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KINETICS OF ARSENIC REMOVAL FROM LIQUID COPPER BY MEANS OF TITANIUM

KINETYKA USUWANIA ARSENU Z CIEKŁEJ MIEDZI PRZY POMOCY TYTANU

The article analyses the process of copper alloy refining by means of chemical bonding; arsenic dissolved in liquid copper reacts with pieces of titanium and a new phase TiAs is being formed. Numerical simulation of the kinetics of this process was performed. It was assumed, that the process is diffusion controlled. Calculations consisted in simultaneous solution of a non-stationary diffusion of Ti and As at variable concentration field of both reagents, variable position of the reaction zone and variable radius of the spherical particle of titanium. The rate of the process and the time of arsenic removal for different size of titanium particles were calculated.

Keywords: copper, arsenic, titanium, refining, kinetics

Praca przedstawia analizę procesu rafinacji ciekłego stopu miedzi. poprzez wiązanie chemiczne; arsen rozpuszczony w miedzi reaguje z kawałkami tytanu tworząc nowa fazę TiAs. Przeprowadzono symulację numeryczną kinetyki tego procesu, opartą na założeniu o kontroli dyfuzyjnej. Obliczenia polegały na równoczesnym rozwiązaniu równań dyfuzji niestacjonarnej obu reagentów, Ti i As, przy zmiennym polu stężenia obu reagentów, zmiennym położeniu strefy reakcji i zmiennym promieniu sferycznej cząstki tytanu. Wyznaczono szybkość reakcji i czas potrzebny na usunięcie arsenu dla różnych wielkości ziaren rafinatora.

1. Introduction

The production of copper in flash smelting process is accompanied with large amount of copper-rich slag, which has to be treated with the aim of copper recovery. As a result of reduction in electric furnace the copper alloy is obtained, which contains iron, lead and arsenic. Due to arsenic toxicity its removal from this alloy and its conversion to non-reactive form is one of the principal problems in copper technology. From this view-point the method of chemical bonding of arsenic from liquid copper seems promising. The results of previous work [1,2] have revealed that RE metals as cerium or lanthanum effectively remove arsenic from liquid copper and from the copper based Cu-Pb-Fe-As alloy. Due to lower costs and weaker negative influence on physical properties of copper titanium and zirconium seem the proper reagents for this purpose. Previous work [3] analysed activities of components in liquid As-Cu-Ti and As-Cu-Zr liquid solutions as well as the phase equilibria in these systems. Present work is aimed at characterization of the refining process itself. The kinetics of reaction of arsenic dissolved in liquid copper with pieces of titanium is studied and an attempt to simulate the stages of process is made.

2. Laboratory experiment of copper-arsenic alloy refining

In order to establish the basic information on refining process, i.e. the total process rate and the size of grains of obtained solid refining product, the laboratory experiment was carried out. The 0.5 kg alloy sample was melted in an induction vacuum furnace VSG10 (Balzers). The furnace cover was equipped with the manipulators for components addition and sampling of liquid alloy. The alloy was obtained by melting copper of 99.99% purity with Cu-As matrix alloy. As direct melting of copper with arsenic is hardly realizable because of high arsenic vapour pressure, matrix alloy of arsenic approximate concentration 25 atomic pct was obtained in non-isothermal vacuum cell of silica glass. Solid arsenic from low-temperature compartment was evaporated to high-temperature compartment containing

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copper, where the liquid alloy was formed. The composition of Cu-As matrix alloy was calculated from mass balance. The concentration of arsenic in Cu-As alloy used in refining experiment in the present work was 2.0 atomic pct. This value may be representative for industrial conditions.

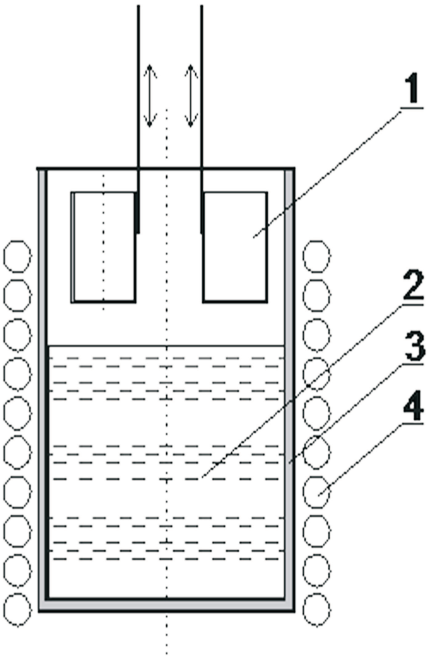

Fig. 1. The schematic diagram of the system for Cu-As alloy refining by means of titanium. 1. Alundum crucible for sampling, 2. Molten metal, 3. Crucible, 4. Induction coil

