

New Information Technology on the Basis of Interval Analysis: Estimation of Aluminum Corrosion Parameters in Real Electrochemical Process

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Abstract. Practical applications of computer technologies are considered. Estimation of parameters of the aluminum corrosion process is investigated. In practice, estimation of parameters of experimental chemical processes is very actual and important for researches for necessary organization of corresponding technological processes by correct choice of the parameters. But usually, determination of the process parameters is hampered by their complicated internal structure and incompleteness of input information for processing. The paper considers application of the interval analysis procedures to estimation of parameters of an experimental chemical process under conditions of corruption, uncertainty of errors (corruption) probability characteristics, and short sample of measurements. For these reasons, the standard statistical approach can be applied only formally; especially, it becomes impossible to determine accurately the confidential intervals for parameters of the process. Under such conditions, namely methods of the interval analysis can work reliably and give exact set of the admissible values of the parameters to be estimated. In this paper, existing interval analysis procedures were advanced and arranged for a concrete experimental process and its data. As a comparison, approximate estimations of parameters have been calculated by the standard statistical approach. It is shown that the standard approach gives very rough and, often, practically senseless estimations of the process parameters.

Keywords: Interval analysis, metal corrosion, uncertainty conditions, estimation, parameters.

1 Introduction

In the paper, the corrosion process and transformations of its components is considered. Components ($NaNO_3$, Al , O_2 , Al_2O_3) are described by a kinetic system

of ordinary differential equations of the first approximation and analytical functions.

The vector of parameters, *i.e.*, the activity coefficients, comprises: $K_{NT,AL}$ of transformation of nitrate in the direct reaction with aluminum, $K_{NT,T}$ of the own nitrate thermal decomposition, and $K_{AL,Ox}$ of aluminum transformation into the aluminum oxide by free oxygen. Moreover, aluminum oxide partially (with the coefficient K_F) precipitates as a film on the aluminum surface but residuary part of oxide sediments in the molten environment and does not participate further in reactions. The coefficients of the reagents activity (of creation and transformations) and redistribution of the aluminum oxide between the oxide film and the powder sediment have to be found and the latter coefficient K_F is also of interest.

But estimation of these coefficients is strongly hampered by complexity of the process description, fatally short length of measurement samples, and complete absence of any probabilistic characteristics of errors in the measurements. Measuring is implemented only at the beginning $t = 0$ of the process (the initial concentration of nitrates and mass of metallic aluminum before the corrosion test) and at its termination $t = t_f$ (the final concentration of nitrates and final mass of the metallic specimen with the oxide sediment on it).

Estimation of the set of admissible values of the coefficients is performed in the following way. On the basis of the measurements, the uncertainty intervals of the direct or indirect measurements (both at the beginning and the end of the process) of the components are built using the prescribed bounds on the measuring errors. The sought-for set is a totality only of such parameters values, for which the integral curves of the process components pass through the mentioned intervals at the beginning and termination instants of the experiment. This excludes application of the standard statistical methods [3] to estimation of parameters of the corrosion process. But under such conditions, methods of the Interval Analysis [7, 8] work efficiently. On their basis, applied procedures and algorithms of estimation were elaborated [9–11]. These algorithms were successfully used for processing the data of chemical experiments.

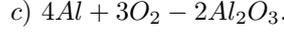
The goal of this work is in further development of a new approach for processing the mentioned experimental data. The paper has the following structure. In Section 1, the process model is described and the estimation problem is formulated. Section 2 is devoted to the main Interval Analysis ideas applied. Section 3 shortly describes structure of the estimation algorithm. Section 4 presents results of numerical simulation of the estimation problem.

2 Model of the process and problem formulation

Earlier, the corrosion process was investigated in [1, 2]. The process is implemented in a molten eutectic mixture of cesium and sodium chlorides that contained up to 30 wt% of the sodium nitrate in the argon atmosphere in the temperature interval 793–903 K. Here, the corrosion is stipulated by both the sodium nitrite and free oxygen appeared as a result of the thermal decomposition of the sodium nitrate. The corrosion process is followed by creation of the aluminum oxide that partially deposits as the oxide film on the surface of the

metallic aluminum electrode and partially leaves the process in the form of the powder sediment.

