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A study of selenium and tellurium distribution behavior, taking the

copper matte flash converting process as the background

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Abstract: Single particle experiments have been carried out in the present study. An industrial copper matte powder, containing 68.04 wt. % Cu, 0.50 wt. % Se and 0.08 wt. % Te has been taken as the starting material. Se and Te phase assemblies and distribution behaviors have been systematically investigated in air atmosphere. After experiments, Se reported to blister copper, matte and oxide phase, whilst Te will enrich in oxide phases, including phases of the Fe-Si-Te-O, Ca-Fe-Te-O, and Ca-Te-O-(S) systems. Along with the increasing of temperature, selenium and tellurium content in copper and matte phases decrease. The introduction of CaO flux and typical impurities, Pb and Si, had significant influence on the Se and Te distribution. Results revealed that CaO addition and Si impurity accelerated the removal of Se and Te from the copper and matte phase, but the Pb impurity helped for more Se and Te in Cu rich phases.

Keywords: Photovoltaic, Anode slime, Slag chemistry, Phase equilibria, Secondary

INTRODUCTION

Selenium and tellurium related materials are widely used in traditional industries such as metallurgy, glass, agriculture, rubber, etc. [1], and they have also become important raw materials for strategic industries such as photovoltaics, thermoelectric power, etc. [2]. The green extraction, integrated usage and efficient recycling of Se and Te have received widely concerns. However, both Se and Te are rare and scattered elements with very low abundance in earth crust. According to the U.S. Geological Survey data in 2019 [3], the global Se and Te reserves are only 99,000 tons and 31,000 tons, respectively, and they are mostly associated with non-ferrous metal minerals of Cu, Pb, Zn, Bi, Au, etc. The current global annual production of Se and Te are about 2,800 tons and 440 tons, respectively. but with the continuous development of traditional industries and the rapid growth of new industries, the demand for Se and Te will continue growing [4-5].

More than 90% of the world's selenium and tellurium are produced as a byproduct the copper smelting industry [6-7], mainly from the treatment of copper anode slime. There are no independent deposits for Se or Te that can be economically exploited. Coal also contains a certain amount of Se, and fly ash is technically feasible to be used as Se resource, but not economically profitable. In addition to the associated Te in copper mines, some Au and Bi minerals also contain some Te, but the industrial scale of Au and Bi is much smaller than Cu. Therefore, to improve the production level of Se and Te and enhance the resource efficiency, efforts should be paid on tapping the potential from copper smelting industry.

Se and Te enter the copper smelting system along with the copper concentrate in the form of associated minerals, having physical and chemical reactions, and distributing among the matte/copper/slag/flue dust and gas phase. The Se and Te that follow with the matte/copper stream will be end up in the anode slime after electrolytic refining process. There are various technologies used in industry to recover Se and Te from anode slime, including the Kaldo method, the hydrometallurgical process, and a combined pyro- and hydro-metallurgical process [8-10]. The Kaldo process is the most widely used method in anode slime treating due to its large processing capacity, good adaptability for raw materials, good environmental behavior and high mechanization level. Researchers have done a lot of work in enhancing the recovery efficiency of Se and Te, Avarmaa et al. [11] studied the distribution behavior of Te in Ag and Na₂O-SiO₂ slag at 1000-1300°C with the Kaldo process as background, Kong [12] reported the behavior of major elements in the Kaldo process and found that more than 98% Se & Te can be efficiently recovered. However, Se and Te reporting to other phases are difficult to recover. The key factor in improving the recovery efficiency of Se and Te in the copper industry is trying to guide more Se and Te entering the matte phase or copper phase.

