REMOVAL OF ARSENIC FROM LIQUID BLISTER COPPER DURING REMELTING IN AN INDUCTION VACUUM FURNACE

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Abstract

Using a reduced pressure during the smelting and refining of alloys removes dissolved gasses, as well as impurities with a high vapor pressure. When smelting is carried out in vacuum induction furnaces, the intensification of the discussed processes is achieved by intensive mixing of the bath, as well as an enhanced mass exchange surface (liquid metal surface) due to the formation of a meniscus. This is due to the electromagnetic field applied to the liquid metal. This study reports the removal of arsenic from blister copper via refining in an induction vacuum furnace in the temperature range of 1423–1523 K, at operating pressures from 8 to 1333 Pa. The overall mass transfer coefficient \( k_{As} \) determined from the experimental data ranged from \( 9.99 \times 10^{-7} \) to \( 1.65 \times 10^{-5} \) ms\(^{-1}\). Arsenic elimination was largely controlled by mass transfer in the gas phase. The kinetic analysis indicated that the arsenic evaporation rate was controlled by the combination of both liquid and gas-phase mass transfer only at a pressure of 8 Pa.

Keywords: Blister copper; Arsenic removal; Vacuum furnace; Evaporation

1. Introduction

Most impurities in copper concentrates produced during pyrometallurgical processes enter blister copper. If their content is sufficiently low, most can be removed during an electro-refining process. During this process, efforts are made to ensure that the concentration of metallic impurities in cathode copper does not exceed 30 ppm and that this copper does not contain impurities that negatively affect its electrical conductivity or recrystallization temperature. Metallic impurities in copper that lower both its electrical and thermal conductivity mainly include arsenic, silicon, manganese, chromium, and antimony. One of the proposed methods for removing arsenic and antimony from liquid copper is remelting refinement carried out under a reduced pressure. The results of the first studies on the use of a reduced pressure during copper-arsenic refining were published in the 1970s [1-5]. Unfortunately, these papers reported a relatively small datasets, and the tests were mainly carried out in resistance furnaces over relatively narrow pressure and temperature ranges. In addition, there are no precise data of the test parameters, especially about the dimensions of the crucibles or the chemical composition of the tested alloys. Thus, it is impossible to perform a more complete analysis of these results, especially their kinetics.

The first papers on the kinetic analysis of arsenic removal from copper by vacuum refining were published by Harris and Lombeck [6-8]. Harris investigated the removal rate of arsenic from cathode and anode copper using 35 kg samples in a vacuum induction furnace with a power of 150 kW. The temperature and pressure ranges were 1450–1610 K and 3–30 Pa, respectively. The values of the general arsenic mass transfer coefficient \( k_{As} \) determined based on the experimental data ranged from \( 0.2 \) to \( 3 \times 10^{-5} \) ms\(^{-1}\). Harris and colleagues also reported the removal of arsenic from copper matte [9]. Danovitch [10] and Ozberk, Guthrie, and Harris [11-13] reported the removal of arsenic from cathode, anode, and blister copper using a similar vacuum aggregate. Despite the use of similar test parameters, the obtained results showed significantly different arsenic removal rates. The higher refining rates achieved by Danovitch probably resulted from the use of copper samples that completely filled the crucibles after melting, which reduced the mass transport resistance in the gas phase. Courso and Szubina [14] investigated arsenic removal from liquid copper with a higher oxygen content. Experiments were carried out in a resistance furnace with argon bath purging, which ensured additional mixing.

Although results concerning arsenic removal from copper by vacuum induction melting (VIM) have...
been published, in most cases, the experiments were carried out in very narrow pressure ranges. Additionally, the analyses did not take into account the actual surface of the liquid metal, which ignored the possibility of the formation of a distinct meniscus in the metallic bath. At the same time, in some studies on the mass transport rate in liquid metal, a constant value of the bath stirring rate was assumed, without taking into account its dependence on the induction furnace parameters, especially the furnace power and the current frequency. In this work, these elements were taken into account, and the obtained results were compared with literature data, taking into account the above comments. The innovation of this study are:

• a wide range of applied working pressures of a vacuum induction furnace;
• consideration of the real surface area of the liquid metal (meniscus formation); and
• evaluation of the real value of the subsurface velocity of metals melted in an induction furnace.

