This paper describes a kinetic analysis of the process of chromium evaporation from ferrous alloys smelted under reduced pressure. The study discussed comprised determination of the liquid phase mass transfer coefficient as well as the value of the constant evaporation rate. By applying these values as well as the values of the overall mass transfer coefficient estimated based on the relevant experimental data, the fractions of resistance of the individual process stages were established.

Key words: chrome, steel, evaporation, pressure

Kinetika isparavanja kroma iz toplinski otpornog čelika pod smanjenim tlakom. Prilog opisuje kinetičku analizu procesa isparavanja kroma iz željeznih legura pod smanjenim tlakom. Studija obuhvaća utvrđivanje koeficijenta prijenosa mase tekuće faze kao i vrijednost konstantne stope isparavanja. Primjenom ovih vrijednosti i vrijednosti koeficijenta ukupnog prijenosa mase utvrđenog na temelju odgovarajućih eksperimentalnih podataka, ustanovljene su frakcije otpora pojedinih faza procesa.

Ključne riječi: krom, čelik, isparavanje, tlak

INTRODUCTION

The problem of losing components of alloy metal baths during smelting is particularly significant when even the slightest change in the content of the evaporated component alters the properties of the alloy being cast. In the case of high-chromium steel smelting, one must deal with losses of chromium, particularly in the processes conducted under reduced pressure conditions. This phenomenon was observed by numerous researchers including Bellot [1] in the process of smelting of stainless steel with the chromium content of 17 % by weight.

ANALYTICAL PART

In order to perform a kinetic analysis of the process of chromium evaporation from liquid iron, results of the experiments discussed in the papers of Ohno [2], Bellot [1] and Blacha [3] were applied. The aforementioned authors investigated chromium evaporation from steel containing from 1 to 25 % by weight of Cr smelted under the conditions of reduced pressure in induction furnaces. The overall mass transfer coefficient values established by the said authors based on experimental data for chromium as well as the basic parameters of the experiments conducted have been collated in Table 1,
For the sake of a description of a mass transfer process in liquids, penetration models are most frequently recommended at present. However, in the evaporation process being analysed, their application is limited, this resulting from the fact that, in those models, in the dependencies describing the mass transfer coefficient, the parameters being used are difficult to estimate. According to Higbie’s model, where transfer coefficient \( k_{l} \) is described by the following dependence:

\[
(1)
\]

where:

- \( D_{A-B} \) – interdiffusion coefficient for the liquid components,
- \( t^{*} \) – time for which the given component remains on the surface.

such a parameter is time \( t^{*} \). Dependence (1) can only be used to determine the value of coefficient \( k_{l} \) in the process of the liquid bubbling with gases, including liquid metallic alloys \([4, 5]\).

In Danckwerts’s penetration model, coefficient \( k_{l} \) is described by the following dependence:

\[
(2)
\]

where:

- \( s^{*} \) – proportionality factor.

Factor \( s^{*} \) determines the relation between the area restored in a unit of time and the liquid’s total area. Also in the above case, this coefficient is difficult to determine. In paper \([6]\), based on an analysis of the flow field of induction stirred liquid Fe-Cu alloy, it was found that the entire surface of metal is practically in motion at any given moment, and hence the value of parameter \( s^{*} \rightarrow 1 \).

When induction stirred mixed liquid volume occurs in the process analysed, it is recommended that for the sake of establishment of mass transfer coefficient \( k_{i} \), Machlin’s model should be applied. According to this model, the coefficient is described by the following dependence:

\[
(3)
\]

where:

- \( v_{m} \) – near surface velocity of liquid metal,
- \( R_{m} \) – melting pot’s internal radius.

Most authors investigating the evaporation rate for volatile components of metal bath assumed after Machlin that velocity \( v_{m} \) is constant for most induction aggregates and equals 0.1 m s\(^{-1}\). Also the authors of publication \([2]\) made such an assumption. A detailed analysis of the flow field for induction stirred liquid metal implied that not only does velocity \( v_{m} \) depend on the current frequency, but also on the melting pot’s arrangement against the inductor \([7, 8]\).

