Electro-thermo-chemical simulation of isomorphic crystallization of thallium in the aluminum-containing anti-corrosion coatings

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Abstract

In the conditions of burning for plasma-generating fuels on the basis of aluminium with calcium additives a formation of anti-corrosion coatings should be classified as an event, which takes place according to both main mechanisms. First, the processes are existing at the lower excess of oxygen and the other are at $\lambda>1$. In the last case we expect the production of oxides conglomerating in the complex salts. This inclination of the aluminate building corresponds to the common tendency of creation for mix crystals during the thermal treatment of slag systems. But the most pressing argument for the process independence discussion from the heat effect of fuel transformation is the isothermal crystallization of main minerals, the content of which stays unchanged with the condensation of solid bodies. In this article we model the isomorphic incoming of thallium composites in the such aluminum rich compounds as pyroxenes and anortith with aim to study the influence of the formation for general agglomerates in the conditions of higher thallium concentrations. It's evident that we should avoid $\lambda<1$ because of the appearance of unpleasant spinels, which could be damaged with the electro-thermo-chemical corrosion.

We studied an important property of this effect in respect of the estimation for the concentrations of substances in the gas and condensed phase as a result of the combustion for metallic mixes at the dissipation influence of the high energy electric impulses.

1. Introduction in the ionized gas spraying skin-films

A stability of thermal treatment products against the solutions with pH from 4 till 12 depends on the binding of mobile substances with silicate films because of the building for the oxide composites. In this context the sintering is enough for the disactivation of metal containing salts. The lack of this method is the localization of mix crystals so that the structure of coatings doesn't become equal.

The homogenization in a molten state is prevailed at the temperatures more than 2000 °C with aim of initiation for diffusion processes of the concentration gradient elimination. On the other hand [1] there were the processes for conglomeration of oxide products with metallic educts in the case of burning for energy fuels with lower coefficients of an air excess. Such spinels are regarded as unpleasant because of their reaction activity with the corrosion environments of combustion outputs according to the difference of the chemical potential between the solid and gas phase. In this aspect it is strongly recommended to enrich the resistance layer with calcium oxides to prevent the appearence of complex metal-containing species, which are characterized with the lower heat resistance.

Incoming of thallium in pyroxenes, anorthite was confirmed by [5] as a consequence of spontaneous formation for minerals. In the conditions of heat incineration for waste takes place the building of compounds, which are exchanged with elements existing in the same group of the periodic table, so that its transfer in the main composites is caused with its isomorphic crystallization thallium($^{3+}$) → aluminium($^{3+}$) in the solid solutions during a condensation (figure 1).

Thus, a feature for the combustion of plasma-producing propellants on a basis of aluminium with potassium additives is the agglomeration of complex oxide components. And at the temperature 3000 K and the pressure 3 MPa (figure 2) the

formation of anti-corrosion coatings is influenced with thallium substances because of its lower activity to react with aggressive species. Grounding on the arguments above we construct the magnesium($^{2+}$) → calcium($^{2+}$) exchange in the stabilizing compounds with aim to increase heat resistance. Now, we summarize the contents of layers consisting from aluminates and thallates with magnesium oxide and silicates.

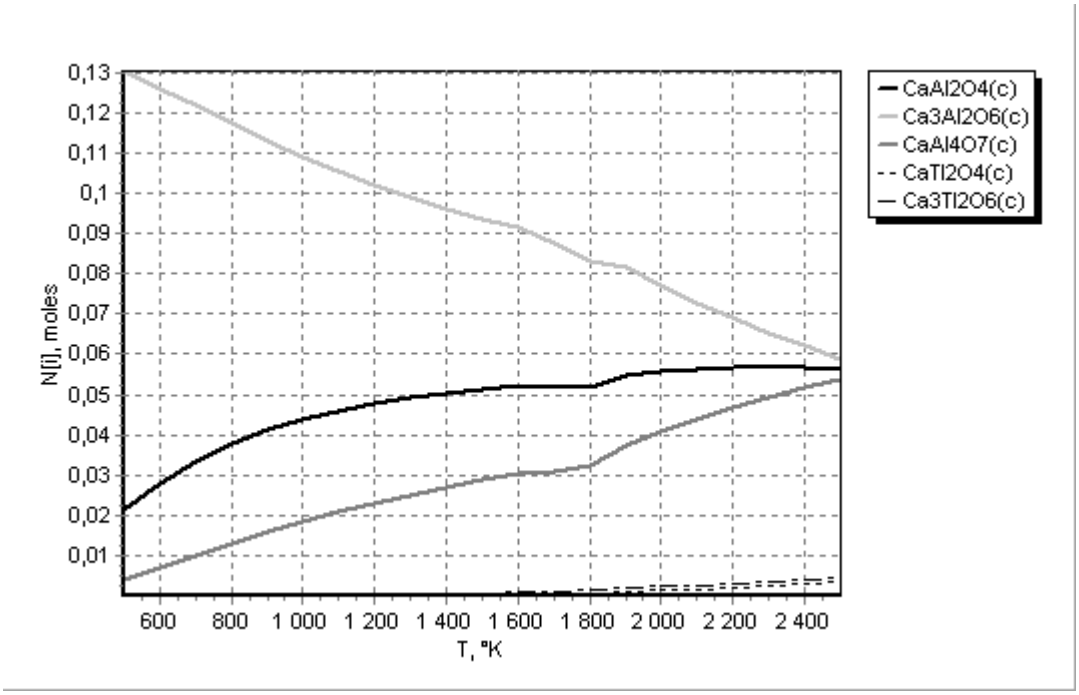


Figure 1. Equilibrium activities of aluminates and thallates at the high temperature conditions during the formation of main mineral systems for the stabilization of anti-corrosion coatings