The original description of chemical reactions (of the first approximation) is



On the basis of this description, the following mathematical model (the first approximation) of the process was built:

$$t \in [0, t_f], \quad (1)$$

$$\dot{NT} = -K_{NT,AL}NTAL - K_{NT,T}NT, \quad (2)$$

$$\dot{AL} = -K_{NT,AL}NTAL - K_{AL,Ox}AL.Ox, \quad (3)$$

$$\dot{Ox} = K_{NT,T}NT - K_{AL,Ox}AL.Ox, \quad (4)$$

$$OxAl(t) = AL(0) - AL(t), \quad (5)$$

$$Flm(t) = K_F OxAl(t), \quad (6)$$

$$M(t) = AL(t) + Flm(t), \quad (7)$$

where, t is time, the independent argument with termination instant t_f ; $NT(t)$ is the nitrate current concentration, wt%; $AL(t)$ is the current mass of the aluminum electrode, grams; $OxAl(t)$ is the current total mass of the oxide, grams; $Ox(t)$ is the current oxygen mass; $Flm(t)$ is the current mass of the film precipitated on the surface of the metal aluminum electrode, this value is a part of the whole oxide mass; $M(t)$ is the auxiliary variable representing the current mass of metal AL and the oxide Al_2O_3 film precipitated on the metal surface; $K_{NT,AL}$, $K_{NT,T}$, and $K_{AL,Ox}$ are the activity coefficients (of corresponding physical dimensions; here and later, their dimensions are omitted for simplicity of description); K_F is a deal coefficient of the film mass. The oxide part $OxAl(t) - Flm(t)$ goes out of the reaction as a sediment and does not participate in the further processes.

It was revealed [1, 2] that corresponding to equations (a)–(c), a large deal of oxides can appear during the process. These oxides precipitate as the film on the metal surface or accumulate as sediment in the volume of the molten salt electrolyte. Such redistribution of the oxides is stipulated by adhesion of oxide layers and velocity of the metal interaction with the melt.

That is why for adequate description of the process in the mathematical model (1)–(7), a special important variable $M(t)$ is introduced that describes the total current mass of the aluminum electrode and film on its surface. Value of this variable can be measured at the termination instant.

Remark 1: Since of description of the process in the differential form (2)–(4), values of the components during the process and at the termination instant can be presented only by numerical integration for each value of the coefficients $K_{NT,AL}$, $K_{NT,T}$, and $K_{AL,Ox}$.

Measured data. Measurements at the initial ($t=0$) instant: $NT_{mes,0}$ with bounded additive error $e_{max,NT}$, $AL_{mes,0}$ with bounded additive error $e_{max,AL}$, $Ox_{mes,0} = 0$, $OxAl_{mes,0} = 0$, $Flm_{mes,0} = 0$, $M_{mes,0} = AL_{mes,0}$.

Measurements at the termination (final $t = t_f$) instant: $NT_{mes,f}$ with bounded additive error $e_{max,NT}$, $M_{mes,f}$ with bounded additive error $e_{max,AL}$.

Values of $AL(t_f)$, $Ox(t_f)$, $OxAl(t_f)$, and $Flm(t_f)$ are not measured. No probabilistic information on measuring errors is known. There are no *a priori* bounds on possible values of the coefficients.

The problem is formulated as follows: *to build the set (i.e., the Information Set or Set-membership) of admissible values of the activity coefficients $K_{NT,AL}$, $K_{NT,T}$, $K_{AL,Ox}$, and to estimate a collection of intervals for the coefficient K_F consistent with the described data.*

Note once more that because of incomplete observability of the process phase coordinates, fatally short length of the measurements sample (only two measurements), absence of probabilistic characteristics of errors, and measurements uncertainty, it is impossible to use standard statistical methods (see, [3]).