Table 1 summarizes the basic parameters and test results for the removal of arsenic from liquid copper during refinement in vacuum induction furnaces.

### Table 1. Summary of previous studies on arsenic removal from copper under a vacuum

| T (K) | P (Pa) | Material | As content (mass%) | As removal (%) | Mass transfer coefficient $k_A$ (ms⁻¹) | Ref. |
|-------|--------|----------|--------------------|----------------|---------------------------------------|------|
| 1423–1573 | 8–40 | Copper cathode and anode and blister copper | 0.33–0.96 | 5–22 | < 0.1·10⁻⁴ | [11–13] |
| 1500–1740 | 7–160 | Copper cathode and anode and | – | – | 2–3·10⁻⁴ | [10] |
| 1445–1626 | 7–27 | Copper cathode and anode | 0.215 – 3.938 | – | 0.24–3.96·10⁻⁴ | [7] |
| 1423–1473 | 5 | Copper with raised oxygen content (up to 1 wt. %) | 0.42–1.02 | 58 – 80 | – | [6] |
| 1373–1523 | 50–130 | Copper mate | 0.019 – 0.059 | 60 – 93 | 0.75–1.3·10⁻⁴ | [9] |
| 1445–1626 | 3–25 | Copper anode | 0.215–3.93 | 2–25 | 0.09–3.64·10⁻⁴ | [8] |

2. Research methodology

All experiments were performed on blister copper containing 0.193 wt.% arsenic (Table 2).

The melting device used in the research was an ISS/III vacuum induction furnace manufactured by Leybold Heraeus with a maximum power 100 kW and operating frequency of 4 kHz (Figure 1). The melting coil allowed the use of crucibles with a volume of up to 0.005 m³. The furnace was equipped with a system that enabled the collection of liquid metal samples during the processing. A system of three pumps was used to create a vacuum in this unit, i.e. a rotary pump, a Roots pump, and a diffusion pump. At the beginning of each experiment, a ~5 kg blister copper sample was placed in a ceramic crucible with an internal diameter of 0.1 m, and then was heated in an argon atmosphere to the set temperature. After heating the metal, the pressure in the melting system was reduced to the set value. The maximum holding time of the metal at a given temperature was 30 minutes. During this process, metal samples were extracted and subjected to chemical analysis for their arsenic content. The experiments were carried out in the temperature range of 1423–1523 K and pressures of 8–1333 Pa. The wide range of pressures used in the tests resulted from the desire to determine the impact of this parameter on the velocity of the evaporation process under study. The temperature range adopted in the tests was similar to the values used in the process of smelting high-purity cooper with similar aggregates.

The concentration of arsenic in copper was determined by an Analytik Jena atomic absorption spectrometer (AAS), operating at a voltage of 10 V and current of 13 mA. The analyses were carried out by using an acetylene-air flame (stoichiometric) with an ionization buffer (1000 ppm KCl).

The arsenic concentration in copper was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). The plasma gas flow was 7.5 dm³/min. Calibration solutions from 0 to 0.5%...
were prepared from ICP-MS-grade multi-element standards in 1% HNO₃. The samples were digested in an open vessel by accurately weighing approximately 1 g of sample in 10 ml of 63% nitric acid. After complete digestion, the vessels were filled to 50 ml. Samples were prepared in duplicate and further diluted 20 fold with distilled water prior to analysis.

3. Results

All experimental results are summarized in Table 3. Apart from the basic parameters of each experiment, the table also includes the initial and final contents of arsenic in copper and the determined degree of arsenic removal. Figures 2 and 3 show a graphical interpretation of these results.

