INTRODUCTION

The phenomenon of evaporation of volatile metal bath components can be observed in numerous processes of both extractive metallurgy and refining. In some of them, this phenomenon can be considered positive, in others, however, to the contrary. In order to intensify the evaporation process or to restrain it, one must necessarily know the factors determining its rate. The most important of those factors include pressure inside the system, the gaseous atmosphere type, temperature and hydrodynamic properties of the system in which the given metallurgical process is being analysed.

From a kinetic point of view, the process of volatile metal bath component evaporation can be divided into three main stages:
- transfer of the evaporating component from the body of the liquid phase to the interface,
- evaporation of the component from the interface,
- transfer of the evaporating component vapours from the interface to the core of the liquid phase.

The mass flux of the evaporating component “i” transferred from the body of the liquid metal to the interface is characterised by the following relation:

\[ N_i^l = \beta_i^l \left( C_i^l - C_i^i \right) \] (1)

where:
- \( \beta_i^l \) – mass transfer coefficient for component “i” in the liquid metal,
- \( C_i^l \) – concentration of component “i” in the liquid phase core,
- \( C_i^i \) – concentration of component “i” in the interface.

The mass flux of component “i” being evaporated from the liquid metal surface can be determined according to the following relation:

\[ N_i^e = k_i^e \left( p_i^{eq} - p_i^i \right) \] (2)

where:
- \( k_i^e \) – constant evaporation rate (evaporation coefficient) for component “i”,
- \( p_i^{eq} \) – equilibrium pressure of component “i” over the bath,
- \( p_i^i \) – actual pressure of component “i” near the interface.

For the gaseous phase, the flux of vapours of component “i” transferred from the interface to the body of the phase is conditioned by the following relation:

\[ N_i^g = \beta_i^g \cdot p_i^i \] (3)

where:
- \( \beta_i^g \) – mass transfer coefficient for vapours of component “i” in the gaseous phase.

If one is to assume that, in the process being analysed, there is an equality of the fluxes in both phases, i.e.:

\[ N_i^l = N_i^e = N_i^g \] (4)

then the overall mass flux from the liquid metal body penetrating the core of the gaseous phase can be described by the following relation:

\[ N_i = \frac{1}{\beta_i^l} + \frac{1}{k_i^e} \cdot \frac{1}{\beta_i^g} \] (5)

or

\[ N_i = k_i \cdot C_{i}^l \] (6)
where:

- $k_i$ – overall mass transfer coefficient

Mass transfer coefficient $k_i$ is described by the following equation

$$\frac{1}{k_i} = \frac{1}{\beta_i} + \frac{1}{\beta_i} + \frac{RT}{\beta_i \phi} \quad (7)$$

where:

- $\phi = \frac{p_i^* \gamma_i M_m}{\rho_m} \quad (8)$

where:

- $\gamma_i$ – activity coefficient for component “i” in the liquid metal solution,
- $M_m$ – molar mass of the main bath component,
- $\rho_m$ – density of the main bath component

The slowest stage of the evaporation process is one that limits or controls – to put it differently – the overall rate of the process progress. The form of equation (8) implies that the evaporation process controlling stages may be the processes of mass transfer in the liquid or gaseous phase as well as the very act of evaporation when taking place on the interfacial surface.

**PRESSURE IMPACT**

It has been proved in the course of various studies that the system pressure exerts a significant impact on the rate of the evaporation process. One may generally speak of four pressure ranges with separate impacts on the process in question. The first one is the range of pressures under which the metal evaporation rate reaches the maximum value and does not change on their further reduction. Under such conditions, one is to deal with a free evaporation process whose characteristic feature is that atoms or particles of the evaporating metal leaving the metal bath surface do not collide with gas particles, and hence they are moving with identical speed as when leaving this surface. Another pressure impact range is one in which the process rate is practically only controlled by the phenomena of the mass transfer in the liquid phase. Having analysed Figure 1 depicting the kinetic curves obtained for the process of lead evaporation from copper [1] and copper evaporation from iron [2], one can conclude that the range of pressures for which the process was indeed determined by the mass transfer in the liquid phase was similar in both cases and equalled less than 10 Pa. Increasing the pressure in the system to exceed this value causes alteration of the stage determining the process being analysed. This principles applies to pressures of even up to several hundreds Pa. Within this range of pressure values, the process rate is usually determined by the mass transfer phenomena taking place in both the liquid and the gaseous phase. Above this range of pressures, the process is in diffusion control, and its rate is only evidenced by the phenomena of the mass transfer in the gaseous phase. One will usually deal with such a process for the pressures of more than 1 000 Pa.