3 Interval approach to solving the problem

Since probabilistic information on errors is unknown, only uncertainty intervals of measurements can be constructed:

$$\mathbf{H}_{NT,0} = [NT_{mes,0} - e_{max,NT}, NT_{mes,0} + e_{max,NT}], \quad (8)$$

$$\mathbf{H}_{AL,0} = [AL_{mes,0} - e_{max,AL}, AL_{mes,0} + e_{max,AL}], \quad (9)$$

$$\mathbf{H}_{NT,f} = [NT_{mes,f} - e_{max,NT}, NT_{mes,f} + e_{max,NT}], \quad (10)$$

$$\mathbf{H}_{M,f} = [M_{mes,f}e_{max,AL}, M_{mes,f} + e_{max,AL}]. \quad (11)$$

Note: here and in the sequel, notations of the interval variables recommended by the Standard [12] are used.

After termination of the process, an interval of the coefficient K_F is calculated as

$$K_F = (\mathbf{H}_{M,f} - AL_f)/OxAL_f, \quad (12)$$

where AL_f and $OxAL_f$ are values of the variables at the terminal instant t_f computed by integration of the describing differential equations system (1)-(7).

Ideas and methods of the Interval Analysis Theory and Applications arose from the fundamental, pioneering work by L.V. Kantorovich [4]. See, also, pioneering works in USA [5, 6]. Nowadays, very effective developments of the theory and computational methods were elaborated by many researchers both in Russia and abroad [7, 8]. Special interval algorithms have been created for estimating parameters of experimental chemical processes [9–11].

In application to the problem under consideration, essence of Interval Analysis Methods consists in estimation (or identification) of a process parameters under bounded measuring errors in the input information and under total absence of probabilistic characteristics of the errors.

The estimation results are represented in the form of so-called the Information Set or Set-membership that approximate (see, for instance, [7, 8, 10, 11]) the estimated desirable totality of admissible values of the parameters from the outer side or from the inner side.

In practice and, especially, in the case of small dimension of the parameters vector to be estimated, the inner grid approach is more preferable since its computational simplicity and smaller computations in comparison with both the outer peeling and inner-box approach.

In our problem, it is just the case: vector of the main parameters is only three-dimensional: $K_{NT,AL}$, $K_{NT,T}$, and $K_{AL,Ox}$. So, the inner grid approach was used.

Definition. A point $(K_{NT,AL}, K_{NT,T}, K_{AL,Ox})$ of the parameters space $K_{NT,AL} \times K_{NT,T} \times K_{AL,Ox}$ is admissible and an initial point (NT_0, AL_0) from the box $\mathbf{H}_{NT,0} \times \mathbf{H}_{AL,0}$ is admissible if the corresponding computed point (NT_f, AL_f) at the termination instant belongs to the box $\mathbf{H}_{NT,f} \times \mathbf{H}_{AL,f}$.

Definition allows one to sift out directly such points $(K_{NT,AL}, K_{NT,T}, K_{AL,Ox})$ and (NT_0, AL_0) that are not consistent with the given experimental data.

4 The main algorithms

Structure of the main algorithms and steps of its performing are illustrated in Fig. 1. The algorithms are implemented in the following steps:

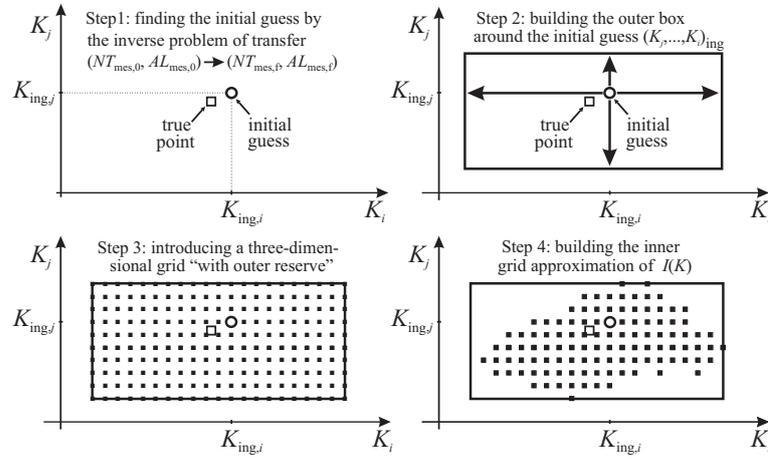


Fig. 1. Structure of the main algorithms and steps of its performing; values of the initial guess coefficients are marked by the ing -index; parameters shown on the axes are illustrative