The schematic diagram of experimental system is presented in Fig. 1. The sample of alloy is placed in the crucible made of fused alumina. The experiment begins with melting the sample in crucible and setting temperature at the level 1400 K. The pressure in the system during experiment was 500 mbar. Then by means of a manipulator tube the weighed amount of titanium was added. After the appropriate time interval the samples of alloy were taken from the top layer of the alloy by means of the sampling manipulator with small Al_2O_3 crucibles. The samples were analyzed with the use of Link Isis X-ray micro-analyzer. The EBS method was used. The results of experiment are presented in Table 1.

TABLE 1
The results of Cu-As alloy refining by means of titanium

Number of the sample	Time [min]	Diameter of inclusion [μm]	Composition of inclusions [mass %]		
			Cu	Ti	As
1	5	2-6	7	51	42
2	15	3	6	42	52
3	25	2-3	20	27	52

It was found that the matrix phase in examined samples is Cu-As solution phase containing 3-6 mass pct of arsenic, i.e. of the composition similar to the initial one. The Ti:As ratio in precipitates obtained after 5 and 15 min suggest that arsenic is bonded with titanium in the compound of atomic ratio 1:1.

It follows from the obtained results that:

- The introduction of titanium to Cu-As alloy results in formation of TiAs compound.
- The introduced titanium reacts mainly with arsenic and does not dissolve in copper,
- The refining reaction takes place during the first 15 min.

3. Modelling of liquid alloy refining by means of a granular refining agent

The present analysis regards the refining operation where a solid reagent is used. In the first approach the refining is a sequence of three stages:

- Transport of reagents to the reaction zone,
- Chemical reaction of TiAs formation,
- Flotation of reaction product to the surface of the melt.

The process begins at the point of introduction of the solid reagent into a liquid alloy of an uniform arsenic concentration. The first simplifying assumption is that equal spherical grains of the radius r_0 are used. Two basic cases may be considered:

- Under the assumption that the movement of a liquid alloy does not influence the process, each particle of a refining agent acts in a spherical zone, corresponding to the part of the total melt volume. The solid reagent dissolves isothermally. The reaction zone is initially situated close to the surface of the reagent particle and during the progress of dissolution it shifts outwards. The transport of substrates: arsenic and titanium to the reaction zone is accomplished through diffusion. This situation is schematically shown in Fig. 2.
- When the liquid metal is intensely stirred the diffusion transport to the reaction zone is restricted to the boundary layer. In the bulk volume of the liquid metal the concentration of reagents is position independent.

This paper presents results of calculation for the first case, that is without stirring. The uniform size of reagent particles was assumed. The mass of liquid alloy is m_a, while its density ρ_a. The mass of refining reagent is m_r, and its density ρ_r. Thus the number n of reagent spherical particles of radius r_0 is:

$$n = \frac{3 \cdot m_r}{4 \cdot \pi \cdot \rho_r \cdot r_0^3} \tag{1}$$

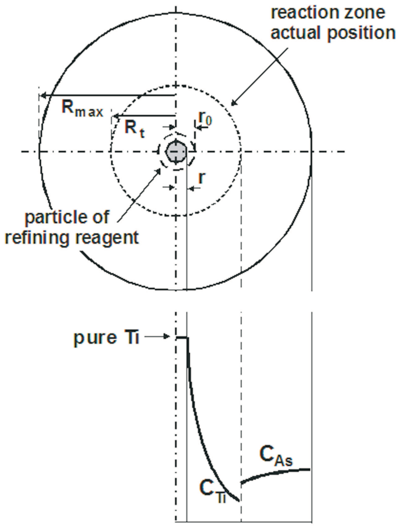

Fig. 2. Scheme of reagents concentrations in As removal from copper – stationary regime

