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CRYOLITE-METAL OXIDE BINARY PHASE DIAGRAMS AND PURIFICATION OF LEAD BULLION AND BLISTER COPPER

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Synopsis:

Partial binary phase diagrams of cryolite-metal oxide were introduced and briefly discussed. Most of them were found to form a simple eutectic in the cryolite rich corner. Their eutectic points were located between 1146 and 1281 K and between 1.1 and 32.2 mole% of metal oxide.

Removal of antimony, arsenic, tin and bismuth in the system of molten cryolite-lead bullion was investigated in the presence of dissolved oxygen. Contents of the first three elements decreased rapidly from 1000 ppm to 40, 30 and 35 ppm, respectively at dissolved oxygen content of 0.2 wt% and 973 K. Removal of impurities, such as antimony, arsenic, tin, lead and bismuth from blister copper by cryolite flux was also attempted at 1473 K. Contents of the first three elements also decreased rapidly from 1200, 1130 and 700 ppm to 60, 14 and 10 ppm at dissolved oxygen content of 0.5 wt%. The cryolite flux, however, had only a moderate effect on the removal of lead and virtually no effect on the removal of bismuth in both cases.

A brief thermodynamic analysis was carried out to estimate the solubilities of impurity oxides and experimental results were discussed, accordingly.

Keywords: cryolite, flux, lead refining, copper refining

1 Introduction

Industrial metal refining processes very often adopt the oxidation technique for the removal of impurity elements from the melt. The formation of insoluble oxides may serve as a refining step in removing the metallic component of the oxide. In this process the effective removal of the oxide formed must certainly be our major concern.

It is well known that cryolite(Na_3AlF_6) has a remarkable dissolving power for metallic oxides. It also has thermal stability, high fluidity and low specific gravity at moderately high temperatures[1]. The utilization of cryolite in metal fire-refining, such as copper and lead refining may provide new perspective in pyrometallurgy.

Knowledge of cryolite-metal oxide phase diagrams gives information on the solubility limits of impurity oxides in the melt and on the selection of the container materials as well. In the early 50's Hayakawa and Kido[2] have reported on the binary phase diagrams of Na_3AlF_6-CaO, -CdO, -MgO, -TiO_2, -ZnO and -ZrO_2. Foster[3,4] has reported on that of Na_3AlF_6-Al_2O_3, and Sterten et al.[5] studied the systems of Na_3AlF_6-Al_2O_3, -NiO, -Cr_2O_3, -Cu_2O, -TiO_2, -ZrO_2 and -FeO by means of thermal and chemical analyses. More recently, the present authors[6,7,8,9] have reported on the systems of Na_3AlF_6-PbO, -NiO, -Cu_2O, and -Co_3O_4 by the thermal analysis and X-ray technique. Those data reported for phase diagrams are rather discordant and improved data are clearly needed.

The interest in using special fluxes in the fire refining of crude copper has been growing in the last few years due to the increasing need to apply impure, complex raw materials in the pyrometallurgical production of primary copper. It has been known for several decades that the alkali slag treatment is an effective method for removing arsenic, antimony and bismuth from

blister copper[10,11]. Several equilibruim studies on copper fire-refining with soda slags[12,13] have been carried out particularly during the last ten years. An analogous process well known as the Harris process adopts caustic flux to remove arsenic, antimony, tellurium and tin from lead bullion under the oxidizing atmosphere. Those treatments, however, have some disadvantages, such as metal loss to the slag, flux consumption, treatment time and metallic oxide inclusions in the metal phase.

The aim of this study was to examine cryolite as a fire-refining flux. Removal of antimony, arsenic, tin and bismuth from lead bullion and blister copper was attempted with cryolite flux. A brief thermodynamic analysis was also carried out to estimate the solubilities of impurity oxides both in liquid copper and lead.

2 Cryolite - Metal Oxide Binary System

Eutectic points for the cryolite-metal oxide(M_xO_y) binary systems are shown in Table 1. As seen in Table 1 eutectic points are somewhat discordant. Recently Sterten et al.[5] reported the melting point of cryolite(T_m) to be 1285 K, which agrees well with the present authors' results. However, that measured by Berul et al.[14] and Hayakawa et al.[2] was 1273 K and 1268~1273 K, respectively. The low melting point of cryolite obvserved may be mainly due to impurities included in cryolite. The lowering of the eutectic temperature as well as the eutectic composition is also attributed to those impurities.

