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ЗАДАЧИ ТЕОРИИ ТЕРМОУПРУГОЙ ДИФФУЗИИ С ХИМИЧЕСКИМИ РЕАКЦИЯМИ

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INTRODUCTION

General characteristics of the work

The problems of thermal elastic diffusion study the interrelation between stress, strain, temperature and concentration fields. This theory is interesting for the situation where material behaviour under intensive thermal and mechanical action is studied. In this case, the processes in solid are irreversible and can be accompanied by chemical reactions. For example, at the condition of surface material treatment by intensive particle beams, the chemical conversion happen which change the materials composition and properties. As a result, stresses and strains appear during composition change. The generalized thermal elastic theory doesn't take into account the chemical conversions. It is necessary to include the chemical reactions in thermal elastic diffusion and investigate as an example the problems for typical experimental situation.

One of the traditional areas of mechanics of deformable solids is to investigate the influence of thermal elastic diffusion in the solid phase. This is due to the theoretical study of the problem of interaction field various physical nature, with the construction of models of multi-component and multiphase media and the challenge of managing physical and chemical processes in modern technology. Mechanical stress can be either static (tensile, shear, torsion, rotation) or dynamic (shock waves, blast vibration, pressing, ultra-sound). In any case, the influence of the external load is associated with the change of transformation modes (speed, direction). This fully applies to the processes of self-propagating high-temperature synthesis and sintering. There are a number of scientists, working on the construction of models of multicomponent media associated with the names A.K.Öhringen, R.M.Bowen and W. Nowacki etc.

Study of mutual influence of stress and diffusion (both theoretical and experimental methods) has a rich history, the first works connected with the name S.A Gorsky devoted to the phenomenon of ascending diffusion. At the moment, there is another surge of interest in both domestic and foreign researchers Lei this matter. This is due to the fact that diffusion processes appearing, on the one hand, defining, and often limiting in large an amount of observable phenomena, and, on the other hand, the mass transfer subject to influence of various physical fields, including temperature, electric electromagnetic field, or the field of mechanical stresses. The impact of recent actively studied in connection with the development and research of various technological processes.

The ion implantation of metal surfaces by particles (ions) of other metal can accompany by intermetallic compounds formation [1, 2]. It promotes the surface properties modification. The model construction for this technology process will assist to physical phenomena study and treatment conditions optimization.

The work is devoted to the models construction for ion implantation with intermetallides, analytical and numerical methods development to realize the models of new phases formation in surface layer under the action of a particle beam. The models are based on the generalization of thermal elastic diffusion theory started from the simple and known problem in classical approximation. Particular problems are solved analytically and numerically with the demonstration of the stresses and strains evolution in treated surface layer with constant and changing properties.

The aim of this work:

Numerical and theoretical study of new models of generalized thermal elastic diffusion with chemical reactions, accompanied by various cross physical effects in the surface layer of material under particle beam action. In accordance with the intended purpose is required:

1. To build the related models of thermal elastic diffusion with chemical reactions under different conditions.
2. To formulate mathematical models taking into account the various cross effects between concentration, stresses and strains.
3. To develop the algorithm for the numerical investigation of formulated models, taking into account the specific condition of diffusion and thermoelasticity.
4. To implement the detailed parametric study of particular problems with the purpose of parameters defining and modes of processing.
5. To analyze the influence of various cross effects and thermal effects on the processes of redistribution of concentrations.

Corresponding to this, we formulate the tasks:

1. To develop mathematical model of generalized thermal elastic diffusion with chemical reaction with and without time relaxation.
2. Find analytical and numerical solution with wide range values of parameters.
3. For solving the problem using the double sweep method and Laplace transformation method and coding in FORTRAN.

Novelty of a scientific work

The thesis for the first time:

1. Formulated and investigated related models on thermal elastic diffusion with chemical reactions.
2. The algorithms were developed excluding the possibility of inconsistency appearance in terms of physical solutions.
3. Based on the results of numerical modeling the new effects were revealed.

Theoretical and practical significance of the work:

The work presents a new knowledge in the thermal elastic diffusion theory with chemical reactions. Results of the study can be used to develop models and methods of composition modification with acceptable stress-strain state of processed samples. Models admit their further development by taking into account the different parameter and conditions of ions deposition. It is the practical and applied value of the work.

The validity of the scientific results is confirmed by thorough testing program, comparing numerical results with exact analytical solutions in various limiting cases. Correct formulation is solved in dissertation work tasks using modern physical understanding of the processes, analytical and computational methods; consistency of the results and their compliance in extreme cases the theoretical results known from literature and available experimental facts.

Personal contribution of the author was to analysis of data in the literature, writing and debugging programs, a numerical study set out particular tasks, judgment of the results, the formulation of basic scientific positions and conclusions. All works published in collaboration, met with the personal participation of the author.