One particle of reagent operates in the region of radius:

$$R_{\max} = r_0 \cdot \sqrt[3]{\frac{m_a}{m_r} \cdot \frac{\rho_r}{\rho_a}} \tag{2}$$

3.1. Model of process in stagnant fluid – without stirring

The radius of operation zone for a single reagent particle is calculated under assumption, that molar proportion of titanium to arsenic is 1:1, which corresponds to the refining product TiAs. This composition was confirmed in the experiment described earlier. If arsenic concentration of 1.0 mass pct in copper alloy is concerned, the corresponding titanium concentration is 1.5 mass pct. Thus $m_r/m_s = 0.015$. Density of solid Ti is 4.5 g/cm^3, while density of liquid copper is 8.8 g/cm^3.

At the chosen time the reaction runs at the spherical surface of radius $R_t (R_{\max} > R_t > r_0)$. The position of the reaction zone is determined with:

1. Thermodynamic condition of formation of refining product inclusions,
2. The rate of dissolution and transport of titanium,
3. The rate of transport of arsenic.

The rate of chemical reactions at the temperature 1400 K is so high that the reaction stage does not influence the position of reaction zone.

3.2. Thermodynamic condition of TiAs formation

The reaction of arsenic removal is as follows:

$$\underline{Ti} + \underline{As} = TiAs(s) \tag{3}$$

The reaction proceeds, if appropriate concentrations of reagents are reached. The equilibrium values of concentrations may be deduced from the equilibrium constant.

$$K = \frac{a_{TiAs(s)}}{f_{Ti} \cdot [\%Ti] \cdot f_{As} \cdot [\%As]} \tag{4}$$

$[\%\ Ti]$ and $[\%\ As]$ denote the concentrations of reagents in mass pct, f_{Ti} and f_{As} – the activity coefficients based on Henry's law.

Gibbs free energy change of reaction (3), $\Delta G^0_{(3)}$ may be presented as a sum of three contributions: a) dissolution of solid titanium to 1 mass pct in copper $\Delta G^0_{Ti,s(Cu)}$, b) dissolution of gaseous arsenic to 1 mass pct in copper $\Delta G^0_{As,g(Cu)}$, and c) formation of TiAs from As(g) and Ti(s), $\Delta G^0_{f,TiAs(s)}$:

$$\Delta G^0_{(3)} = -\Delta G^0_{Ti,s(Cu)} - \Delta G^0_{As,g(Cu)} + \Delta G^0_{f,TiAs(s)} \tag{5}$$

Gibbs free energy of solid titanium dissolution was determined from the Redlich-Kister parameters for liquid Cu-Ti solution given by [4]:

$${}^0L_{Cu-Ti} = -19330 + 7.651 \cdot T J/mole \tag{6}$$

$${}^1L_{Cu-Ti} = 0 \tag{7}$$

$${}^2L_{Cu-Ti} = +9382 - 5.448 \cdot T J/mole \tag{8}$$

From the above parameters the limiting value of the activity coefficient was deduced as $\ln \gamma^0_{Ti(Cu)} = 0.555$ for the temperature 1400 K. Thus the free energy change of titanium dissolution is given as:

$$\Delta G^0_{Ti(Cu)} = RT \cdot \ln\left(\gamma^0_{Ti(Cu)} \cdot \frac{M_{Cu}}{100 \cdot M_{Ti}}\right) \tag{9}$$

where: $M_{Cu} = 63.55$ and $M_{Ti} = 47.87$.

It results from (9) that $\Delta G^0_{Ti,l(Cu)} = -\ 43\ 850$ J/mole. Taking into account the free energy change of melting, $\Delta G^0_{Ti(s-l)} = +\ 4080$ J/mole [5], the value of free energy change for solid titanium dissolution becomes: $\Delta G^0_{Ti,s(Cu)} = -\ 39\ 770$ J/ mole.

The Redlich-Kister parameters for liquid Cu-As solution according to [6] are as follows:

$${}^0L_{As-Cu} = -45857.442 - 7.0593 \cdot T J/mole \tag{10}$$

$${}^1L_{As-Cu} = +8941.709 + 18.2381 \cdot T J/mole \tag{11}$$

$${}^2L_{As-Cu} = -789.0528 + 8.0076 \cdot T J/mole \tag{12}$$

On the basis of the above parameters the average value of arsenic activity coefficient in the range $X_{As}=0$ to $X_{As}= 0.1$ is $\gamma^0_{As(Cu)} = 1.161 \cdot 10^{-3}$ at 1400 K. The Gibbs free energy change of formation of 1 wt pct solution is:

$$\Delta G^0_{As,l(Cu)} = RT \cdot \ln\left(\gamma^0_{As(Cu)} \cdot \frac{M_{Cu}}{100 \cdot M_{As}}\right) \tag{13}$$

where $M_{As} = 74.92$.