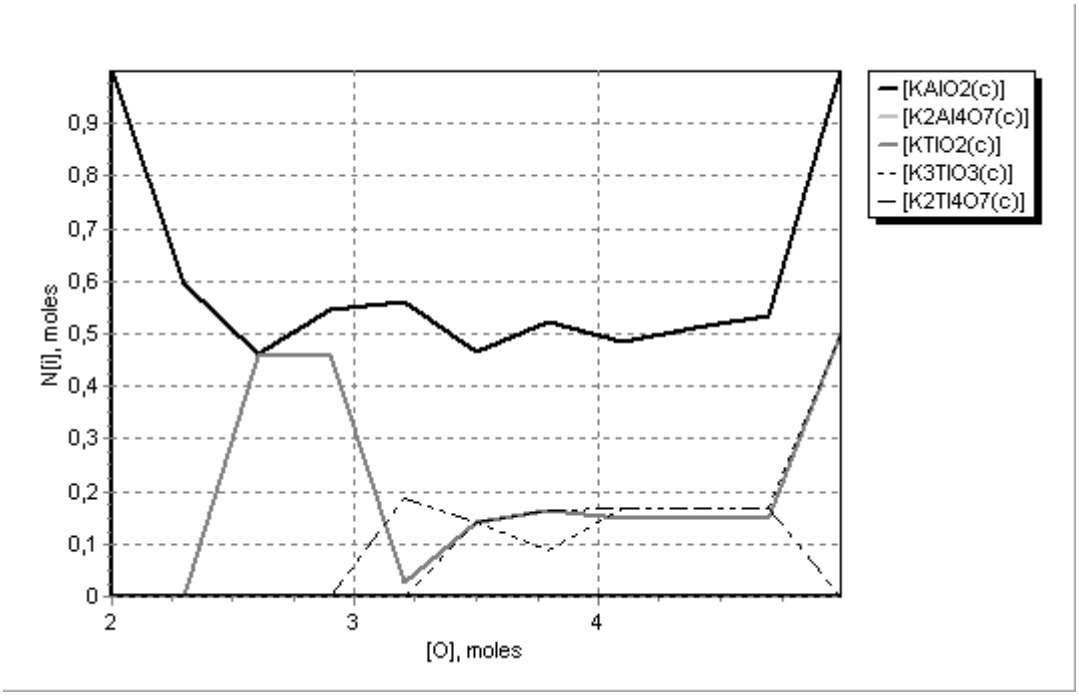


Figure 2. The burning products of aluminium-containing fuels in the processes of the building of thallium skin-layers

The technology of formation for anti-corrosion coatings is spraying. An ion gas state is reached with burning of the aluminium and magnesium- containing fuels and the electric arc between contacts after discharging of a capacitor battery, which creates the initial conducting area. Combustion species are the positive and negative bearers, the existence conditions of which are supported with the additional injecting of dissipation energy impulses of the voltage source. The flow of product compounds enriching with thallium silicates is directed to the sample with an influence of static pressure of reaction components and dynamic power of an electric field.

2. Kinetic mechanisms of phase contribution in slag

The experiments of transformation for fuel from waste were carried on the rosts of the incineration plant TAMARA [2] in the Karlsruhe Institute of Technology. They proved the good combustion quality and the formation of slag, which consisted from main minerals: pyroxenes, melilith, wollastonite [3]. At a higher concentrations of

aluminium oxide the phase content is characterized with anorthite, mullite, gehlenite on the figure 3.

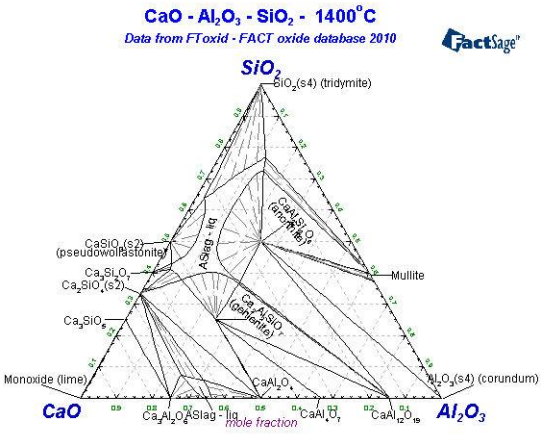


Figure 3: The phase diagram of slag systems according to the dates of scientific group thermodynamic Europe

A stability of thermal treatment products against ground water depends on the binding of the toxic substances with silicate films because of the building of the oxide composites. In this context the sintering is enough for a minimization of the hazardous influence of metal containing salts, but the high energy expenses for melting are not sufficient in terms of the better exploitation characteristics. The lack of this method is the localization of combustion mixes so that the structure of slag doesn't become equal. In compare with the THERMOSELECT technology the homogenization of the molten bottom ash was prevailed at 2000 °C with aim of its purification in a periphery, where the active complex additives of metals diffuzed according to the difference of the chemical potential between the solid phase and oxygen atmosphere. Berthod [4] proved a softening of the surface layer of steels as a result of the reaction ability of the carbides at a contact with aggressive environments. On the other hand there were the processes for conglomeration of oxide products with metallic educts in the case of burning for energy fuels with lower coefficients of air excess. The

enriching of *Tl* in pyroxenes, anorthite was confirmed by [5] as a consequence of spontaneous geological activities. Thus, in the conditions of heat incineration for waste takes place the formation of mix crystals, which are exchanged with elements existing in one group of the periodic table so that the transfer of thallium in the main minerals is caused with its isomorphic incoming $Tl^{3+} \rightarrow Al^{3+}$ in the solid solutions during a condensation.

