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VACUUM REFINNING COOPER BLISTER TO REMOVE ANTIMONY

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Preliminary Note – Prethodno priopćenje

A research on kinetics of antimony evaporation from molten copper blister was made in a vacuum induction melting (VIM) furnace at temperatures of 1 473 and 1 523 K, and operating pressures of 8 - 133 Pa. The evaporation rate of Sb was found to be first order with respect to your content in the melt. The overall mass transfer coefficient of antimony evaporation from cooper blister are from $1{,}82\times10^{-5}$ ms^{-1} to $3{,}43\times10^{-5}$ ms^{-1} at 1 473 K (8 Pa) - 1 523 K (133 Pa).

Key words: vacuum refining, blister copper, antimony, evaporation of metals, induction vacuum furnace

INTRODUCTION

In the process of vacuum copper refining, the removal of arsenic, antimony and lead is of fundamental importance. Some of them must be removed from molten metals, because of their deleterious effects on copper electrical properties. In the case of the first two elements, they can be removed from the bath by evaporation. For Antimony due to its low vapour pressure, it is difficult.

In the work, the results of investigations on vacuum melting of copper blister conducted under pressure within the range of 8 - 133 Pa and at temperature 1 473 - 1 523 K, are presented. The copper input contained 0,02 % mass of antimony and 0,41 - 0,44 % mass of oxygen. The metallurgical process was carried out in the IS5/III vacuum furnace produced by the Leybold Heraeus company. The results were discussed and allowed to determine experimental overall mass transfer coefficient for antimony.

COPPER AND ANTIMONY VAPOUR PRESSURE OVER THE LIQUID Cu-Sb-O ALLOYS

The outotec HSC chemistry software thermodynamic database data shows that for copper alloys containing antimony and oxygen it is possible to have Sb (g), Sb_2 (g), Sb_4 (g), SbO (g) and Sb_4O_6 (g) in the gas phase. Thus, the removal of antimony from blister copper, takes place by evaporation not only of pure antimony, but also its volatile oxides. Following thermodynamic condition of this process can be considered:

$$\frac{X_{Sb(l)}}{X_{Cu(l)}} < \frac{p_{Sb(g)} + 2p_{Sb_2(g)}}{p_{Cu}} + \frac{4p_{Sb_4(g)} + p_{SbO(g)} + 4p_{Sb_4O_6(g)}}{p_{Cu}} \quad (1)$$

where:

$X_{Sb(l)}$, $X_{Cu(l)}$ - molar fraction of antimony and copper respectively in a liquid metallic bath,

p_{Sb}, p_{Sb2}, p_{Sb4}, p_{SbO}, p_{Sb4O6} - vapour pressure in the gas phase Sb, Sb_2, Sb_4, SbO, Sb_4O_6 respectively

Table 1 shows the values of equilibrium vapour pressure of the gas phase components determined based on thermodynamic data collected during the experiments at temperatures of 1 473 K and 1 523 K. The simulation concerns a three-component Cu-Sb-O alloy with a composition similar to the blister copper used in the research.

The condition (1) was verified taking into account the vapour pressure values of Sb, Cu and Sb_2, Sb_4 , SbO and Sb_4O_6, summarized in Table 1, which showed its fulfilment with respect to the analyzed initial material, i.e. copper blister.

The analysis shows that condition (1) is not met for oxygen-free copper, while for copper blister with increased copper content is met. This means that from a thermodynamic point of view the removal of antimony from the copper blister by its evaporation is possible.

METHODOLOGY

The tests were carried out using two batches of copper blister with the chemical composition given in Table 2.

The Leybold Heraeus IS5 / III vacuum induction furnace with an operating frequency of up to 4 kHz was used as the melting equipment in this work. A system of two pumps, i.e. a rotary pump and a Roots pump, was used to form the vacuum.