Step 1: finding the initial guess $(K_{NT,AL}, K_{NT,T}, K_{AL,Ox})_{ing}$, *i.e.*, the initial admissible point of coefficients inside the information set;

Step 2: constructing the auxiliary outer guaranteeing box of coefficients;

Step 3: introducing the three-dimensional grid on the auxiliary box of coefficients;

Step 4: building the inner grid approximation of the information set $I(K_{NT,AL}, K_{NT,T}, K_{AL,Ox})$ of coefficients.

5 Computation results

Numerical results are presented in Figs. 2 and 3. Computation was performed with the model prescribed true coefficients of values $K_{NT,AL}^* = 0.001$, $K_{NT,T}^* = 0.001$, $K_{AL,Ox}^* = 0.001$, and $K_F^* = 0.1$ and with the initial values $NT_{mes,0}$, $AL_{mes,0}$. The true model values $NT_0^* = 10$ and $AL_0^* = 0.3$ are pointed with arrows.

The general picture (Fig. 2) shows decreasing the nitrate concentration $NT(t)$ (dash-two-points curve). Also, the initial $NT_{mes,0}, AL_{mes,0}$ corrupted measurements and ones $NT_{mes,f}, M_{mes,f}$ at the termination instant are marked by crosses.

Processes on the components $AL(t), M(t), ALOx(t), Ox(t)$, and $Flm(t)$ are given in the lower part in Fig. 3 and in zoomed images in Fig. 5. It is seen both active decreasing the aluminum mass (since corrosion) and increasing the oxide and film masses.

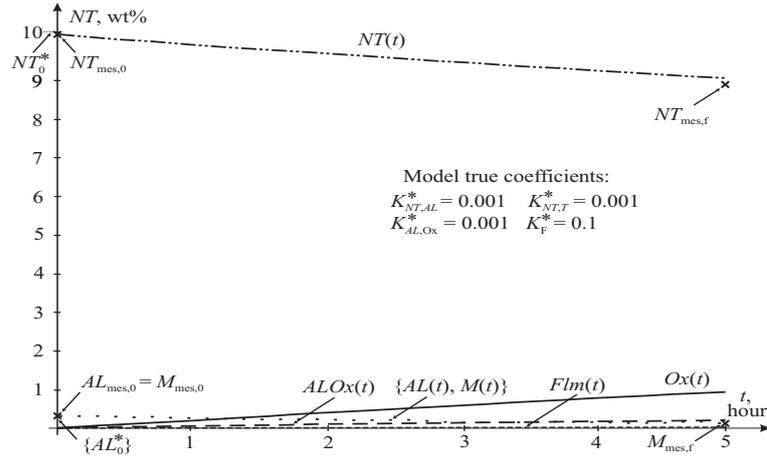


Fig. 2. Results of computations; general picture of the process

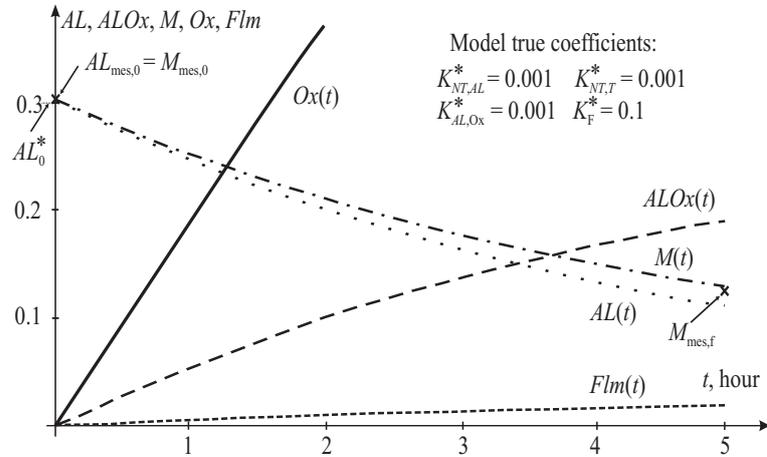


Fig. 3. Results of computations; picture in small components (zoomed)

