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KINETICS OF LEAD REMOVAL FROM THE Cu-Pb-Fe ALLOY BY BARBOTAGE WITH INERT GASES

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Discussion of the of kinetics of lead removal from the Cu-Pb-Fe alloy by barbotage with argon and helium. The values of the mass penetration coefficient for the liquid and solid phase as well as the mass transfer coefficient were calculated for the temperatures of 1 473 K and 1 548 K, and for the gas flow rate of $5{,}55 \cdot 10^{-6}$, $6{,}94 \cdot 10^{-6}$, $8{,}33 \cdot 10^{-6}$ and $9{,}72 \cdot 10^{-6}$ $\text{m} \cdot \text{s}^{-1}$.

Key words: metallurgy, barbotage, kinetics, refining, alloy

Kinetika odstranjivanja olova iz Cu-Pb-Fe legure pročišćavanjem inertnim plinom. Diskusija o kinetici odstranjivanja olova iz Cu-Pb-Fe legure pročišćavanjem argonom i helijem. Vrijednosti koeficijenta masene penetracije za tekuću i krutu fazu kao i za koeficijent masenog prijenosa su izračunati za temperature 1473 K i 1548 K, te za protok plina $5{,}55 \cdot 10^{-6}$; $6{,}94 \cdot 10^{-6}$; $8{,}33 \cdot 10^{-6}$ i $9{,}72 \cdot 10^{-6}$ ms^{-1}.

Ključne riječi: metalurgija, pročišćavanje, kinetike, rafiniranje, legura

INTRODUCTION

One of products of the single step copper smelting from concentrate in fluidized-bed furnace in Glogow Copperworks is the slag containing up to 20 % wt. copper. This product is then submitted to a decopperizing process in electric furnace. As product in this technology, a Cu-Pb-Fe alloy containing over 20 % wt. of lead and dusts containing up to 40 % wt. of this element are obtained [1, 2].

Cu-Pb-Fe alloy is processed in the converter to obtain copper suitable for the fire refining process, i.e. containing below 0,3 % wt. of lead. At the same time, this technology is aimed at the removal of possible higher quantity of lead to dust and to obtain low concentration of arsenic in copper. As result of this process, approx. 70 % wt. of lead contained in this alloy is passed to dusts and the remaining part is collected in converter slag. Because the copper content in slag (even above 35 % wt.) is higher than that of lead, this material is returned back to electric furnace. It can be assumed then, that the lead in converter slag is circulating in the process cycle [1, 2].

RATE OF LEAD EVAPORATION FROM THE CU-PB-FE ALLOY

In the processes analysed, it was assumed that the lead wonted be removed from the Cu-Pb-Fe alloy with evaporation in to bubbles of gas flowing through the liquid alloy. Therefore, for the processes, the general mass balance equation can assume the following form [3]:

$$dn_{Pb_{(c)}} = dn_{Pb_{(g)}} \tag{1}$$

where:

$dn_{Pb_{(c)}}$ – quantity of lead removed from the alloy,

$dn_{Pb_{(g)}}$ – quantity of lead transferred to the gaseous phase (bubbles).

The speed of the process can be determined based on the following dependence [3]:

$$\begin{aligned} \frac{dn}{dt} &= F \cdot \frac{\beta_g}{R \cdot T} \cdot (P_{Pb}^* - P_{Pb}^P) = \\ &= F \cdot \beta_c \cdot (C_{Pb} - C_{Pb}^*) \end{aligned} \tag{2}$$

where:

F – mass transfer area / m^2,

P_{Pb}^* – balance pressure for lead vapours at the phase boundary / Pa,

P_{Pb}^P – lead pressure inside a gas bubble / Pa,

C_{Pb} – lead concentration in the liquid phase core,

C_{Pb}^* – lead concentration in the alloy near the phase boundary,

R – gas constant / $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$,

T – temperature / K,

β_g – mass penetration coefficient in the gaseous phase / $\text{m} \cdot \text{s}^{-1}$,

β_c – mass penetration coefficient in the liquid phase / $\text{m} \cdot \text{s}^{-1}$.