At the beginning of each experiment, copper blister with a specified mass was placed in crucibles made of Al_2O_3 MgO with an internal diameter of 0,22 m. After heating the metal to the desired temperature (this process was carried out in an argon atmosphere), the pressure in the melting system was reduced to a certain value. The maximum holding time of the metal at a

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Table 1 **Equilibrium vapour pressure of copper, antimony, SbO and Sb_4O_6 over the liquid Cu-Sb-O alloy**

Temperature / K	Antimony content in the alloy / %mass	Oxygen content in the alloy / %mass	Vapour pressure of the gas phase ingredients / Pa					
			p (Cu)	p (Sb) × 10^3	p (Sb_2) × 10^{10}	p (Sb_4) × 10^{20}	p (SbO) × 10^4	p (Sb_4O_6) ×10^{14}
1 473	0,2	-	0,513	0,222	4,04	1,53	-	-
1 573	0,2	-	1,190	0,446	8,30	6,80	-	-
1 473	0,2	0,4	0,501	0,371	0,256	1,40	5,02	9,78
1 573	0,2	0,4	1,170	0,752	0,159	3,60	7,31	1,88

Table 2 **Chemical composition of investigated copper blister**

Type of copper	The content of basic admixtures of copper blister / % mas.				
	Pb	S	O_2	As	Sb
Cu blister I	0,24	0,05	0,41	0,193	0,020
Cu blister II	0,33	0,04	0,44	0,181	0,019

given temperature was 30 min. During the process, metal samples were taken and, subjected to chemical analysis for lead content. The tests were carried out for an operating pressure of 8 to 133 Pa in a temperature range of 1 473 - 1 523 K.

OUTCOMES

The changes in the concentration of antimony in copper blister observed for selected experiments are presented graphically in the Figures 1-2.

The data summarized in Table 3 show that the operating pressure decrease from 133 Pa to 8 Pa results in the reduction of the final concentration of antimony in the copper blister down to 0,0131 % by mass for the process conducted at 1 473 K and 0,0118 % mass for one at 1 523 K.

For the assumed F/V = 8,8 - 8,9 ratio, the increase in the process temperature from 1 473 to 1 523 K, with the reduction of the operating pressure in the furnace from 133 Pa to 8 Pa, caused the increase in the mass flux of the evaporating antimony from 1,35 10^{-4} to 2,24 10^{-4} g cm^{-2} min^{-1}.

DISCUSSIONS

The value of the mass flux of antimony evaporating from the molten copper blister can be determined from the general relationship [1]:

$$N_{Sb} = k_{Sb} F \Delta\pi \tag{2}$$

where:

k_{Sb} – antimony transport coefficient also called the overall mass transport coefficient,

F – mass exchange surface area (interface between liquid metal and gas phase),

$\Delta\pi$ – general process drive module.

In order to determine the value of the general antimony transport coefficient in the analysed evaporation process, it was assumed, according to the previous studies, that it can be described by the first order kinetic equation [2-5]. Thus, its rate can be described by the following relation:

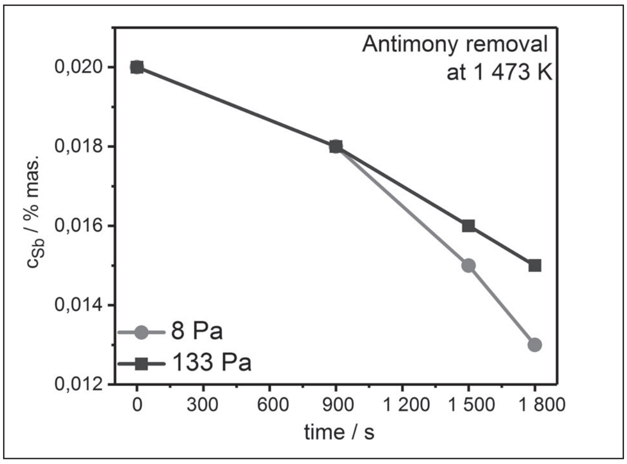

Figure 1 Change of antimony concentration in copper blister during melting carried out at the temperature of 1 473 K

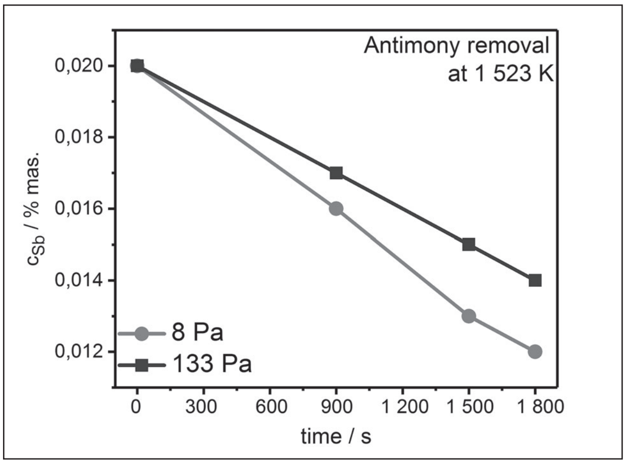

Figure 2 Change of antimony concentration in copper blister during melting carried out at the temperature of 1 523 K, F/V = 8,7

$$\frac{dC_{Sb}}{dt} = k_{Sb} \cdot \frac{F}{V} \cdot C_{Sb} \tag{3}$$

Using equation (3) to determine k_{Sb} values from experimental data, the relationship was used:

$$2{,}303 \log \frac{C^t_{Sb}}{C^0_{Sb}} = -k_{Sb} \cdot \frac{F}{V} \cdot (t - t_0) \tag{4}$$

where:

