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ISSN 0543-5846
METABK 51(3) 317-320 (2012)
UDC – UDK 669.26:669.15:669.083:66.047.3=111

KINETICS OF CHROMIUM EVAPORATION FROM HEAT-RESISTING STEEL UNDER REDUCED PRESSURE

Received – Prispjelo: 2011-12-05
Accepted – Prihvaćeno: 2011-03-20
Preliminary Note – Prethodno priopćenje

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 loosing 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, whereas Figure 1 depicts the pressure impact on the overall mass transfer coefficient for the process of chromium evaporation being analysed.

Table 1 **Basic parameters assumed in the study of the process of chromium evaporation from ferrous alloys and the overall mass transfer coefficient values**

Temp. / K	Press. / Pa	Initial chromium concentration in bath / % wt.	Overall mass transfer coefficient value k x 10-6 / ms^{-1}	Ref
1 873	1,33	0,98	2,10	[2]
1 873	1,33	1,89	2,00	[2]
1 873	0,13	2,83	2,83	[2]
1 993	1,33	17,00	5,56	[1]
1 993	4,27	17,00	5,29	[1]
1 993	13,3	17,00	3,21	[1]
1 993	26,7	17,00	2,21	[1]
1 993	48,0	17,00	1,15	[1]
1 993	66,7	17,00	0,78	[1]
1 993	133	17,00	0,59	[1]
1 773	150	23,56	0,80	[3]
1 773	150	23,56	0,95	[3]
1 823	150	23,47	1,40	[3]
1,823	150	23,50	1,37	[3]
1 773	70	23,84	1,21	[3]
1 773	70	23,71	1,14	[3]
1 823	70	23,37	1,46	[3]
1 823	70	23,11	1,57	[3]
1 773	10	23,36	2,16	[3]
1 773	10	23,07	2,68	[3]
1 823	10	22,21	2,98	[3]
1 823	10	22,43	3,12	[3]

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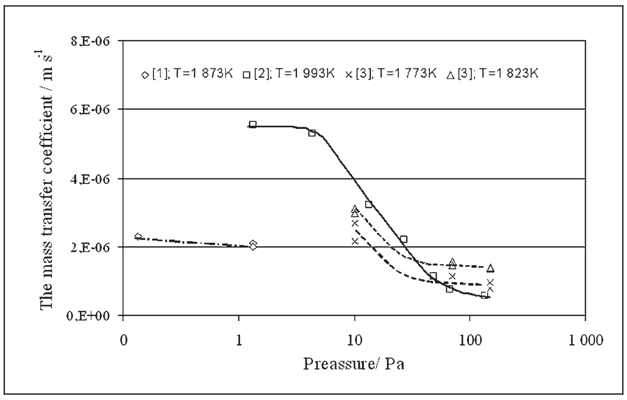

Figure 1 Change of the mass transfer coefficient (k) depending on pressure established for the process of chromium evaporation from liquid iron based on [1-3].

MASS TRANSFER COEFFICIENT FOR THE LIQUID METALLIC PHASE

Or 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:

$$k_l = \left(\frac{D_{A-B}}{\pi \cdot t^*}\right)^{0,5} \tag{1}$$

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

$$k_l = (D_{AB} \cdot s^*)^{0,5} \tag{2}$$

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* → 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 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* → 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_l Machlin's model should be applied. According to this model, the coefficient is described by the following dependence:

$$k_l = \left(\frac{8D_{AB} \cdot v_m}{\pi \cdot R_m}\right) \tag{3}$$

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 ms^{-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 $D_{Cr\text{-}Fe}$ 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.

CONSTANT VELOCITY OF THE EVAPORATION PROCESS

According to Langmuir's equation, the maximum mass flux of the component being evaporated from the surface is determined by the following dependence:

$$N_i = \frac{\alpha \cdot p_i}{\sqrt{2\pi RTM_i}} \tag{4}$$

where:

α – evaporation constant,

p_l – 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:

$$\kappa_e = \frac{\alpha \cdot p_i^0 v_i M_p}{\rho_p \sqrt{2\pi RTM_i}} \tag{5}$$

where:

p_i^0 – equilibrium pressure of component "i" over pure bath,

γ_i – activity coefficient for component "i",
M_p – molar mass of primary metal,
ρ_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 2 **Values of constant evaporation velocity and mass transfer coefficient for chromium evaporation from liquid ferrous alloy**