Testing of work:

The main results of the thesis were reported and discussed at the following international conferences:

1. International Conference of young scientist "High Technology Research and Application 2014" (HTRA 2014) held at Tomsk Polytechnic University Tomsk, Russia: March 26th - 28th, 2014.
2. Russian-German School of young scientists Conference "Biotechnology, Energy and nanotechnology" Tomsk Polytechnic University Tomsk, Russia: May 20th -23rd, 2014.
3. International Conference on Physical Mesomechanics of Multilevel Systems 2014. Tomsk, Russia: 3 -5 September, 2014.
4. International Congress on Energy Fluxes and Radiation Effects 2014. (EFRE-2014) Tomsk, Russia: September 21 -26, 2014.
5. International Conference of young scientist "High Technology Research and Application 2015" (HTRA 2015) held at Tomsk Polytechnic University Tomsk, Russia: April 21 -24, 2015.

The structure and scope of the thesis: The thesis is composed of introduction and three chapters, conclusion, appendix and bibliography. The work is described on page 114, including 37 figures and 01 table.

Chapter 1
Theory of thermal elastic diffusion

1.1. Definitions

In the mechanics we speak about behavior of bodies at the loading. To describe the behavior of real bodies it is necessary to introduce some conditional concepts and definitions.

The linear theory of elasticity deals with problems in which deformations, displacements, and rotations are small. In this case we determine the relations between stresses and strains.

Thermal elastic diffusion theory deals with the elastic body behavior when not homogeneous fields of temperature and species concentrations exist.

Firstly it is necessary to introduce some definitions and postulate governing equations.

1.2. Elasticity theory

Elasticity theory is based on two experimental laws: Hook and Poisson [3, 4] First law speaks that strain linearly connects with stress when external load is applied to rod

$$\sigma = E\varepsilon, \tag{1.1}$$

where

$$\varepsilon = \frac{l - l_0}{l_0} -$$

is relative elongation of the rood; l_0-is its initial length E; is proportional coefficient called as elasticity modulus or Young modulus.

Besides the strain in the tension direction, the lateral strain ε' exists, where

$$\varepsilon' = \frac{b - b_0}{b_0} -$$

where b_0 and b - are lateral size of the rod before and after deformation.

Second law ascertains the relation between lateral ε' and longitudinal ε strains. For isotropic material the value ε' is the same for all directions in the cross-section. If strain is elastic and satisfies to Hook's law (1.1), so the value ε'/ε is constant:

$$\varepsilon' = -\nu\varepsilon = -\nu\frac{\sigma}{E}. \tag{1.2}$$

This is Poison relation and the coefficient ν is called as Poisson's coefficient.

For three-dimensional case in arbitrarily coordinate system Hook's law has the form

$$\sigma_{ij} = 2\mu\varepsilon_{ij} + \delta_{ij}\lambda\varepsilon_{kk}. \tag{1.3}$$

where λ and μ are Lame coefficients; δ_{ij} is Kronecker delta,

$$\delta_{ij} = \begin{bmatrix} 1, & i = j; \\ 0, & i \neq j, \end{bmatrix}$$

σ_{ij} are stress tensor components; ε_{ij} are small strain tensor components satisfying to Cauchy relations

$$\varepsilon_{ik} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i}\right), \tag{1.4}$$

u_i are components of displacement vector, x_i are components of radius-vector.

The equations (1.3) and (1.4) are constitutive equations of thermal elasticity theory.

In Cartesian coordinate system,

$$x_1 = x, x_2 = y, x_3 = z\,;\; u_1 = u_x, u_2 = u_y, u_3 = u_z \text{ etc.}$$

and, instead (1.4), we have

$$\varepsilon_{xx} = \frac{\partial u_x}{\partial x},\quad \varepsilon_{yy} = \frac{\partial u_y}{\partial y},\quad \varepsilon_{zz} = \frac{\partial u_z}{\partial z},$$

$$2\varepsilon_{xy} = 2\varepsilon_{yx} = \frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x} = \gamma_{xy},\quad 2\varepsilon_{yz} = 2\varepsilon_{zy} = \frac{\partial u_z}{\partial y} + \frac{\partial u_y}{\partial z} = \gamma_{yz}, \tag{1.5}$$

$$2\varepsilon_{zx} = 2\varepsilon_{xz} = \frac{\partial u_x}{\partial z} + \frac{\partial u_z}{\partial x} = \gamma_{zx},$$

where u_x, u_y, u_z are the components of displacement vector in Cartesian coordinate system.

The Hook's law takes the form

$$\sigma_{xx} = 2\mu\varepsilon_{xx} + \lambda\varepsilon_{kk},\quad \sigma_{yy} = 2\mu\varepsilon_{yy} + \lambda\varepsilon_{kk},$$

$$\sigma_{zz} = 2\mu\varepsilon_{zz} + \lambda\varepsilon_{kk}, \tag{1.6}$$

$$\sigma_{xy} = 2\mu\varepsilon_{xy},\quad \sigma_{yz} = 2\mu\varepsilon_{yz},\quad \sigma_{zx} = 2\mu\varepsilon_{zx}$$

The value $\varepsilon_{kk} = \varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33}$ is first invariant of strain tensor and describes the small change of the volume of elastic body.

