



Removal of Lead From Blister Copper by Melting in the Induction Vacuum Furnace

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Abstract

The usage of the reduced pressure in the processes of smelting and refining of metal alloys allow to remove not only the gases dissolved in the metal bath, but also the impurities having a higher vapour pressure than the matrix metal. Blister copper produced in flash furnace contains many impurities such as lead, bismuth and arsenic. Some of them must be removed from molten metals, because of their deleterious effects on copper electrical properties. When the smelting process is carried out in the induction vacuum furnaces, the above-mentioned phenomenon is being intensified, one or another mixing of bath and increase in the surface area of mass exchange (liquid metal surface). The latter results from the formation of a meniscus being an effect of the electromagnetic field influence on the liquid metal. In the work, the results of refining blister copper in terms of removing lead from it, are presented. The experiments were carried out in the induction crucible vacuum furnace at temperatures of 1473 and 1523 K, and operating pressures in a range of 8 - 533 Pa.

Keywords: Vapour pressure, Blister copper, Induction vacuum furnace, Evaporation of metals, Refining of cooper

1. Introduction

Vacuum induction furnaces are modern metallurgical equipment's used for smelting and refining of various metals. During alloys smelting in vacuum induction furnace, impurities with high vapour pressure can be removed from the melts. Blister copper produced in flash furnace contains many impurities such as lead, bismuth and arsenic. Some of them must be removed from molten metals, because of their deleterious effects on copper electrical properties. In the vacuum refining process of copper, the removal of lead contaminants plays a significant role. Intensification of this process may allow to apply other input materials than electrolytic copper for production of high purity copper. In the work, the results of investigations on vacuum melting of copper blister conducted under pressure being in the range of 8 - 533 Pa and at temperature 1473 and 1523 K, are

presented. The input copper contained 0.24 % mass of lead and 0.41 % mass of oxygen. The metallurgical process was carried out in the IS5/III vacuum furnace of the Leybold Heraeus company. The obtained results were discussed and allow to determine experimental overall lead mass transfer coefficient.

2. Copper and lead vapour pressure over the liquid Cu-Pb-O alloy

Based on the results of the thermodynamic analysis presented in [1], assuming that the most common additives of copper are lead and oxygen, it can be stated that in practice only copper, lead and lead oxide vapours are present above the bath. 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 1473 K and 1523 K. The simulation concerns a three-component Cu-Pb-O alloy with a

composition similar to the blister copper used in the research.

Table 1.

Equilibrium vapour pressure of lead, copper and PbO over the liquid Cu-Pb-O alloy

Temperature, K	Lead content in the alloy, %mass	Oxygen content in the alloy, %mass	Vapour pressure of the gas phase ingredients, Pa		
			p (Cu)	p (Pb)	p (PbO)
1473	0.2	-	0.513	8.288	-
1573	0.2	-	1.191	12.39	-
1473	0.2	0.4	0.506	13.85	16.05
1573	0.2	0.4	1.75	22.48	22.88

Assuming that during the removal of lead from copper blister evaporation not only of lead but also of its volatile oxides occur, the following formula can be considered as the thermodynamic condition of this process:

$$\frac{X_{\text{Pb(l)}}}{X_{\text{Cu(l)}}} < \frac{X_{\text{Pb(g)}}}{X_{\text{Cu(g)}}} \quad (1)$$

where:

$X_{\text{Pb(l)}}$, $X_{\text{Cu(l)}}$ – molar fraction of lead and copper respectively in a liquid metallic bath,

$X_{\text{Pb(g)}}$, $X_{\text{Cu(g)}}$ – mole fraction of lead and copper respectively in the gas phase.

The relation (1) can also be presented in the form :

$$\frac{n_{\text{Pb(l)}}}{n_{\text{Cu(l)}}} < \frac{n_{\text{Pb(g)}}}{n_{\text{Cu(g)}}} \quad (2)$$

where:

n – the number of moles of the respective component.

