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V.P. Gritsaj, manager by a department, c.t.s., professor
V.I. Ivanov, senior research worker
T.N. Nesterenko, associate professor, c.t.s.
V.R. Rumyantsev, associate professor, c.t.s.

TO MASS TRANSFER OF IONS FOR REFRACTORY METALS AT ELECTROLYSIS OF MOLTEN SALTS

(Report 2)

Zaporozhe state engineering academy, Ukraine

The task of heat conductivity has been formulated and it has been decided in the cylinder of endless length with a moving border for the process precipitation of main metal on a cathode at the electrolysis of melted salts. Results of numeral experiment for the study of influence of thermal stream on a rise speed of metal layer thickness on a cathode indicate about essential influence of running direction for discharged ions and active hashing of electrolyte melt.

Keywords: electrolysis of melted salts, refractory metals, ions, cathode, mass transfer, deposition of metal.

The electrolysis of ionic fusions with depositing of crystalline metal on a cathode is widely used at the production of refractory metals: titan, vanadium, zirconium and other.

There are give an account in detail the aspects of influence of electric and related with him mass streams on crystallization of metals from fusions of salts on the process of delivery of ions to the cathode and post reduction of layer of the depositing metal on his surface [1]. The features of forming hydrodynamic, thermal and concentration boundary layers on length of generatrix of cathode are described and the high-quality estimation of influence of thermal stream on the process of electro-deposition of metal from ionic fusions of salts is carried out at article [2].

The quantitative estimation of influence of thermal stream parameters in the process of electrolysis on the dynamics of forming of metal layer on a cathode has been carried out.

At the modeling of metal deposition of with the moving border of the most complete approaching to the real process are arrived at realization a task about a phase transition [3].

The mathematical model of process was developed at next assumptions: calculation range for a cathode and metal, deposited on him, has axial and thermal symmetry; fusion is assumed monophase, id est consolidation of layer of metal, carried out at the temperature of phase transition; the coefficient of heat emission on the surfaces of cathode is accepted by constant; the thermophysical parameters of the developed metal and fusion of electrolysis do not depend from a temperature.

Then change of temperature for the metal layer on a cathode in time and on a co-ordinate is described one-dimensional non-linear equation of heat conductivity at cylindrical co-ordinates for an range with the moving border ($R < r < R+\xi$):

$$\rho_m c_m \frac{\partial T_m}{\partial \tau} = \frac{\lambda_m}{r}\left[\frac{\partial}{\partial r}\left(r\frac{\partial T_m}{\partial \tau}\right)\right], \quad \tau > 0 \tag{1}$$

at initial and border conditions

$$\xi(r,\tau)\big|_{\tau=0} = 0 \tag{2}$$

$$T_m(0,\tau)\big|_{r=R} = T_c \ ; \qquad T_m(\xi,\tau)\big|_{r=R+\xi(\tau)} = T_{cr} \tag{3}$$

$$\lambda_m \frac{\partial T_m}{\partial r}\bigg|_{r=(R+\xi)-0} = \lambda_l \frac{\partial T_l}{\partial r}\bigg|_{r=(R+\xi)+0} + \rho\cdot L\frac{d\xi}{d\tau} \ , \tag{4}$$

where ρ_m and c_m are a closeness and heat capacity of the deposited metal; λ_m and λ_l are a coefficient of heat conductivity for metal and fusion of electrolyte; T_c and T_{cr} are a tem-perature of cathode and phase transition; T_m and T_l are a temperature of metal and fusion of electrolyte; r and τ are radial and time co-ordinates; R is a radius of cathode; ξ is a co-ordinate of metal front; L is a specific warmth of phase tran-sition.