Picture of the measured data is given in Fig. 4 and 5. Here, the true model values are marked, the measurements and calculated values $NT_{mes,f}, M_{mes,f}$ (at the termination instant) are pointed by arrows; uncertainty boxes (sets)

$\mathbf{H}_{NT,0} \times \mathbf{H}_{AL,0}$ and $\mathbf{H}_{NT,f} \times \mathbf{H}_{M,f}$ of measurements are drawn by rectangles. Integration of system (1)-(7) with true coefficients gives the values NT_f, M_f .

Note that this point lies inside the uncertainty box $\mathbf{H}_{NT,f} \times \mathbf{H}_{M,f}$ that proves admissibility of taken values of the coefficients and the initial position $NT_{mes,0}, AL_{mes,0}$. Consider steps of the suggested algorithm.

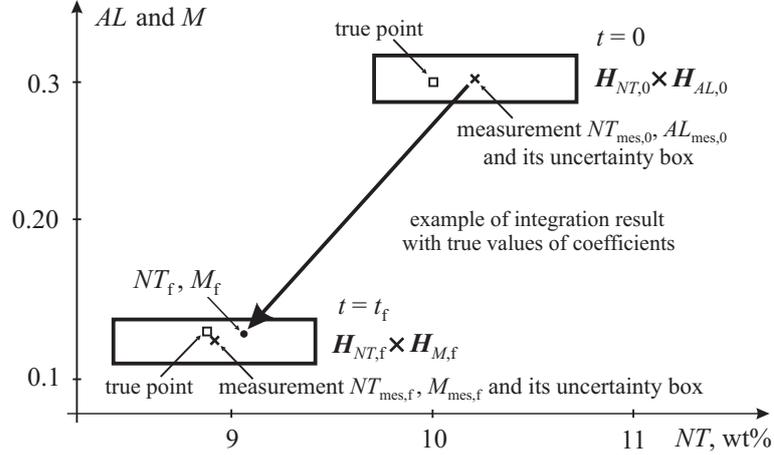


Fig. 4. Picture of the measured data

Step 1. The initial guess of admissible values of coefficients

$$(K_{NT,AL} = 0.001046, K_{NT,T} = 0.001163, K_{AL,Ox} = 0.001)_{ing} \quad (13)$$

are found as a solution of an usual inverse problem of dynamics with the initial (left) value of the process $NT_{mes,0}, M_{mes,0}$ and the termination (right) value $NT_{mes,f}, M_{mes,f}$.

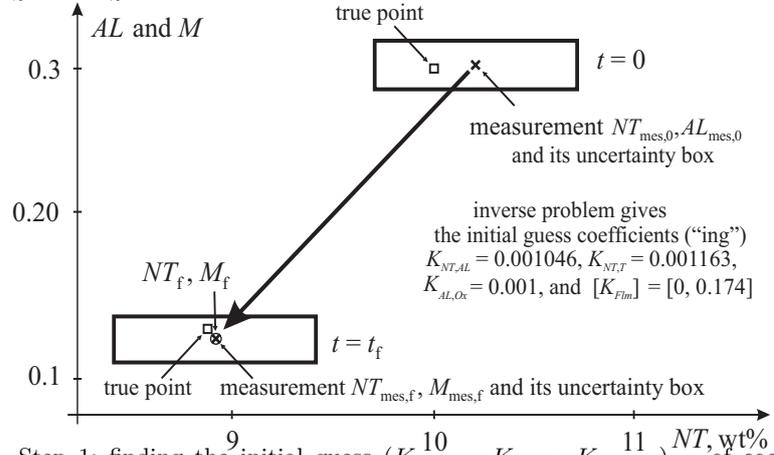


Fig. 5. Step 1; finding the initial guess $(K_{NT,AL}, K_{NT,T}, K_{AL,Ox})_{ing}$ of coefficients $K_{NT,AL}, K_{NT,T}, K_{AL,Ox}$

Step 2. Constructing an auxiliary outer box around the initial guess $(K_{NT,AL}, K_{NT,T}, K_{AL,Ox})_{ing}$. The procedure consists of:

- coordinate-wise variation of each coefficient under fixed values of two other ones with verification of admissibility each changed value of the coefficient under variation;
- variations are implemented for two directions to find the minimal and maximal values on each coefficient, *i.e.*, to find approximate intervals of each coefficient.

