J. ŁABAJ*

## KINETICS OF COPER EVAPORATION FROM THE Fe-Cu ALLOYS UNDER REDUCED PRESSURE

## KINETYKA PAROWANIA MIEDZI ZE STOPÓW Fe-Cu W WARUNKACH OBNIŻONEGO CIŚNIENIA

This paper provides an analysis of the results of studies concerning the impact of pressure on the process of copper removal from liquid ferrous alloys by evaporation. The research was conducted in vacuum induction furnace. Iron alloys with 0.509 to 1.518 %wt. Cu content were used for the tests. Kinetics analysis of the examined process was performed for the obtained results and the Speed of the process partial stages was estimated.

*Keywords*: iron alloys, evaporation, vacuum, mass transfer coefficient

W prezentowanej pracy przedstawiono wyniki badań nad możliwością usuwania miedzi z ciekłego żelaza na drodze odparowania. Badania realizowano w indukcyjnym piecu próżniowym. Wykorzystano stopy żelaza zawierające od 0.509 do 1.518% mas. Cu. Dla uzyskanych wyników przeprowadzono analizę kinetyczną badanego procesu i oszacowano szybkości jego etapów cząstkowych.

## 1. Introduction

A considerable decrease in the input of home scrap leads to a necessity of using increased amounts of demolition scrap, which may constitute one of the possible sources of the steel impurities, in the metallurgical processes. Those sources of impurities include metallic coatings or components of electrotechnical devices. When one deals with impurities easily removed in the metallurgical process, the increase of their content in the charge material does not a serious problem. It is otherwise when the charge material contains increased contents of impurities the removal of which in the steel smelting process is particularly difficult. An example of such an impurity may be copper. Due to the fact that copper forms low-melting eutectic compounds with iron, that are released during solidification at the grain boundary, it is possible that, on high content of the problematic metal, the hot steel becomes brittle. It was indeed the negative influence of copper on the properties of steel that has led to the necessity of undertaking studies concerning the possible options of removing it from liquid steel alloys.

## 2. Research methodology

The studies consisted in examining synthetic Fe-Cu alloys based on the ARMCO iron and grade M00B oxygen-free copper, produced through melting in an induction furnace in the inert gas atmosphere. The copper content in the alloys examined varied from 0.509 to 1.518% by weight.

All the experiments were performed using the VIM 20-50 one-chamber vacuum induction furnace manufactured by SECO-WARWICK. During the experiment, a sample of alloy of specific weight was placed in a magnesite or zirconium melting pot. After the furnace was closed, a system of pumps was switched on to attain the pressure assumed for the unit. The pressure was set through a cooperation between a mechanical pump, a Roots pump and, when necessary, a diffusion pump. Another stage of the experiment was heating of the charge material up to the specific temperature. After the metal had reached the temperature assumed, melting was conducted for 30 minutes. Samples of the metal were collected at specific and precise time intervals. The process temperature was measured using a pyrometer and type PtRh-Pt thermocouples. After the test completion, the liquid metal was poured into a graphite ingot mould. Once the metal had solidified and the fur-

* SILESIAN UNIVERSITY OF TECHNOLOGY, DEPARTMENT OF METALLURGY, 40-019 KATOWICE, 8 KRASIŃSKIEGO STR., POLAND

nace cooled down, the chamber was opened. The copper content in the alloys tested was by atomic absorption spectrometry using an apparatus manufactured by Perkin Elmer.

The tests were conducted at the temperature of 1923 K and within the range of pressures from 0.06 to 1074 Pa.

## 3. Test results

The change of the copper concentration in the liquid iron during the melting process was correlated by the following logarithmic function:

$$-\log \frac{C_{Cu}^t}{C_{Cu}^0} = A \cdot t \qquad (1)$$

where: $C_{Cu}^t$ – copper concentration in the alloy after time t [% by wt.]

$C_{Cu}^0$ – initial copper concentration [% by wt.]
$t$ – time [s]
$A$ – constant [$s^{-1}$]

### 3.1. Kinetic process model assumed

From a kinetic point of view, the process of copper evaporation from liquid iron being analysed can be divided into three main stages (Fig. 1):
- copper transfer from the body of the liquid phase to the interface,
- copper evaporation from the liquid metal surface,
- transfer of the copper vapours from the interface to the core of the gaseous phase.