3. Modeling of contact and movement for the electric arc of plasma generator

Electromagnetic energy streams in the area $\Phi = \Phi_1 \cup \Phi_2$ from an external circuit with the capacitor C_0, inductivity L_0, resistance R_0. *U(t) is* a dependence for the voltage on time and *I(t)* is the discharge current. Φ is described with the system of cylinder coordinates:

$$\Phi_1 = \left\{ (r,\varphi,z) : 0 < r < r_0, 0 < \varphi < \frac{\pi}{4}, z = 0 \right\}, \tag{1}$$

$$\Phi_2 = \left\{ (r,\varphi,z) : r_0 < r < r_e, 0 < \varphi < \frac{\pi}{4}, z = l \right\}.$$

Hence, the electro-technical part of our model is

$$L_X \frac{dI}{dt} + R_X I - U + \int_{\Phi_1} (E - [u \times H])\, dl = 0, \tag{2}$$

$$C_0 \frac{dU}{dt} = -I,$$

$$I(0) = 0, U(0) = U_0,$$

where r_0 is a conducting zone, U_0 – the start voltage. An initiation of the contact and a movement u of an ionized medium cause a fall for the voltage, which characterizes the integral in (2), and create the internal circuit so that we increase the total inductivity L_X and resistance R_X.

According to the differential equations we construct the difference schema and solve it with help of the Euler method

$$I_{k+1} = I_k + h \cdot \frac{U_k - I_k R_0}{L_0},$$

$$U_{k+1} = U_k - h \cdot \frac{I_{k+1}}{C_0},$$

$$h = \left| t_{k+1} - t_k \right|.$$

On the figure 4 we can see the calculated values for the total current *[I,A]* during the discharging of four capacitors.

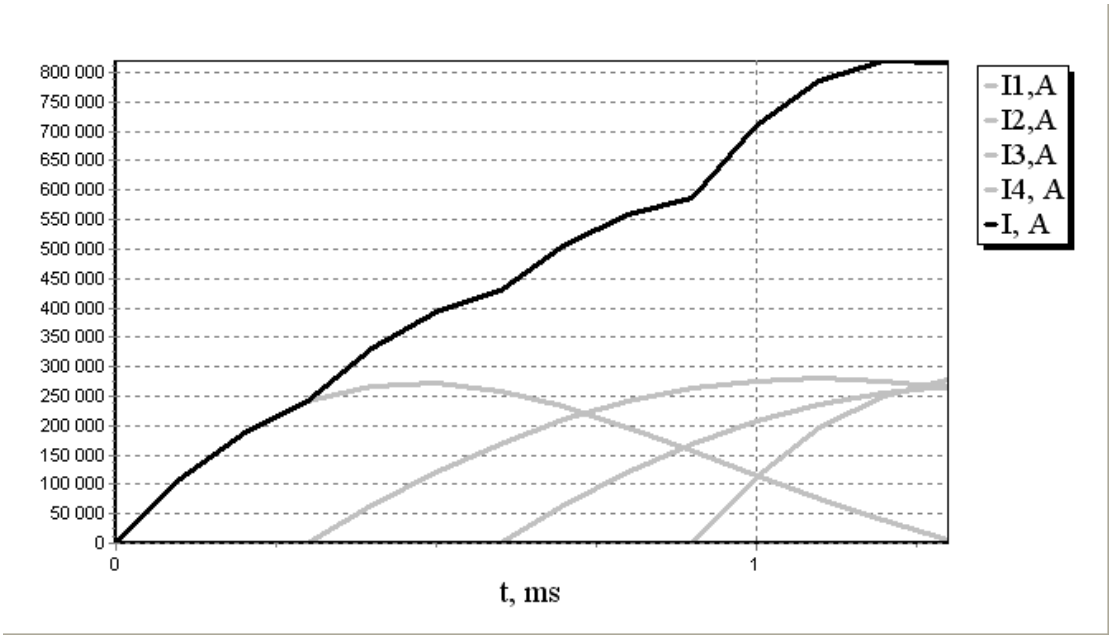


Figure 4. Executing regime with the time delay of 0,3 *мsec* after an initiation of the forerunner

Each method of finite elements means a transaction from the continuous environment to its discrete analogy. But it's necessary to notice that conservation laws mustn't break their power during such simulation. We write the postulates for the energy contribution [6] in Φ

$$\frac{\partial}{\partial t} \int_{\Phi} H^2 dV + \int_{\Phi} \sigma E^2 dV + \int_{\Phi_2} [E \times H] dV = 0. \qquad (3)$$

The first term is the transformation rate of energy density for the electromagnetic field. We regard the second one, which describes the source of dissipation for Joule's heat in plasma generator. Transfer of the electric arc introduces the third.

On the figure 5 the dependences of value I^2R_x and movement of plasma propulsion on time are shown.