Results of this procedure are shown in Fig. 6. The maximal upper points are marked by white squares; the minimal ones are represented by black squares. The following marginal boundary values were found:

$$\begin{aligned} K_{NT,AL} &= [0.000896, 0.00125], & K_{NT,T} &= [0.000618, 0.001738], \\ K_{AL,Ox} &= [0, 0.004225]. \end{aligned} \quad (14)$$

Remark 2: Because of independent coordinate-wise variations, the box found can have inadmissible points, for example, the box apices or, even, parts of the edges.

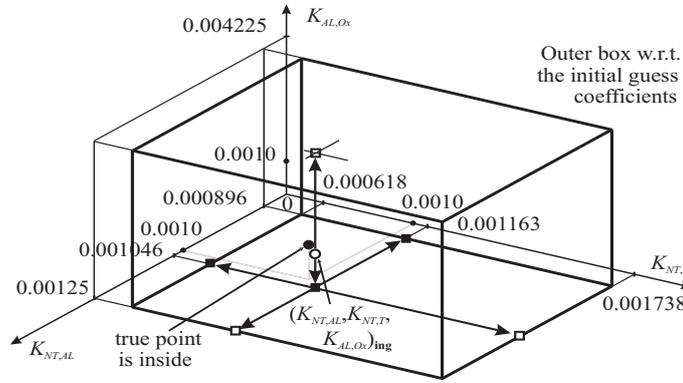


Fig. 6. Step 2; the auxiliary outer box of parameters $K_{NT,AL}$, $K_{NT,T}$, $K_{AL,Ox}$ around the initial guess point $(K_{NT,AL}, K_{NT,T}, K_{AL,Ox})_{ing}$

Step 3. Having boundaries (14), introduce grid in each of these intervals with some reasonable values of the grid step on each parameter. In model computations, the number of nodes in each grid was sufficiently given as 51.

Step 4. The concluding operation is in simple direct verification of each node of the introduced three-dimensional grid. Only admissible nodes are included further into the inner part of the information set.

Results of constructing a cross-section of the inner approximation of the information set $I(K_{NT,AL}, K_{NT,T}, K_{AL,Ox})$ for the fixed value of the icoefficient $K_{NT,T} = 0.001163$ is shown in Fig. 7.

The similar pictures are obtained for presentations of the initial grid and final inner approximation of the cross-sections of the information set $I(K_{NT,AL}, K_{NT,T}, K_{AL,Ox})$ for fixed values of the coefficient $K_{AL,Ox}$, and the initial grid and final inner approximation of the cross-section of the information set $I(K_{NT,AL}, K_{NT,T}, K_{AL,Ox})$ for fixed values of the coefficient $K_{NT,AL}$.

By the similar procedures, the whole informational set $I(K_{NT,AL}, K_{NT,T}, K_{AL,Ox})$ for all points from the initial uncertainty box $\mathbf{H}_{NT,0} \times \mathbf{H}_{AL,0}$ is built

