Influence of process parameters on quality of copper in electron-beam melting

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Abstract. Results are presented and discussed obtained by experimental and theoretical investigation concerning the influence of process parameters (melting power and refining time) on the quality of copper metal ingots in electron-beam melting. The thermodynamic and kinetic conditions are analyzed. Possible refining process mechanisms under different technological conditions are investigated. Appropriate processing regimes are proposed for efficient refining of copper and for obtaining high-quality metal after e-beam melting.

1. Introduction

Analyses of the world's raw material resource for copper production show that copper ore reserves are decreasing, while the global copper consumption continues to grow every year [1]. Copper is the third most important metal after iron and aluminum used in a variety of applications (energy and electrical systems and networks, architecture, electronics and telecommunications, transportation, industrial machinery and equipment, chemical industry, agriculture, etc.) that are necessary for a reasonable standard of living. The requirements for the chemical composition, structure and quality of the final product are also increasing. The development of effective methods for the production of metals and alloys with a low content of metal, non-metal and gas impurities and the preservation of the chemical composition obtained during further processing are important problems that modern metallurgy is successfully solving.

As part of the vacuum metallurgy, electron-beam melting (EBM) for refining is a key method for producing new micro- and nanoelectronics materials that require high purity and quality. This method combines well the advantages of the electron beam (EB) as an unconventional source of heat without the limitations of the achieved temperature and the high vacuum as an environment for refining processes [2-4].

In the EBM process, favorable conditions are created for carrying out fully reactions and processes that involve a gas phase, since it is possible to shift their thermodynamic equilibrium in the desired direction. In EBM, degassing, deoxidation, reduction, and evaporation of volatile impurities occur that are unrealizable at atmospheric pressure. Refining takes place at the boundary surface between superheated liquid metal and vacuum (reaction surface), where various processes run simultaneously, such as mass transfer (from volume to boundary surface and vice versa), chemical interactions

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between components (elements and chemical compounds) present in the surface region, and evaporation from the boundary surface of impurities in atomic form or bonded in compounds [3, 5].

To provide an efficient realization of a concrete refining process in EBM processing, it is important to know the concentration of the investigated components at thermodynamic equilibrium under concrete conditions (temperature and pressure) giving in principle a possibility of refining. Also, to achieve a thermodynamic equilibrium, the rates and limits of the processes and the parameters influencing them should be known.

In this paper, we analyze the thermodynamic conditions of and the kinetic limitations on the flow of refining processes and the possible refining mechanisms in electron beam refining of copper. The influence of the beam power (temperature) and the duration of the melting process on the quality of the refined metal is studied as well.

2. Results and discussion

The experiments on EBM of copper disks with a height of 50 mm and diameter of 60 mm were conducted using the 60-kW ELIT 60 plant at the Physical Problems of the EB Technologies Laboratory of the Institute of Electronics, Bulgarian Academy of Sciences. The EBM furnace consists of a melting chamber, one electron gun with an accelerating voltage of 25 kV, a vacuum system, and an extraction system [6]. The operation vacuum pressure is 3 – 6 × 10⁻² Pa.

The investigated material contained 99.83% Cu and impurities such as As, Sb, Pb, Sn, Ni, Bi, Zn, Ag and O₂. The initial material was processed at melting powers of 7.5 kW (T = 1400 K), 10 kW (T = 1500 K) and 15 kW (T = 1700 K) for different refining times – 3 min, 10 min, 15 min, 20 min and 30 min. Using emission spectral analysis, the chemical composition of the samples before and after EBM was determined.

During EBM of Cu, the liquid metal is a complex system of Cu, Cu₂O, metal impurities, and their oxides, in a liquid and solid state depending on the operating temperature. The refining processes take place simultaneously and should be considered in their interdependence. By analyzing the thermodynamic and kinetic refining conditions under each of the technological regimes studied, the qualitative composition of the metals and oxides reaching the reaction surface can be predicted.

Equations (1-3) present possible chemical interactions between the base metal (Cu) and metal components (Me) with the oxygen:

\[
\begin{align*}
Cu_2O + Me &= MeO + 2Cu + \Delta F_{r}^T, \\
Cu + 1/2O_2 &= Cu_2O + \Delta F_{T,Cu/Cu_2O}, \\
Me + 1/2 O_2 &= MeO + \Delta F_{T,Me/MeO}.
\end{align*}
\]

where \(\Delta F_{r}^T, \Delta F_{T,Cu/Cu_2O}\) and \(\Delta F_{T,Me/MeO}\) are the free energies of the respective process. According to the thermodynamics laws [7], these reactions can take when the value of the respective free energy is negative. In EBM, dissociation of oxides stable at atmospheric pressure is possible and proceeds completely due to the continuous separation of the gas phase from the reaction surface (the respective free energy should be negative).