Assuming that the change of temperature on the radius of cell and thickness of metal layer complies to the linear law, get linear equation in full differentials relative to the change of thickness of metal layer E at the electrolysis Fo

$$\frac{EdE}{\left[D_2\cdot\ln(1-D_1\cdot E)+C_2\cdot\theta_2\cdot E\right]} = \frac{2dFo}{(\theta_1-2K)_1\cdot D_2} \ . \tag{5}$$

Non-dimensional variables and criteria similarities, included in equation (9), are determined by correlations: $E = \xi/H$ is a relative thickness of deposited metal layer (H is a depth of dip of cathode in fusion of electrolyte); $D_1 = H/R$ is a relative depth of dip of cathode in fusion; $D_2 = \delta/H$ is a relative thickness of dynamic bo-undary layer of fusion (δ is a thickness of dynamic boundary layer of fusion); θ_1 is a relative temperature of cathode; $\theta_1 = (T_c - T_{cr})/(T_{cr} - T_c)$; θ_2 is a relative temperature of fusion; $\theta_2 = (T_l - T_{cr})/(T_{cr} - T_c)$; C_1 is a relative warmth of phase transition and dis-charge of ions on a cathode; $C_1 = \rho\cdot L/c_p\cdot(T_{cr} - T_c)$; C_2 is a relative coefficient of heat conductivity of the system «fusion of electrolyte - deposited metal»; Fo is a criterion of Fourier.

After simple transformations equation (5) will take form

$$E^2 + \frac{4(C_2\theta_2 - D_1D_2)\cdot E}{D_1^2\cdot D_2} + \frac{8(C_2\cdot\theta_2 - D_1\cdot D_2)^2\cdot Fo}{D_1^2\cdot D_2\cdot(\theta_1-2C)_1} = 0 \ . \tag{6}$$

Size of thermal stream closeness from fusion of electrolyte to the surface of cathode it is possible to expect by formula:

$$q = \lambda_l \left. \frac{\partial T}{\partial r} \right|_{r=R+\xi} ; \tag{7}$$

$$q = \alpha \cdot \left(T_l - T_{cr} \right) . \tag{8}$$

Comparison of right parts of equations (7) and (8) allows writing down $D_2 = 1/Nu$.

Then after the substitution of the got correlation in equation (6) at $E > 0$ and $Fo > 0$ and $Z = \left(C_2 \cdot \theta_2 \cdot Nu - D_1 \right)/D_1^2$ it is possible to write down:

$$E = 2Z \cdot \left[\left(1 - \frac{2Nu \cdot D_1^2 \cdot Fo}{\theta_1 - 2C_1} \right)^{0,5} - 1 \right] . \tag{9}$$

A calculable experiment with the use of computer has been executed at the next values of relative parameters: D_1 = 2.0-10.0; θ_1 = 1.0; θ_2 = 1.0-1.2; C_1 = 1.0-2.0; C_2 = 0.7-1.0; Nu = 3.0-12.0. There are set: independence of value $E(Fo)$ from the parameter C_2, insignificant influence on him parameter θ_2 and increase of him with the height of parameter Nu. The last is related to convective character of motion of molten electrolyte in a cell from the presence of difference of closeness's of his elementary volumes. Definition influences of parameter of D_1 at $E(Fo)$ it is possible to specify on his complied character.

The decision of equation (9) does not have physical sense at non fulfillment of condition (θ_1 - $2C_1$) < 0, id est the processes of delivery of ions from fusion of electrolyte to the surface of cathode and discharging on her take place at $2C_1 > \theta_1$. So, the size of parameter C_1 determines the conditions of behavior of the directed deposition of crystals of parent metal on the surface of cathode.

Conclusions. The results of decision of thermal task for electrolysis of molten salts allowed fixing desisting influence of parameters C_1 and Nu on the height of thickness of metal layer $E(Fo)$. Thus if on the size of parameter C_1 determine the presence of the directed motion of ions, then on the size of parameter Nu estimate intensity of heat emission a convection on the border of division «fusions - depositing metal», the increase of which is attain at by active interfusion of electrolyte fusion.

LIST OF LITERATURE

1. Барабошкин, А. Н. Электрокристаллизация металлов из расплавленных солей [Текст] / А. Н. Барабошкин. – М. : Наука, 1976. – 371 с. – Библиография в конце разделов.
2. До перенесення маси під час електролізу розплавлених солей, які містять іони тугоплавких металів (Повідомлення 1) [Текст] / І. Є. Лукошніков, В. І. Іванов, Т. М. Нестеренко, В. П. Грицай // Металургія : наукові праці Запорізької державної інженерної академії. – Запоріжжя : РВВ ЗДІА, 2013. – Вип. 1 (29). – С. 42-47.
3. Рубинштейн, Л. И. Задача Стефана [Текст] / Л. И. Рубинштейн. – Рига : Звайгзне, 1957. – 409 с. – Библиография в конце разделов.