form: $\ln p_{Sb_2Te_3(o)} [Pa] = 31,776 - 25181 \cdot T^{-1}$

The change in the enthalpy and entropy of evaporation corresponds to the following values:

$$\Delta H_{Sb_2Te_3(l)}^{vap} = 209,39 \text{ kJ/mol},$$

$$\Delta S_{Sb_2Te_3(l)}^{vap} = 168,36 \text{ J/(mole} \cdot \text{K)}.$$

The boiling point of liquid antimony telluride at atmospheric pressure corresponds to 971 °C, and it will be extracted into the vapor phase under the vacuum conditions of matte.

Distribution of chalcogenides in Sb_2S_3 - Sb_2Se_3 , Sb_2S_3 - Sb_2Te_3 and Sb_2Se_3 - Sb_2Te_3 systems

Measurements of microhardness and thermal conductivity of Sb_2S_3 - Sb_2Se_3 alloys and X-ray diffractometry established the formation of solid solutions between these compounds which crystallize in a rhombic lattice, in the same way as the initial compounds [44]. When antimony selenide is added to sulfide, sulfur atoms statistically replace selenium atoms, and the lattice parameters gradually increase as sulfur atoms are replaced by selenium atoms with a larger atomic radius. In connection with the formation of a continuous series of solid solutions and the unlimited solubility of antimony chalcogenides in the liquid phase, the boundaries of vapor-liquid equilibrium are calculated in Sb_2S_3 - Sb_2Se_3 , Sb_2S_3 - Sb_2Te_3 and Sb_2Se_3 - Sb_2Te_3 systems.

There are no studies on vapor-liquid equilibrium in binary systems of antimony chalcogenides.

Due to the fact that the chalcogenides of one metal, as a rule, have a very slight deviation or lack thereof under the Raoult law [16], Sb_2S_3 - Sb_2Se_3 , Sb_2S_3 - Sb_2Te_3 and Sb_2Se_3 - Sb_2Te_3 binary systems were regarded as ideal ones.

The boundaries of the vapor-liquid equilibrium fields were calculated based on the partial pressure values of the saturated vapor of the alloy components. At the same time, the temperature at

which the sum of the partial pressures of the vapor of the components is equal to atmospheric pressure or another one corresponding to the conditions of vacuum distillation of mattes (15 - 0.7 kPa) was considered as the boiling point of the melt.

The composition of the vapor phase at the boiling point was determined on the basis of the Clapeyron–Mendeleev equation as the ratio of the partial pressure of one component to the total pressure at this temperature. The boundaries of vapor-liquid equilibrium in binary systems of antimony chalcogenides are shown in Figure 1.

State diagrams of condensed systems are constructed only for binary Sb_2S_3 - Sb_2Se_3 and Sb_2Se_3 - Sb_2Te_3 [44]. Sb_2S_3 - Sb_2Te_3 system liquidus line is drawn between the melting points of chalcogenides conditionally, by a dotted line.

It can be concluded based on the position of the boundaries of the liquid and vapor phase coexistence fields that it is impossible to separate binary systems of chalcogenides into separate compounds in the process of one evaporation cycle - condensation. The different influence of the decrease in pressure over the melts should be noted. A decrease in pressure from atmospheric to 0.7 kPa does not change the position of the boundaries of the liquid and vapor fields ($L + V$) in temperature in Sb_2S_3 - Sb_2Se_3 system; field width ($L+V$) decreases with decreasing pressure in Sb_2S_3 - Sb_2Te_3 system; the field width first decreases with temperature, then increases in Sb_2Se_3 - Sb_2Te_3 system. Apparently, inaccuracies in determination of the vapor pressure values of the initial antimony chalcogenides are the reason for such a change in the position of field boundaries ($L+V$) in the last two systems.