Assuming that :

$$\sum n_{\text{Pb(g)}} = n_{\text{Pb(g)}} + n_{\text{PbO(g)}} \quad (3)$$

and knowing that under the analyzed temperature and pressure conditions

$$p_i \approx n_i \quad (4)$$

following formula is obtained:

$$\frac{n_{\text{Pb(l)}}}{n_{\text{Cu(l)}}} < \frac{p_{\text{Pb(g)}} + p_{\text{PbO(g)}}}{p_{\text{Cu}}} \quad (5)$$

which may be transformed into:

$$\frac{X_{\text{Pb(l)}}}{X_{\text{Cu(l)}}} < \frac{p_{\text{Pb(g)}} + p_{\text{PbO(g)}}}{p_{\text{Cu}}} \quad (6)$$

The condition (6) was verified taking into account the vapour pressure values Pb, Cu and PbO, summarized in Table 1, which showed its fulfilment with respect to the analyzed starting material, i.e. copper blister.

The value of $\frac{X_{\text{Pb(l)}}}{X_{\text{Cu(l)}}$ ratio for the analyzed temperature range is 0.00074, while $\frac{p_{\text{Pb(g)}} + p_{\text{PbO(g)}}}{p_{\text{Cu}}}$ ratio is in the range between 25 and 60.

2.1. Methodology

All experiments were carried with copper bath having composition given in the Table 2.

Table 2.

Chemical composition of investigated copper blister

The content of basic admixtures of copper blister, % mas.				
Pb	S	O ₂	As	Sb
0.24	0.05	0.41	0.193	0.029

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. The melting coil of the aggregate allowed to use the crucibles up to 0.005 m³. The furnace was equipped with the system enabling the sampling of liquid metal during its processing. A system of two pumps (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 Al₂O₃ MgO with an internal diameter of 0.1 and 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 given temperature was 30 min. During the process, metal samples were taken and subjected to chemical analysis for lead content. The basic parameters of experiments are summarized in Table 3.

Table 3.

Experiment parameters

Operating pressure, Pa	Sample mass, kg	Crucible diameter, m
8 - 533	5, 35	0.01, 0.22

2.2. Outcomes

The changes in the concentration of lead in copper blister, observed for selected experiments, are presented graphically in Figures 1-4.

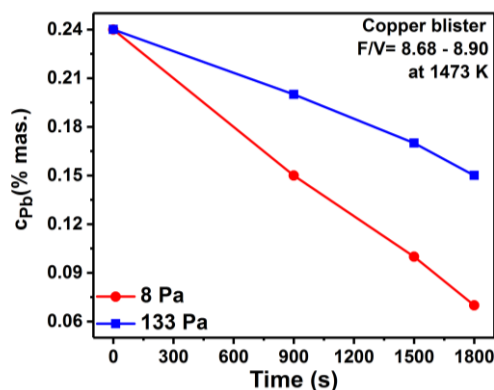


Fig. 1. Change of lead concentration in copper blister during melting carried out at the temperature of 1473 K, $F/V=8.8$

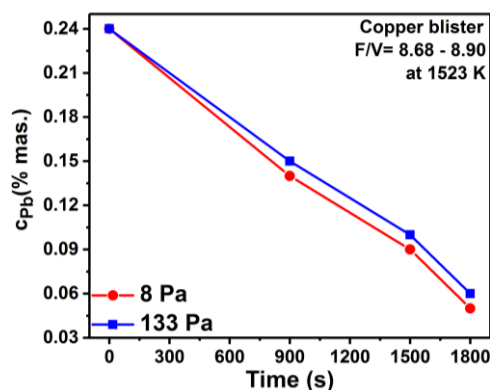


Fig. 2. Change of lead concentration in copper blister during melting carried out at the temperature of 1523 K, $F/V=8.7$

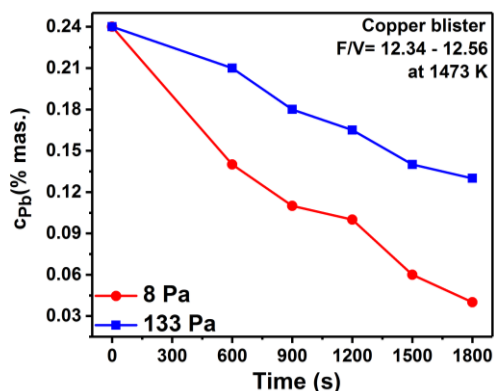


Fig. 3. Change of lead concentration in copper blister during melting carried out at the temperature of 1473 K, $F/V=12.4$

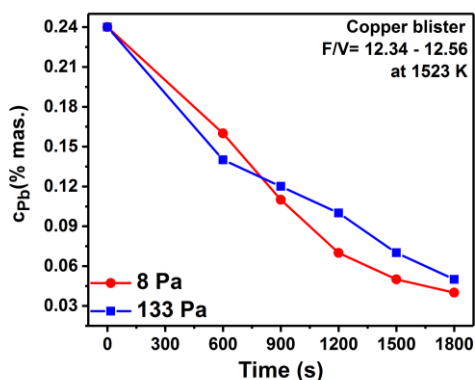


Fig. 4. Change of lead concentration in copper blister during melting carried out at the temperature of 1523 K, $F/V=12.3$

The final lead concentrations in copper for all experiments are given in the Table 4.