The value of balance pressure can be determined using the following dependence:

$$P_{Pb}^* = P_{Pb}^o \cdot \gamma_{Pb} \cdot X_{Pb}^* \tag{3}$$

where:

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X_{Pb} – lead mole fraction,
γ_{Pb} – activity coefficient for lead in solution.

By applying dependence (2) and analysing the processes with reference to a single bubble, i.e. when:

$$F = \pi \cdot d_p^2 \tag{4}$$

where:
d_p – bubble diameter / m.
the following relation is obtained:

$$\frac{dn}{dn} = \pi \cdot d_p^2 \cdot \frac{\beta_g}{R \cdot T} \cdot (P_{Pb}^{*} - P_{Pb}^{p}) = \\ = \pi \cdot d_p^2 \cdot \beta_c \cdot (C_{Pb} - C_{Pb(r)}) \tag{5}$$

Using dependence (3) and Clapeyron equilibrium, dependence (5) can be transformed in the form:

$$\frac{d}{dt} = \left(\frac{\pi \cdot d_p^3 \cdot P_{Pb}^{P}}{6R \cdot T} \right) = \\ = \pi \cdot d_p^2 \cdot \frac{\beta_g}{R \cdot T} \cdot (P_{Pb}^{o} \cdot \gamma_{Pb} \cdot X_{Pb}^{*} - P_{Pb}^{P}) = \\ \pi \cdot d_p^2 \cdot \frac{\beta_c}{\alpha} \cdot (X_{Pb} - X_{Pb}^{*}) \tag{6}$$

where:

$$\alpha = \frac{m_s}{\sum n_i \cdot \rho_s} \tag{7}$$

where:
m_s – alloy mass / g,
n_i – number of moles of the ith alloy component,
ρ_s – alloy density.

The total speed of the process can be ultimately expressed with the following dependence:

$$\frac{d}{dt} = \left(\frac{\pi \cdot d_p^3 \cdot P_{Pb}^{P}}{6R \cdot T} \right) = \\ = \pi \cdot d_p^2 \cdot k \cdot (P_{Pb}^{o} \cdot \gamma_{Pb} \cdot X_{Pb}^{*} - P_{Pb}^{P}) \tag{8}$$

where:

$$\frac{1}{k} = \frac{R \cdot T}{\beta_g} + \frac{\alpha \cdot P_{Pb}^{o} \cdot \gamma_{Pb}}{\beta_g} \tag{9}$$

where:
k – mass transfer coefficient.

From the relation (9) the value of the mass transfer coefficient of the processed analysed could the calculated.

CHANGE OF LEAD PRESSURE IN THE GAS BUBBLE

In the analysis of the process, one must bear in mind the fact that the lead concentration in the bubble changes not only with time but also with the bubble position in the metal bath, which means that it is necessary to consider the a change of the process driving modulus also the change of position of the bubble in the bath. The lead pressure change depends on its position in the bath and can be described as follows [3]:

$$\frac{dP_{Pb}^{P}}{dz} = \frac{6R \cdot T}{u_p \cdot d_p} \cdot k \cdot \\ \cdot (P_{Pb}^{o} \cdot \gamma_{Pb} \cdot X_{Pb} - P_{Pb}^{P}) \tag{10}$$

where:

$$u_p = \frac{dz}{dt} \tag{11}$$

where:
z – distance between the gas nozzle outlet point and the bubble.

By transforming the relation (10), it is obtained [3]:

$$\frac{dp_{Pb}^{P}}{\int (P_{Pb}^{o} \cdot \gamma_{Pb} \cdot X_{Pb} - P_{Pb}^{P})} = \int \frac{6R \cdot T \cdot k}{d_p \cdot u_p} \cdot dz \tag{12}$$

and furthermore:

$$(P_{Pb}^{o} \cdot \gamma_{Pb} \cdot X_{Pb} - P_{Pb}^{P}) = e \frac{-R \cdot T \cdot k \cdot y}{d_p \cdot u_p} \cdot c \tag{13}$$