The copper mass flux transferred from the body of the liquid metal to the interface is characterised by the following relation [1]:

$$N_{Cu}^l = \beta_{Cu}^l \left( C_{Cu}^l - C_{Cu}^s \right) \qquad (2)$$

where: $\beta_{Cu}^l$ – mass transfer coefficient for copper in the liquid phase (liquid iron) [$m \cdot s^{-1}$]

$C_{Cu}^l$ – copper concentration in the liquid phase core
$C_{Cu}^s$ – copper concentration near the interface

The mass flux of the copper being evaporated from the liquid metal surface can be determined according to the following relation:

$$N_{Cu}^e = k_{Cu}^e \left( p_{Cu}^{eq} - p_{Cu}^s \right) \qquad (3)$$

where: $k_{Cu}^e$ – constant copper evaporation rate [$m \cdot s^{-1}$]

$p_{Cu}^{eq}$ – equilibrium pressure of copper over liquid iron [Pa]

$p_{Cu}^s$ – actual pressure of copper near the interface [Pa]

For the gaseous phase, the flux of copper transferred from the interface to the body of this phase is conditioned by the following relation:

$$N_{Cu}^g = \beta_{Cu}^g \cdot p_{Cu}^s \qquad (4)$$

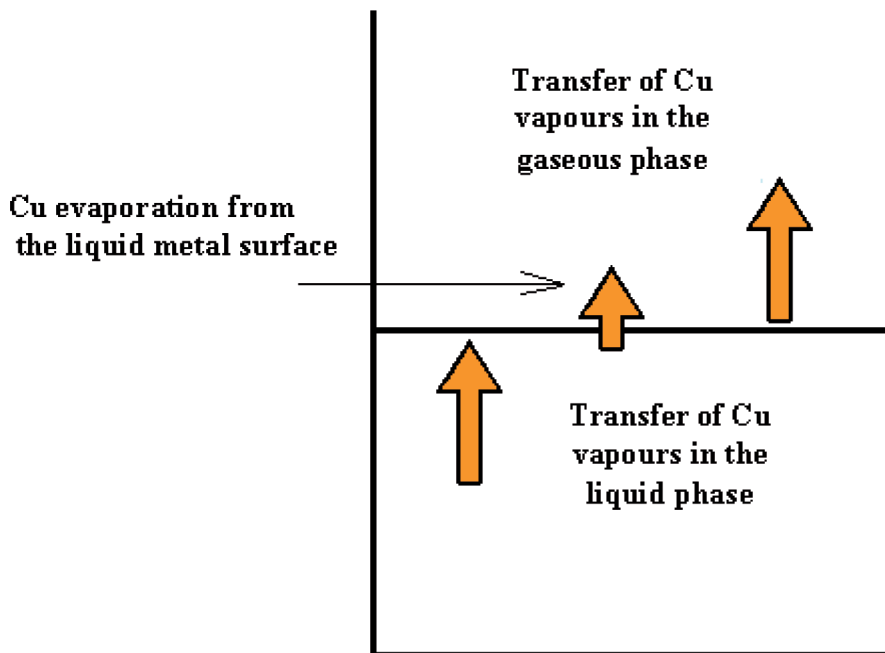where: $\beta_{Cu}^g$ – mass transfer coefficient for copper in the gaseous phase



Fig. 1. Stages of the process of copper evaporation from liquid iron

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

$$N_{Cu}^l = N_{Cu}^e = N_{Cu}^g \qquad (5)$$

then the overall flux of copper mass transfered from the liquid iron body to the gaseous phase core can be described by the following relation:

$$N_{Cu} = \left( \frac{1}{\beta_{Cu}^l} + \frac{1}{k_{Cu}^e} + \frac{1}{\beta_{Cu}^g} \right)^{-1} \cdot C_{Cu}^l \qquad (6)$$

or

$$N_{Cu} = k_{Cu} \cdot Cu_{Cu}^l \qquad (7)$$

where: $k_{Cu}$ – overall mass transfer coefficient.