In the analysis discussed, in order to establish the value of coefficient \( k_{l} \) with regard to the studies referred to in publications \([1, 3]\), dependence (3) was applied. In the calculations, according to Ohno and Yamamoto \([9]\), the value of \( D_{C_{x-Fe}} \) for temperatures of 1 823 K and 1 873 K was assumed to equal 3.04 and 3.42 · 10\(^{-9}\) m\(^{2}\) s\(^{-1}\) respectively. At the same time, the near surface velocity value of \( v_{m} \) was assumed to equal 0.1 ms\(^{-1}\). Table 2 contains values of coefficient \( k_{l} \) estimated for all the experiments discussed.

\[
(4)
\]

where:

- \( \alpha \) – evaporation constant,
- \( p_{i}^{e} \) – balance pressure of component “i” being evaporated over the liquid solution,
- \( M_{i} \) – molar mass of component “i”.

Constant evaporation velocity \( k_{e} \) is described by the following equation:

\[
(5)
\]

where:

- \( p_{i}^{e} \) – equilibrium pressure of component “i” over pure bath,
γᵢ – activity coefficient for component “i”,
\( M_p \) – molar mass of primary metal,
\( \rho_p \) – density of primary metal.

The values of constant evaporation velocity \( k_e \) determined based on equation (5) have been collated in Table 2. In the calculations, the activity coefficient values for chromium in liquid metal were assumed after publication [10].

<table>
<thead>
<tr>
<th>Temp. / K</th>
<th>Mass transfer coefficient for the liquid phase ( k_l \cdot 10^6 / \text{ms}^{-1} )</th>
<th>Constant evaporation velocity ( k_e \cdot 10^6 / \text{ms}^{-1} )</th>
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<tr>
<td>1 873</td>
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**PROCESS RESISTANCE ESTIMATION**

Having established the values of overall mass transfer coefficient \( k \) for the chromium evaporation process being analysed, determined based on the relevant experimental data, as well as the estimated values of coefficients \( k_l \) and \( k_e \), one could determine the fractions of resistances of the individual stages in the total process resistance. As for the resistance due to the mass transfer in the liquid phase, its total resistance fraction did not exceed several per cent (Figure 2). An exception can be found in Ohno’s studies [2], where the resistance exceeded 25%. This discrepancy probably results from the fact that, for the sake of calculations, the said author assumed the diffusion coefficient value for chromium in liquid iron being an order of magnitude larger than those provided in other publications. Therefore, one may generally assume that within the pressure range from 1 to 150 Pa, in the range of temperatures being analysed, the mass transfer does not determine the process of chromium evaporation from iron for the alloys containing from 1 to 24% of Cr.

Figure 3 depicts the fraction of resistance related to the reaction of the chromium evaporation occurring on the liquid metal surface in the total process resistance. It is evident that this fraction increases considerably as the pressure in the system is dropping, and it decreases with the temperature increase. For temperatures below 1860 K, this fraction reaches the values exceeding 50%, which implies that the process analysed is then determined by the rate of the surface reaction. Figure 4, on...
the other hand, depicts the fraction of overall resistance due to the mass transfer in the liquid phase and the evaporation reaction in the total process resistance. It is also evident that the dependence in question is identical as compared with only the evaporation reaction. Therefore, at high temperatures, the stage actually determining the chromium evaporation process being analysed is the mass transfer in the gaseous phase, since the overall fraction of resistances of other stages does not exceed 30 %.

CONCLUSIONS

The results obtained by the authors in the study of the chromium evaporation process during vacuum smelting of ferrous alloys have been confirmed in other publications. By indicating the stages determining the chromium removal from the ferrous alloy one may obtain relevant information on the option of reducing or even avoiding this phenomenon. The mass transfer coefficient values calculated for the liquid phase as well as the constant evaporation velocity and the values of the overall mass transfer coefficient obtained based on experimental data have enabled determination of the resistances of the individual stages as well as their fraction in the total process resistance.

The resistance fraction of the chromium evaporation stage occurring in the liquid alloy/gaseous phase interfacial surface in the total process resistance clearly implies a strong dependence on the pressure in the system as well as the temperature. For temperatures below 1860 K, this fraction accounts for more than 50 % which may imply that the process analysed is determined by the rate of the surface evaporation itself. For the overall fraction of the resistance due to the mass transfer in the liquid phase and the evaporation reaction, an identical dependence is clearly observed as for the fraction of the evaporation reaction only. Consequently it may be claimed that, at high temperatures, the stage actually determining the chromium evaporation from ferrous alloys is the mass transfer in the gaseous phase, since the overall fraction of resistances of other stages does not exceed 30 %.

REFERENCES


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