At present, there are limited researches on the reaction behavior of Se and Te reaction behavior or distribution behavior during pyro-stages of copper making [13-17]. Johnson et al.[13] studied the interaction among As, Sb, Bi, Se and Te in slag phase at 1250 °C and found that the dissolved amount of Te in slag phase has little influence with the content of other elements or slag components CaO, MgO and Al₂O₃, while the dissolved amount of Se in slag phase decreased with the increasing of other elements content and CaO portion in slag. Sukhomlinov et al.[14] studied the effect of matte grade (55wt. % - 75wt. %) on the distribution behavior of Ga, In, Sn and Te in matte and slag phases at 1300 °C, the result showed that with the increase of matte grade, Te content in matte phase increased, and with the increasing of CaO content in slag, Te content in slag phase increased. Klemettinen et al.[15] studied the behavior of Te in WEEE smelting and found that the Te content in copper phase decreased with the increasing of oxygen partial pressure. Brenan [16] studied the distribution of Te between sulfide and silicate under high pressure, and results showed that the partition coefficient of Te is related to the activity coefficient of FeO component, and Te content decreases with the increasing of FeO activity in silicate phase. Schlit et al.[17]. Studied the distribution of Te in copper phase and matte phase, and reported that Te is more easily enriched in matte phase. The distribution behavior of Se and Te in slag/matte/Cu phase have been investigated in the above studies, but there is incomplete conclusion on the occurrence form, reaction mechanism, distribution behavior and transformation law of Se and Te in the pyrometallurgical copper process.

In order to collect more data in answering the above unknowns, effects of CaO flux, temperature and typical impurities (Pb, Si) on the distribution behavior and phase transformation of Se and Te in slag/copper/matte phase were studied by the single particle experiment in this study. The copper matte flash converting process has been

considered as the background, and the data will be useful in improving the recovery efficiency of Se and Te in copper industry.

EXPERIMENTAL SECTION

Raw material

The copper matte powder used in this study is produced by one large domestic copper producer, using the "flash smelting----flash converting" technology, and materials were taken from the matte powder warehouse above the reaction shaft. Particle size distribution has been measured by laser particle size analyzer (MS2000, Malvern, England), the d10, d50 and d90 cut-sizes of the matte particles are 5.165 µm, 15.326 µm and 40.345 µm, respectively. The chemical composition of the matte powder was analyzed with ICP-OES, and results are presented in table I.

Table I. Chemical composition of copper matte powder (wt. %)

Cu	Fe	Mg	Pb	S	Se	Te
68.04	6.63	0.01	0.51	20.65	0.50	0.08

Procedure and Apparatus

The experimental process has been conducted in two stages. In the first stage, Pb and Si doping, pre-sintered 2FeO·SiO₂ and commercial PbS (purity 99.5 wt. %, supplied by Sigma-Aldrich, Shanghai, China) were used as doping materials, copper matte powder was mixed thoroughly with 2FeO·SiO₂ and PbS in different ratio, and then pressed with 2 MPa in a Ø 10 mm pressing tool, pellets were placed in a sealed graphite crucible, and the crucible was heated up to 1200 °C for 4 h in a gas flow of 99.99 % N₂, then the whole crucible was air quenched. Samples were collected by breaking the crucible after cooling to room temperature, then grounded into fine powder, and the particle size was smaller than 75 μ m. In the doping procedure, the addition of 2FeO·SiO₂ and PbS were calculated based on the weight of matte powder, and the added amount of Si or Pb were 0.01 %, 0.10 %, 0.50 %, 1.00 % and 2.00 % respectively on

basis of matte powder weight. In the second stage of the experiment, single particle experiment, the original or doped copper matte powder was fed into a corundum working tube alone or together with 10 % CaO flux (purity 99.99 wt. %, supplied by Sigma-Aldrich, on basis of matte powder), and an Al₂O₃ sheath was used as guiding tube in the vertical electric furnace. Particles passed through the hot zone at different temperatures in air atmosphere to simulate the reaction behavior of matte powder in the reaction shaft. When passed through the corundum working tube, particles were quenched on a water-cooled copper plate. The detailed information about the equipment has been presented in the previous publication [18]. In the single particle experiment, samples can be divided into four big groups, and they are produced from Pb doped matte powder, Pb doped matte powder with CaO flux, Si doped matte powder, and Si doped matte powder with CaO flux.

Special attention has been paid to the experimental temperature. The temperature profile of the working tube was measured by a S-type thermocouple beforehand and the temperature of the hot zone was measured by a working thermocouple during the experiment and the value was recorded as the experimental temperature. Referring to the practice of flash converting process, the temperature range was set between 600 °C and 1600 °C, with an interval of 200 °C. Taking all parameters (doping elements, impurity content, temperature and fluxing condition) into consideration, there are 120 samples in total.