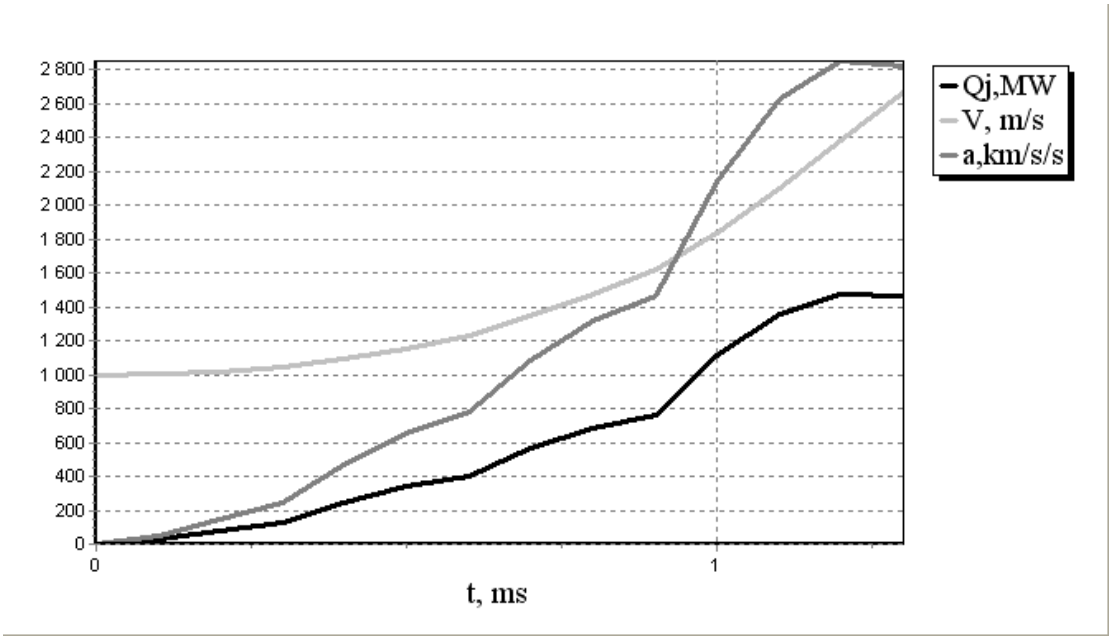


Figure 5. Dissipation energy *Qj*, velocity *V* and acceleration *a* of the current arc

The first shorting initiates ablation of a skin-layer and inflammation of the metallic fuel. The burning processes increase the static pressure in the combustion chamber and generate the conducting area of ionized gas products streaming in the direction to a covered detail. The dynamic part of the moving power is the electro-magnetic field, which acts in the plasma propulsion pushing the general anti-corrosion content at higher velocities. The additional injection of dissipation energy of the current is reached with the next discharging impulses of the capacitor battery. The balance equation should be rewritten in the form

$$\rho\frac{\partial \Phi^{\circ}(T)}{\partial t}+\rho(u,\nabla)\Phi^{\circ}(T)=(j,E)+\operatorname{div}(\kappa\,\operatorname{grad}T)+Q_{comb}, \qquad (4)$$

where ρ – substance density, $\Phi°(T)$ – temperature divided Gibbs energy for the arc continuum, which was produced with electro- erosion processes of contacting materials and the combustion products of the aluminium and magnesium fuel during the vaporization of thallium-containing silicates, κ – coefficient of the heat transfer, Q_{comb} - exothermal effect of the fuel transformation.

In the case of a condensed phase let us write $\Phi°(T)$ in the form

$$\Phi°(T) = A + B \cdot T + C \cdot ln(T) + \frac{D}{T} + \frac{E}{T^2}, \quad (5)$$

presented the integral dependence of the experimental results approximation $f(T, \Phi°(T))$ for differential scanning calorimetric (DSC) measures of the heat capacity

$$A_h \Phi°(T) = f(T, \Phi°(T)), \ \Phi°(298{,}15) = A_{T_0} \quad (6)$$

$A_{298,15}$ is the function value at the temperature 298,15 K and A_h – the differential operator. A solution of (6) exists because (5) is continuous at the interval $I = (T_0, T_0 + H)$ and the condition $\| f(T, \Phi°(T)) - f(T, \Phi'(T)) \| \le L \cdot \| \Phi°(T) - \Phi'(T) \|$ converges [7].

The task for the calculation of concentrations for equilibrium composites, which are building as a result of inflammation and burning of metal containing mixes, is the estimation of activities for species arising and disappearing at the stable conditions. The selection of an *i*-substance from a database is realizable according to the qualitative analyze of elements in chemical formulas. On their quantity *N* depends the number of all possible transformation reactions, which were investigated with the program complex "*MeRS-data*" [8-9], but the quantitative elementary content comes in the term for the computation of stoichiometric coefficients.

The equation of potential difference for the main *k*-process

$$\mu_i^\circ = \frac{-\Delta_{ik} G(T,p,n)}{R \cdot T} = \frac{\Delta_{ik} \Phi(T,p,n)}{R} - \frac{H^\circ(0)}{R \cdot T} \qquad (7)$$

we write so that the closed isobar-isothermal system of crystal bodies reaches the global minimum.

An opportunity to describe the solid-gas interactions appears in the case of combustion of energy fuels, which takes place at the surface between the both phases, and we implement it with help of fugasities $f_{ik} = f_{ik}(p)$. They are the source of a power influencing the substance at the heterogeneous equilibrium. Thus, the chemical potentials of each component are

$$\mu_{ik} = \mu_i^\circ + \sum_{k=1}^{K} In \frac{f_{ik}}{p_k}. \qquad (8)$$

The contribution φ_{ik} of each *k*-reaction for creation of the *i*-substance in the moving engine of an inter-phase transformation inputs the fugacity together with partial pressures $p_{ik} = x_i p$ of a gas existence above a solid solution

$$f_{ik} = \phi_{ik} x_i p. \qquad (9)$$

And the formula for computation of an isothermal activity is

$$c_i = \left(\mu_i^\circ + \sum_{k=1}^{K} ln \frac{\varphi_{ik} x_i p}{p_k} \right) \Big/ \sum_{i=1}^{N} \mu_{ik}. \qquad (10)$$

According to regarded formalisms we introduce the difference schema of the start task for the system of *i* linear differential equations