The Lame elastic constants λ and μ are connects with technical characteristics E and ν as

$$\lambda = \frac{\nu E}{(1+\nu)(1-2\nu)}\,;\; \mu = \frac{E}{2(1+\nu)} = G,$$

where G is shear module.

Note that the following relation hold [5, 6]:

$$3\lambda + 2\mu = 3K,\; E = \frac{(3\lambda + 2\mu)\mu}{(\lambda + \mu)},\; \nu = \frac{\lambda}{2(\lambda + \mu)}.$$

To describe the mechanical behavior of the elastic body we must add the above equations the equilibrium equations for quasistatic problems

$$\frac{\partial \sigma_{xx}}{\partial x} + \frac{\partial \sigma_{xy}}{\partial y} + \frac{\partial \sigma_{xz}}{\partial z} + X = 0;$$

$$\frac{\partial \sigma_{xy}}{\partial x} + \frac{\partial \sigma_{yy}}{\partial y} + \frac{\partial \sigma_{yz}}{\partial z} + Y = 0; \tag{1.7}$$

$$\frac{\partial \sigma_{xz}}{\partial x} + \frac{\partial \sigma_{yz}}{\partial y} + \frac{\partial \sigma_{zz}}{\partial z} + Z = 0,$$

where X, Y, Z are the components of the volume forces in the x, y, z directions respectively.

For the dynamical problems the inertia forces are taken into account. In the general form the motion equations have the form

$$\nabla \cdot \boldsymbol{\sigma} + \rho \mathbf{F} = \rho \frac{\partial^2 \mathbf{u}}{\partial t^2},$$

where t is the time, $\mathbf{F}$ is vector of volume forces with components X, Y, Z.

For Cartesian coordinate system we have

$$\begin{gathered}
\frac{\partial \sigma_{xx}}{\partial x} + \frac{\partial \sigma_{xy}}{\partial y} + \frac{\partial \sigma_{xz}}{\partial z} + X = \rho \frac{\partial^2 u_x}{\partial t^2}; \\
\frac{\partial \sigma_{xy}}{\partial x} + \frac{\partial \sigma_{yy}}{\partial y} + \frac{\partial \sigma_{yz}}{\partial z} + Y = \rho \frac{\partial^2 u_y}{\partial t^2}; \\
\frac{\partial \sigma_{xz}}{\partial x} + \frac{\partial \sigma_{yz}}{\partial y} + \frac{\partial \sigma_{zz}}{\partial z} + Z = \rho \frac{\partial^2 u_z}{\partial t^2}.
\end{gathered} \tag{1.8}$$

In elasticity theory, it is assumed that temperature and body composition do not change.

1.3. Thermal conductivity theory

Thermal conductivity theory studies the temperature field change in the bodies under different thermal actions. In this case, it is assumed that the body is none deformed, and their composition does not change.

Corresponding to Fourier law, heat flux is proportional to temperature gradient

$$\mathbf{q} = -\lambda_T \nabla T, \tag{1.10}$$

where λ_T is thermal conductivity coefficient. In Cartesian coordinate system and for isotropic body, we can write

$$q_x = -\lambda_T \frac{\partial T}{\partial x}; \quad q_y = -\lambda_T \frac{\partial T}{\partial y}; \quad q_z = -\lambda_T \frac{\partial T}{\partial z}.$$

Using balance equation

$$c\rho \frac{\partial T}{\partial t} = -\nabla \cdot \mathbf{q},$$

we come to thermal conductivity equation

$$c\rho \frac{\partial T}{\partial t} = \nabla \cdot (\lambda_T \nabla \mathbf{q}) = \frac{\partial}{\partial x}\left(\lambda_T \frac{\partial T}{\partial x}\right) + \frac{\partial}{\partial y}\left(\lambda_T \frac{\partial T}{\partial y}\right) + \frac{\partial}{\partial z}\left(\lambda_T \frac{\partial T}{\partial z}\right),$$

where c is heat capacity. It is parabolic differential equation. Here

$$\nabla \cdot \ldots \equiv div\ldots; \quad \nabla \ldots \equiv grad\ldots$$

If we take into consideration the generalized thermal conductivity law [7]

$$\mathbf{q} = -\lambda_T \nabla T - t_R \frac{\partial \mathbf{q}}{\partial t}, \tag{1.11}$$

we come to hyperbolic equation with finite relaxation time t_R of heat flux

$$c\rho\left[t_R\frac{\partial^2 T}{\partial t^2}+\frac{\partial T}{\partial t}\right]=\nabla\cdot\left(\lambda_T\nabla\mathbf{q}\right)=\frac{\partial}{\partial x}\left(\lambda_T\frac{\partial T}{\partial x}\right)+\frac{\partial}{\partial y}\left(\lambda_T\frac{\partial T}{\partial y}\right)+\frac{\partial}{\partial z}\left(\lambda_T\frac{\partial T}{\partial z}\right).$$

This equation is suitable for description of thermal problems for irreversible conditions.