Figure 1. Schematic view of the Leybold Heraus IS5/III vacuum induction furnace. 1 – rotary vacuum pumping system; 2 – root pumping system; 3 – chamber with form; 4 – vacuum chamber with crucible; 5 – sampling port valve; 6 – high-vacuum pumping system

Figure 2. Change in the final concentration of arsenic in the blister copper depending on the operating pressure in the furnace

Figure 3. Change in the degree of arsenic removal from the blister copper depending on the operating pressure in the furnace

| Temperature, K | Pressure, Pa | Cu blister Cᵦ₁₀₀ = 0.193 | Final content As, wt.% | As elimination, % |
|---------------|-------------|----------------------------|------------------------|------------------|
| 1423          | 1333        | 0.188                      | 2.6                    |
| 1423          | 533         | 0.181                      | 6.2                    |
| 1423          | 133         | 0.175                      | 9.3                    |
| 1423          | 80          | 0.171                      | 11.4                   |
| 1423          | 27          | 0.158                      | 18.1                   |
| 1423          | 8           | 0.152                      | 21.2                   |
| 1473          | 1333        | 0.184                      | 4.7                    |
| 1473          | 533         | 0.178                      | 7.8                    |
| 1473          | 133         | 0.171                      | 11.4                   |
| 1473          | 80          | 0.167                      | 13.5                   |
| 1473          | 27          | 0.158                      | 18.1                   |
| 1473          | 8           | 0.147                      | 23.8                   |
| 1523          | 1333        | 0.169                      | 12.4                   |
| 1523          | 533         | 0.159                      | 17.6                   |
| 1523          | 133         | 0.149                      | 22.8                   |
| 1523          | 80          | 0.144                      | 25.4                   |
| 1523          | 27          | 0.137                      | 29.0                   |
| 1523          | 8           | 0.125                      | 35.2                   |

4. Discussion of Results

Impurity removal via vacuum induction melting is generally observed to follow first-order kinetics [15]. The resulting overall rate of arsenic removing can be described by equation (1):
which in integral form is (2):

\[
\int_0^t \frac{dC_{As}}{dt} = k_{As} \frac{F}{V} \int_0^t C_{As} dt
\]  

(2)

After integration, this equation takes the form (3):

\[
2.303 \log \frac{C_{As}^f}{C_{As}^i} = -k_{As} \frac{F}{V} (t-t_0)
\]  

(3)

where:

- \(C_{As}^i\) and \(C_{As}^f\) – initial and final arsenic concentration in copper,
- \(k_{As}\) – overall mass transfer coefficient of arsenic,
- \(F\) – melt surface area,
- \(V\) – volume of the melt, and
- \((t-t_0)\) – time of melting.

Equation (3) shows that to determine the value of \(k_{As}\), the volume of the melt and its surface area must be known. In the analyzed experiments, in the temperature range of 1373–1523 K, the estimated value of the liquid metal volume was in the range of 645–656 \(10^{-6}\) m\(^3\). The liquid copper density in the analyzed temperature range was determined based on the data contained in ref. [16]. It is more difficult to estimate the actual evaporation surface (liquid copper surface). When metals or their alloys are melted in induction furnaces (vaccum induction melting - VIM or induction skull melting - ISM), the metal surface area is highly dependent on the electromagnetic field acting on the melt and the properties of the liquid metal [17-22]. This is shown by the formation of a distinct meniscus on the surface of the bath. To illustrate this, Figure 4 shows a photo of the surface of the molten copper in an induction furnace crucible [23].

Ref. [24] presents the flow field analysis and the coupling of an electromagnetic field with the geometry of the molten metal that was melted in an induction furnace crucible. Numerical simulations related to the determination of the actual surface of the metal bath discussed in ref. [24] also concerned the process of melting copper and its alloys in the aggregate in which the above-mentioned experiments were carried out. The determined values of the actual evaporation area for blister copper melting conditions were 105 cm\(^2\) (average), with the calculated crucible cross-sectional area of 78.5 cm\(^2\). It should be noted that none of the studies that discussed the kinetics of arsenic evaporation from liquid copper during its melting using VIM took into account meniscus formation.

The values of the overall arsenic transfer coefficient \(k_{As}\) determined from equation (3) are presented in Table 4. Figure 5 presents a graphical representation of changes in \(k_{As}\) as a function of the operating pressure of the induction furnace. By analyzing the influence of pressure and temperature on the rate of arsenic removal from blister copper, it can be concluded that upon increasing the temperature from 1423 K to 1523 K and reducing the pressure from 1333 Pa to 8 Pa, the overall mass transfer coefficient increased 16 times with a simultaneous increase in the degree of arsenic removal from 2.6% to 35.2 %. The obtained \(k_{As}\) values (9.99 \(10^{-7}\) to 1.65 \(10^{-5}\) m s\(^{-1}\)) were in good agreement with the values given by other authors who have studied this process (Table 2).