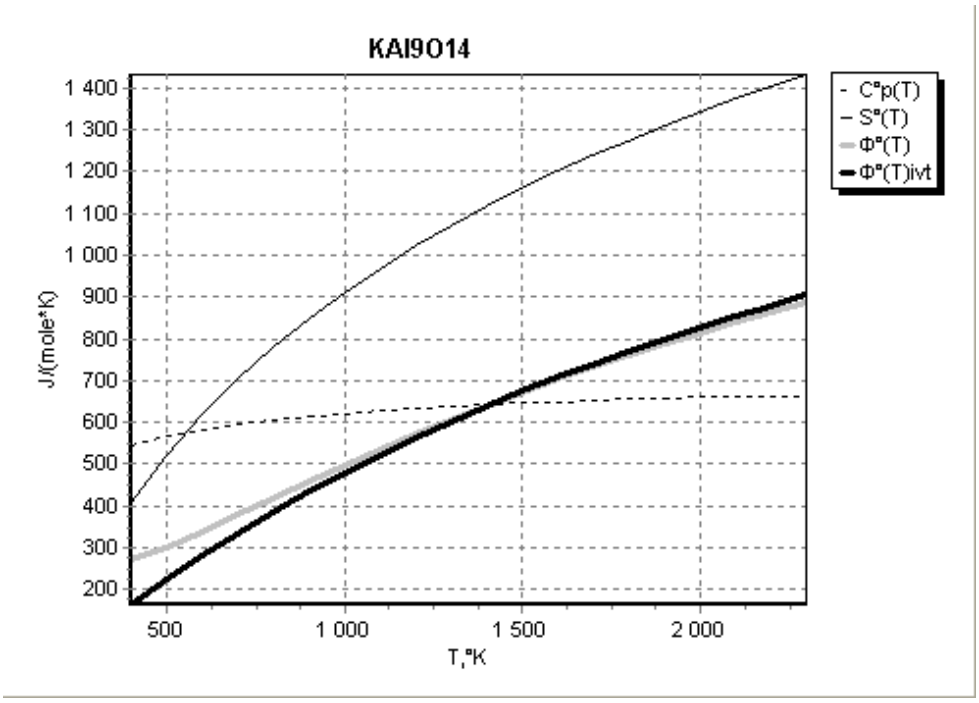
$$A_h n_{h,i}(b_j) = c_i,\ 0 < b_j < \kappa_j,\ n_i(0) = 0,\ n_i(\kappa_j) = \upsilon_i,$$

$$\kappa_j, \upsilon_i \in I = (0,\infty) \qquad (11)$$

at the condition of elementary balances [10-11] $\sum_{i \in I_T} a_{ji} n_i = b_j$, $j = \overline{1,m}$, where m is the number of chemical elements, which build the system, a_{ji} - the quantity of atoms j in the i substance.

The key value $n_i = c_i \sum_{l=1}^{L} \tau_{li}$ is met with Ritz's variation method in a approximation of the discretization error 10^{-7}. (11) is stable at the interval $\lfloor 0, \kappa_j \rfloor$, if we use all calculated parameter of the inconstant step width. Thus, at each iteration on the fixed temperature level the concentration of an essence is equal to the multiplication of its activity and τ_{li}.

The picture 6 shows results of the numerical investigation for thermodynamic properties of KAl_9O_{14} at the temperatures of waste treatment. The functions of heat capacity, enthropy, $\Phi°(T)$ are approximated with coefficients [12] (with index 'ivt') in compare with calorimetric measures [13].



Picture 6. The good combination of the dates for the calculation of thermo-chemical functions

4. Thermo-chemical simulation of formation for thallates

Chlorine fell in waste together with polyvinyl-chlorides of role materials on the textile basis and isolation coatings. The solubility of slag is characterized with chlorides, which are from 0,024 till 0,6 mass.-%, and sulfates 0,036 – 2 [14]. An estimation for the quantity of first ones was limited with the transformation processes because of a presence of sulfur in the reaction zone. The content of metallic hydroxy-anions in a dissociation equilibrium of water mobile compounds for lead were introduced in [15].

In terms of the destruction in the environments of titration with pH from 4 to 12 we regarded a formation of oxy-anionic salts in the conditions of waste incineration, which was investigated by Paoletti [16] "as a Lewis acid-base neutralization reaction". For example of thallium oxides coming in interaction with calcium and potassium ones at the temperatures of 500-3000 °K we modeled the building of thallates, which were analogous to aluminates, according to the following reactions:

$$0{,}5 \cdot K_2O + 0{,}5 \cdot Tl_2O_3 = KTlO_2$$

$$CaO + Tl_2O_3 = Ca(TlO_2)_2$$

$$1{,}5 \cdot K_2O + 0{,}5 \cdot Tl_2O_3 = K_3TlO_3$$

$$3 \cdot CaO + Tl_2O_3 = Ca_3(TlO_3)_2$$

The calculations were made with help of the program complex "MeRS-data" [8-9] using the thermodynamic properties of [12] and [13].

The calcium thallates (presented in the figure 7) have the lower activity in compare with the aluminates. They are detected at the higher temperatures 2000-2500 K, than the potassium ones in the figure 8, the existence area of which likewise extends on the all interval of heat cultivation. The figure 9 shows the phase diagram in the system K-Ca-Tl-O at 1500 K. The calculation confirms the thermodynamic

prevalence of the Ca- compounds at the low values of the oxygen excess, but at the higher O- concentrations the synthesis of the K- complexes takes place.