For the temperature 1400 K $\Delta G^0_{As,l(Cu)} = -134\ 200 J/mole$.

This value corresponds to dissolution of liquid arsenic. To calculate the corresponding value for gaseous arsenic the free energy change of evaporation must be taken into account.

According to Wypartowicz [7] $\Delta G^0_{As(l-g)} = -106\ 865 J/mole$.

Thus the free energy change of gaseous arsenic dissolution is:

$$\Delta G^0_{As,g(Cu)} = \Delta G^0_{As,l(Cu)} - \Delta G^0_{As(l-g)} \qquad (14)$$

The obtained value of $\Delta G^0_{As,g(Cu)} = -$ 27 335 J/mole.

The free energy of solid TiAs formation from solid titanium and gaseous arsenic at $\Delta G^0_{f,TiAs(s)}$ is not known so far. However, the expected values of equilibrium concentrations of Ti and As may be obtained from (5) on the basis of the $\Delta G^0_{As,g(Cu)}$ and $\Delta G^0_{Ti,s(Cu)}$ values calculated above and assumed values of $\Delta G^0_{f,TiAs(s)}$.

If $\Delta G^0_{f,TiAs(s)} = -$ 150 000 J/mole, one obtains [%Ti] = [%As] = 0.034, while for $\Delta G^0_{f,TiAs(s)} =$ 200 000 J/mole [%Ti] = [%As] = 0.0039 is obtained. This simulation suggests low concentrations of reagents in the reaction zone, i.e. high efficiency of refining.

Discussion in the chapter 3.2. is aimed at the estimation of reagents concentrations in solution in equilibrium with TiAs precipitate. These determine the final concentrations of reagents in reaction zone, which influence the calculation of diffusion fluxes.

3.3. Diffusion of titanium and arsenic to reaction zone at stagnant fluid

For the stationary state of process, i.e. for fixed positions of $R_{\max}$ and R_t in space the condition of constant flux of diffusing species in radial direction is valid. This is equivalent to mass conservation law:

$$\frac{d}{dR}\left[R^2 \cdot J_i\right] = 0R^2 \cdot J_i = const \qquad (15)$$

where J denotes diffusion flux.

The diffusion flux is the function of position and time: $J_i = f(R,t)$

Introducing the dependence for diffusion flux (Fick's law)

$$J_i = -D \cdot \frac{dX_i}{dR} \qquad (16)$$

one obtains the differential equation:

$$\frac{d}{dR}\left[R^2 \cdot \frac{dX_i}{dR}\right] = 0 \qquad (17)$$

This equation should be solved under boundary conditions:

$$X_i = X_{i\max} \quad for \quad R = R_{\max} \quad and$$
$$X_i = X_{i0} \quad for \quad R = R_0$$

First integration yields:

$$R^2 \cdot \frac{dX_i}{dR} + a = 0 \qquad (18)$$

Separation of variables and second integration yields:

$$X_{i\max} - X_i = a \cdot \left(\frac{1}{R_{\max}} - \frac{1}{R}\right) \qquad (19)$$

The constant α may be deduced from boundary conditions:

$$a = \frac{X_{i\max} - X_{i0}}{\frac{1}{R_{\max}} - \frac{1}{R_0}} \qquad (20)$$

The diffusion flux of reagent is:

$$J_i = 4\pi \cdot R^2 \cdot \frac{dX_i}{dR} \qquad (21)$$

To obtain the stoichiometric compound TiAs, the diffusion fluxes of both reagents must be equal.

$$J_{Ti} = J_{As} \qquad (22)$$

Two additional assumptions were used in calculations:

- The reaction of TiAs formation proceeds at the spherical surface of radius R_t. The thickness of the reaction zone may be neglected. The rate of TiAs precipitation is equal to the rate of reagents delivery:

$$v_{TiAs} = J_{Ti} \cdot 4\pi \cdot R_t^2 = J_{As} \cdot 4\pi \cdot R_t^2 \qquad (23)$$

- The dissolution rate of titanium is sufficiently high in relation to diffusion transport rate, so it does not affect the total process rate.

