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THERMODYNAMICS AND KINETICS OF PROCESS SECONDARY ELECTRO-THERMAL ALLOYING AND AFFINAGE OF METAL

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The analysis of factors, influencing on the charge of slag in the system «metal-slag», concerned as an electrolytic condenser has been carried out. System of equations for thermodynamics equilibrium of the system «metal-slag» modified as it applies to the secondary electro-thermal alloying and affinage of metal (BEAA). As a result of decision of the system of kinetic differential equations the trajectories of motion of the system to the equilibrium in the BEAA process as individual curves for maintenance of separate chemical elements have been got.

Keywords: steel, alloying, refining, kinetics, thermodynamics equilibrium, electroneutrality

Introduction. Process of the secondary electro-thermal alloying and affinage of metal (BEAA), first offered in work [1], got posited-action experimental confirmation [2] and presently is on the stage of development for practical applications. At the same time row of theoretical questions, pertaining thermodynamics and kinetics for BEAA process, require additional researches. In particular, presentation of interphase border for the system a «metal-slag» as an electrolytic condenser did not execute before. Such presentation allows to calculate the row of sizes, necessary for an adequate control and planning of BEAA process for the wide class of law- and hidhalloyed steels with especially subzero content of oxygen and sulphur. In addition, the accurate conception understanding of sequencing for renewal of elements and kinetic trajectory of motion for the system absents «metal-slag» to the equilibrium.

Problem formulation. The task for modify equations of thermodynamics equilibrium as it applies to BEAA is set in work; to decide the system of kinetic differential equations, describing the trajectory of motion to the equilibrium of the system a «metal-slag» at BEAA steel 14ХГС; and also to execute the analysis of factors, influencing on the charge of slag in the system «metal-slag», examined as a condenser.

Basic part of researches. As an object researches chose deoxidated liquid steel 14ХГС at a temperature 1620 °C, covered by the layer of deoxidated slag. Mass of metal was accepted by equal 151.8 t, mass of slag – 1.2 t. If tension to attach to the slag (one electrode) and to the metal (other electrode), then system a «metal-slag» begins to work as an electrolytic condenser the charge of which is equal

$$Q = C \cdot U\,, \tag{1}$$

where C is a capacity of condenser; U is a difference of potentials, id est. tension between plates.

Thus, displacement of abscise axis on the graphic of electroneutrality (fig. 1) will be proportional to the applied tension and capacity of condenser. In the good condenser loss of current does not almost take place, but in the case of BEAA such loss exists and exactly it is responsible for electrolysis renewal, id est. on Faraday.