1.4. Thermal elasticity theory

The development of the theory of thermal stresses connects with the names of Duhamel J.M.S [8], Neumann F.E. [9], Gatewood B.E. [10] of 1941 and Boley B. [11] of 1956. The first papers of importance seem to be those of Duhamel J**.** M.S, published in Paris in 1.837, 1838, and 1856, and a paper by Neumann F. E, published in Berlin in 1841. With the passage of time, more and more researchers became interested in thermal stresses. We should also need to mention the work that appeared after the Second World War by J. Lighthill and J. Bradshaw [12] of 1949 on thermal stresses in turbine blades, by S.S. Manson [13] of 1947 on gas turbine disks, and by J. Aleck [14] of 1949 on thermal stresses in rectangular plates.

The phenomenon of thermal expansion is taken into account here. Compared to the history of the theory of elasticity, which is traced to Robert Hooke and Edm´e Mariotte in the seventeenth century or, even earlier, to Galileo Galilei in the 16th century, the history of thermoelasticity and thermal stresses is much younger [8]. Thermal elasticity theory appearing is connected in 19 Century with Duhamel (1837) and Neumann (1885). Thermal action on the body leads to thermal strains appearing. In this case the additional term appears in the constitutive equations (1.3). We have

$$\sigma_{ij}=2\mu\varepsilon_{ij}+\delta_{ij}\left[\lambda\varepsilon_{kk}-3K\alpha_T\left(T-T_0\right)\right] \tag{1.12}$$

where α_T is linear thermal expansion coefficient, K is the bulk modulus

$$K=\lambda+\frac{2}{3}\mu.$$

New form of constitutive equations is accompanied by new form balance equation

$$c_\varepsilon\rho\frac{\partial T}{\partial t}=-\nabla\cdot\mathbf{q}-3K\alpha_T T\frac{\partial\varepsilon_{kk}}{\partial t}, \tag{1.13}$$

where c_ε is the heat capacity at the constant strains.

Classical quasistatic thermo elasticity theory includes equilibrium equations (1.7), balance equation (1.13), and constitutive equations (1.5), (1.10) and (1.12). Thermal conductivity equation takes the form

$$c_\varepsilon\rho\frac{\partial T}{\partial t}=\nabla\cdot\left(\lambda_T\nabla\mathbf{q}\right)-3K\alpha_T T\frac{\partial\varepsilon_{kk}}{\partial t}.$$

Generalized quasistatic thermo elasticity theory uses the generalized equation (1.11) instead of (1.10) and comes to the thermal conductivity equation

$$\left[1+t_R\frac{\partial}{\partial t}\right]\left(c_\varepsilon\rho\frac{\partial T}{\partial t}+3K\alpha_T T\frac{\partial\varepsilon_{kk}}{\partial t}\right)=\nabla\cdot\left(\lambda_T\nabla\mathbf{q}\right).$$

or

$$\rho c_\varepsilon\left[\frac{\partial T}{\partial t}+t_R\frac{\partial^2 T}{\partial t^2}\right]+3K\alpha_T\left[T\frac{\partial\varepsilon_{kk}}{\partial t}+t_R\frac{\partial}{\partial t}\left(T\frac{\partial\varepsilon_{kk}}{\partial t}\right)\right]=\nabla\cdot\left(\lambda_T\nabla T\right).$$

Most of early works of thermal elasticity theory were devoted to static problems [15]. Integration of thermoelasticity equations was reduced to problems of action of body forces with the potential of which density is the temperature of the body. Besides the development of the theory, a number of specific problems were solved. We should mention the work of C.W. Borchardt of 1873 on a solution in integral representation for a sphere acted upon by an arbitrarily distributed temperature, by J. Hopkinson on thermal stresses in a sphere in 1874, by A. Leon on a hollow cylinder in 1905, and by S. Timoshenko on bi-metallic strips in 1925.

Dynamical theories using motion equations (1.8) instead (1.7) study the wave phenomena [16]. The theory of thermal elasticity is usually studying in two approaches: Coupled and uncoupled thermal elasticity [17]. Although J.M.C. Duhamel presented equations of thermo elasticity with coupling of field of deformation with field of temperature already in 1837, only papers published 120 years later by M.A. Biot and M. Lessen in 1956 [18] and 1957 [19] respectively, gave a new impulse to do research in this area. In classic thermo elasticity, a problem of temperature was solved first, and then stresses were received from Duhamel-Neumann equations.