Coefficient $k_{Cu}$ is described by the following equation:

$$\frac{1}{k_{Cu}} = \frac{1}{\beta_{Cu}^l} + \frac{1}{\varphi k_{Cu}^e} + \frac{RT}{\beta_{Cu}^g \cdot \varphi} \qquad (8)$$

where:

$$\varphi = \frac{p_{Cu}^o \cdot \gamma_{Cu} M_{Fe}}{\rho_{Fe}} \qquad (9)$$

where: $p_{Cu}^o$ – *equilibrium pressure of copper over pure bath*

$\gamma_{Cu}$ – *copper activity in a liquid Fe-Cu solution*
$M_{Fe}$ – *iron molar mass* [gmol − 1]
$\rho_{Fe}$ – *liquid iron density* [gm − 3]

The form of equation (7) implies that in order to establish the overall mass transfer coefficient values, one must first estimate the values of coefficients $\beta_{Cu}^l, \beta_{Cu}^g$ and $k_{Cu}^e$.

For the sake of description of the mass transfer in the liquid phase, the Nernst boundary film model as well as penetration models were originally applied. In accordance with the Nernst model, mass penetration coefficient $\beta^l$ is described by the following relation [2]:

$$\beta^l = \frac{D_{A-B}}{\delta_x} \qquad (10)$$

where: $D_{A-B}$ – *interdiffusion coefficient of the liquid phase components* [$m^2 s^{-1}$] $\delta_x$ – *boundary film thickness* [m]

The boundary film thickness marked as $\delta_x$ depends on the hydrodynamic conditions in the system, and it is a relatively difficult to determine.

Among the models much more frequently used to describe the mass transfer in the liquid phase than the boundary film model one should mention the penetration models [3, 4]. The first of them proposed by Higbie was based on the assumption that the liquid surface is composed of multiple components, each being in contact with the gaseous phase for a specific period of time, and subsequently passing deeper into the liquid. This means that the turbulent swirls occurring deeper in the liquid are not suppressed near the interfacial area and so they approach it causing its continuous restoration. In this model, the time all elements of the liquid spend near the surface is identical and the relation describing the mass transfer coefficient assumes the following form:

$$\beta^l = \left( \frac{D_{AB}}{\pi \cdot \tau} \right)^{0,5} \qquad (11)$$

$\tau$ – *time for which the given component remains on the surface* [s]

The second penetration model was proposed by Danckwerts who managed to modify Higbie's assumption that time $\tau$ is not constant and it is random. According to Danckwerts, however, the constant quantity is the relation between the area restored in a unit of time and the liquid's overall area. In this model, the mass transfer coefficient is described by the following relation:

$$\beta^l = (D_{AB} \cdot s)^{0,5} \qquad (12)$$

$s$ – *proportionality factor* [$s^{-1}$]

The penetration models use quantities that are difficult to determine. They include both time $\tau$ and proportionality factor $s$. Therefore, using these models to describe the mass transfer in a liquid metallic phase in hydrodynamic systems, usually occurring in steelmaking units, is limited in scope. While analysing the velocity field present in induction stirred liquid copper on the frequency of current from 1 to 5 kHz, the authors of paper [1] evidenced that all the liquid metal components are moving near its surface. This implies with a considerable degree of probability that the value of coefficient $s$ for induction stirring of metals assumes the value of 1.

Based on the penetration models, Machlin [5] developed a mass penetration model for induction stirred liquid metal. This model assumed that the liquid metal components were moving along a tangent line of liquid metal – gas or liquid metal – melting pot, and the surface normal velocity gradient is close to zero. In order to establish the value of mass transfer coefficient $\beta^l$, Machlin proposed the following relation:

$$\beta^l = \left( \frac{8 D_{AB} \cdot v_m}{\pi \cdot r_m} \right)^{0,5} \qquad (13)$$

where: $v_m$ – *near surface velocity of induction stirred liquid metal* [$m\ s^{-1}$]

$r_m$ – *radius of the liquid metal surface (assumed to be the melting pot inner radius)* [m]