Depending on the thermodynamic melting conditions and the type of individual impurities, the refining of the metal at the boundary surface can proceed by (a) degassing – evaporation of impurities having a vapor pressure \(p_i\) higher than the vapor pressure of copper (the base metal), i.e. \(p_i > p_{Cu}\); (b) distillation – evaporation of volatile compounds of metallic impurities when \(p_{MeO} > p_{Me}\), which also applies to the re-melted metal oxide. Effective refining requires the implementation of the following inequalities: \(p_{MeO} > (p_{Me}) > (p_{Cu2O}) > (p_{Cu})\).

Table 1 shows data on the concentration of metallic impurities during e-beam refining of Cu, with the oxygen content varying from 1500 ppm (in the initial material) to 10 ppm (after EBM). It can be seen that the removal of the impurities Sb, Pb, Sn depends on the temperature of the liquid metal. Increasing the temperature \(T\) enhances the removal of these impurities (table 1). At \(T = 1700 K\) and melting time \(\tau = 30 \) min, the refining efficiency \(\eta_r\) for each of them reaches 90%. Under the
melting regimes investigated, the degree of oxygen refining is in the range of 80% – 99.3%. The temperature has little effect on the removal of Ni, Bi, As, Ag (Table 1).

Table 1. Concentration of impurities at EBM of Cu.

| $T$ (K) | $\tau$ (min) | $C_{Sn}$ (ppm) | $C_{Sb}$ (ppm) | $C_{Pb}$ (ppm) | $C_{Bi}$ (ppm) | $C_{Ni}$ (ppm) | $C_{Ag}$ (ppm) | $C_{As}$ (ppm) | $C_{Zn}$ (ppm) | $C_{O2}$ (ppm) |
|---------|--------------|----------------|----------------|----------------|----------------|---------------|---------------|---------------|---------------|---------------|
| 3       | 10           | 10.7           | 26.6           | 36.1           | 1.5            | 49.0          | 8.2           | 11.7          | -             | 300           |
| 10      | 9.7          | 9.7            | 25.2           | 33.8           | 1.8            | 47.1          | 7.8           | 11.3          | 17            | 50            |
| 20      | 9.4          | 9.4            | 24.6           | 32.9           | 1.9            | 46.3          | 7.7           | 11.2          | 18            | 60            |
| 30      | 8.6          | 8.6            | 23.4           | 31.0           | 2.0            | 44.7          | 7.4           | 10.8          | 11            | 100           |
| 3       | 5.3          | 5.3            | 19.2           | 25.6           | 1.4            | 46.3          | 7.7           | 10.3          | 13            | 250           |
| 10      | 5.1          | 5.1            | 18.7           | 24.7           | 1.6            | 45.5          | 7.7           | 10.2          | -             | 30            |
| 15      | 4.9          | 4.9            | 18.3           | 24.1           | 1.7            | 45.0          | 7.7           | 10.0          | -             | 40            |
| 20      | 4.7          | 4.7            | 17.9           | 23.4           | 1.9            | 44.4          | 7.7           | 9.9           | -             | 70            |
| 30      | 4.5          | 4.5            | 17.1           | 22.1           | 2.1            | 43.3          | 7.6           | 9.7           | 34            | 120           |
| 3       | <1           | 4.4            | 5.0            | 1.2            | 41.0           | 6.9           | 7.6           | -             | 210           |
| 10      | <1           | 4.4            | 4.9            | 1.5            | 40.9           | 7.2           | 7.6           | 5             | 30            |
| 15      | <1           | 4.4            | 4.9            | 1.7            | 40.8           | 7.4           | 7.2           | 6             | 20            |
| 20      | <1           | 4.4            | 4.8            | 1.9            | 40.7           | 7.7           | 7.6           | 7             | 11            |
| 30      | <1           | 4.4            | 4.7            | 2.3            | 40.5           | 8.1           | 7.5           | 95            | 10            |
| Before EBM | 27          | 42              | 63             | 1.6            | 55             | 8             | 16            | 7             | 1500          |

The results show that Zn release is possible during the first 10 min at $T = 1700$ K. With continuous refining at $T = 1700$ K, the content of Ag in the base metal increases. For all impurities tested, the removal efficiency was the highest during the first 3-10 min, after which the refining time $\tau$ did not significantly affect their removal. The highest purity of Cu (99.991%) and an oxygen content of 20 ppm was obtained at $T = 1700$ K for $\tau = 10$ min; the degree of refining was 94.7%.