4. Results of simulations

Mathematical simulation of the process consists in simultaneous solution of non-stationary diffusion of both reagents Ti and As at variable concentration field of both reagents, variable position of the reaction zone and the variable radius of the spherical particle of titanium in order to determine the time of dissolution of the titanium particle, which is approximately equivalent to the time of the refining process.

The solution to the problem of simultaneous diffusion of two reagents to the reaction zone was carried out numerically with the use of Mathematica program [8]. Calculations were executed for three values of initial radius r_0 of refining agent particles: 1.5 mm, 3.0 mm and 7.5 mm. Diffusion coefficients of both components were assumed as

$D = 9 \cdot 10^{-9} m^2 \cdot s^{-1}$, according to Ohno [9]. The density of liquid Ti was assumed 4.51, liquid As – 5.72, liquid Cu – 8.92 kg/dm^3.

The calculations for various sizes of refining agent particles were performed at the variable time step, which was adopted to the size of the reaction zone. The spherical particle of the refining agent was accepted as dissolved, if its radius became smaller than 0.01 mm. The results of calculations were presented in Figs. 3-9 and in Table 2. Figs. 3-8 present the calculated distribution of titanium and arsenic concentration for two stages of process:

1. When the radius of titanium particle is reduced to 0.001 m,

2. When the particle is practically dissolved, i.e. its radius is 0.01 mm.

Fig. 3 describes the behavior of titanium sphere of initial radius 0.0015 m. The diameter of 0.001 m is reached after 42 s, and that of 0.01 mm after 209.7 s. Fig. 4 presents the corresponding distribution of arsenic concentration after 42 s and after 209.7 s. It may be observed, that when titanium sphere radius is 0.01 mm, considerable amount of arsenic is still present at the outermost region of spherical zone around titanium particle. This amount is of course equivalent to the amount of remained titanium in spherical particle.

Figs. 5 and 6 present the behavior of reagents within spherical process zone around titanium particle of radius 0.003 m. In comparison to the case of 0.0015 m radius of titanium sphere, the radius of reaction zone, as well as dissolution time are considerably higher, as the mass of titanium to be dissolved is 8 times larger.

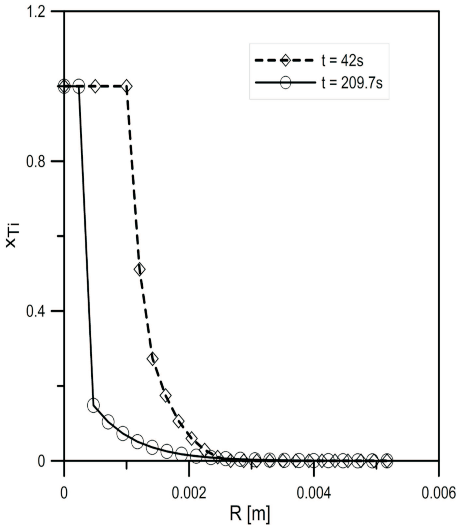

Fig. 3. Distribution of titanium concentration in the refining zone after t = 42 s and t = 209.7s (termination of the refining period). Initial radius of titanium particle – 0.0015 m

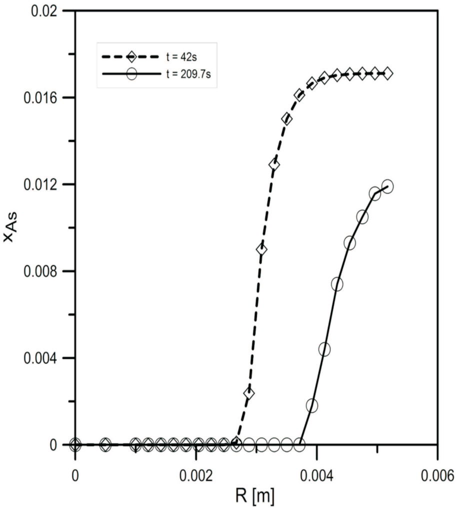

Fig. 4. Distribution of arsenic concentration in the refining zone after t = 42 s and t = 209.7s (termination of the refining period). Initial radius of titanium particle – 0.0015 m