Generalized theory appears when H. Lord and Y. Shulman [20] postulates new thermal conductivity law in mechanics (1.11) instead of classical Fourier Law. Numerous problems of generalized thermal elasticity theory with finite time of heat flux relaxation were described in [21-23].

1.5. Thermodynamical basis for thermal elasticity theory

Based on thermodynamical theory of potentials, we can give thermodynamical definitions for elastic and thermal physical properties and ascertain thermodynamical constitutive equations [5-7].

Internal energy U is basic thermodynamical potential. It depends on entropy and volume, $U = U(S,V)$. The first and second laws of thermodynamics together lead to Gibbs equation

$$dU = TdS - pdV \,, \tag{1.14}$$

where

$$\left(\frac{\partial U}{\partial S}\right)_V = T \;;\; \left(\frac{\partial U}{\partial V}\right)_S = -p \,.$$

Using other thermodynamical potentials

$F = U - TS$ - free energy (Helmholtz energy);

$G = U - TS + PV$ Gibbs energy;

$H = U + pV$ - enthalpy (heat content),

we can write Gibbs equation in different forms.

$$dF = -SdT - pdV \,,\; dG = -SdT + Vdp \,,\; dH = TdS + Vdp \,, \tag{1.15}$$

where p is the pressure.

The laws of classical thermodynamic cannot establish why irreversible processes occur and why all real processes are irreversible.

To describe irreversible processes (deformation and diffusion etc.) there are different ways in thermodynamics and in continua mechanics. The choice of the description way depends on the phenomena under study.

If we know one of thermodynamical potentials, we can use the properties of potential functions and can find all thermodynamical properties of the system.

For deformable medium instead of (1.14) and (1.15) we have

$$dU = TdS + \rho^{-1}\sigma_{ij} d\varepsilon_{ij}, \quad dF = -SdT + \rho^{-1}\sigma_{ij} d\varepsilon_{ij}, \tag{1.16}$$

$$dG = -SdT - \rho^{-1}\varepsilon_{ij} d\sigma_{ij}, \quad dH = TdS - \rho^{-1}\varepsilon_{ij} d\sigma_{ij}.$$

In this case, all thermodynamical variables are the functions of the spatial coordinates and the time.

According to thermodynamical definition, the heat capacity at the constant pressure is

$$C_p = \left(\delta Q_\tau / dT\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p,$$

where δQ_τ is the heat supplied to the thermodynamical system. By analogy, for deformable media, we can write

$$C_\sigma = T\left(\frac{\partial S}{\partial T}\right)_\sigma.$$

Because we have from Gibbs equations

$$S = -\left(\frac{\partial G}{\partial T}\right)_\sigma,$$

we obtain

$$C_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_\sigma.$$

It is the heat capacity at the constant stresses.

Similarly to previous we shall find the heat capacity for constant strains

$$C_\varepsilon = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_\varepsilon.$$

Thermodynamical state equations in differential forms also follow from theory of thermodynamical potentials.

Really, from Gibbs equation for Helmholtz energy, we have $F = F\left(T, \varepsilon_{ij}\right)$. Hence $S = S\left(T, \varepsilon_{ij}\right)$ and $\sigma_{ij} = \sigma_{ij}\left(T, \varepsilon_{kl}\right)$. Then we can write

$$dS = \left(\frac{\partial S}{\partial T}\right)_\varepsilon dT + \left(\frac{\partial S}{\partial \varepsilon_{ij}}\right)_T d\varepsilon_{ij}; \tag{1.17}$$

$$d\sigma_{ij} = \left(\frac{\partial \sigma_{ij}}{\partial T}\right)_\varepsilon dT + \left(\frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}}\right)_T d\varepsilon_{kl}. \tag{1.18}$$

Some derivatives in these equalities are known for us.

First equation contains the heat capacity

$$C_\varepsilon = \left(\frac{\partial S}{\partial T}\right)_\varepsilon .$$

Second equations give the generalized Hook's law, if $T = const$

$$(d\sigma_{ij})_T = \left(\frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}}\right)_T d\varepsilon_{kl} = C_{ijkl} d\varepsilon_{kl} , \tag{1.19}$$

where C_{ijkl} is tensor of elastic modulus. Fir isotropic medium and small strain, the equation (1.3) is obtained from (1.19).

Other derivatives describe the known cross effect connecting with interrelation between temperature and strain fields:

$$\left(\frac{\partial S}{\partial \varepsilon_{ij}}\right)_T = -\left(\frac{\partial}{\partial \varepsilon_{ij}}\left(\frac{\partial F}{\partial T}\right)_\varepsilon\right)_T = -\left(\frac{\partial}{\partial \varepsilon_{ij}}\left(\frac{\partial F}{\partial T}\right)_\varepsilon\right)_T =$$

$$= -\rho^{-1}\left(\frac{\partial \sigma_{ij}}{\partial T}\right)_\varepsilon = \rho^{-1}\beta_{ij}^T = \rho^{-1} C_{ijkl}\alpha_{kl} ,$$

where α_{kl} is tensor of thermal expansion coefficients.