Metal oxides of group II in the periodic table generally form a eutectic system with a solid solution region in the cryolite rich corner. On the other hand, metallic oxide of group VIII (FeO, Co_3O_4 and NiO) form a simple eutectic and the eutectic temperature increases in the order of FeO, Co_3O_4 and NiO, whereas the eutectic composition decreases in the same order. In the case of lanthanides, only few systems(CeO_2,Nd_2O_3 and Sm_2O_3) were reported and the phase diagrams lack to give useful informations on phase relations.

The majority of works to date are not well defined and improved phase diagrams are needed. It is also necessary to extend experimental work to other metal oxide systems for the utilization of cryolite flux in the fire-refining process.

Table 1 Na_3AlF_6-M_xO_y binary systems

Group	Binary System	T_C(K)	T_E(K)	N_E(mole %)	Source
II	Na_3AlF_6-MgO	1268	1178	28.7	Hayakawa[2]
	-CaO	1268	1168	32.2	Hayakawa[2]
	-ZnO	1273	1246	5.9	Hayakawa[2]
	-CdO	1273	1243	9.3	Hayakawa[2]
IV	Na_3AlF_6-TiO_2	1273	1243	10.1	Hayakawa[2]
	-TiO_2	1273	1253	10.0	Belyaev[5]
	-TiO_2	1277	1255	8.3	Madhaven[5]
	-TiO_2	1282	1261	12.0	Rolin[5]
	-TiO_2	1284±1	1268±1.5	11.7±0.3	Sterten[5]
	-ZrO_2	1273	1238	18	Hayakawa[2]
	-ZrO_2	1284±1	1268±1.5	5.3±0.4	Sterten[5]
VIII	Na_3AlF_6-FeO	1285	1258	14.2	Choi[9]
	-FeO	1284±1	1255.9±2	14.2±0.5	Sterten[5]
	-Co_3O_4	1285	1225	4.4	Choi[9]
	-NiO	1277	1236	6.0	Lee[7]
	-NiO	1284±1	1278.9±1	2.80±0.2	Sterten[5]
Others	Na_3AlF_6-Al_2O_3	1285	1234	19.45	Foster[3]
	-Al_2O_3	1285	1233.7	19.8	Suh[6]
	-Al_2O_3	1284±1	1236.9±1	19.1±0.5	Sterten[5]
	-PbO	1285	1176	30.7	Suh[6]
	-Cu_2O	1285	1146.5	74.1	Suh[6]
	-Cu_2O	1284±1	1281.2±1	1.1±0.1	Sterten[5]
	-Cr_2O_3	1284±1	1281.5±1.5	0.95±0.1	Sterten[5]
Lanth.	Na_3AlF_6-CeO_2	1273	(1155)	(5.4)	Berul[13]
	-Nd_2O_3	1263	-	-	Berul[13]
	-Sm_2O_3	1273	(1173)	(2.0)	Berul[13]

T_C: Melting point of cryolite in Kelvin, T_E: Eutectic temperature in Kelvin and N_E: Eutectic composition in mole percent,( ): the point of lowest solubility.

3 Experimental

The experimental apparatus used in this work is shown in Fig.1 The working tube was located in a vertical tube furnace heated by a SiC heating element. Water cooled brass heads were used to seal the working tube. Temperature of the crucible was controlled by an automatic temperature controller to better than ±3 K. Atmosphere over the melt was dry argon which was purified before use by passing through silica gel and pyrogallic acid traps. Its flow rate was controlled to 3 ml/sec(STP).

Synthetic cryolite, with a purity of 99.9% Na_3AlF_6 was used through the experiment. Electric copper and lead were used for the metal phase. Sb, As, Sn and Bi were chemical pure and taken as impurity elements. As seen in Fig. 1 a small stainless steel container was placed inside of the carbon crucible to avoid possible contamination of the melt by reduced impurity elements.

A 300g of electric copper(lead) was melted in a stainless steel crucible at 1473K (973K) under

the argon atmosphere. The impurity elements were added in metallic form and the bath was sampled for chemical analysis. A 50g of cryolite in the form of compacted tablet was added into the crucible. Molten materials in the crucible were well mixed for 2 to 3 min by a quartz rod through the sampling hole and held for 15 min to allow the slag-metal phase separation. Oxygen contents in the melt was controlled by successive additions of Cu_2O and PbO for copper and lead melts respectively.

The slag and metal samples were sucked from the crucible using a quartz tube through the sampling hole. The metal phase was analyzed spectroscopically and by the I.C.P. method, and the slag phase by the standard wet method.