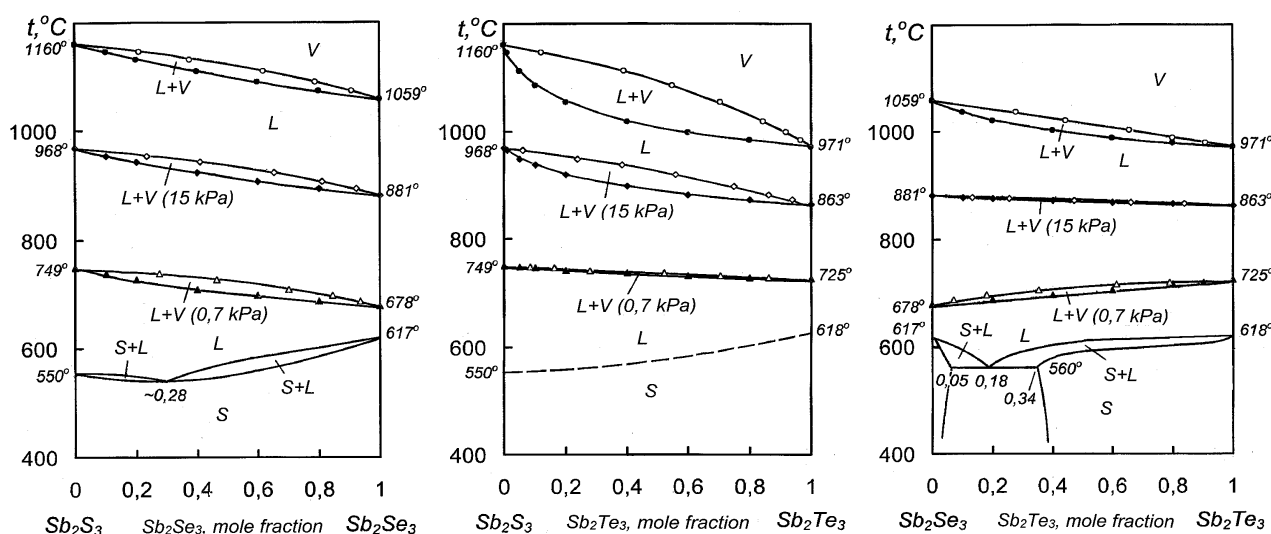


Figure 1 - Liquid-vapor phase equilibria in binary systems of antimony chalcogenides.

At the same time, the position of the boiling curves for the solutions of antimony chalcogenides indicates the complete transfer of compounds into the vapor phase under the conditions of distillation processing of mattes (at 1100-1250 °C) even at atmospheric pressure.

Conclusions

It was established based on the saturated vapor pressure values for antimony monochalcogenides and the construction of the boundaries of vapor-liquid equilibrium in Sb_2S_3 - Sb_2Se_3 , Sb_2S_3 - Sb_2Te_3 and Sb_2Se_3 - Sb_2Te_3 systems that antimony monochalcogenides, as well as solutions of

antimony chalcogenides will be completely transferred to the condensate under the conditions of distillation processing of polymetallic mattes performed, as a rule, at 1100-1250 °C and with a rarefaction of 15 - 0.7 kPa. Separation of antimony chalcogenides into individual compounds during distillation is not possible.

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ШТЕЙНДЕРДІ ВАКУУМДЫҚ-ТЕРМИЯЛЫҚ ҚАЙТА ӨНДЕУ ЖАҒДАЙЫНДА СҮРМЕ ХАЛЬКОГЕНИДТЕРІНІҢ ТАРАЛУЫ