**IMPACT OF GASEOUS ATMOSPHERE**

When discussing the impact of gaseous atmosphere on the evaporation process being analysed, one must separately consider inert gases as well as those reacting with the bath components. Let us start with inert gases. While analysing the relations describing the mass transfer coefficient for the gaseous phase, one will easily notice that it mainly depends on the diffusivity of the evaporating metal vapours in the gas above the bath. The values of overall mass transfer coefficient for lead evaporation from the Cu-Pb alloy in the atmosphere of argon, carbon monoxide and helium are in Table 1. The table also contains diffusivity values calculated based on Hirschfelder’s equation for lead vapours in the said gases. The data provided in the table in question clearly imply that in the atmosphere of helium, the lead evaporation process proceeds much more quickly than in carbon monoxide and argon, and it is still faster in carbon monoxide than in argon. One should also notice that the lead vapour diffusion coefficients for the gaseous atmospheres being analysed fall into a similar series of values as the overall mass transfer coefficients. However, one must bear in mind that the process discussed proceeded under atmospheric pressure, i.e. under such conditions where it is determined by the mass transfer in the gaseous phase. When the pressure is being reduced below 1 000 Pa, the impact of the gaseous atmosphere type on the evaporation rate drops significantly and ultimately fades out. What should be clearly emphasised at this point is that one speaks of using inert gas atmospheres only.

In the case of metal evaporation in a reactive (oxidising) atmosphere, one must frequently deal with complete inhibition of the process which is due to intense oxidation of the bath surface that blocks the volatile component of the liquid alloy from penetrating the bath. This phenomenon was observed by many researchers including Turkdogan [3] who was investigating the
evaporation of metals into a gas flux being a mixture of inert gas and oxygen.

**IMPACT OF THE METAL BATH STIRRING RATE**

This factor is particularly important when the process is conducted under the conditions of high vacuum, when the evaporation rate is conditioned by the mass transfer in the liquid phase. When the metal is heavily stirred, the mass penetration of the evaporation surface is enhanced. Yamamoto [4] was one of those who observed this phenomenon while investigating the rate of evaporation of alloy components from liquid metal. This author proved that when the smelting was performed in an induction furnace, the rate of copper evaporation was higher than with the process taking place in a resistance furnace. However, he did not observe the same phenomenon when tin was evaporated. It is quite understandable, since on such pressures, the tin evaporation rate is not determined by the mass transfer in the liquid phase but in fact by the evaporation from the surface. The results of the studies in question have been provided in Table 2.

Table 1 **Values of the overall mass transfer coefficient for the lead evaporation process in various gaseous atmospheres**

<table>
<thead>
<tr>
<th>Temp. / K</th>
<th>Type of gaseous atmosphere</th>
<th>Overall mass transfer coefficient / ( \text{ms}^{-1} \cdot 10^6 )</th>
<th>Lead vapour diffusion coefficient for the given gas / ( \text{m}^2 \text{s}^{-1} \cdot 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 523</td>
<td>He</td>
<td>1,20</td>
<td>5,12</td>
</tr>
<tr>
<td>1 523</td>
<td>CO</td>
<td>0,43</td>
<td>2,24</td>
</tr>
<tr>
<td>1 523</td>
<td>Ar</td>
<td>0,24</td>
<td>1,83</td>
</tr>
</tbody>
</table>

Table 2 **Values of overall mass transfer coefficient for copper and tin evaporation from liquid iron smelted using various aggregates**

<table>
<thead>
<tr>
<th>Temp. / K</th>
<th>Bath heating method</th>
<th>Component being evaporated</th>
<th>Overall mass transfer coefficient / ( \text{ms}^{-1} \cdot 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 570</td>
<td>induction</td>
<td>Cu</td>
<td>4,44</td>
</tr>
<tr>
<td>1 572</td>
<td>induction</td>
<td>Cu</td>
<td>4,52</td>
</tr>
<tr>
<td>1 574</td>
<td>induction</td>
<td>Cu</td>
<td>4,54</td>
</tr>
<tr>
<td>1 560</td>
<td>resistance</td>
<td>Cu</td>
<td>3,35</td>
</tr>
<tr>
<td>1 576</td>
<td>resistance</td>
<td>Cu</td>
<td>3,71</td>
</tr>
<tr>
<td>1 589</td>
<td>resistance</td>
<td>Cu</td>
<td>3,73</td>
</tr>
<tr>
<td>1 574</td>
<td>induction</td>
<td>Sn</td>
<td>1,82</td>
</tr>
<tr>
<td>1 574</td>
<td>induction</td>
<td>Sn</td>
<td>1,84</td>
</tr>
<tr>
<td>1 593</td>
<td>induction</td>
<td>Sn</td>
<td>2,04</td>
</tr>
<tr>
<td>1 581</td>
<td>resistance</td>
<td>Sn</td>
<td>1,82</td>
</tr>
<tr>
<td>1 579</td>
<td>resistance</td>
<td>Sn</td>
<td>1,91</td>
</tr>
<tr>
<td>1 592</td>
<td>resistance</td>
<td>Sn</td>
<td>2,04</td>
</tr>
</tbody>
</table>