To carry out a kinetic analysis of the arsenic evaporation from copper, it was necessary to take into account its three main stages:

- transport of arsenic through the molten copper to the metal–gas interface;
- evaporation of arsenic \(\text{As}_{l} \rightarrow \text{As}_{g}\); and
- mass transfer of the evaporating component to the condensed surface.

The overall mass transfer coefficient of arsenic is related to these three steps and can be described by...
equation (4):
\[
\frac{1}{k_e} = \frac{1}{\beta} + \frac{1}{k_e} + \frac{1}{\beta^g}
\]  
(4)

where:
\( \beta_l \) – mass transfer coefficient of arsenic in the liquid phase;
\( \beta^g \) – mass transfer coefficient of arsenic in the gas phase; and
\( k_e \) – evaporation rate coefficient of arsenic.

Mass transfer in the liquid phase

The transfer of alloy components through the molten metal to the melt surface can be described by the Machlin model [25]. According to this model, the value of the arsenic transport coefficient \( \beta_l \) is given by equation (5):
\[
\beta_l = \frac{8D_{As}v_m}{\pi r_m} \theta_{l}
\]  
(5)

where:
\( v_m \) – mean surface velocity;
\( r_m \) – radius of the surface of the liquid metal (most often taken as the inner radius of the crucible); and
\( D_{As} \) – diffusivity of arsenic in molten copper.

1. By analogy to the penetration models of mass transport, Machlin assumed that elements in liquid metal moved along the tangent: liquid metal–gas or liquid metal–crucible, and the velocity gradient normal to the surface was close to zero. This dependency showed that the value of \( \beta_l \) was directly proportional to the value of the near-surface velocity of the liquid metal. According to Machlin, most authors who have investigated the evaporation kinetics of inductively-mixed metallic bath components assumed that this rate was practically independent of the electrical parameters of the furnace operation. It was assumed for induction furnaces with a mass of liquid metal up to 1 ton, the value of \( v_m \) was constant (0.1 ms\(^{-1}\)); however, later studies showed that this speed depended on factors such as the current frequency, the geometry of the crucible, and the position of the crucible in the furnace relative to the inductor [25-31].

Ref. [24] also presented a simulation model for determining the value of the mean surface velocity of copper during its melting for the same furnace in the analyzed studies on arsenic removal. This model consisted of two successive elements, i.e. an analysis of the electromagnetic field generated in the liquid metal, and an analysis of the field velocity in the liquid metal. The measured average volumetric velocity of copper determined from this model was 0.103 ms\(^{-1}\), and the average surface velocity was 0.129 ms\(^{-1}\).

Table 3 presents the values of the \( \beta_l \) coefficient determined from equation (5), which ranged from 1.4 to 1.44x10\(^{-4}\) ms\(^{-1}\). In these calculations, the values of the near-surface velocity estimated based on the above-discussed model were used.

The Darken equation was used to determine arsenic diffusion coefficients in liquid copper [32]. The values of self-diffusion in both liquid metals were taken from refs. [33, 34]. The estimated values of the \( D_{As-Cu} \) coefficient in the temperature range 1423–1523 K were in the range of 3.46–3.67x10\(^{-5}\) cm\(^2\) s\(^{-1}\). Figure 5 shows the estimated contribution of the liquid-phase transport resistance to the total resistance of the arsenic evaporation process. This was determined using the following equation:
\[
R_l = \left( \frac{1}{\beta_l} \right) \cdot 100\%
\]  
(6)

For comparison, the figure also shows the values of R\(_l\) shares estimated from Harris's experimental data [8]. The data in Fig. 6 show that for the temperature and pressure ranges used in the experiments, the analyzed arsenic evaporation process was not
determined by mass transport in the liquid phase. The contribution of mass transfer resistance in the liquid metallic phase to the total process resistance did not exceed 12%. As the pressure was lowered, this resistance increased slightly. The same conclusions can be drawn from an analysis of the experimental data presented in ref. [8].