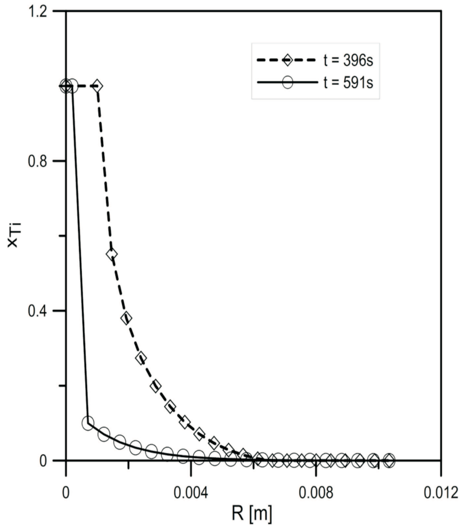

Fig. 5. Distribution of titanium concentration in the refining zone after t = 396 s and t = 951s (termination of the refining period). Initial radius of titanium particle – 0.003 m

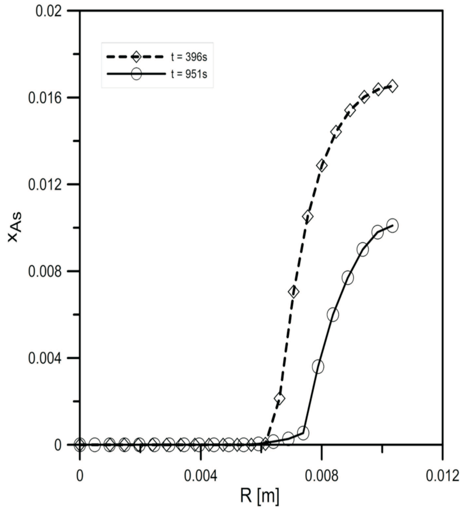

Fig. 6. Distribution of arsenic concentration in the refining zone after t = 396 s and t = 951s (termination of the refining period). Initial radius of titanium particle – 0.003 m

Figs. 7 and 8 present the results for titanium particle of radius 0.0075 m. In this case the time of total particle dissolution exceeds 2 h, and for this reason so large titanium grains are out of practical application.

It is important to notice, that the initial concentrations of titanium and arsenic differ very strongly, and for this reason the concentration profiles are strongly asymmetric.

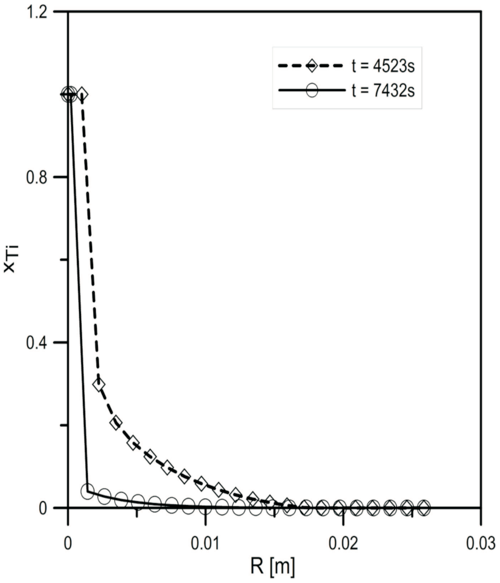

Fig. 7. Distribution of titanium concentration in the refining zone after t = 4523 s and t =7432s (termination of the refining period). Initial radius of titanium particle – 0.0075 m

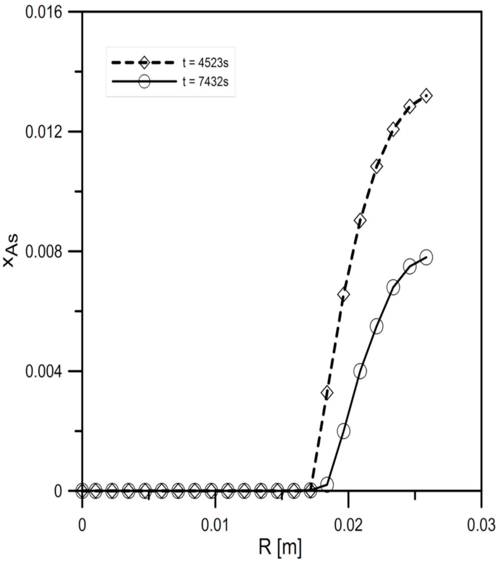

Fig. 8. Distribution of arsenic concentration in the refining zone after t = 4523 s and t = 7432s (termination of the refining period). Initial radius of titanium particle – 0.0075 m