Table 2. Overall removal efficiency $\eta$ at e-beam melting of Cu.

| $T/\tau$ | 3 min | 10 min | 15 min | 20 min | 30 min |
|----------|-------|--------|--------|--------|--------|
| 1400 K   | 74.2% | 88.9%  | 88.1%  | 87.7%  | 86.1%  |
| 1500 K   | 78.0% | 91.7%  | 91.2%  | 89.5%  | 84.9%  |
| 1700 K   | 84.0% | 94.7%  | 94.6%  | 94.6%  | 90.2%  |

The evaluated values of the overall removal efficiency (removal efficiency of all the impurities in the sample) are presented in Table 2. It is seen that the increase of the temperature (beam power) and also the increase of $\tau$ up to 10 min lead to an increase of the overall removal efficiency of the controlled impurities. Table 3 presents data for the material losses which are mainly due to evaporation and also to splashes. The results show that prolonged melting does not increase the refining efficiency due to the higher weight losses of the base metal (tables 2, 3).

Table 3. Material losses $W_{loss}$ in EBM of Cu.

| $T/\tau$ | 3 min | 10 min | 15 min | 20 min | 30 min |
|----------|-------|--------|--------|--------|--------|
| 1400 K   | 0.14 g| 0.62 g | 0.96 g | 1.31 g | 2 g    |
| 1500 K   | 0.82 g| 3.56 g | 5.52 g | 7.48 g | 10.83 g|
| 1700 K   | 2.18 g| 10.02 g| 14.64 g| 19.83 g| 30.21 g|
Under EBM conditions (temperature range 1400 – 1700 K and pressure $10^{-1} – 10^{-3}$ Pa), $p_{Ni} < p_{Cu}$ so that Ni cannot be atomically removed (figure 1). It is possible to separate some of the other controlled impurities such as As, Sb, Pb, Zn, Bi ($p_{i} > p_{Cu}$) from the reaction surface.

We further calculated the free energy values $\Delta F_{T,Me/MeO}$ for the chemical interactions between metal impurities and $O_2$ (equation (3)), in the studied temperature range. It was found that the probability for oxidation of impurities is the highest for Zn and decreases for the other impurities in the order Ni, As, Sn, Cu, Sb, Bi, Pb. As the temperature $T$ increases, the likelihood of oxidation of each of these impurities in the volume of liquid metal increases.

The oxidation processes are reversible (equations (2, 3)); the equilibrium constant $k_e$ for reactions of the oxygen with each of the metallic components at given temperature and pressure is calculated from:

$$k_e = \exp(\frac{-\Delta F^0_O}{RT}),$$

where $\Delta F^0_O$ is the variation of the free energy of oxidation at atmospheric pressure, R is the gas constant [8]. The values of $k_e$ for the oxidation reactions occurring in the liquid pool were calculated, from which the electron affinity to $O_2 (E_{ea})$ of the studied impurities can be determined. It was found that $E_{ea,Me}$ decreases in the following sequence $E_{ea,Sb} > E_{ea,As} > E_{ea,Zn} > E_{ea,Bi} > E_{ea,Ni} > E_{ea,Pb} > E_{ea,Cu}$. Any metal for which $E_{ea,Me} > E_{ea,Cu}$ is fulfilled can reduce Cu$_2$O and can be separated by distillation of its oxide (equation (1)).

The volatility of the metal oxides at a certain temperature is determined by the oxygen pressure released during the thermodynamic equilibrium of their decomposition to metal and oxygen (dissociation pressure of the oxide $p_{MeO}$). If $p_{MeO} > p_{Me}$ is satisfied for a stable metal oxide, then its separation from the boundary surface is accomplished by distillation. The $p_{Me}$ of the impurities and the base metal were compared with the $p_{MeO}$ of their oxides; table 4 shows the values of the $p_{MeO}/p_{Me}$ ratios, which decrease in the order $p_{MeO}/p_{Sn} > p_{MeO}/p_{Sb} > p_{MeO}/p_{Cu} > p_{MeO}/p_{Bi} > p_{MeO}/p_{Pb} > p_{MeO}/p_{Ni} > p_{MeO}/p_{Zn} > p_{MeO}/p_{As}$. It can be seen that the oxides of Sn and Sb are the most volatile, while the least volatile is the oxide of As. Therefore, upon reaching the reactive surface, the stable oxides of Sn and Sb will be separated by distillation, while the removal of the stable oxide of As is impossible by distillation; i.e., separation of As is only possible by degassing (in atomic form). For the refined metal, $p_{CuO} > p_{Cu}$ is satisfied and the $p_{CuO}/p_{Cu}$ ratio