In order to establish the value of coefficient $\beta^l$ based on relation (12), one must first know the values of $v_m$ and $r_m$. Most authors studying the kinetics of evaporation of induction stirred liquid metallic phase assumed after Machlin that velocity $v_m$ is practically independent of the electric parameters of the furnace operation as well as

its geometry (melting pot arrangement against the inductor). For induction furnaces of the capacity not exceeding 1 Mg, it was assumed that the value of velocity $v_m$ is constant and equals 0.1 ms$^{-1}$. However, it was proved that the nature of motion of induction stirred metal is a function of multiple factors such as the furnace type and geometry or the current frequency [6-7].

For instance, the authors of paper [6] evidenced based on the simulation performed that, for an induction stirred Cu-Pb alloy, as the current frequency is increasing to 3 kHz, the value of the near surface velocity is dropping. For the changes in the current frequency from 1 kHz to 5 kHz, a slight drop in the metal mean velocity deeper in the liquid was observed. Paper [7] provides a proof that the near surface velocity of metal depends on the changes in the symmetry of the melting pot arrangement against the furnace inductor.

Bearing in mind the foregoing reservations as regards the accuracy of determination of near surface value $v_m$, in order to estimate the values of the mass transfer coefficient for the liquid phase, relation (11) was applied having previously assumed the value of parameter $s$ equal to 0.9 based on the liquid Fe-Cu alloy flow field analysis conducted.

In order to determine the mass penetration coefficient for the liquid phase, it is also necessary to know the value of the coefficient of copper diffusion in liquid iron (i.e. $D_{Cu-Fe}$). Unfortunately, one will not find any data concerning such values in the literature of the subject, this being mainly due to the fact that considerable experimental obstacles are encountered while conducting the relevant measurements. In order to determine the value of $D_{Cu-Fe}$, the Darken equation for binary solutions was applied. Values of the self-diffusion coefficient for liquid copper and iron within the range of temperatures analysed were determined based on the following relations [8, 9]:

$$D_{Cu} = 14,6 \cdot 10^{-8} \cdot exp(-9700/RT) \qquad (14)$$

$$D_{Fe} = 3,66 \cdot 10^{-9} \cdot exp(-2860/RT) \qquad (15)$$

The diffusion coefficients calculated for copper in liquid iron equalled from 7.87 to 7.93E-09 m$^2$s$^{-1}$ for the alloys containing 0.509 and 1.518% of Cu by weight respectively. The diffusion coefficient values estimated for copper in liquid iron are highly consistent with the diffusion coefficient values of other metals in liquid iron [10].

The values of coefficient $\beta^l_{Cu}$ calculated based on equation (11) have been collated in Table 1.

The maximum flux of the component being evaporated from the liquid metal surface to the gaseous phase is determined by the Langmuir-Knudsen equation [11]. It assumes the following form:

$$N^e_{Cu} = \frac{\alpha \cdot p^o_{Cu} \cdot \gamma_{Cu} \cdot M_{Fe} \cdot C_{Cu}}{\rho_{Fe} \sqrt{2\pi RT M_{Cu}}} \qquad (16)$$

The above equation implies the following relation for a constant evaporation rate:

$$k^e_{Cu} = \frac{\alpha}{(2\pi RT M_{Cu})^{0,5}} \qquad (17)$$

The values of coefficient $k^e_{Cu}$ calculated based on equation (16) have also been collated in Table 1.

In order to establish the value of the copper mass transfer coefficient based on the experimental data available, the process velocity was described with the following equation:

$$\frac{dC_{Cu}}{dt} = k \cdot \frac{F}{V} \cdot C_{Cu} \qquad (18)$$

which assumed the following notation in the integral form:

$$\int_o^t \frac{dC_{Cu}}{C_{Cu}} = -k \cdot \frac{F}{V} \int_o^t dt \qquad (19)$$

Having integrated this relation, one obtains the following:

$$2,303 \log \frac{C^t_{Cu}}{C^o_{Cu}} = -k \cdot \frac{F}{V}(t - t_o) \qquad (20)$$

*where: F – evaporation areas (interfacial areas) [m$^2$]*
   *V – liquid metal volume [m$^3$]*
   *(t - t_o) – process duration time [s]*

The overall mass transfer coefficient value for the copper evaporation process was established based on equation (19) by applying the value of coefficient "A" from equation (1) as one describing the change of this metal concentration in the function of time.