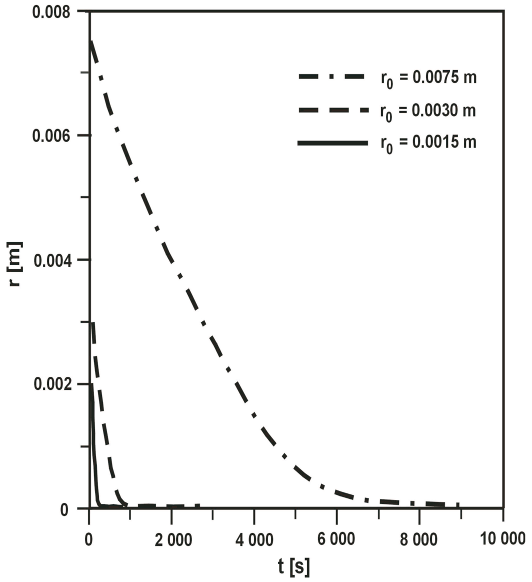

Fig. 9. Decrease of titanium particle radius in the course of refining. Initial particle radius – 0.0015, 0.003, and 0.0075 m

The variations of titanium particle radius with time for three values of initial particle radii are presented in Fig. 9. Large difference between calculated curves may be observed.

5. Discussion

The most characteristic features of obtained results are summarized in Table 2, which collects the obtained times of total dissolution and a partial dissolution (down to 0.001 m radius). The total time of process increases strongly with the titanium grain radius. However, the dissolution time does not change proportionally to grain volume, i.e. to third power of grain radius, but rather proportionally to $r^{2.2}$. This effect may be attributed to the radius of process zone of given titanium particle, as well as to comparatively low arsenic concentration in the melt.

TABLE 2

Results of calculations

Radius of the particle of refining element [m]	0.0015	0.003	0.0075
Radius of the reaction zone [m]	0.00517	0.01034	0.02585
The time of dissolution [s]	209.2	963	7432
The time of particle's radius reduction to 1 mm [s]	42	396	951
Time step [s]	0.2	0.5	0.5

In the present work the diffusion flux was expressed with the Fick's law in the form valid for the component in considerable dilution. The calculation of the diffusion flux of substance "i" in solution should also take into account the fluxes of other components. This becomes important at high concentrations of species "i". The correct expression for diffusion flux is as follows [10]:

$$J_i = D \cdot \frac{\Delta X_i}{\Delta x} \cdot \frac{1}{(X_{solv})_{lm}} \qquad (24)$$

$$(X_{solv})_{lm} = \frac{X_{solv,2} - X_{solv,1}}{\ln X_{solv,2} - \ln X_{solv,1}} \qquad (25)$$

where the index "solv" denotes solvent.

This suggests that the logarithmic mean of copper (solvent) concentration should be taken into account. However, in the conditions of present simulation, the titanium concentration falls rapidly in first few time steps and the deviation of results obtained by means of equation (25) is negligible.

6. Conclusions

Refining operation by means of the solid refining agent is a complex process in which several stages can be distinguished:

- Dissolution of the particle of the refining reagent,
- Transport of reagents to the reaction zone,
- Chemical reaction of compound (TiAs) formation,
- Formation and growth of inclusions
- Flotation of reaction product to the surface of the melt.

As the experimental investigation of kinetics of all stages is impossible, various mathematical models are used. The case presented in this paper has not been considered yet, it resembles, in some ways, the process of metal's dissolution in a liquid alloy [9, 11] or injection of carbon particles [12].

Results of calculations presented in this article state, that the diffusion of reagents is the slowest stage of the process and it determines the total rate of the process while the size of the particles of the refining reagent determines the efficiency of the process. For the particles diameter ratio 1:5, the time of the process ratio is 1:35 (see Table 2 and Fig. 9).

In relation to process of refining in industrial vessel the conclusion may be drawn, that the particles size of refining agent is of great importance in process efficiency under stagnant fluid conditions. In strongly agitated fluids this is no longer valid.

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