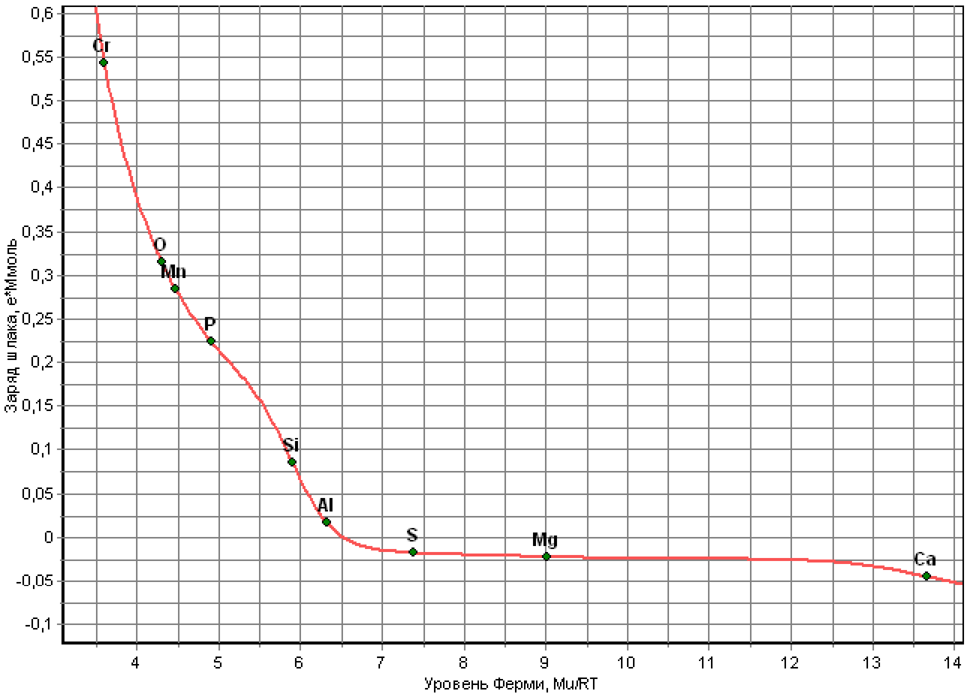


Figure 1 is fragment of the curse of electroneutrality at the applied charge to the slag 0,05 unit Faraday for 14ХГС steel BEAA

The capacity of condenser, in turn, is determined by expression (in the system SI):

$$C = \varepsilon \cdot \varepsilon_0 \cdot S / d \ , \tag{2}$$

where ε is an inductivity of environment between plates; ε_0 - electric constant, ε_0 = $8.854 \cdot 10^{-12}$ F/m; S is an area of contact for metal and slag; d is a thickness of interphase layer between a metal and slag.

From all transferred sizes, except for electric constant, in a formula (2) it is reliably possible to measure parameter S. Id est., except for voltage, displacement of abscise axis of the curse electroneutrality also will be proportional to the area for contact of metal and slag. It is experimentally possible to define only a relation ε/d at the temperature of the experienced melting, however it will be enough for the calculation of effective charge on the interphase border of metal and slag. For the estimation of electrolysis constituent of BEAA it is necessary also to measure the voltage-current characteristic of the system «metal-slag», which can be substantial nonlinear at small currents and voltages [2].

The system of equations, describing a thermodynamics equilibrium in the system «metal-slag» in the conditions of BEAA, differs from traditional, described in work [3], that equation of electroneutrality in right part contains the charge of slag Q, shown in units Faraday constant (F):

$$\sum_{i=1}^{k} n_{(i)} \cdot \nu_i = Q \, , \tag{3}$$

where $n_{(i)}$, ν_i - accordingly number of moles and valence i element in a slag; k is a number of chemical elements, making the system «metal-slag».

Transformation of the required sizes of number moles of elements for the metal and slag to the phase variables Y and μ allows to reduce the initial system $k+1$ nonlinear equations to two equations in relation to unknown Y and μ:

$$\begin{cases} F_1 = \sum\limits_{i=1}^{k} \dfrac{n_i \nu_i}{1+\exp\left(-A_i + Y + \mu \cdot \nu_i\right)} - Q = 0; \\ F_2 = \sum\limits_{i=1}^{k} \dfrac{n_i}{1+\exp\left(-A_i + Y + \mu \cdot \nu_i\right)} - \dfrac{N}{1+\exp(Y)} = 0, \end{cases} \qquad (4)$$

where $Y = \ln\left(N_m / N_s\right)$ is natural logarithm of inverse value of mole multipleness of slag; N is a sum of moles of all elements in the system; n_i is a number of moles i element in the system; μ is a oxidized-reduce for the system (Fermi level); A_i are logarithms of the consolidated (or effective) constants for equilibrium «metal-slag» on i element.

For description of kinetics of BEAA process the off-line dynamic system of $2k$ differential equations [4] in relation to the numbers of moles in a metal and slag have been used, from which independent it is served as either k equations in relation to the numbers of moles in a metal or k equations in relation to the numbers of moles in a slag:

$$\begin{cases} \dfrac{dn_{(i)}}{d\tau} = \theta_{[i)} \cdot \Delta\mu_{[i)} \\ \dfrac{dn_{[i]}}{d\tau} = -\theta_{[i)} \cdot \Delta\mu_{[i)} \end{cases}, \quad i = 1, 2, \ldots.k \ , \qquad (5)$$

where $n_{(i]}$ are numbers of moles i element in a slag and metallic phases, accordingly; $\Delta\mu_{[i)}$ are motive forces (gradients of chemical potentials i element) on a interphase border «metal-slag»; $\theta_{[i)}$ are kinetic coefficients, proportional to the temperature and area of interphase surface «metal-slag»; in the first approaching these coefficients can be considered by identical for all elements on this interphase border; τ is a temporal co-ordinate.