For isotropic medium and small strains we shall obtain from (1.18) the Dugamel relations (1.12).

In general case, we have in differential form

$$d\sigma_{ij} = C_{ijkl} d\varepsilon_{kl} - \beta_{ij}^T dT ; \tag{1.20}$$

$$ds = \rho^{-1}\beta_{ij}^T d\varepsilon_{ij} + \frac{C_\varepsilon}{T} dT . \tag{1.21}$$

These are thermodynamical irreversible state equations in differential form.

In first equality, the summation goes with indexes *k* and *l*. In second one, summation goes with indexes *i* and *j*.

1.6. Theory of multi component diffusion

As a rule, multi component diffusion in solid bodied has been studied for isothermal conditions and without stresses and strains. And strain – stressed state has been analyzed without taking into account the composition change.

When we have simple body which contains the admixture of one kind, or this admixture enters in the body from environment, only one diffusion equation for one species is necessary to describe this process.

According to Fick law, the diffusion flux of species is proportional to concentration gradient

$$\mathbf{J} = -\rho D \nabla C , \tag{1.22}$$

where C is species concentration, D is diffusion coefficient.

Balance equation

$$\rho \frac{\partial C}{\partial t} = -\nabla \cdot \mathbf{J}$$

together with (1.22) gives the diffusion equation

$$\rho \frac{dC}{dt} = \nabla \cdot \left(\rho D \nabla C \right).$$

For $\rho = const$ and immobile medium, we obtain

$$\frac{\partial C}{\partial t} = \nabla \cdot \left(D \nabla C \right).$$

In Cartesian coordinate system and for isotropic medium, we have

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y}\left(D \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z}\left(D \frac{\partial C}{\partial z} \right).$$

This is similar to usual thermal conductivity equation

For multi component body, the generalized Fick law takes a place

$$\mathbf{j}_j = -\sum_{k=1}^{n-1} D_{jk} \nabla C_k,$$

where D_{jk} are partial diffusion coefficients,

$$\sum_{k=1}^{n} C_k = 1, \qquad (1.23)$$

because the definitions are assumed:

$$M = M_1 + M_2 + \ldots + M_n \text{ -}$$

is the mass of the system (body),

$$\rho = \frac{M}{V} = \frac{M_1 + M_2 + \ldots + M_n}{V} = \rho_1 + \rho_2 + \ldots + \rho_n = \sum_{k=1}^{n} \rho_k \text{ -}$$

is density of the system (body),

$$\rho_k = \frac{M_k}{V} \text{ -} \qquad (1.24)$$

are partial densities of species (components),

$$C_k = \frac{\rho_k}{\rho} \text{ -} \qquad (1.25)$$

are the mass concentrations of species.

For particular problems in the chemistry and diffusion theory, molar concentrations are used:

$$y_k = \frac{\rho_k / m_k}{\sum_{i=1}^{n} \rho_i / m_i}, \qquad (1.27)$$

where m_k are molar masses of species.

Nowadays, theory of multi component diffusion has thermodynamical basis and used for numerous applications [24-27].

However, these laws are simplified laws that does not take into consideration the mutual interaction between the introduced substance and the medium into which it is introduced or the effect of the temperature on this interaction. Thermal diffusion utilizes the transfer of heat across a thin liquid or gas to accomplish isotope separation. There is a certain degree of coupling with temperature and temperature gradients as temperature speeds up the diffusion process. The thermo diffusion in elastic solids is due to coupling of fields of temperature, mass diffusion and that of strain in addition to heat and mass exchange with the environment. Due to these cross effects the thermal excitation results in an additional mass concentration, this generates the additional temperature field. The diffusion kinetics is described by a parabolic equations under corresponding initial and boundary conditions. The thermal stress field is caused by non-uniform distribution of temperature.

1.7. Thermal elastic diffusion

Thermoelastic diffusion involves the coupling of the fields of temperature, mass diffusion and strain. It has a wide range of applications in geophysics and industries. In particular, diffusion is used to form the base and emitter in bipolar transistors, form integrated resistors, form the source regions in Metal oxide semiconductors transistors and dope poly silicon gates in Metal oxide semiconductors transistors. Using the coupled thermoelastic model, Nowacki [28-30] developed the theory of thermoelastic diffusion. In this theory the relations

$$\sigma_{ij} = 2\mu\varepsilon_{ij} + \delta_{ij}\left[\lambda\varepsilon_{kk} - Kw\right], \tag{1.28}$$

where

$$w = 3\left[\alpha_T\left(T - T_0\right) + \alpha_C\left(C - C_0\right)\right] \tag{1.29}$$

are used. New coefficient α_C is called concentration expansion coefficient. The fluxes of the heat and mass satisfy to Fourier and Fick laws.