Having analysed the impact of the metal bath stirring rate on the evaporation rate, one should also discuss in a more detailed manner the process of metal smelting and processing in induction aggregates. These devices are commonly used for smelting of numerous metal alloys as well as for their refining. The mass transfer coefficient for induction stirred liquid metal is determined by the following relation [5,6]:

\[
\beta_I = \left( \frac{8D_{A,B} \cdot v_m}{\pi \cdot r_m^2} \right)^{0.5}
\]

where:

- \( v_m \) – near surface velocity of induction stirred liquid metal,
- \( r_m \) – radius of the liquid metal surface (assumed to be the melting pot inner radius),
- \( D_{A,B} \) – diffusion coefficient of the component transferred in the liquid phase.

This relation used many authors for description mass transport in molten metals [7-11].

The above relation implies that the value of coefficient \( \beta_I \) is directly proportional to the value of the near surface liquid metal velocity. As evidenced by numerous studies conducted [12,13], this velocity depends on such factors as current frequency or the melting pot arrangement inside the furnace against the inductor. Table 3 contains values of velocity \( v_m \) established for the liquid Cu-Pb alloy. Analysing the data provided, one may notice that as the distance between the bottom surface of the metal inside the melting pot and the inductor’s bottom edge increases, the metal velocity near the surface decreases.

Table 3 **Liquid Cu-Pb alloy velocity on various melting pot arrangements in the furnace against the inductor [12]**

<table>
<thead>
<tr>
<th>Melting pot's position</th>
<th>Distance between the liquid metal's lower surface and the inductor’s lower edge / mm</th>
<th>Mean velocity on the surface / ( \text{ms}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>0,259</td>
</tr>
<tr>
<td>B</td>
<td>37</td>
<td>0,234</td>
</tr>
<tr>
<td>C</td>
<td>74</td>
<td>0,211</td>
</tr>
</tbody>
</table>

where:

- \( A \) – liquid’s bottom surface = inductor’s bottom edge,
- \( B \) – melting pot arranged in the centre of the inductor,
- \( C \) – liquid’s upper surface = inductor’s upper edge.

Certain studies have also proved a considerable impact of the current frequency on the mass transfer coefficient for the induction stirred liquid metallic phase. This is caused by the change of the stirring intensity along with the said parameter and thus the stirring velocity as well. On the current frequency change from 1 kHz to 5 kHz, the near surface velocity value drops (Figure 2) [13].

However, one must also bear in mind that this impact is relevant when the process is conducted under the conditions of high vacuum, when the evaporation rate is conditioned by the mass transfer in the liquid phase.
The evaporation rate also depends on the phenomena occurring on the interface, such as adsorption, chemisorption and desorption. In this respect, the key factors are the metal bath components from a group of surfactants, namely oxygen, sulphur, selenium or tellurium. They tend to rapidly accumulate on the liquid metal / gas interface, thus causing the surface tension to change. This may hinder penetration of the liquid metal component from the phase body to the surface. These phenomena were observed by Hayakawa investigating the impact of oxygen present in liquid metal on the copper and iron evaporation rate with the pressure in the measurement system being fixed below 13 Pa [14]. He proved that not only does an increase of the oxygen content in the liquid metal cause the surface tension of those metals to drop, but also the evaporation rate decreases (Figure 3). Also sulphur decreases the evaporation rate of iron under the conditions of reduced pressure (Figure 4).

It is also possible that a surface active bath component causes the evaporation rate to increase. An example of this phenomenon may be removal of antimony from liquid copper in the vacuum refining process. When copper does not contain oxygen, removing the antimony in the aforementioned process is impossible, since partial pressure of antimony is lower than that of copper. When the content of oxygen in copper was increased above 0.3 %, one could observe the antimony content in the bath to drop by even as much as 30 % after the refining. The antimony removal was due to the formation of volatile SbO whose equilibrium pressure is much higher than that of antimony as well as copper. The impact of the oxygen content in liquid copper on the extent of antimony removal in the vacuum refining process has been depicted in Figure 5.
CONCLUSIONS

In numerous high-temperature metallurgical technologies related to metal smelting from both primary and secondary raw materials, the evaporation process is among the most important ones. Its rate depends on such factors as temperature, pressure in the system, metal bath composition as well as the bath stirring method. In the case of pressure, one may observe its considerable impact on the evaporation rate through alteration of the stages being the process determinants. The influence of the bath stirring method is mainly relevant for the processes taking place in high vacuum, since mass transfer in the liquid phase determines the evaporation process. As regards the impact of the metal bath composition, it is clearly noticeable when it contains surfactants.

REFERENCES


Note: Nowak P is responsible for English language, Katowice, Poland