The system of equations (5) is hard, because sizes of the required functions $n_{(i)}(\tau)$ and $n_{[i]}(\tau)$ can differ on a few orders. For its numeral decision there is used Rozenbrok algorithm [5] in composition separate program «Excalibur» [6]. The results of decision for this system are brought reduced on a fig. 2 and fig. 3.

Kinetics of renewal for elements with positive valence and transition of them in a metal is characterized by monotony except for calcium (fig. 2). Elements are reduced practically simultaneously at motion to the equilibrium; here aluminum is reduced by the last. The contents of calcium is described by the difficult curve with inflections and local minimum. In addition, in complete accordance with the experienced data [2], there is desulphurizing of metal and monotonous decline in it content of sulphur. The content of oxygen in a metal goes down to the balanced value 0.007 % without noticeable features.

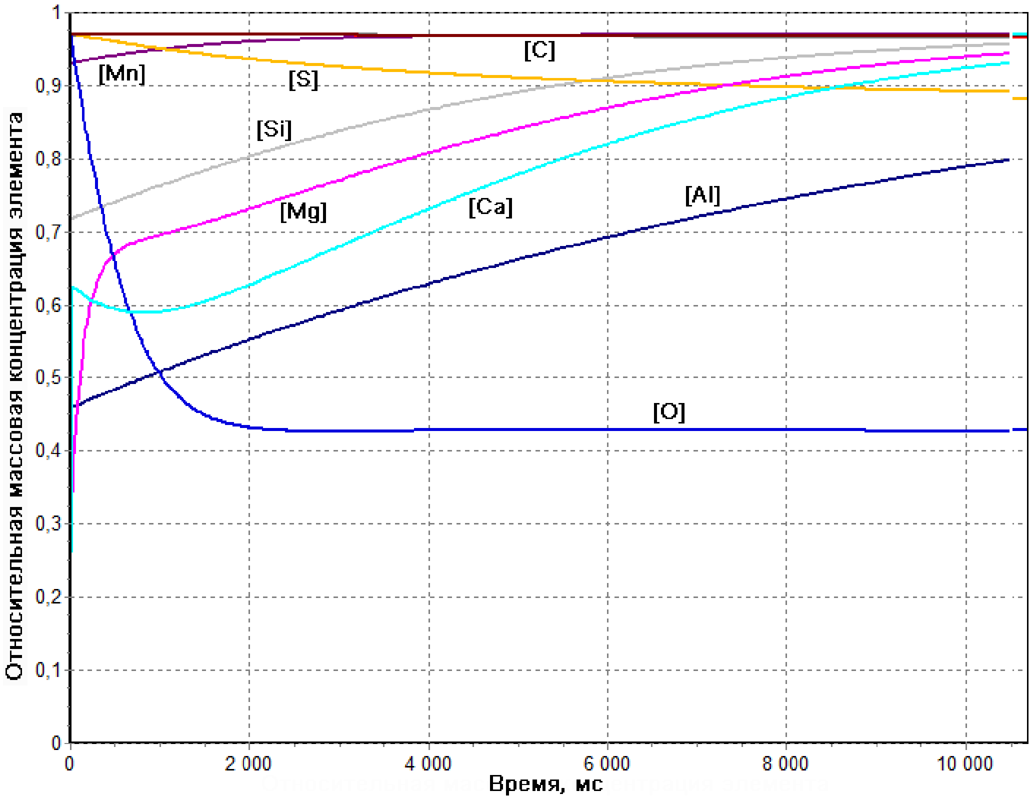
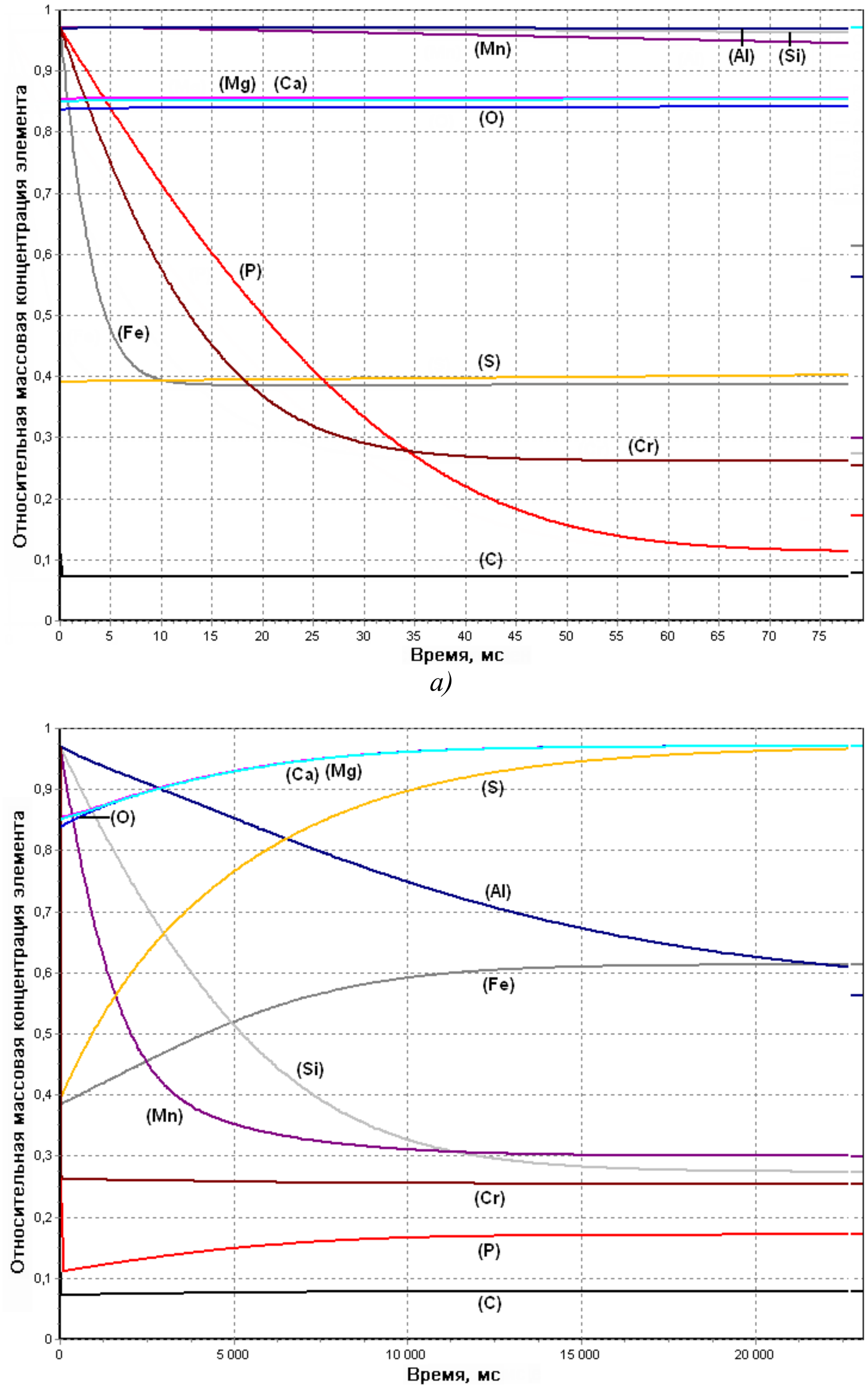


Figure 2 - Trajectories of motion to the equilibrium of concentrations for elements in a metal in the BEAA process of steel 14ХГС

In a slag on the whole there is an opposite pattern, illustrated by a fig. 3. All elements with positive valence have a clear tendency to the decline of their content. There is an increase of content of oxygen and sulphur at the decline of content of iron and phosphorus. A slag in a state of equilibrium becomes by electric charged, that is supported by internals source of direct-current.

