論文内容の要旨

論文題目　Physicalchemistry of Chlorination Reaction for Separation of Metal Elements in Copper
(塩化反応による銅中金属元素の分離の物理化学)

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In Japan, a large quantity of copper scrap are recycled every year from the viewpoints of efficient use of resources, environmental protection and energy saving. Because of the low mineral reserve and large production, the production of copper must depend on the recovery of copper scrap in the future. Copper scraps are mainly recycled to the conventional copper smelting process. However, it has to be faced with the fact whether the pyrometallugical process of copper can be applicable to the recycling of copper scrap in the future. Therefore, a new recycling process of copper scrap should be taken into account. In this study, a new recycling process of copper scrap by using Cu_2O-based and CuCl-based fluxes based on the experimental results was proposed, and the possibility of new process was discussed from the thermodynamic viewpoint and the mass balance.

In Chapter 1, the present state of copper metal production and copper scrap recycling were investigated. The possibility to apply the chlorination reaction for refining copper scrap was discussed according to the thermodynamic calculation. Based on the above-mentioned investigation and analyses, the necessity to establish a new process aiming at the future recycling of copper scrap was presented.

In Chapter 2, the partition ratios of Pb and Sb between the MgO saturated Cu_2O-SiO_2-$MgO_{satd.}$, Cu_2O-CaO-$MgO_{satd.}$, and Cu_2O-CaO-SiO_2-$MgO_{satd.}$ fluxes and liquid copper from at 1523 to 1673 K were measured. For Cu_2O-SiO_2-$MgO_{satd.}$ system, the effect of SiO_2 content on partition ratios of Pb and Sb was small and their partition ratios were lower than 20 at 1573 K. For Cu_2O-CaO-$MgO_{satd.}$ system, the partition ratio of Pb was not affected by the CaO concentration. The partition ratio of Sb increased with increasing CaO content. For Cu_2O-CaO-SiO_2-$MgO_{satd.}$ system, two liquid phases of calcium silicate phase and Cu_2O rich phase were observed at 1573 K. In Cu2O rich phase, the effect of slag composition on partition ratios of Pb and Sb was small. In calcium silicate phase, the partition ratio of Pb decreased and that of Sb increased with increasing the (mass%CaO)/(mass%SiO_2) ratio.

In Chapters 3 and 4, the removal rate of Pb and Sb from liquid copper by using the CuCl,

$CuCl\text{-}Na_2CO_3$ and CuCl-CaO fluxes from 1423 K to 1523 K was measured. The vaporized amounts of Pb and Sb from the flux-metal system were also discussed according to the mass balances. Lead from liquid copper could be easily removed by using only CuCl flux, and a relatively low concentration was reached at 1423 K. The removal of antimony from liquid copper was difficult by using CuCl flux at 1423 K. However, the addition of Na_2CO_3 or CaO to CuCl flux was effective for the removal of antimony. The concentration of antimony largely decreased with time or with increasing Na_2CO_3 content. It could reach a relatively low value after 15 minutes. According to the mass balances, a large part of removed lead of copper vaporized from CuCl flux. The vaporized amount of antimony from the CuCl flux was small. However, the addition of Na_2CO_3 or CaO to the CuCl flux increased the vaporized amount of Sb. The CuCl-based fluxes system were effective for the removal and recycling of Pb and Sb.

In Chapter 5, the vaporization behavior of Sb by using $CuCl\text{-}Sb_2O_3$, $CuCl\text{-}CaO\text{-}Sb_2O_3$ and $CuCl\text{-}NaSbO_3$ fluxes without liquid copper and the source of oxygen by using $CuCl\text{-}Cu_2O\text{-}Cu$ system at 1423 K to clarify the mechanism of removal and recycling of Sb from liquid copper by using CuCl-based fluxes were investigated. For the vaporization experiments, the SbCl3 and SbOCl were formed in flux, and vaporized to gas phase. The decomposition of Cu_2O in the CuCl flux was confirmed, and resulted in an increase of oxygen content in copper. Based on the experimental results, the mechanism of removal and recycling of Sb by using the $CuCl\text{-}Na_2CO_3$ and CuCl-CaO fluxes was discussed. The Cu_2O was formed by the reaction between CuCl and Na_2CO_3 or between CuCl and CaO, and resulted in an increase of oxygen content in liquid copper. The antimony of liquid copper was oxidized to form the antimony oxide. The formed Sb_2O_3 in flux was chlorinated by CuCl, and resulted in the formation of $SbCl_3$ and SbOCl in flux. Finally, the formed $SbCl_3$ and SbOCl vaporized from flux.

In Chapter 6, the possibility of chlorination reaction utilized in the recycling process of copper scrap was discussed based on the experimental results from the thermodynamic viewpoint and the mass balance. A new recycling process of copper scrap containing the copper-iron separation, oxidation refining, chlorination refining and chloride separation processes was proposed. In the oxidation refining process, the concentrations of impurities including Ni could decrease to 0.01 mass% by using 60 kg of the Cu_2O-15mass%SiO_2 and Cu_2O-15mass%CaO fluxes at 1573 K. In the chlorination refining process, the concentrations of impurities such as Pb and Sb except Ni could reach the lower values than those of JIS standard (H 2121) by using 60 kg of the CuCl-25mass%CaO flux with two times at 1423 K. A small part of impurities vaporized to gas phase, and the vaporized amount of Pb was largest in all impurities. In the chloride recycling process, the vaporization behaviors of ZnOCl and PbOCl were investigated at 1423 K from the thermodynamic viewpoint. The ZnOCl could be ignored, and the PbOCl might exist in gas phase in the chlorination refining process. The source of chlorine was investigated based on the mass balance. The production of Cl2 was calculated to be 291200 ton for treating 1140000 ton of PVC

and was enough for refining copper scrap while the PVC was recycled. The necessary amount of PVC was calculated to be 18750 ton for refining 1400000 ton of copper scrap.

According to the above-mentioned experimental results and analyses, the possibility of chlorination reaction utilized in the recycling process of copper scrap is shown. The proposed new process by utilizing Cu_2O-based and CuCl-based fluxes is feasible for recycling the copper scrap in the future. In the process, both the chlorine from the waste PVC can also be effectively used.