The rate of arsenic evaporation from the liquid phase to the gas phase at the liquid copper surface was analyzed, and the maximum evaporation rate coefficient \( k_{e\text{As}} \) was calculated by (7):

\[
k_{e\text{As}} = \frac{\alpha \cdot \psi}{(2\pi RT_{M_{\text{As}}})^{0.5}}
\]

(7)

where:
- \( M_{\text{As}} \) – molar mass of arsenic,
- \( R \) – gas constant,
- \( T \) – temperature,
- \( \alpha \) – relative volatility coefficient, and
- \( \psi \) – multiplier.

\[
\psi = \frac{\gamma_{\text{As}} M_{\text{Cu}} p_{0\text{As}}}{\rho_{\text{Cu}}}
\]

(8)

where:
- \( \gamma_{\text{As}} \) – activity coefficient of arsenic,
- \( M_{\text{Cu}} \) – molar mass of copper,
- \( p_{0\text{As}} \) – equilibrium arsenic vapor pressure, and
- \( \rho_{\text{Cu}} \) – density of molten copper.

This study used data from the thermodynamic database HSC Chemistry ver. 6.1 [12] to determine the arsenic vapor pressure \( p_{0\text{As}} \) and the arsenic activity coefficient in liquid copper \( \gamma_{\text{As}} \) [35]. Based on these estimations, for the temperature range of 1423–1523 K, the value of \( p_{0\text{As}} \) changed from 464 to 608 Pa, and the activity coefficient \( \gamma_{\text{As}} \) changed from 0.001 to 0.0016. In analogous calculations presented by Harris et al. [8] for the same temperature range, the assumed values of \( p_{0\text{As}} \) changed from 1720 to 15256 Pa, and the assumed value of \( \gamma_{\text{As}} \) was 0.006. Such differences in the values of the discussed thermodynamic quantities resulted in significant differences in the estimated values of \( k_{e\text{As}} \).

Figure 7 shows the estimated contribution of the transport resistance associated with the reaction on the surface of liquid copper to the total resistance of the arsenic evaporation process. The equation used to determine this was (9):

\[
R^e = \left( \frac{1}{k_{e\text{As}}} \right) \cdot 100\%
\]

(9)

The data in Fig. 8 show that for the temperature and pressure ranges applied in the experiments, the contribution of \( R^e \) resistance to the total process resistance varied from 5% to 45%. Figure 8 shows the estimated contribution of the transport resistance related to the reaction on the surface of liquid copper \( R^e \) and mass transport in the liquid phase \( R_l \) to the total resistance of the arsenic evaporation process. The resistance ranged from 7% to 55%.
7. Mass transfer in the gas phase

None of the known hydrodynamic models used to describe mass transport in the gas phase provide accurate estimations of the mass transport coefficient $\beta_g$, for the measuring system used in this research. Similarly, there are no criteria equations in the literature that enable the correct determination of this coefficient. For this reason, the overall pressure ratio (OPR) parameter was used to determine the role of mass transfer in the gas phase in the analyzed arsenic evaporation process, as proposed in ref. [36]. The OPR parameter is defined as the ratio of the total initial pressure of the bath components above the alloy to the pressure in the furnace chamber, as shown in equation (10):

$$\text{OPR} = \sum_i \frac{P_i}{P_{ch}}$$   \hspace{1cm} (10)

It is assumed that transport in the gas phase does not determine the rate of the analyzed metal evaporation under reduced pressure when OPR $> 1$. By analyzing the obtained results, the OPR was estimated for the experimental temperature range. It was a sum, by taking into account the composition of the blister copper, that the vapor pressure of arsenic, as well as lead, copper, antimony, and their compounds with oxygen and sulfur. Figure 9 shows the relationship between the OPR and temperature. The data show that for a pressure of 8 Pa, the analyzed process was not determined by mass transport in the gas phase (OPR $> 1$).

8. Conclusions

The kinetic analysis of arsenic evaporation from blister copper during its melting in a vacuum induction furnace was performed. The analysis included:

- determining the value of the overall mass transfer coefficient of the evaporating component based on experiments performed in this paper; and
- estimating the mass transport coefficients in the liquid phase and the constant evaporation rate.