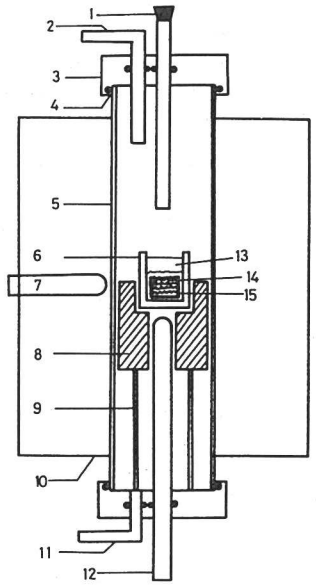

Fig. 1 Experimental apparatus
1. Sampling tube
2. Ar gas outlet
3. Brass water jacket
4. O-ring
5. Müllite tube
6. Carbon crucible
7. Thermocouple well
8,9. Refractory support
10. SiC furnace
11. Ar gas inlet
12. Thermocouple well
13. Flux
14. Blister copper
15. Stainless steel crucible

4 Results and Discussion

In view of the fact that oxygen plays a major role in the liquid metal refining process, equilibria between dissolved oxygen and other elements i.e. impurity elements in the melt being refined are of prime importance. Reaction equilibrium between the dissolved oxygen and the resulting oxide may be expressed by the reaction,

$$x\underline{M}+y\underline{O}=M_xO_y \qquad (1)$$

where $\underline{M}$ and $\underline{O}$ represent the impurity metal and oxygen dissolved in the bulk metal, respectively. Assuming that the metallic oxide, M_xO_y is at its standard state and that the dissolved elements obey the Henry's law the solubility product of M_xO_y, K_{SP} may be expressed by the equation,

$$K_{SP}=[\underline{M}]^x[\underline{O}]^y=\exp(\Delta G^\circ_1/RT) \qquad (2)$$

where ΔG°_1 stands for the standard free energy change of eq(1). The value of ΔG°_1 may be calculated from thermodynamic quantities at the given temperature i.e. the standard free energy of formation of M_xO_y, ΔG°_1 and Henrian activity coefficients of dissolved elements, γ°. The standard free energy of formation[15] and the activity coefficients[16] are presented in Table 2 and 3, respectively.

Table 2 Standard free energy of formation

Reaction	Temp.(K)	ΔG°(cal)
$2Sb(l) + 3/2O_2(g) = Sb_2O_3(s)$	928~1698	$-173940 - 32.84T\log T + 0.75\times10^{-3}T^2 - 0.3\times10^5T^{-1} + 166.52T$
$2Bi(l) + 3/2O_2(g) = Bi_2O_3(s)$	544~1090	$-142270 + 2.30T\log T - 3.25\times10^{-3}T^2 - 0.3\times10^5T^{-1} + 67.55T$
	1090~1600	$-147350 - 32.84T\log T + 0.75\times10^{-3}T^2 - 0.3\times10^5T^{-1} + 174.59T$
$Sn(l) + O_2(g) = SnO_2(s)$	505~1898	$-143080 - 7.37T\log T - 0.70\times10^{-3}T^2 - 2.38\times10^5T^{-1} + 76.53T$
$Pb(l) + 1/2O_2(g) = PbO(s)$	600.5~1153	$-53520 + 3.06T\log T + 2.95\times10^{-3}T^2 - 0.10\times10^5T^{-1} + 18.08T$
	1159~1745	$-53980 - 12.94T\log T + 0.25\times10^{-3}T^2 - 0.10\times10^5T^{-1} + 64.22T$
$Cu(l) + 1/2O_2(g) = CuO(s)$	1357~1720	$-39410 - 4.17T\log T - 2.15\times10^{-3}T^2 - 0.10\times10^5T^{-1} + 12.05T$
$1/2O_2(g) = \underline{O}$(1 wt% in Pb)	1073~1323	$-28300 + 8.47T$
$1/2O_2(g) = \underline{O}$(1 wt% in Cu)	1273~1523	$-21600 + 5.3T$

Table 4 shows solubility products estimated for oxides of impurity elements in lead and copper melts at 973 K and 1473 K, respectively. Those for arsenic couldn't be estimated because thermodynamic data were not available. Equilibrium plots of dissolved elements in lead and copper melts with respect to the oxygen content were made from solubility product values and are shown respectively in Figs. 2 and 3.

One can easily see that in both cases antimony and tin are readily oxidized from lead and copper melts to the cryolite flux, while bismuth is never oxidized in lead and copper melts before lead and copper are oxidized. In general, stability areas of oxides decrease as oxygen content in the melt decreases. It is also interesting to point out that antimony oxide, Sb_2O_3 becomes the more stable phase than copper oxide, CuO in the copper melt containing oxygen over 2.63 wt%.