The values calculated for the overall mass transfer coefficient for the copper evaporation from liquid iron have been provided in Table 1.

## 4. Analysis of the study results

The studies to determine the impact of pressure on the copper evaporation rate were conducted at the temperature of 1923 K for the alloys containing 0.509 and 1.518% of Cu by weight. The measuring system pressure was altered within the range from 0.06 to 1074 Pa.

Based on the studies conducted, the authors managed to establish the values of experimental mass transfer coefficient $k_{Cu}$, estimate the values of coefficients of mass transfer in the liquid phase $\beta^l_{Cu}$ as well as constant evaporation velocity $k^e_{Cu}$. By means of these coefficients, values of theoretical mass transfer coefficient $k_{Cu}$ were established. At the same time, the estimated values of

TABLE 1

Experimental mass transfer coefficients for the process of copper evaporation from Fe-Cu alloys

| Item | Process temperature, K | Working pressure, Pa | $k_{Cu} \times 10^6$ m s$^{-1}$ | $\beta^l_{Cu} \times 10^6$ m s$^{-1}$ | $k^e_{Cu} \times 10^6$ m s$^{-1}$ |
|---|---|---|---|---|---|
| 1 | 1923 | 1,074 | 4.09 - 4.19 | 52.39 | 135.80 |
| 2 | 1923 | 212 | 6.47 - 6.94 | 52.39 | 135.80 |
| 3 | 1923 | 101 | 9.69 - 10.0 | 52.39 | 135.80 |
| 4 | 1923 | 56 | 14.6 - 15.3 | 52.39 | 135.80 |
| 5 | 1923 | 49 | 16.8 - 17.9 | 52.39 | 135.80 |
| 6 | 1923 | 40 | 21.9 - 23.1 | 52.39 | 135.80 |
| 7 | 1923 | 5 | 41.2 - 41.9 | 52.39 | 135.80 |
| 8 | 1923 | 0.5 | 47.0 - 49.0 | 52.39 | 135.80 |
| 9 | 1923 | 0.06 | 44.3 - 48.1 | 52.39 | 135.80 |
| 10 | 1923 | 1013 | 1.75 - 3.64 | 52.74 | 135.80 |
| 11 | 1923 | 526 | 5.87 - 6.09 | 52.74 | 135.80 |
| 12 | 1923 | 425 | 5.83 - 7.88 | 52.74 | 135.80 |
| 13 | 1923 | 202 | 7.43 - 7.94 | 52.74 | 135.80 |
| 14 | 1923 | 101 | 8.63 - 8.95 | 52.74 | 135.80 |
| 15 | 1923 | 5 | 28.5 - 30.8 | 52.74 | 135.80 |
| 16 | 1923 | 1.2 | 37.6 - 37.7 | 52.74 | 135.80 |
| 17 | 1923 | 0.13 | 43.8 - 45.1 | 52.74 | 135.80 |
| 18 | 1923 | 0.06 | 44.2 - 47.8 | 52.74 | 135.80 |

TABLE 2

Experimental mass transfer coefficients for the process of copper evaporation from iron alloys

| Item | Temperature range, K | Pressure range, Pa | Experimental mass transfer coefficient, ms$^{-1} \times 10^{-5}$ | References item |
|---|---|---|---|---|
| 1 | 1873 | | 2 – 2.3 | [11] |
| 2 | 1683 – 1873 | 1 – 100 | 1.95 – 6.38 | [12] |
| 3 | 1923 – 1973 | 133 – 101,325 | 0.1 – 4 | [13] |
| 4 | 1898 – 1998 | 0.06 – 1,074 | 0.4 – 4.9 | own studies |

coefficients $\beta^l_{Cu}$ and $k^e_{Cu}$ enabled determination of resistances of the individual stages of the evaporation process analysed.