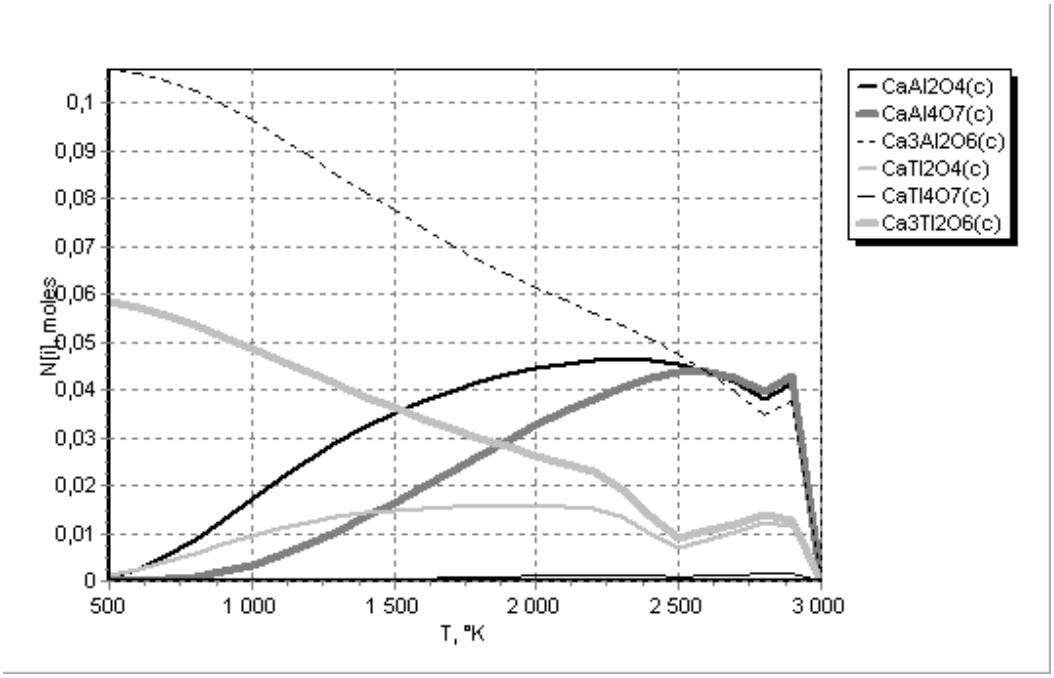


Figure 7: Phase diagram for species created in a chemical reactor of the system Ca-Al-Tl-O at the atmosphere pressure

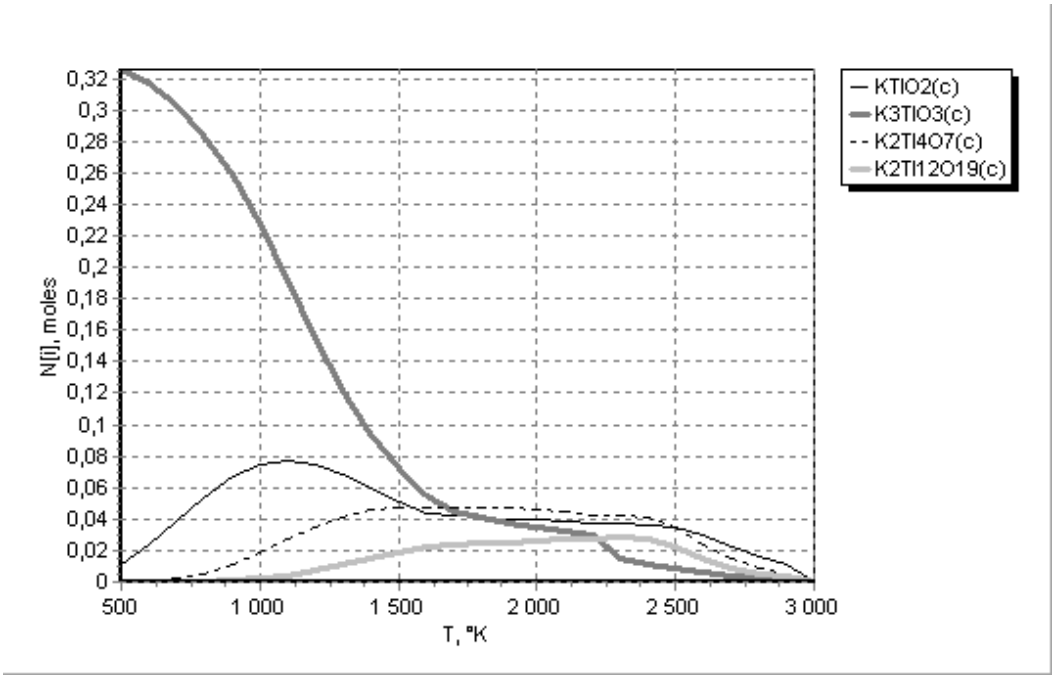


Figure 8: The activities of condensed phases for the potassium thallates in the conditions of a high-temperature transformation of MeRS