Table 3 Henrian activity coefficients in liquid lead and copper

Element	Solvent metal	Temp.(K)	γ°	Atomic wt.
Bi	Pb	983	0.43	208.98
	Cu	1473	2.7	
Sb	Pb	773	0.80	121.74
	Cu	1473	0.014	
Sn	Pb	773	2.30	118.70
	Cu	1473	0.048	
Pb	Cu	1473	5.27	207.19

Table 4 Solubility products of oxides in melts

Reactions	Solvent metal	Temp.(K)	log K_{SP}
$2\underline{Sb} + 3\underline{O} = Sb_2O_3(s)$	Pb Cu	973 1473	- 6.72 2.50
$2\underline{Bi} + 3\underline{O} = Bi_2O_3(s)$	Pb Cu	973 1473	1.86 4.10
$2\underline{Sn} + 2\underline{O} = SnO_2(s)$	Pb Cu	973 1473	- 9.92 - 2.12
$\underline{Sn} + \underline{O} = SnO(s)$	Pb	973	- 4.04
$\underline{Pb} + \underline{O} = PbO(s)$	Pb Cu	973 1473	- 2.08 0.98
$\underline{Cu} + \underline{O} = CuO(s)$	Cu	1473	1.04

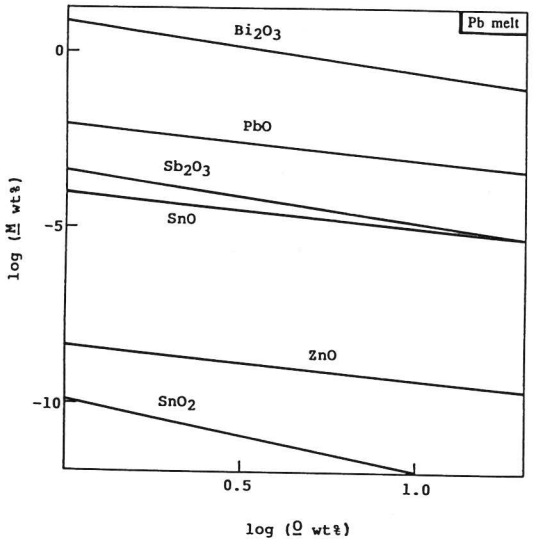

Fig. 2 Equilibrium plot of dissolved elements in Pb melt at 973 K; M stands for Bi, Pb, Sn and Sb

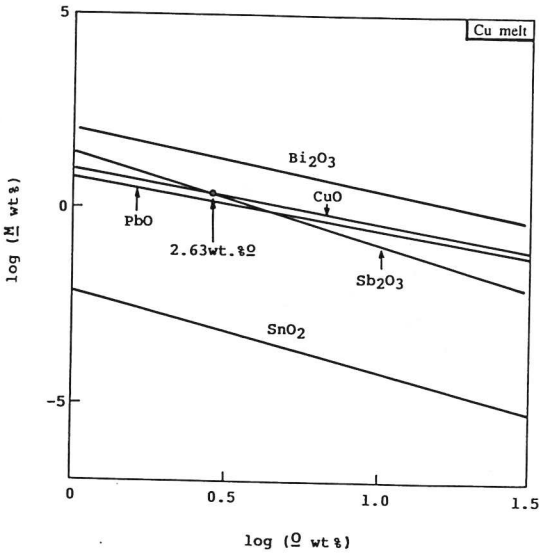

Fig. 3 Equilibrium plot of dissolved elements in Cu melt at 1473 K; M stands for Bi, Pb, Cu, Sb and Sn

The thermodynamic analysis suggests that antimony and tin can easily be oxidized and dissolved into the cryolite flux. The oxidation, however, is not an effective process to remove bismuth from lead bullion as well as blister copper. This observation is in good agreement with the industrial practice known as the Harris process where other methods must be adopted for the bismuth removal[17].

Figs. 4 and 5 show experimental results for removal of impurity elements in lead and copper melts to the cryolite flux, respectively. The initial concentrations of impurities in the lead melt was 0.1 wt%. The oxygen concentrations studied were in the range of 0 to 1 wt%. As can be seen antimony, arsenic and tin except bismuth were easily oxidized from the lead melt and dissolved into the cryolite flux. Their concentrations were lowered below the resolution of the analytical methods used at about 0.3 wt% oxygen. Fig.4 indicates that concentrations of antimony, arsenic and tin were decreased to below 40, 35 and 30 ppm at 0.2 wt% oxygen, respectively. This result is excellent compared to the industrial practices.