Knowing that for z=0, which corresponds to the bubble position at the moment of separation from the nozzle, one assumes that:

$$P_{Pb}^{P} = 0 \tag{14}$$

and consequently:

$$c = P_{Pb}^{0} \cdot \gamma_{Pb} \cdot X_{Pb} \tag{15}$$

By applying the relations (10) and (14), one can express the change of pressure of lead vapours inside the bubble as function of its position as bath. The dependence in question assumes the following form:

$$P_{Pb}^{P}(z) = P_{Pb}^{0} \cdot \gamma_{Pb} \cdot X_{Pb} \cdot \left(1 - \exp\left(\frac{-6R \cdot T \cdot k \cdot z}{d_p \cdot u_p} \right) \right) \tag{16}$$

For the sake of calculation, the assumed bubble diameter is the arithmetic mean of the values obtained from relations (17) and (18) [4, 5]:

$$d_p = 0{,}54 \cdot (q \cdot d_w^{0{,}5})^{0{,}289} \tag{17}$$

where:
d_p – bubble diameter,
d_w – nozzle internal diameter,
q – gas flow intensity

$$d_p = \left\{ \left(\frac{6 \cdot \sigma_m \cdot d_z}{\rho_m \cdot g} \right)^2 + 0{,}0242 \cdot (q^2 \cdot d_z)^{0{,}867} \right\}^{\frac{1}{6}} \tag{18}$$

where:
σ – surface tension of liquid metal,
ρ_m – liquid metal density,
d_z – nozzle external diameter.

In Figure 1 an exam file of change of pressure of lead vapours in the gas bubble depending on its position in the bath is shown:

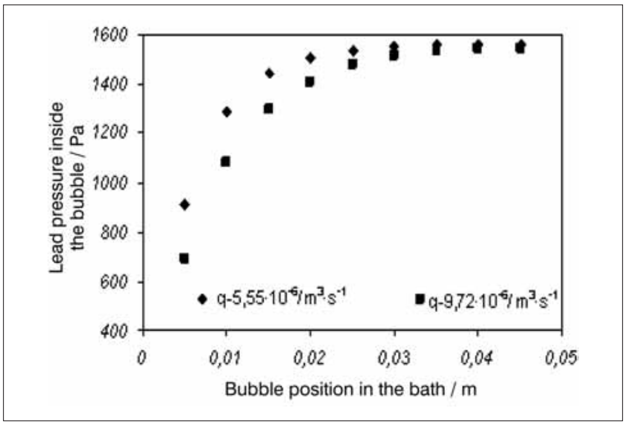

Figure 1 Pressure change for lead inside the gas bubble depending on its position in the metal bath (argon; T = 1 548 K).

By calculating the value of pressure inside a gas bubble released from the bath applying dependence (16) for pressure value P_{Pb}^{P}, it ispossible to determine the speed of lead evaporation from the alloy by applying the dependence [3]:

$$\frac{dn_{Pb}}{dt} = \frac{q \cdot P_{Pb}^{P}(L)}{R \cdot T} \tag{19}$$

where:

q – gas flow rate / $m^3 \cdot s^{-1}$,

L – distance between the nozzle bubble outlet and the bath surface.

ESTIMATING THE VALUE OF THE MASS PENETRATION COEFFICIENT FOR THE LIQUID AND GASEOUS PHASE

With the aim to calculate the mass penetration coefficient for the liquid phase, the following dependence was applied:

$$\beta_c = 2 \cdot \sqrt{\frac{D_{Cu-Pb}}{t \cdot \pi}} \tag{20}$$

where:

D_{Pb-Cu} – coefficient of lead diffusion in liquid copper.

For determining the mass penetration coefficient for the liquid phase, it is necessary to know the value of the coefficient of lead diffusion in liquid copper, shown in Table 1.

For to determining the mass penetration coefficient for the gaseous phase, the following dependence was applied:

$$\frac{\beta_g \cdot d_p}{D_{Pb-Ar,He}} \cong 6{,}6 \tag{21}$$

Table 1 **Change of diffusion coefficient of lead in copper depending on temperature [6].**

Temperature / K	$D_{Pb-Cu} \cdot 10^8$ / $m^2 \cdot s^{-1}$
1 473	2,02
1 548	2,25

For determining the mass penetration coefficient for the gaseous phase, it is necessary to know the value of the diffusion coefficient of lead vapours in argon and helium, shown in Table 2.