![Figure 1](image-url). Partial pressure of the studied metals and their oxides in the temperature range 1400 – 1700 K.

| $T$    | $p_{MeO}/p_{Sn}$ | $p_{MeO}/p_{Sb}$ | $p_{MeO}/p_{Cu}$ | $p_{MeO}/p_{Bi}$ | $p_{MeO}/p_{Pb}$ | $p_{MeO}/p_{Ni}$ | $p_{MeO}/p_{Zn}$ | $p_{MeO}/p_{As}$ |
|--------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| 1400 K | 3.51x10$^{-1}$   | 4.53             | 1.09             | 1.12x10$^{-1}$   | 8.53x10$^{-2}$   | 7.8x10$^{-3}$    | 1.11x10$^{-13}$  | 4.35x10$^{-38}$  |
| 1500 K | 4.7x10$^{3}$     | 3.28             | 2.06             | 2.55x10$^{-1}$   | 1.2             | 1.4x10$^{-2}$    | 4.7x10$^{-13}$   | 2.25x10$^{-34}$  |
| 1700 K | 4.98x10$^{3}$    | 3.18             | 3.89             | 5.77x10$^{-1}$   | 5.86            | 4.3x10$^{-2}$    | 6.4x10$^{12}$    | 8.3x10$^{-25}$   |
increases with increasing the temperature, which explains the greater weight loss at \( T = 1700 \) K.

Under certain thermodynamic conditions, an interaction is possible between a metal impurity and the molecule of \( \text{Cu}_2\text{O} \) (equation (1)), with the impurity reducing that molecule to Cu and the free energy \( \Delta F_T = \Delta F_{T\text{ Me}/\text{MeO}} - \Delta F_{T\text{ Cu/CuO}} \). The values of \( \Delta F_T \) were calculated; the results show that \( \Delta F_T > 0 \) for the impurities \( \text{Pb}, \text{Bi}, \text{and Sb} \), i.e. withdrawal of oxygen from the \( \text{Cu}_2\text{O} \) molecule is not possible. For \( \text{Zn}, \text{Ni}, \text{As}, \text{and Sn} \), \( \Delta F_T < 0 \), i.e. these impurities exhibit reducing properties and extract \( \text{O}_2 \) from the liquid metal. Subsequent distillation of the metal oxides reduces the content of these impurities and of \( \text{O}_2 \) in the base metal. At 1700 K, the distillation from the reaction surface mainly involves \( \text{SnO}_2 \) and \( \text{Sb}_2\text{O}_3 \) and to a lesser extent \( \text{NiO} \) (table 4). In EBM of \( \text{Cu} \) with a high content of \( \text{Sn}, \text{Sb}, \text{Ni} \), the removal of oxygen and of these metal impurities is more efficient due to their good reducing properties.

3. Conclusions

The thermodynamic and kinetic conditions for EBM of copper were investigated in view of process optimization. Possible mechanisms and reactions for refining processes under different technological conditions were analyzed. The results show that the refining processes are most intense during the first 3 – 10 minutes. Separation of the impurities \( \text{Sb}, \text{Pb}, \text{Sn} \) depends on the processing temperature, while it affects only slightly the removal of \( \text{Ni}, \text{Bi}, \text{As}, \text{Ag} \). It was also found that by distilling the oxides of the possible reducers \( \text{Ni}, \text{Sb} \) and \( \text{Sn} \), mainly \( \text{Sb} \) and \( \text{Sn} \) are released from the reaction surface, resulting in a reduction in the oxygen content of the refined metal. The contribution of the \( \text{Ni} \) reducer to the removal of oxygen from \( \text{Cu} \) is smaller. Separation of \( \text{As} \) is possible by degassing. Prolonged melting processing does not reduce significantly the content of the impurities investigated due to the higher weight losses of the refined metal; even a relative increase in the concentration of some of the impurities is possible. The highest purity of \( \text{Cu} \) (99.991%) and an oxygen content of 20 ppm was obtained at 1700 K for a melting time of 10 min with a removal efficiency of 94.7%.

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