SEM-EDS analyzes

Samples prepared in the single particle experiments were mounted in epoxy resin, then a polished cross section of the specimen was prepared using the conventional metallographic grinding and polishing technique. Samples were coated with carbon and then analyzed by SEM (Tescan, Brno, Czech Republic)-EDS (Thermo Fisher Scientific, Waltham, Ma, USA). The working parameters of SEM analysis were, voltage 15 kV, beam current 10.9 nA, working distance 20 mm. The standard and reference spectral lines used in EDS analysis were, calcite (Ca, K α), copper (Cu, K α), haematite (Fe, K α), quartz (oxygen, K α), lead (Pb, M α), marcasite (S, K α), quartz (Si, K α), elemental selenium (Se, K α) and tellurium (Te, L α). For each phase detected in these samples, 5 to 10 points/regions were selected and analyzed.

RESULTS AND DISCUSSION

Morphology and Phase Composition

In the single particle experiments, copper matte powder passed through the hot zone and react with O₂ in air. The morphology and phase assemblies of these particles changed obviously after melting, ignition, slag making and copper making reactions. Taking the sample series produced from Si doped matte powder with CaO flux as example, the SEM-EDS results are shown in Fig. 1.



Fig. 1. BSE-EDS results of these samples prepared from Si doped matte powder with CaO flux, and the Si content in starting Si-dope matte powder is 0.01 wt. %, (a) Si-doped matte powder at room temperature, (b) sample reacted at 800 °C (c) sample reacted at 1200 °C, (d) & (e) sample reacted at 1600 °C, (f) EDS mapping result of the particle in (e).

Fig. 1(a) shows that the original Si doped copper matte powder has an irregular morphology, some 2FeO·SiO₂ well attached the matte particle, and others were isolated particles. It can be seen from Fig. 1(b) that after passing through the hot zone, there was no difference with matte particles, but the 2FeO·SiO₂ started to melt and a new Fe-Si-

Te-O phase formed within the 2FeO·SiO₂ phase, indicating some Te species vaporized from the matte phase and were captured by the oxide phase. Along with the increase of temperature, the phase boundary became distinct in Fig. 1 (b)-(e) due to the melting of irregular matte powder particles, which gradually forms spherical particles. Ca-S-Te-O phase can be observed in Fig. 1 (c) to Fig. 1 (e), which is the product of reaction between CaO, SO₂ and Te gaseous species. The Cu-Fe-O phase in Fig. 1 (c) was the product of matte oxidation. Small Cu droplets can also be found in the matte phase, representing the copper making reactions. Blister Cu, matte phase, Cu₂O phase, Cu-Fe-Te-O phase and Ca-S-Te-O phase co-existed in Fig. 1 (d), the porous Cu₂O phase was the product of over-oxidized matte. Fig. 1 (e) and (f) show the BSE images and EDS mapping results of the samples treated at 1600 °C. Starting from particle core and moving to the surface, there were blister copper, matte and Cu-Fe-Te-O phase in turn. The relative position of the phases indicated that Fe was preferentially oxidized, migrated to the outer layer and formed the slag phase with CaO flux during the process. Cu accumulated to the particle core, and formed the blister copper phase. The EDS results showed that the matte phase had very low iron content and its composition was very close to 'white matte'. Se reported to blister copper, matte and Cu-Fe-Te-O phases. Te was highly enriched in the Cu-Fe-Te-O phase, indicating that Te was easily oxidized and preferentially absorbed by oxide phase. The original copper matte powder contains 0.51 wt. % Pb that it mainly followed the matte phase in the process.

Se and Te in the Matte Phase

The matte powder was treated with different temperature, different impurities contents, and different flux condition, there were 120 samples in total which were carefully and systematically examined with SEM-EDS. All composition data have been collected and 435 matte phase regions/points have been found in all samples. They have been graphically depicted along with their processing parameters in Fig. 2.



Fig. 2. Se and Te contents in matte phase from whole batch sample, (a) Se content, Pb doped matte, (a') Se content, Pb doped matte with CaO flux, (b) Se content, Si doped matte, (b') Se content, Si doped matte with CaO flux, (c) Te content, Pb doped matte, (c') Te content, Pb doped matte with CaO flux, (d) Te content, Si doped matte, (d') Te content, Si doped matte with CaO flux.