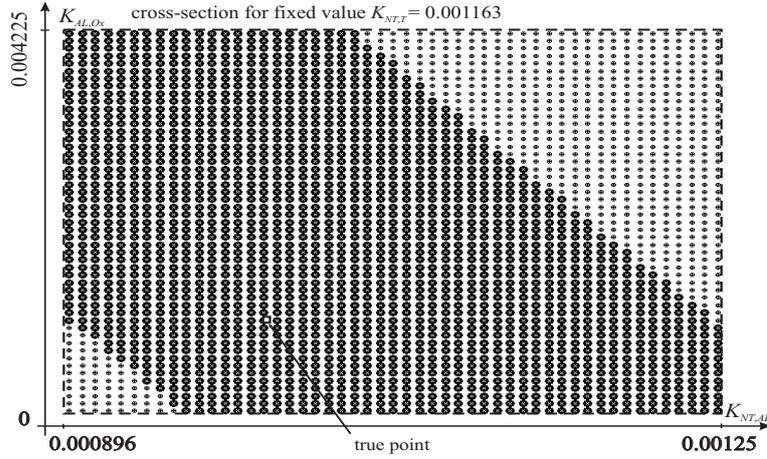


Fig. 7. Step 4; the initial grid and final inner approximation of the cross-section of the information set $I(K_{NT,AL}, K_{NT,T}, K_{AL,Ox})$ for fixed value of the initial guess coefficient $K_{NT,T} = 0.001163$; circles denote admissible nodes; points denote inadmissible ones

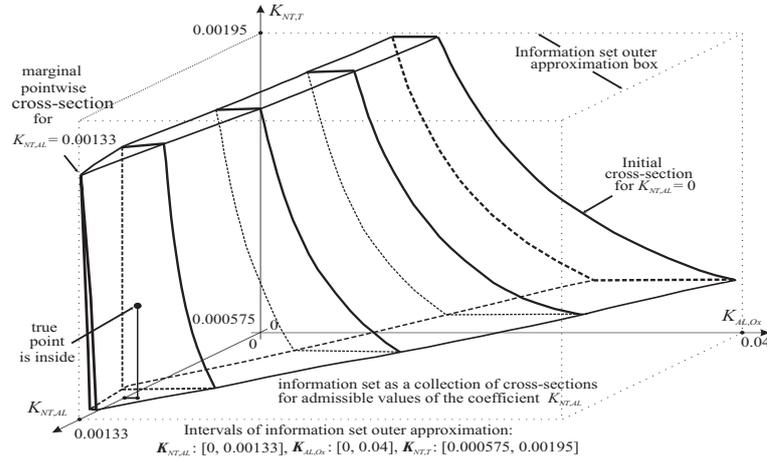


Fig. 8. The three-dimensional image of the information set $I(K_{NT,AL}, K_{NT,T}, K_{AL,Ox})$ for fixed $K_F = 0.1$

as a totality (see ideology and techniques of such representation in [9–11]) of all admissible cross-sections; its spatial image is shown in Fig. 8.

Underline that the results represented in Figs. 7, 8 have the guaranteed character since the true values of the coefficients $K_{NT,AL}^* = 0.001$, $K_{NT,T}^* = 0.001$, and $K_{AL,Ox}^* = 0.001$ obligatory (by construction) lie inside the final inner approximation of the information set $I(K_{NT,AL}, K_{NT,T}, K_{AL,Ox})$ for all initial values $NT(t=0)$, $AL(t=0)$ from the initial uncertainty box $\mathbf{H}_{NT,0} \times \mathbf{H}_{AL,0}$.

Analysis of experimental data has shown that for practical applications, the mentioned point-wise initial guess of type (13) with approximate estimating intervals of type (14) are sufficient and acceptable.

6 Conclusion

In contrast to now existing approaches to estimation of experimental process parameters under mentioned conditions of uncertainty, the interval approach allows one:

- to built verified inner approximation of the information set for the activity coefficients;
- to find verified interval estimations of the important coefficient of the oxide film precipitated on the aluminum surface for various values of admissible coefficients from the information set;
- if necessary, to enhance the box (set) of the initial (or termination) measurements for some fixed prescribed values of coefficients.

7 Acknowledgment

The work was supported by the Russian Foundation for Basic Research, Project 18-01-00410 and by the Ural Federal University's Center of Excellence in "Quantum and Video Information Technologies: from Computer Vision to Video Analytics" (according to the Act 211 Government of the Russian Federation, contract 02.A03.21.0006). M. Hladík was supported by the Czech Science Foundation Grant P402/13-10660S.

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