Table 4.

Results of the study on the lead removal from copper blister by melting in the induction vacuum furnace

Nr	Operating temperature, K	Operating pressure, Pa	F/V , cm^{-1}	Final lead concentration, % mas	Lead removal fraction, %	Mass flux $\text{gcm}^{-2}\text{min}^{-1}$
1	1473	533	12.4	0.20	16.6	$6.29 \cdot 10^{-4}$
2	1473	133	12.4	0.13	45.8	$1.73 \cdot 10^{-3}$
3	1473	8	12.4	0.04	83.3	$3.14 \cdot 10^{-3}$
4	1473	533	8.8	0.19	20.8	$1.35 \cdot 10^{-3}$
5	1473	133	8.8	0.15	37.5	$2.44 \cdot 10^{-3}$
6	1473	8	8.8	0.07	70.8	$4.61 \cdot 10^{-3}$
7	1523	533	12.3	0.16	33.3	$1.26 \cdot 10^{-3}$
8	1523	133	12.3	0.05	79.1	$2.98 \cdot 10^{-3}$
9	1523	8	12.3	0.04	83.3	$3.15 \cdot 10^{-3}$
10	1523	533	8.7	0.14	41.6	$2.71 \cdot 10^{-3}$
11	1523	133	8.7	0.06	75.0	$4.88 \cdot 10^{-3}$
12	1523	8	8.7	0.05	79.2	$5.15 \cdot 10^{-3}$

The data compiled in the Table 4 show that the operating pressure decrease from 533 Pa to 8 Pa result in the reduction of the final concentration of lead in the copper blister down to 0.07% by mass for the process conducted at 1473 K and 0.05% by mass for 1523 K. In the same time, the increase in the degree of lead removal from 16.6 % to 83.3 % was observed.

For the assumed F/V ratio, the increase in the process temperature from 1473 to 1523 K, with the reduction of the operating pressure in the furnace from 533 Pa to 8 Pa, caused the increase in the mass flux of the evaporating lead from $6.29 \cdot 10^{-4}$ to $3.15 \cdot 10^{-3}$ ($F/V=12.3$) and from $1.35 \cdot 10^{-3}$ to $5.15 \cdot 10^{-3}$ ($F/V=8.7$). Thus, the higher the value of the F/V ratio, the lower the mass flux of the evaporating lead.

2.3. Discussion

The value of the mass flux of lead evaporating from the metal bath can be determined from the general relationship [2]:

$$G_{pb} = k_{pb} \cdot F \cdot \Delta\pi \quad (7)$$

where:

k_{pb} - lead 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 lead transport coefficient in the analyzed evaporation process, it was assumed, according to the previous studies, that it can be described by the first order kinetic equation [3-9]. Thus, its rate can be described by the following relation:

$$\frac{dC_{pb}}{dt} = k_{pb} \cdot \frac{F}{V} \cdot C_{pb} \quad (8)$$

This relationship in the integral form can be written as:

$$\int_0^t \frac{dC_i}{C_i} = k_{pb} \cdot \frac{F}{V} \cdot \int_0^t dt \quad (9)$$

After integrating the relationships (9):

$$2.303 \log \frac{C_{pb}^t}{C_{pb}^0} = -k_{pb} \cdot \frac{F}{V} \cdot (t - t_0) \quad (10)$$

where:

C_{pb}^0, C_{pb}^t - lead concentration in the bath, initial and after time t , % mas.,

F - evaporation surface, m^2 ,

V - volume of liquid metal, m^3 ,

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

The form of the formula (10) shows that the value of the mass transport coefficient k_{pb} depends, among others, on the evaporation surface area, which is the actual mass exchange surface area in the analyzed evaporation 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 [3-5]. The effect of the electromagnetic field causes the formation of the distinct meniscus on the surface of the bath. Figure 5 shows a photograph of the surface of fused copper in the induction crucible furnace at the furnace operating power of 38 kW.