Based on the measurement data, values of experimental mass transfer coefficients were established on the level of 0.4-4.9·10$^{-5}$ ms$^{-1}$. They conform well with the values provided in various publications (see Table 2) as reported by other authors.

The studies conducted implied a considerable impact of pressure on the process rate. For the pressure below 10 Pa, there was practically no pressure impact on the process rate observed (Fig. 3). This means that for such pressure values, the process analysed is not de-termined by the mass transfer in the gaseous phase. In order to confirm the legitimacy of the above observation, the theoretical mass transfer coefficient values were calculated on the assumption that the process rate depends on two other constituent stages, i.e. the mass transfer in the liquid phase and the evaporation from the interface. Therefore, it was assumed that for the pressures below 10 Pa, the following relation is satisfied:

$$\frac{1}{k_{Cu}} = \frac{1}{\beta^l_{Cu}} + \frac{1}{k^e_{Cu}} \qquad (21)$$

The overall mass transfer coefficient values calculated based on relation (20) are highly consistent with the val-

ues established for experimental mass transfer coefficient $k_{Cu}$. The foregoing has been illustrated in Fig. 2.

The mass transfer resistance in the gaseous phase accounts for ca. 2% of the range of pressures being discussed.

The largest impact of pressure on the process studied was observed in the pressure range from 10 to 100 Pa. An identical impact was also noticed in other processes including evaporation of manganese from liquid iron [2, 12], lead from liquid copper [14] or zinc from the Zn-Ag-Pb alloy [15]. For the said range of pressure values, the process in question is determined by the mass transfer in the liquid and gaseous phase.

The studies conducted also implied that for the process executed on pressures exceeding 100 Pa, one will observe its diffusion control, and the determining stage is the mass transfer in the gaseous stage. The overall resistance of two other stages accounts for merely 5 to 25% of the total resistance. The foregoing has been illustrated with the data provided in Fig. 3.

The change in the share of transfer resistance in the liquid phase and the transfer resistance in the gaseous phase in the total copper evaporation resistance in the function of pressure (for T=1923 K), as obtained in the course of the studies conducted, has been depicted in Fig. 4.
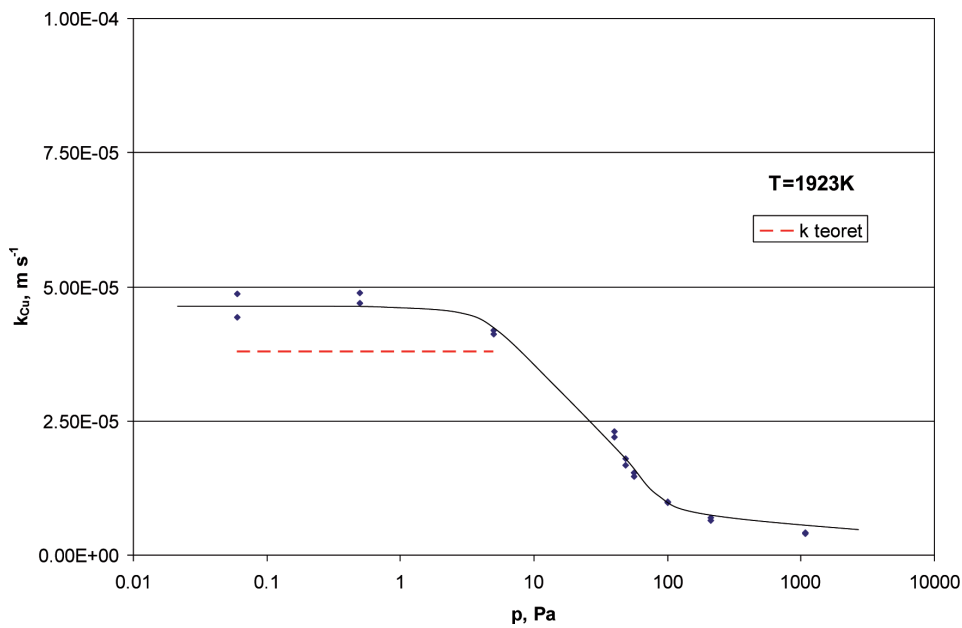