As shown in the Fig. 2, along with the variation of processing parameters, Se content in the matte phase varies from 0.001 wt. % to 1.16 wt. % and Te content varies

from 0.001 wt. % to 0.16 wt. %. Temperature variation has a major influence on-the Se and Te distribution behavior, less Se and Te reported to matte phase in most cases along with increasing temperature, and this can be explained by the high vapor pressure of Se and Te containing species at elevated temperatures [19]. Fig. 2 (b) and (d) show that higher Si content in the matte powder, the more Se and Te entrapped to matte phase. This phenomenon should result from the difference of the reaction progress. Si doping will influence the oxide layer formation, which will hinder mass transfer of the system. When CaO flux was introduced into the system, the influence mechanism changed dramatically. Generally speaking, Pb doping will hold more Se and Te in matte phases at high temperature, but Si doping has opposite influence, which can be explained by the formation of Ca-Fe-O oxide phase and the high melting of Ca-Si-O system compound. PbS containing matte phase has lower ignition temperature than original ones, thus FeS oxidation and Ca-Fe-O oxide phase formation occurred at lower temperature and at an early stage. The low melting point oxide phase will slow down the oxidation and evaporation process. However, when Si content was high in matte powder, high melting point compound from the Ca-Si-O system was neutral in influencing the oxidation or evaporation process at the beginning. But when it started to melt, it may hinder the matte phase.

Se and Te in the Blister Copper Phase

When matte powder is oxidized, blister copper may form. All samples have been examined and 570 blister copper regions/points have been detected, all data have been collected and graphically depicted along with their processing parameters in Fig. 3.



Fig. 3. The Se and Te contents in the blister copper phase, and samples were prepared with different parameters, (a) Se content, Pb doped matte, (a') Se content, Pb doped matte with CaO flux, (b) Se content, Si doped matte, (b') Se content, Si doped matte with CaO flux, (c) Te content, Pb doped matte, (c') Te content, Pb doped matte with CaO flux, (d) Te content, Si doped matte, (d') Te content, Si doped matte with CaO flux.

As shown above, along with the variation of processing parameters, Se content in

the matte phase varies from 0.001 wt. % to 2.02 wt. % and Te content varies from 0.001 wt. % to 0.25 wt. %, which are comparable with that in the matte phase, indicating that matte and copper have similar capability in absorbing Se and Te. In Fig. 3 (a), Se content in Cu phase increased along with increasing temperature or Pb doping dosage, but when temperature continuously increases, Se content will decrease due to its evaporation. When Pb doped matte powder co-treated with CaO flux in Fig. 3 (a'), remaining Se in Cu phase will decrease obviously, Se in Cu phase will be higher along with increasing Pb doping dosage. In Fig. 3 (b), it is easy to find out that increasing temperature enhances the Se distribution to other phases, and Si doping dosage changing has no obvious influence on Se content in copper phase. When Si doped matte powder cotreated with CaO flux in Fig. 3 (b'), the remaining Se in Cu phase was very low, yet along with increasing of Si doping dosage. It can also be explained by the formation of Ca-Fe-O oxide phase and the Ca-Si-O compound. The result in Fig. 3 (c) shows that when Pb doped matte powder was treated, Te content in Cu phase was very low. However, when CaO was introduced into the system, Te behavior changed obviously. Te in Cu phase can be as high as 0.25 wt.% along with the increasing of Pb doping dosage, which is higher than that in the origin industrial matte powder or that in matte phase after treatment. In Fig. 3 (d), Te content in Cu phase increased along with temperature increasing along with low Si doping dosage condition due to the reaction progress of these particles, samples treated at high temperature required less time in forming the oxide phase. When Si doping dosage was high, the Te content in Cu phase was also high due to low melting point compound of 2FeO·SiO₂. When CaO flux was introduced into the system in Fig. 3 (d'), Te behavior has the same law with Fig. 3(d).

Te in Oxide Phases

Ca-Fe-Te-O System Oxide

The Ca-Fe-O slag system was used in the Mitsubishi converting process and in the flash converting process, which has been revealed to be suitable in solving the Fe₃O₄ saturation problem. The studying of Te distribution behavior in the Ca-Fe-O system can be helpful in improving the Te recovery efficiency. The sample series produced from 0.01 wt.% Pb doping matte powder with CaO flux has been taken as subject in investigating the Te behavior in the Ca-Fe-O phase, 439 groups of data have been collected. Fig. 4 presents the BSE-EDS results.