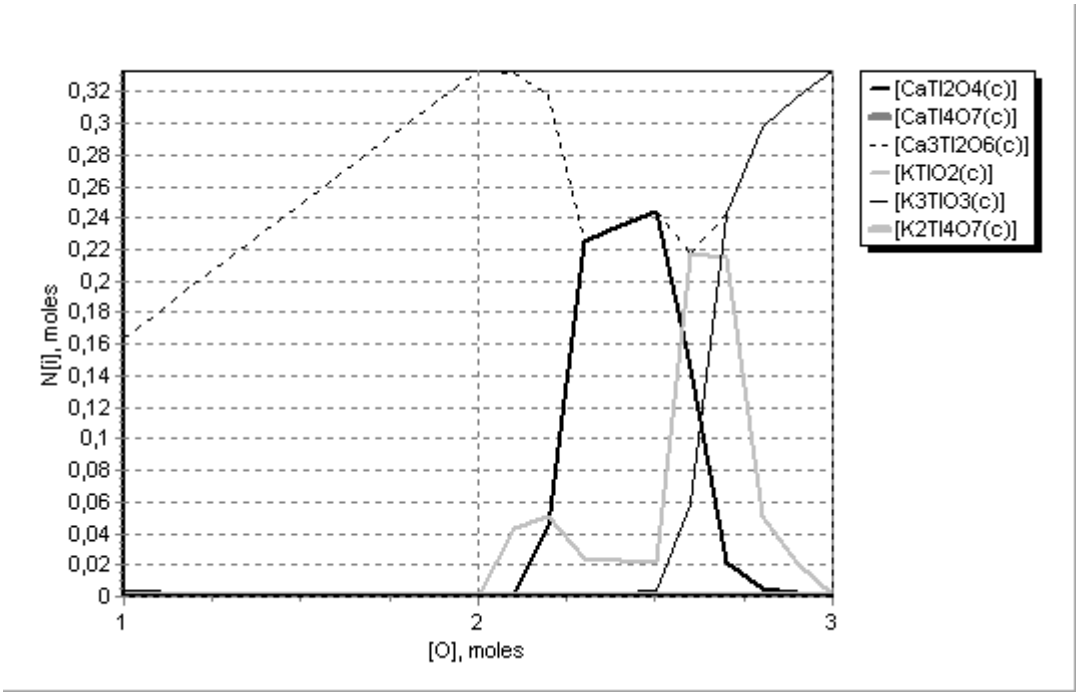


Figure 9: Dependence of the equilibria in slag Ca-K-Tl-O on the oxygen excess from 2 till 3 moles in the fuel at T=1500 K

5. Distribution of package

The program complex “ETCh“ (Electro-Thermo-Chemistry) was produced and designed with help of the language ‘object Pascal’. It creates and visualizes databases, views and edits information, inserts new substances and experimental inventions, presents the calculation results in the form of protocols and graphics.

The main panel of page "ETCh" includes the TabSheets "Electro" (Figure 10) and "Thermo" (Figure 11). In the first one man computes voltages and currents of the in- and external circuits, resistances and inductions of plasma continuums, the energy of Joul’s dissipation and movement of the electric arc; in the second one the activities of components for ETCh- transformation products of metallic fuels.

5.1. Movement of the electric arc

Discretization of electro-technical equations and of the second Newton law begins with clicking on the button “Calculate”. The results are visualized in the string greed. Their redaction is possible in the group “Deleting of dates”. If the dataset is to empty we must check the box “Delete all”. The input parameters are relevant when the date of test is found. The coefficients *Kel*, *Ktr* and *Kl* are shown with aim to approximate the experimental measures and to define the moving engine, friction and air resistance forces. The most important stage is the test prognoses and the strategy implementation for future campaigns during the program recognition of research directions.

5.2. Calculation of equilibrium concentrations

After the definition of an elementary content and the conditions of combustion at the TabSheet “Fuel” of the panel “Experiment” it is necessary to choose the pure species of the equilibrium calculation with help of the button “Filter”. The list of essences appears and we can click them with the right mouse in the column “Choice”. The successful action is completed when the sign ‘*’ fills the cell direct near the chemical formula. The output parameters are situated in the radio groups “Temperature”, “Pressure” ore “Substance”. The last corresponds to an element with variable concentrations during the burning process and is marked with the right mouse button. In this case we see another radio “Excess” and the substances of balancing are visualized according to the start inventory in “Experiment”. Now it’s high time to push "Balance". The numerical values and graphical dependences are saved in the panel "Output".

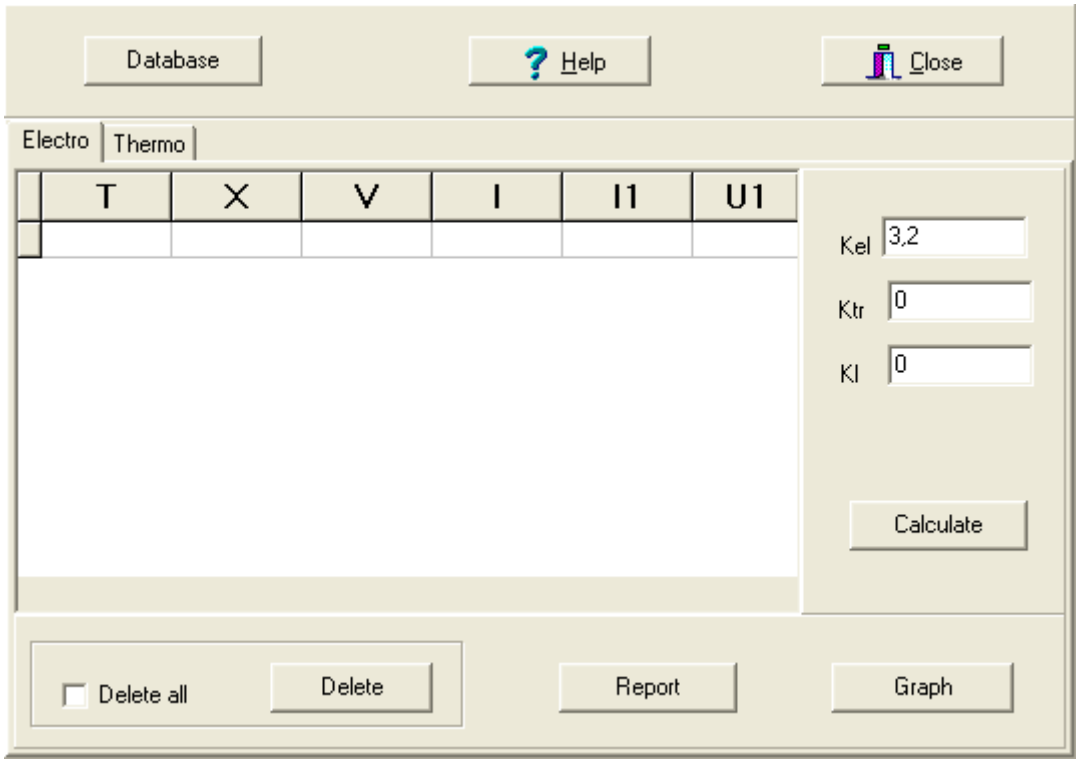


Figure 10: TabSheet "Electro" of program page "ETCh"