The results of the analysis led to the following conclusions:

- Increasing the remelting temperature from 1423 K to 1523 K at a working pressure of 1333 Pa was accompanied by a decrease in the arsenic content in the alloy from 12.4% to 2.6% compared with the initial concentrations;
- For a furnace operating pressure of 8 Pa, the decrease was 21.2 and 35.2%, respectively;
- In the analyzed temperature and pressure ranges, the total arsenic mass transport coefficient increased from $0.99 \times 10^{-6}$ ms$^{-1}$ to $1.65 \times 10^{-5}$ ms$^{-1}$;
- The removal of arsenic was largely controlled by mass transfer in the gas phase;
- Only at a pressure of 8 Pa, the kinetic analysis indicated that the rate of arsenic evaporation was controlled by a combination of both liquid and gas-phase mass transfer; and
- In the entire pressure range, the contribution of resistance related to mass transport in the liquid phase to the total process resistance did not exceed 32%, and the resistance related to the act of evaporation itself did not exceed 31%.

References

[1] G. Kim, A. Kvyatkovskii, Vacuum Processing of Crude Copper, Trudy Altaisk Gorno-Met Nauczno-isled Inst., 13 (1963) 86-89.
[2] V. Golovko, R. Isakova, Trans. Inst. Metal. Akad. Nauk. Kazakhstan, 13 (1965) 32-37.
[3] H. Kametani, C. Yamauchi, Trans. Jpn. Inst. Met., 13 (1) (1972) 13-20.
[4] L. Komorova, Hutnicke listy, 8 (1973) 577-582.
[5] H. Kametani, C. Yamauchi, K. Murao, M. Hayashida, Trans. Jpn. Inst. Met., 14 (1) (1973) 218-223.
[6] K. Lombeck, J. Krueger, H. Winterhager, Metall., 36 (11) (1982) 1192-1196.
[7] R. Harris, Metall. Trans. B, 15 B (1984) 251-257.
[8] R. Harris, R.J. McClincy, E.F. Riebling, Can. Metall. Q. 26 (1) (1987) 1-4.
[9] D. Danovitch, Vacuum Refining of Copper Melts, M. Eng. Thesis, Mc. Gill University Montreal, 1982.
[10] B. Ozberk, R.I.L. Guthrie, Inst. Min, Met. Section C, 94 (1985) 146-157.
[11] B. Ozberk, R.I.L. Guthrie, Metall. Trans. B, 17 B (1986) 87-103.
[12] B. Ozberk, R.I.L. Guthrie, Proc. 6th Int. Vacuum Metallurgy Conf. American Vacuum Society, San Diego, USA, 1979, p. 248-267.
[13] A. Allaire, R. Harris, Metall. Trans. B, 20 B (1989) 793-804.
[14] P. Coursol, N. Stubina, Metall. Mate. Trans. B, 36 (3)
J. Labaj et al. / J. Min. Metall. Sect. B-Metall. 57 (3) (2021) 371 - 378

UKLANJANJE ARSENA IZ BLISTER BAKRA U TEĆNOM STANJU TOKOM TOPLJENJA U VAKUUMSKOJ INDUKCIJNOJ PEĆI

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Apstrakt

Nizak pritisak tokom topljenja i rafinacije legura doprinosi ukljanjuju rastvorenih gasova, kao i nečistoća sa visokim naponom pare. Kada se topljenje vrši u vakuumskoj indukcionoj peći, podsticanje razmjene mase (površina tečnog metal) usled stvaranja meniska zbog primene elektromagnetskog polja na tečnometal. U ovom radu je prikazano ukljanje arsena iz blister bakra rafinacijom u vakuumskoj indukcionoj peći u temperaturom opsegu od 1423 – 1523 K pri radnom pritisku od 8 do 1333 Pa. Ukupan koeficijent transfera mase kAs je utvrđen na osnovu eksperimentalnih podataka i iznosio je između 9.99·10^-7 i 1.65·10^-5 ms^-1. Ukljanje arsena je uglavnom bilo kontrolisano prenosom mase u gasnoj fazi. Kinetička analiza je pokazala da je brzina isparavanja arsena uslovljena kombinacijom prenosa mase u tečnoj i gasnoj fazastim pritiskom od 8 Pa.

Ključne reči: Blister bakar; Ukljanje arsena; Vakuumska peć; Isparavanje