If we use (1.28), (1.29) and (1.5), we come from (1.8) to equations

$$\rho\frac{\partial^2 \mathbf{u}}{\partial t^2} = \left(\lambda + \mu\right)\nabla\nabla\cdot\mathbf{u} + \mu\Delta\mathbf{u} - 3K\left(\alpha_T\nabla T + \alpha_C\nabla C\right) + \rho\mathbf{F} \tag{1.30}$$

These are the motion equation or Lame equation in thermal elastic diffusion.

Classical theory deals with equation (1.30) and parabolic equations thermal conductivity and diffusion. The theories based on thermodynamics use the equation

$$\mathbf{J} = -D'\nabla g$$

instead (1.22). The species flux is proportional to gradient of chemical potential corresponding to this component. The relation

$$\mathbf{J} = -L\nabla\left(\frac{g}{T}\right)$$

is more correct.

When the composition change and temperature gradient presents, we should speak about the thermodynamical system, state of which and internal energy depends not only entropy, but on concentration. Hence, in this case (in the literalized theory) we have three types of thermal state equations [31, 32].

$$\rho T_0 S = \rho c_\varepsilon \Theta + \beta_T T_0 \varepsilon_{kk} + T_0 a C,$$
$$\sigma_{ij} = 2\mu\varepsilon_{ij} + \delta_{ij}\left[\lambda\varepsilon_{kk} - \left(\beta_T\Theta + \beta_C C\right)\right], \tag{1.31}$$

$$P = -a\Theta - \beta_C \varepsilon_{kk} + \beta C,$$

where P is difference between chemical potentials of admixture and basic material for unit of mass ($P = \rho(g_2 - g_1)$, $a = s_{21}\rho$ is difference between their partial entropies;

$$\beta_T = 3K\alpha_T;\ \beta_C = 3K\alpha_C;\ \Theta = T - T_0.$$

Different theories (coupling and no coupling) admit the infinite propagation velocity for thermal and concentration waves [33].

Sherief end etc. [34] develops the theory of generalized thermal elastic diffusion with finite velocity of thermal and diffusion waves. However there are numerous inaccuracies in this and other papers. Furthermore, the linearization for the equations is not justifying.

Based on irreversible thermodynamics [35] we can derive the constitutive equation containing known theories [5,6] necessary for the following investigations.

Really [36], for two-component body, internal energy depends on entropy, strains and concentrations C_1 and C_2, and free energy F depends on temperature, , strains and concentrations:

$$F = F(T, \varepsilon_{ij}, C_1, C_2),$$

$$dF = -SdT + \rho^{-1}\sigma_{ij} d\varepsilon_{ij} + g_1 dC_1 + g_2 dC_2.$$

Hence, entropy S, stresses σ_{ij} and chemical potentials g_1 and g_2 (they are partial Gibbs energies, $G = C_1 g_1 + g_2 C_2$) depend on the same thermodynamical variables. Therefore, we can write

$$\begin{gathered}
dS = \frac{C_\varepsilon}{T} dT + \frac{\beta_{ij}{}^T}{\rho} d\varepsilon_{ij} + s_1 dC_1 + s_2 dC_2, \\
d\sigma_{ij} = -\beta_{ij}{}^T dT + C_{ijkl}^T d\varepsilon_{kl} - \beta_{ij}{}^1 dC_1 - \beta_{ij}{}^2 dC_2, \\
dg_1 = -s_1 dT - \beta_{ij}{}^1 \rho^{-1} d\varepsilon_{ij} + \beta_1^1 dC_1 + \beta_2^1 dC_2, \\
dg_2 = -s_2 dT - \beta_{ij}{}^2 \rho^{-1} d\varepsilon_{ij} + \beta_1^2 dC_1 + \beta_2^2 dC_2.
\end{gathered} \tag{1.32}$$

We have

$$g_1 = \left(\frac{\partial F}{\partial C_1}\right)_{T,\varepsilon,C_2};\quad g_2 = \left(\frac{\partial F}{\partial C_2}\right)_{T,\varepsilon,C_1};$$

$$\beta_2^1 = \left(\frac{\partial g_1}{\partial C_2}\right)_{T,\varepsilon,C_1} = \left(\frac{\partial^2 g}{\partial C_2 \partial C_1}\right)_{T,\varepsilon} = \left(\frac{\partial^2 g}{\partial C_1 \partial C_2}\right)_{T,\varepsilon} = \beta_1^2.$$