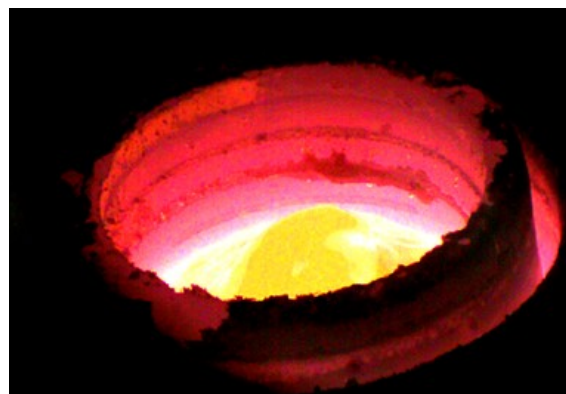


Fig. 5. Photograph of fused copper surface in an induction furnace - operating power 53 kW

The results of flow field analysis and coupling of the electromagnetic field with the geometry of the metal bath presented in [10-13] for the melting process carried out in the induction crucible furnace showed a significant influence of the electromagnetic forces on this geometry. For example, in the case of melting of copper and its alloys in the induction furnace, it is possible to increase the area of the bath surface (which is the actual evaporation surface area), even by 50% compared to the cross-sectional area of the crucible. Numerical simulations related to the determination of the actual surface of the metallic bath discussed in the above works dialled also with the process of melting of copper and its alloys in the furnace in which the above-discussed experiments were carried out [13]. The determined values of the actual size of the evaporation surface for the copper melting conditions were 106 and 430 cm^2 respectively, with the values calculated as crucible cross-sectional areas 78.5 and 380 cm^2 , respectively.

Table 5 presents the values of the k_{pb} coefficient for the studied process of evaporation of lead from copper blister determined from the relationship (10), taking into account the slope of the straight line being a function of lead concentration ($\log \frac{C_{pb}^t}{C_{pb}^0}$) in time. The table also compares the values of these coefficients obtained by other Authors including the basic parameters of the cited results.

Table 5.

Values of experimental mass transport coefficients k_{pb}

Nr	Operating temperature, K	Operating pressure, Pa	The material	F/V , cm^{-1}	General mass transport coefficient, k_{pb} , ms^{-1}	Author
1	1473	8-533	Cu blister	16.74	$1.59-5.62 \cdot 10^{-5}$	Presented study
2	1473	8-533	Cu blister	9.66	$2.24-6.79 \cdot 10^{-5}$	Presented study
3	1573	8-533	Cu blister	16.74	$1.92-6.18 \cdot 10^{-5}$	Presented study
4	1573	8-533	Cu blister	9.66	$2.32-7.96 \cdot 10^{-5}$	Presented study
5	1423-1623	8-13	Cu blister, cathode and anode copper	6.7-10.2	$1.5-4.5 \cdot 10^{-5}$	Ozberk, Guthrie [3]*
6	1473-1573	0.1-1.0	synthetic alloys Cu-Pb	6.5-7.5	$1.0-3.0 \cdot 10^{-4}$	Ohno [14,15]*
7	1373-1523	8-1333	synthetic alloys Cu-Pb	8.8	$0.3-9.6 \cdot 10^{-5}$	Blacha [1]*
8	1373-1523	8-1333	Cu blister	8.8	$0.6-8.2 \cdot 10^{-5}$	Blacha [16]*

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

When analyzing the results presented in the Table 5, it can be stated that the increase in the process temperature from 1473 K to 1523 K together with the decrease in operating pressure in the system from 533 Pa to 8 Pa causes an increase in the rate of lead removal, which is indicated, among others, by the values of the general lead transport coefficient k_{pb} determined from the experimental data. With the assumed increase of the temperature and simultaneous decrease of the pressure, these values increased from $1.59 \cdot 10^{-5}$ to $7.96 \cdot 10^{-5} \text{ ms}^{-1}$. These values are in good agreement with the results of other Authors. The slight differences may arise from the usage of the actual values of the mass exchange surface area in the data analysis, which has been done for the first time. In the presented study, the evaporation surface value was assumed to be equal to the crucible cross-sectional area, which in turn may result in the small uncertainties in estimating the k_{pb} coefficient value.

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