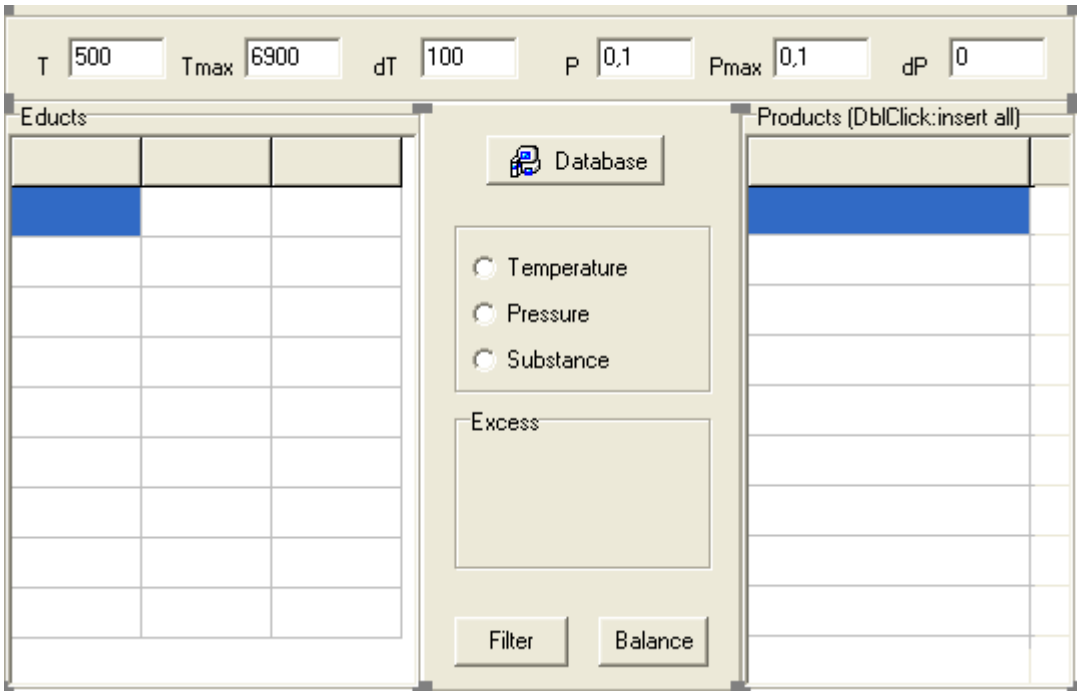


Figure 11: TabSheet "Thermo" of program page "ETCh"

5.3. Linking in the computational facility

The linking with other program pages is succeeded with the buttons "Database", "Report" and "Graph".

Summary

Thus, it’s necessary to say that the combustion processes of metallic fuels cause the agglomeration of oxides in the sustainable complex compounds, which are characterized with own crystal cell parameters, creation enthalpies, electric conductivity and pigment dimensions. We are certainly about the spontaneous inclination of these events because of the common tendency for the formation of main minerals in natural conditions and of the differential scanning calorymetry for the composites.

With aim to produce anti-corrosion coatings the aluminium-composites were studied with x-ray diffraction analyze in compare with thallates, which showed less activity during the building of mix components. This property were used with opportunity to stabilize the reaction activity of the resistance for the skin-layer against aggressive environments. In respect to the heat treatment the calcium complexes were more passive at the influence of chlorine and sulfur- containing species. According to the above transferred arguments it’s evident to conclude the isomorphic exchange of calcium with magnesium as a logical consequence for the formation of stable films.

The technological features for burning of aluminium and magnesium fuels gives us a chance to model the creation of plasma contents in terms of electrical and thermo-chemical transformation of the energy and substance. We regard the solid (liquid) -gas equilibrium with aim to simulate the formation of aluminium-containing crystals in the processes, which take place in the conditions of burning for energy fuels at a surface between the condensed and the gas phase, and to correct the theoretical considerations according to the experimental measures of heat capacities. The fugacities are imputed in the terms for chemical potential and they are the source of a power influencing the substance at the heterogeneous reactions.

The main minerals, which are formed with thermal processes of waste incineration, introduce a good hydrolytic qualities and their soluble content is characterized with oxides of potassium and calcium. But the result of combustion is slag consisting partly from water mobile chlorides and sulfates of toxic metals and their dissociation products (cations and hydroxy-anions) are dangerous for environmental objects. This lack of the bottom ash improves the temperature influence directing the burning reactions to the vaporization of substances, which compounds with halogens and oxygen have the low boiling points, and binding the hazardous composites in the cemented and silicate matrix. The experience shows that the homogenization of slag in the molten state has a priority of the building for the equal structure and of the purification from the additives of metal spinels in a periphery during the contact with the aggressive gas phase of waste pyrolyse and combustion products. In this aspect we should notice the transformation reactions of oxides in chlorides and sulfates too.

In this work we have studied the phase diagrams, which were calculated with the dates of Scientific Group Thermodynamic Europa, compared them with the thermo-chemical functions estimated in the Russian Academy of Sciences and obtained the good combination of numerical results. The model of equilibrium building for thallium composites was constructed with Euler's differential operator of the first order, solved with Ritz's variation method of the inconstant step width and converged with the error of 10^{-7} so that at each iteration on the fixed temperature level the concentration of the substance was equal to the multiplication of its activity and the stoichiometric coefficient.

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