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ТҮЙІНДЕМЕ

Жарияланған жұмыстардағы және авторлар алған нәтижелерді талдау негізінде 1100-1250 °C температурада және қысымды 15-0,7 кПа дейін сирету кезінде жүзеге асырылатын полиметалл штейндерді вакуумдық қайта өңдеу жағдайында Sb_2S_3 , Sb_2Se_3 , Sb_2Te_3 сүрме халькогенидтерінің, сондай-ақ Sb_2S_3 - Sb_2Se_3 , Sb_2S_3 - Sb_2Te_3 және Sb_2Se_3 - Sb_2Te_3 қос жүйелерінің әрекеті мен таралуы туралы мәліметтердің жоқ екендігі анықталды. Монохалькогенидтердің қаныққан бу қысымы мөлшерлерінің негізінде 1100°C кезінде – технологиялық аралықтың төменгі шекарасында бос сүрме сульфидінің бу қысымы 58,95 кПа-ны құрайтыны анықталды, бұл штейндерді вакуумдау кезінде оның бу фазасына толық ауысатынын көрсетеді; 1100°C-та бос сүрме селенидінің бу қысымы атмосфералық қысымның шамасынан асады (101,3 кПа) және вакуумдағы Sb_2Se_3 толығымен бу фазасына өтеді; сұйық сүрме теллуридін атмосфералық қысымдағы қайнау температурасы 971°C-ға сәйкес келеді және штейндерді вакуумдау жағдайында ол бу фазасына шығарылады. Сүрме халькогенидтерінің булануының термодинамикалық сипаттамалары табылды. Қос жүйелерде сұйық және бу фазаларының қатар болатын өрістерінің шекарасын орналастыру негізінде сүрме халькогенидтерінің қос жүйелерінің бір булану – конденсация циклі барысында жеке қосылыстарға бөлінбейтіні туралы қорытынды жасалды. Sb_2S_3 - Sb_2Se_3 жүйесінде қысымның атмосфералық қысымнан 0,7 кПа-ға дейін төмендеуі температура бойынша сұйықтық пен бу (L+V) өрістері шекараларының жағдайын өзгертпейді; Sb_2Se_3 - Sb_2Te_3 жүйесінде – өрістің ені (L+V) қысым төмендеген сайын азаяды; Sb_2Se_3 - Sb_2Te_3 жүйесінде өрістің ені температура бойынша алдымен азаяды, содан кейін ұлғаяды. Сонымен қатар, сүрме халькогенидтері ерітінділерінің қайнауының қисық сызығының орналасуы атмосфералық қысымда штейндерді дистилляциялық қайта өңдеу жағдайында (1100-1250°C температурада) қосылыстардың бу фазасына толық ауысатынын көрсетеді, бұл сүрме және сирек кездесетін металдардың – селен мен теллурдың қайта өңдеу өнімдері бойынша таралуын бағалау үшін маңызды.

Түйін сөздер: сүрме, күкірт, селен, теллур, халькогенид, бу қысымы, вакуум, штейн, термодинамика, таралу.

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РАСПРЕДЕЛЕНИЕ ХАЛЬКОГЕНИДОВ СУРЬМЫ В УСЛОВИЯХ ВАКУУМ-ТЕРМИЧЕСКОЙ ПЕРЕРАБОТКИ ШТЕЙНОВ

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АННОТАЦИЯ

На основании анализа полученных авторами результатов и опубликованных работ установлено отсутствие сведений о поведении и распределении халькогенидов сурьмы Sb_2S_3 , Sb_2Se_3 , Sb_2Te_3 , а также двойных систем $Sb_2S_3-Sb_2Se_3$, $Sb_2S_3-Sb_2Te_3$ и $Sb_2Se_3-Sb_2Te_3$ в условиях вакуумной переработки полиметаллических штейнов, осуществляемой при температуре 1100-1250°C и разрежении 15 – 0,7 кПа. На основании величин давления насыщенного пара монохалькогенидов было установлено, что давление пара свободного сульфида сурьмы при 1100°C – нижней границе технологического интервала будет составлять величину 58,95 кПа, что свидетельствует о его полном переводе в паровую фазу при вакуумировании штейнов; давление пара свободного селенида сурьмы при 1100°C превышает величину атмосферного давления (101,3 кПа) и в вакууме Sb_2Se_3 полностью будет извлечен в паровую фазу; температура кипения жидкого теллурида сурьмы при атмосферном давлении соответствует 971°C и в условиях вакуумирования штейнов он будет извлечен в паровую фазу. Найденны термодинамические характеристики испарения халькогенидов сурьмы. В двойных системах на основании размещения границ полей сосуществования жидкой и паровой фаз сделан вывод о невозможности разделения двойных систем халькогенидов сурьмы на отдельные соединения в процессе одного цикла испарение – конденсация. Отмечено разное влияние понижения давления над расплавами. В системе $Sb_2S_3-Sb_2Se_3$ понижение давления от атмосферного до 0,7 кПа не изменяет положение границ поля жидкости и пара (L+V) по температуре; в системе $Sb_2S_3-Sb_2Te_3$ – ширина поля (L+V) уменьшается с понижением давления; в системе $Sb_2Se_3-Sb_2Te_3$ – ширина поля по температуре вначале уменьшается, затем увеличивается. Вместе с тем, положение кривых кипения растворов халькогенидов сурьмы свидетельствует о полном переводе соединений в паровую фазу в условиях дистилляционной переработки штейнов (при температурах 1100-1250°C) при атмосферном давлении, что важно для оценки распределения сурьмы и редких металлов – селена и теллура по продуктам переработки.

Ключевые слова: сурьма, сера, селен, теллур, халькогенид, давление пара, вакуум, штейн, термодинамика, распределение.

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