Similar experimental results could also be observed in the copper-oxygen-cryolite system(see Fig. 5). Antimony, arsenic and tin contents in the copper melt were readily decreased from 0.12,

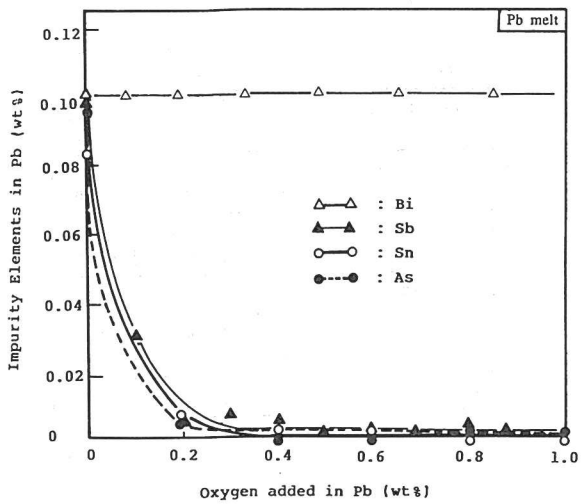

Fig. 4 Effect of oxygen concentration on the elimination of impurity elements from Pb melt at 973 K

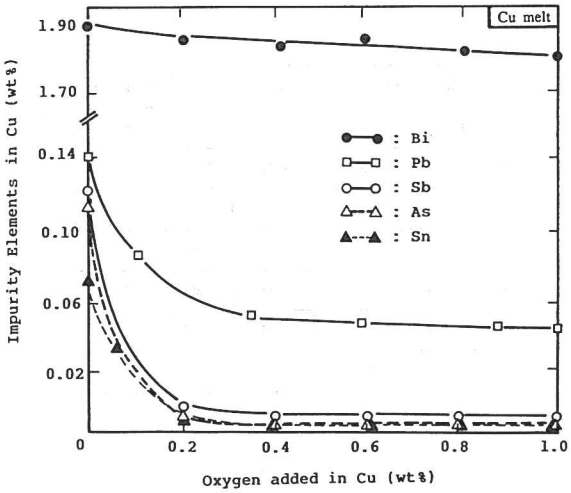

Fig. 5 Effect of oxygen concentration on the elimination of impurity elements from Cu melt at 1473 K

0.113 and 0.07 wt% to 60, 14 and 10 ppm at 0.5 wt% oxygen, respectively. Lead and bismuth, in particular, were not significantly affected in oxygen-bearing copper melts. Those results are in good agreement with thermodynamic predictions.

As for the effect of time on the removal of the impurity elements in copper melt(see Fig. 6), it only took about fifteen minutes for equilibrium to be established between the cryolite flux and the metal phase at 0.5 wt% oxygen and 1473K. This is very advantageous compared to other fluxes(e.g.Na_2CO_3) which require substantial amount of time for the treatment. Cryolite thus is proved to be a practical flux with great applicable potential.

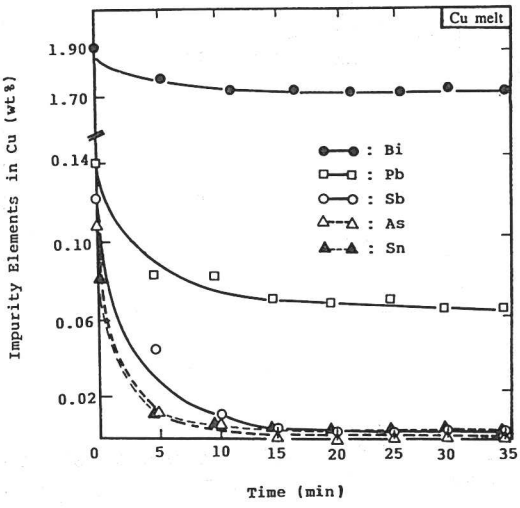

Fig. 6 Effect of time on the elimination of impurity elements from Cu melt at 1473 K, and oxygen content, 0.5 wt%

5 Conclusion

An attempt was made to remove impurity elements from lead bullion and blister copper by using the cryolite flux. Antimony, arsenic and tin could easily be removed from oxygen-bearing lead and copper melts at 973 K and 1473 K, respectively. Those elements decreased rapidly from 700~1200 ppm to 10~60 ppm depending upon melts and oxygen content in the melts. The oxygen content was the most important factor in those systems. The optimum oxygen contents were 0.2 and 0.5 wt% for the lead and copper melts, respectively.

The cryolite flux, however, had only a moderate effect on the removal of lead from the copper melt and virtually no effect on the removal of bismuth in both lead and copper melts. Those results are in good agreement with thermodynamic prediction.

The equilibrium in the copper-oxygen-cryolite system could be attained in 15 min at 0.5 wt% oxygen and 1473K. This is an advantageous factor compared to other fluxes.

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