Fig. 2. Influence of pressure on the overall mass transfer coefficient for the process of copper evaporation from liquid iron
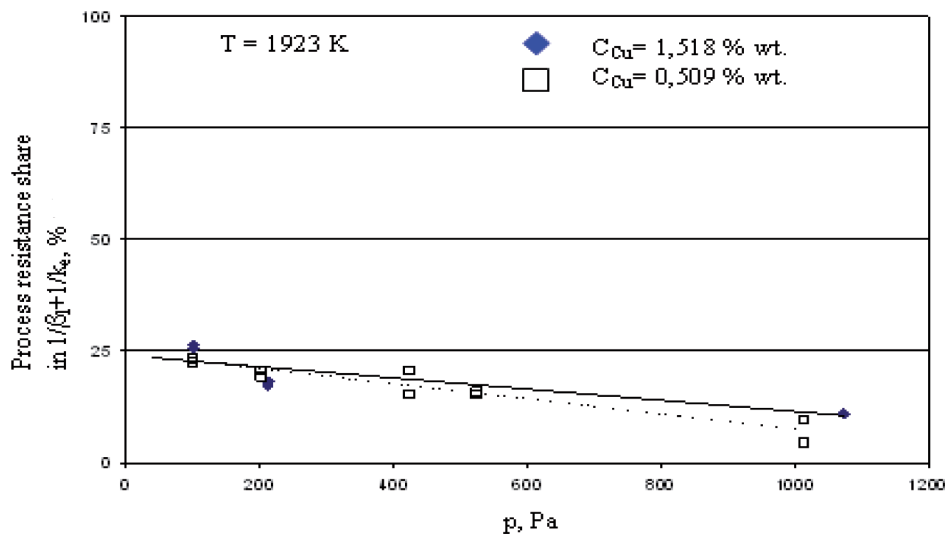


Fig. 3. Share of total resistance in the liquid phase and the evaporation process resistance in the total copper evaporation resistance (for the tests conducted at p > 100 Pa)
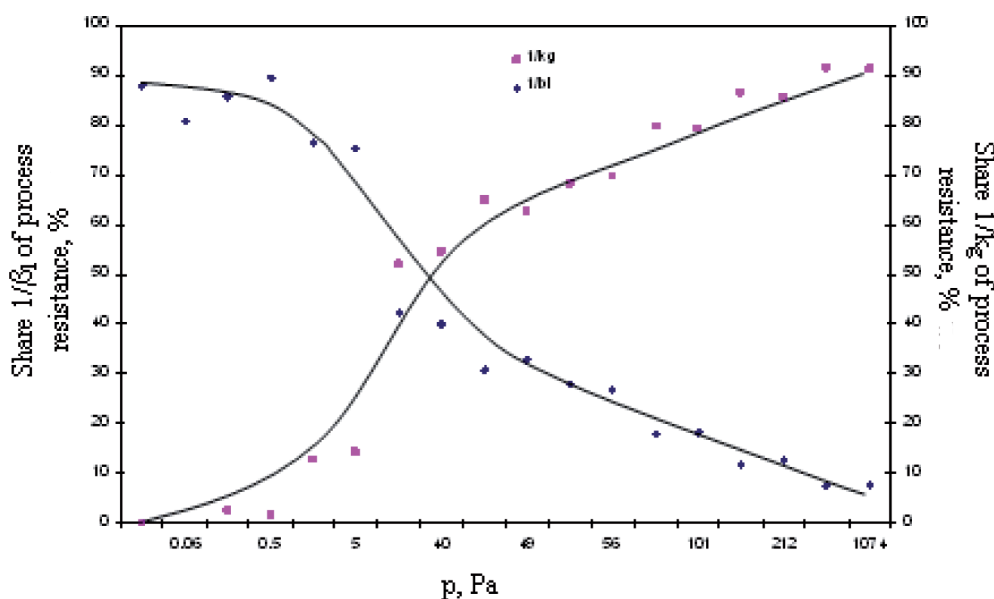
Fig. 4. Change of the share of transfer resistance in the liquid phase and the transfer resistance in the gaseous phase in the total copper evaporation resistance in the function of pressure (for T = 1923 K)

## 5. Conclusions

The analysis performed under the study discussed as well as the results obtained in the course of the experiments of vacuum refining of Fe-Cu alloys in an induction furnace enabled the authors to draw the following conclusions:

1. Within the whole range examined, in terms of pressure and chemical composition, the change in the copper concentration in iron during smelting in a vacuum induction furnace can be described by means of a $1^{st}$ order chemical reaction equation.