Fig. 4. BSE picture of samples produced from 0.01 wt.% Pb doped matte treating with CaO flux, (a,a₁,a₂), 800 °C, (b,b₁,b₂), 1200 °C, (c,c₁,c₂) 1600 °C and (d) EDS result of the Ca-Te-O system, (e) Ca-S-Te-O system and (f) Ca-Fe-Te-O system.

As shown in Fig. 4 (a), (b) and (c), the copper phase in the sample continuously converges and liquefies into a ball with increasing of temperature. There were several oxide phases containing Te, including the Ca-Fe-Te-O, the Ca-S-Te-O, and the Ca-Te-O phase [20-22]. The Ca-Fe-Te-O phase mainly exists at high temperature, and should be the most stable oxide phase among these three. According to Fig. 4 (a), Te in the matte powder can react with CaO flux at early stage and form the Ca-Te-O compound. Along with the oxidation of matte powder, the produced SO₂ could react with CaO and form the Ca-S-Te-O phase with Te species. The oxidized Fe will form the Ca-Fe-Te-O phase with CaO flux and Te species. According to the corresponding EDS data in Fig. 4 (d), the Ca, Te, O atomic ratio of the Ca-Te-O compound has been confirmed to be 3:1:6 at 800 °C, and shifted to 3:1:3 + X (X: 0 < X < 1) at 1600 °C, which indicated that Ca-Te-O compound decomposes at high temperature. Te content slightly decreased along with increasing temperature in the Ca-S-Te-O phase [23-24] in Fig. 4 (e) and in the Ca-Fe-Te-O phase in Fig. 4 (f) due to the evaporation of Te species.

Fe-Si-Te-O System Oxide

Si is a typical impurity element in copper making process, and the content of Si in matte should be carefully monitored in practice especially in the flash converting process. Fe-Si-O slag system is also widely used in P-S converter, bottom blowing converting, and some other bath converting technologies. Thus, the behavior of Te in Fe-Si-O system is a widely concern topic. The sample series produced from 0.01 wt. % Si doping matte powder has been taken as the subject in studying Te behavior in the Fe-Si-Te-O system, and 182 groups of data have been collected. Fig. 5 presents the BSE-EDS results of these samples.



Fig. 5. BSE picture of samples produced from Si doped matte powder, processed at (a), 800 °C, (b), 1200 °C, (c) 1600 °C and (d) EDS result of the Fe-Si-Te-O phase.

As shown in Fig. 5, the Fe-Si-Te-O phase can be found in the specimen from the experiment at 800 °C, and it was stable at the whole temperature range in this study. The Te content in the Fe-Si-Te-O phase was much higher than that in the matte phase or the blister copper phase. According to the recorded data, Te content in the oxide phase was about 45 wt. % at 800 °C. Along with increasing temperature, Te content decreased linearly, which is explained by the change of Te and Fe. Along with the increasing of temperature, vapor pressures of Te related species will increase, and more Te will report to gas phase, which resulting the decrease of Te content in the Fe-Si-Te-O phase. The oxidation reaction of FeS will be accelerated at high temperature, and more FeO_x product will report to the the Fe-Si-Te-O phase. When larger amount of Fe

was oxidized, more Cu will be oxidized as well, which explain the increasing the Cu content in the Fe-Si-Te-O phase at high temperatures.

CONCLUSIONS

Se and Te distribution behaviors and occurrence form have been systematically investigated in this study, and the flash converting process has been taken as the reference. Influence made by impurity elements, temperature and flux condition have been studied in single particle experiments, and major results were 1) Se and Te were originally introduced into the process with the industrial matte powder, and they averagely distributed in particles; 2) after single particle experiments in air atmosphere, Se and Te were observed in blister Cu, matte phase, and the oxide phase. Se mainly follows blister copper and matte, Te enriches in oxide phase, including the Fe-Si-Te-O, Ca-Fe-Te-O, Ca-S-Te-O and Ca-Te-O phase, and the Ca-Te-O system compound decomposes at high temperature,; 3) Se and Te in the blister copper and matte phase were observed to decrease with increasing temperature; 4) when introducing CaO flux into the system, the Se and Te in oxide phases were found to increase; 5) more Se and Te were observed in Cu rich phases, when Pb content was high in the starting material; 6) when Si content was high in matte powder, more Se and Te reported to oxide phases.

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