Temp. / K	Mass transfer coefficient for the liquid phase $k_l \cdot 10^6$ / ms^{-1}	Constant evaporation velocity $k_e \cdot 10^6$ / ms^{-1}
1 873	5,90	3,30
1 873	5,00	3,30
1 873	7,40	3,30
1 993	472	23,6
1 993	472	23,6
1 993	472	23,6
1 993	472	23,6
1 993	472	23,6
1 993	472	23,6
1 993	472	23,6
1 773	176	2,02
1 773	176	2,02
1 823	176	2,02
1 823	176	2,02
1 773	176	2,02
1 773	176	2,02
1 823	185	3,95
1 823	185	3,95
1 773	185	3,95
1,773	185	3,95
1 823	185	3,95
1 823	185	3,95

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.

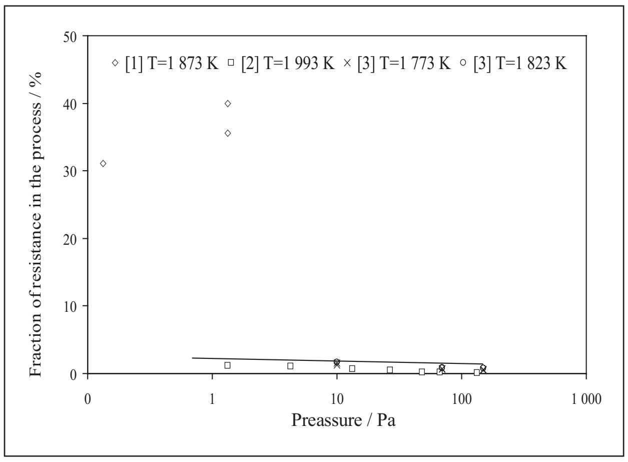

Figure 2 Fraction of the liquid phase mass transfer resistance in the total process resistance.

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 1 860 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

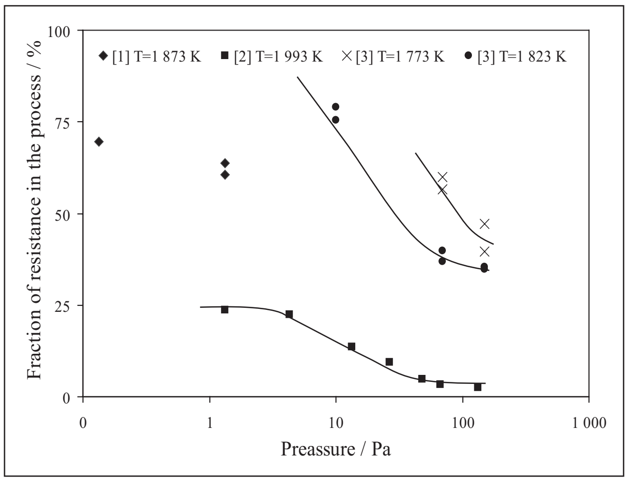

Figura 3 Fraction of the evaporation process resistance in the total process resistance during smelting under the reduced pressure conditions.

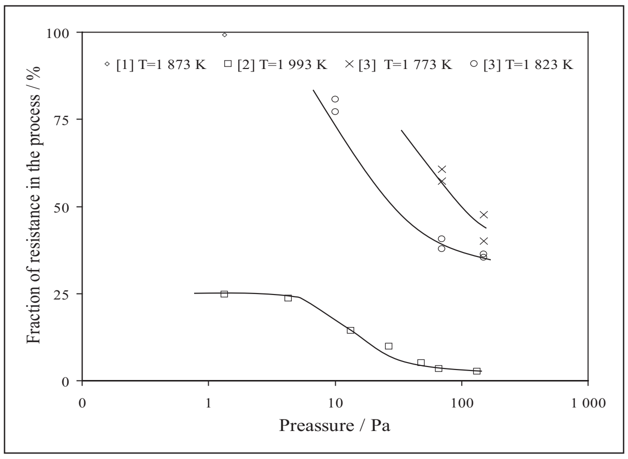

Figure 4 Overall fraction of the liquid phase mass transfer resistance and the evaporation reaction resistance in the total process resistance.

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 1 860 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 %.

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