2. From the kinetic point of view, it has been proved that within the range of pressures from 0.06 to 1074 Pa, the copper evaporation from liquid iron is determined by the phenomena of mass transfer and is a diffusion-controlled reaction.

3. For the pressure value below 10 Pa, the process is determined by the mass transfer in the liquid phase. In this case, the share of the transfer resistance in the gaseous phase, within the whole range of the process resistance, does not exceed 20%.

4. As the pressure increases in the system above the threshold of 10 Pa, also the mass transfer resistance increases in the gaseous phase. For the pressure exceeding 100 Pa, the share of this resistance in the total process resistance assumes the values above 70%. The foregoing means that for the given range of pressures, the controlling stage is the mass transfer in the gaseous phase.

REFERENCES

[1] J. Ł a b a j, L. B l a c h a, Report from a research project of the Ministry of Science and Higher Education 3T08B 05926 entitled Kinetic model of the metal evaporation process under the reduced pressure conditions (unpublished).

[2] R. W a r d, Evaporative Losses During Vacuum Induction Melting of Steel, Journal of the Iron and Steel Inst **201**, 920-923 (1963).

[3] R. H i g b i e The Rate of Absorption of a Pure Gas into a still Liquid During Short periods of Exposure, Trans. AICHE **31**, 365-368 (1935).

[4] P. Danckwerts, Unsteady-state diffusion or heat-conduction with moving boundary, Trans. Faraday Soc. **46**, 101-103 (1950).

[5] B. B a k i s h, O. W i n k l e r, Vacuum Metallurgy, Elsevier, Amsterdam (1972).

[6] L. B l a c h a, R. P r z y ł u c k i, S. G o l a k, B. O l e k s i a k, Influence of an induction furnace's electric parameters on mass transfer velocity in the liquid phase, Archives of civil and mechanical engineering Archives of Civil and Mechanical Engineering **11**, 1, 171-179 (2011).

[7] R. P r z y ł u c k i, S. G o l a k, B. O l e k s i a k, L. B l a c h a, Influence o fan induction furnace's electric parameters on mass transfer velocity In the liquid phase, Metalurgija **51**, 1, 67-70 (2012).

[8] E. O z b e r k, R. G u t h r i e, Application of Vacuum Refininq in Copper Production, Inst. Min. Metall. Trans. C **94**, 146-157 (1985).

[9] E. O z b e r k, R. G u t h r i e, Kinetic Model for the Vacuum Refining of Inductively Stirred Copper Melts, Metall. Trans. B **17**, 87-103 (1986).

[10] Y. O n o, S. M a t s u m o t o, Diffusion of Chromium, Manganese, and Nickel in Molten Iron, Trans of the Japan Institut of Metals **16**, 415-422 (1975).

[11] R. Ohno, T. I s h i d a, Solution rate of solid iron in liquid copper, ISIJ International Japan Inst. Met. **31**, 10, 1164-1169 (1967).

[12] L. S a v o v, D. J a n k e, Evaporation of Cu and Sn from Induction-stirred Iron-based Melts Treated at Reduced Pressure, ISIJ International **40**, 2, 95-104 (2000).

[13] A.I. Z a i t s e v, I, Evaporation of Copper from Iron, SIJ International **44**, 4, 639-646 (2004).

[14] L. B l a c h a, Bleientfernung aus Kupferlegierungen im Prozess der Vakuumraffination, Archives of Metallurgy and Materials **48**, 1, 105-127 (2003).

[15] J. Ł a b a j, J. B o t o r, R. S o s n o w s k i, Kinetik der Zinkverdampfung aus Zn-Ag-Pb Legierungen bei Unterdruck, Archives of Metallurgy and Materials **47**, 3 307-320. (2002).