Table 2 **Change of diffusion coefficient of lead vapours in gases depending on temperature [7].**

Temperature/K	$D_{Pb-Ar} \cdot 10^4/m^2 \cdot s^{-1}$	$D_{Pb-He} \cdot 10^4/m^2 \cdot s^{-1}$
1 473	1,76	8,5
1 548	1,93	9,8

The values of the mass penetration coefficient for the liquid and gaseous phases calculated based on dependence (20) and (21) are shown in Table 3. The table also contains values of the mass transfer coefficient calculated based on dependence (9). The measurement parameters were denoted in the following manner: inert gas symbol – temperature at which the measurements were conducted – gas flow rate.

Table 3 **Coefficients of transfer and penetration of lead in liquid and gaseous phase.**

Measurement parameters	Mean value of penetration coefficient in liquid phase /$\beta_c \cdot 10^4/m \cdot s^{-1}$	Mean value of penetration coefficient in gaseous phase/ $m \cdot s^{-1}$	Mass transfer coefficient k /$mol \cdot s^{-1} \cdot atm^{-1} \cdot m^{-2}$
Ar-1473-5,55	7,22	0,093	0,886
Ar-1473-6,94	7,11	0,087	0,855
Ar-1473-8,33	7,02	0,083	0,830
Ar-1473-9,72	6,94	0,079	0,810
Ar-1548-5,55	7,59	0,101	0,921
Ar-1548-6,94	7,47	0,095	0,889
Ar-1548-8,33	7,37	0,090	0,864
Ar-1548-9,72	7,29	0,086	0,843
He-1473-5,55	7,22	0,449	2,958
He-1473-6,94	7,11	0,422	2,829
He-1473-8,33	7,02	0,401	2,728
He-1473-9,72	6,94	0,384	2,646
He-1548-5,55	7,59	0,511	3,202
He-1548-6,94	7,47	0,480	3,062
He-1548-8,33	7,37	0,456	2,953
He-1548-9,72	7,29	0,436	2,865

Considering the relation (9) and assuming that relation

$$\left(\frac{R \cdot T}{\beta_g}\right) : \left(\frac{1}{k}\right) = z \cdot 100\% \tag{22}$$

represents a contribution of mass transport resistance in gaseous phase in the total process resistance, it has been shown that in the range of temperatures analysed, as well as for the gas flow rates applied, the lead removal process is determined by penetration of mass in the gaseous phase. In all experiments, the fraction of penetra-

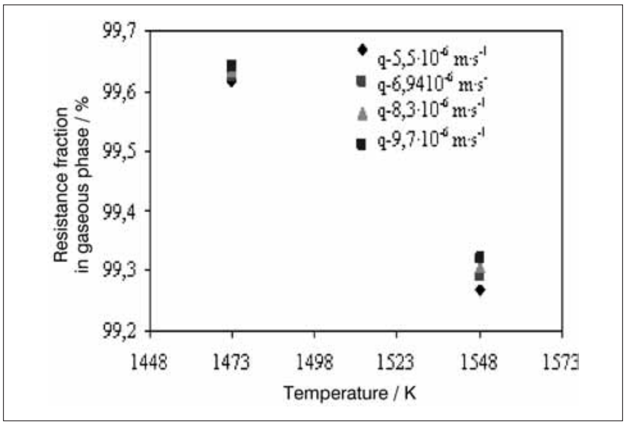

Figure 2 Resistance fraction in the gaseous phase in the total resistance of lead evaporation process from Cu-Pb-Fe alloy (helium).

tion resistance in the gaseous phase exceeded 99 %. This is illustrated by the data provided in Figure 2.

CONCLUSIONS

1. The process of lead removal from the Cu-Pb-Fe alloy by way of barbotage with inert gases in the range of temperatures and gas flow rates analysed is characterised by diffusion control and it is determined by the mass transport in the gaseous phase.
2. In the course of the process, the gas bubbles are quickly saturated with lead vapours to attain the value close to the balance pressure and the further increase of the lead removal at the given temperature is possible by increasing the gas flow rate through the bath.

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