In the experimental melting due to an electrolysis constituent mass of the recovered elements (silicon and aluminum) exceeds such, calculated only on equilibrium in the system «metal-slag». It promotes efficiency of BEAA process, although requires the additional expenses of electric power.



a)

б)

Figure 3 - Trajectories of motion to the equilibrium for concentrations of elements in a slag in BEAA process of steel 14ХГС at self-control 80 ms (a) and 23 s (б)

In a table 1 initial and eventual concentration over of elements are reduced in a metal (14ХГС steel) and slag, corresponding to the charts, introduced on a fig. 2 and fig. 3. As be obvious from the reduced data over, in a metal most noticeable is an increase of silicon content on 0.19 % with the simultaneous decline of its content in a slag on 12.66 %. There is also a more than double increase of aluminum content and magnesium content in a metal accordingly to the level 0.009 % and $2{\cdot}10^{-4}$ %. Decline of content of oxygen in a metal to 0.007 % guarantees its cleaning from an oxide nonmetallic. Sulphur content in a metal goes down insignificantly - on 0.003 %, however in a slag it is observed its more than double increase from 0.15 to 0.39 %.

Table 1 is Initial and final concentrations of elements in metal and slag 14ХГС steel in BEAA process

M / S	Content of chemical elements is in a metal and slag, %										
	Fe	*C*	*Si*	*Mn*	*Al*	*S*	*P*	*Mg*	*Cr*	*O*	*Ca*
M_{ini}	97.7	0.14	0.56	0,92	0.004	0.029	0.027	$1 \cdot 10^{-4}$	0.64	0.016	trace
M_{fin}	97.4	0.14	0.75	0.96	0.009	0.026	0.027	$2 \cdot 10^{-4}$	0.64	0.007	trace
M_{ini}	0.93	trace	18.0	4.07	0.69	0.15	0.004	2.24	0.03	38.3	35.6
M_{fin}	0.61	trace	5.34	1.32	0.42	0.39	$7 \cdot 10^{-4}$	2.67	0.008	46.6	42.7

By the important feature of BEAA process for steel 14ХГС at the positive slag charge there is a substantial decline on 31 % its mass that must be taken into account at planning of BEAA industrial options.

Conclusions. The systems of equations, describing equilibrium thermodynamics of BEAA process and kinetic trajectories of motion for the system «metal-slag» to the equilibrium, have been got. The got numeral decisions give the detailed pattern of change for concentrations of chemical elements in a metal and slag that allows to construct the effective technological BEAA process. The analysis of factors, influencing on the charge of slag in the system «metal-slag», examined as an electrolytic condenser has been executed, that allows to calculate sizes, necessary for BEAA steels with especially subzero content of oxygen and sulphur.

REFERENCES

1. **Харченко, А. В.** Вторичное легирование и рафинирование стали в установках печь-ковш / А. В. Харченко, Н. В. Личконенко, Н. В. Горяйнова // Металургія : наукові праці Запорізької державної інженерної академії, 2012. – Вип. 1(26). – С. 17-21.
2. **Харченко, А. В.** Экспериментальные исследования технологии вторичного электро-термического легирования и рафинирования / А. В. Харченко, Д. А. Лаптев, Д. А. Лупол и др. // Металургія : наукові праці Запорізької державної інженерної академії, 2014. – Вип. 1(31). – С. 30-35.
3. **Харченко, А. В.** Дифференциальные коэффициенты усвоения в компьютерных системах управления плавкой и внепечной обработкой стали / А. В. Харченко, А. Г. Пономаренко, С. В. Довгонюк // Металлургическая и горнорудная промышленность. – 2002. – № 10 (   ). – С. 131-137.
4. **Харченко, А. В.** О кинетике межфазного массопереноса в металлургических агрегатах / А. В. Харченко, А. Г. Пономаренко // Металл и литье Украины. – 2002. – № 12. – С. 41-42.
5. **Rosenbrock H. H.** Some general implicit processes for the numerical solution of differential equations / H. H. Rosenbrock // Comput. J. – 1963. – Vol. 5, No 4. – P. 329-330.
6. **Харченко, А. В.** Программа «EXCALIBUR» - возможности и перспективы использования в металлургическом производстве / А. В. Харченко, Р. В. Синяков // Сборник научных трудов ДонНТУ. Серия: Металлургия, 2005. – Вып. 102. – С. 82-91.