C^0_{Sb}, C^t_{Sb} – antimony concentration in the bath, initial and after time t, % mas

V – volume of molten copper, m^3,

$(t - t_0)$ – duration of the process, s.

The form of the formula (4) shows that the value of the mass transport coefficient k_{Sb} depends, among others, on the evaporation surface area, which is the actual mass exchange surface area in the analysed evaporation

Table 3 **Results of the study on the antimony removal from copper blister by melting in the induction vacuum furnace**

Type of copper	Operating temperature, K	Operating pressure, Pa	F/V, cm^{-1}	Final antimony concentration, % mas	Antimony removal fraction, %
Cu blister I	1 473	133	8,8	0,0151	25,0
Cu blister I	1 473	8	8,8	0,0136	35,1
Cu blister I	1 523	133	8,9	0,0140	30,1
Cu blister I	1 523	8	8,9	0,0120	39,9
Cu blister II	1 473	133	8,8	0,0158	25,7
Cu blister II	1 473	8	8,8	0,0131	34,8
Cu blister II	1 523	133	8,9	0,0139	31,1
Cu blister II	1 523	18	8,9	0,0118	41,0

Table 4 **Values of experimental mass transport coefficients k_{Sb}**

No	Operating temperature / K	Operating pressure / Pa	Material	F/V / m^{-1}	General mass transport coefficient / k_{Sb}, ms^{-1}	Literature
1	1 473 - 1 523	8 - 133	Cu blister	8,8 - 8,9	1,82 - 3,43×10^{-5}	This article
2	1 445 - 1 626	3 - 27	Cu anode	6,5 - 7,2	<0,1×10^{-5}	[8-10]*
3	1 423 - 1 523	8 - 533	Cu catode	6,7 - 10,2	<0,1×10^{-5}	[2]*
4	1 573	8 - 1 333	Cu blister	12,34 - 12,58	1,08 - 2,13×10^{-5}	[12]*
5	1 573	7 - 125	Cu anode	6,8 - 10,2	<0,5×10^{-5}	[11]*

* the value of evaporation area equal to the cross-sectional area of the crucible was assumed.

process. When the melting of metals and their alloys is carried out in the induction furnaces (VIM and ISM technology), the size of the metal surface depends significantly on the electromagnetic field affecting the metal bath and the properties of the liquid metal.

The results of flow field analysis and coupling of the electromagnetic field with the geometry of the metal bath presented in [6-7] for the melting process carried out in the induction crucible furnace showed a significant influence of the electromagnetic forces on this geometry. The determined values of the actual size of the evaporation surface for the copper melting conditions were 430 cm^2, with the values calculated as crucible cross-sectional areas 380 cm^2.

Table 4 summarizes the values of the k_{Sb} coefficient for the studied process of evaporation of antimony from copper blister determined from the relationship (4), taking into account the slope of the straight line being a function of antimony concentration ($\log \frac{C^t_{Sb}}{C^0_{Sb}}$) over time.

CONCLUSIONS

Analysis of the effect of pressure and temperature on the rate of removal of Sb from copper blister showed that an increase in temperature from 1 473 to 1 523 K with a simultaneous decrease in pressure in the system from 133 to 8 Pa causes an increase antimony removal effectiveness from 25 % to 41 %. This corresponds to an increase in the value of the total mass transport coefficient k_{Sb} from 1,82×10^{-5} ms^{-1} to 3,43×10^{-5} ms^{-1}. The obtained values of the overall mass transport coefficient k_{sb} are lower compared to the results obtained by most of other authors. This is due to the fact that, there is a significant amount of oxygen in the copper blister (0,40 % mass) which intensifies the process of antimony evaporation by creating volatile oxides of this metal.

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Note: The responsible translator for English language is Ling House. Poland.