Because $C_1 + C_2 = 1$, we obtain

$$dS = \frac{C_\varepsilon}{T} dT + \frac{\beta_{ij}{}^T}{\rho} d\varepsilon_{ij} + (s_2 - s_1) dC_2,$$

$$d\sigma_{ij} = -\beta_{ij}{}^T dT + C_{ijkl}^T d\varepsilon_{kl} - \left(\beta_{ij}{}^2 - \beta_{ij}{}^1\right) dC_2,$$

$$d(g_2 - g_1) = -(s_2 - s_1) dT - \left(\beta_{ij}{}^2 - \beta_{ij}{}^1\right)\rho^{-1} d\varepsilon_{ij} + \left(\beta_2^2 - \beta_1^2\right) dC_2.$$

Now it is convenient to use the above designations (1.31) for isotropic body

$$\rho dS = \frac{\rho C_\varepsilon}{T} dT + \beta_T d\varepsilon_{kk} + adC \,,$$

$$d\sigma_{ij} = 2\mu d\varepsilon_{ij} + \delta_{ij}\left[\lambda d\varepsilon_{kk} - \left(\beta_T dT + \beta_C dC\right)\right] , \qquad (1.33)$$

$$dP = -adT - \beta_C d\varepsilon_{kk} + \beta dC \,.$$

Generalized Fourier and Fick laws in extended thermodynamics [37] for multi component system can be presented in the form

$$\mathbf{J}_q = L_{qq}\mathbf{X}_T + \sum_{k=1}^{n} L_{qk}\mathbf{X}_k + t_R \frac{d\mathbf{J}_q}{dt} \,,$$

$$\mathbf{J}_k = L_{kq}\mathbf{X}_q + \sum_{j=1}^{n} L_{kj}\mathbf{X}_j + t_k \frac{d\mathbf{J}_k}{dt} \,,$$

where

$$\mathbf{X}_q = -\frac{\nabla T}{T^2}, \;\; \mathbf{X}_k = \left[\mathbf{F}_k - \left(\nabla g_k\right)_T\right]\frac{1}{T} \; -$$

are the generalized thermodynamical forces, $\mathbf{F}_k$ - are the part of external mass force acting to the component with number k; $L_{qq}, L_{qk} = L_{kq}, L_{kj} = L_{jk}$ - are the phenomenological coefficients;

$$\mathbf{J}_q = \mathbf{q} - \sum_{k=1}^{n} H_k \mathbf{J}_k \,,$$

$\mathbf{q}$ - is heat flux for simple body.

Using (1.32) we can present the fluxes formulae in the form suitable for the following investigation [38, 39].

Based on [39], we shall obtain now the equations for the fluxes containing cross-effects known in literature. Note that the description of cross effects (Sore and Dufour effects, for example, and diffusion under pressure gradient action) should be made step-by step, because the simple summation of the phenomena known from experiment leads sometimes to the appearing of superfluous independent coefficients or to loss of important terms.

Let we have two species. In two-component system [39]

$$C_1 + C_2 = 1 \,; \;\; \mathbf{J}_1 + \mathbf{J}_2 = 0 \,.$$

Then we have only two formulae

$$\mathbf{J}_1 = L_{11}\left(\mathbf{X}_1 - \mathbf{X}_2\right) + L_{1q}\mathbf{X}_q + t_M \frac{d\mathbf{J}_1}{dt} \,,$$

$$\mathbf{J}_q = L_{q1}\left(\mathbf{X}_1 - \mathbf{X}_2\right) + L_{qq}\mathbf{X}_q + t_R \frac{d\mathbf{J}_q}{dt} \,.$$

where

$$\mathbf{X}_q = -\frac{\nabla T}{T^2}, \;\; \mathbf{X}_1 = \left[\mathbf{F}_1 - \left(\nabla g_1\right)_T\right]\frac{1}{T} \,; \;\; \mathbf{X}_2 = \left[\mathbf{F}_2 - \left(\nabla g_2\right)_T\right]\frac{1}{T} \,.$$

Hence

$$\mathbf{J}_1 = \frac{L_{11}}{T}\left(\mathbf{F}_1 - \mathbf{F}_2 + \left(\nabla g_2\right)_T - \left(\nabla g_1\right)_T\right) - L_{1q}\frac{\nabla T}{T^2} + t_M \frac{d\mathbf{J}_1}{dt} \,,$$

$$\mathbf{J}_q = \frac{L_{q1}}{T}\left(\mathbf{F}_1 - \mathbf{F}_2 + (\nabla g_2)_T - (\nabla g_1)_T\right) - L_{qq}\frac{\nabla T}{T^2} + t_R\frac{d\mathbf{J}_q}{dt} . \qquad (1.34)$$

Gibbs energies are the functions of temperature, concentration and stress tensor components, because $G = G(T, C_1, C_2, \sigma_{ij})$ and g_1, g_2 are partial Gibbs energies. Then we can write [39]

$$(\nabla g_1)_T = -\rho^{-1}\alpha_{ij}^1 \nabla \sigma_{ij}^e + \beta_1^1 \nabla C_1 + \beta_2^1 \nabla C_2 ,$$

$$(\nabla g_2)_T = -\rho^{-1}\alpha_{ij}^2 \nabla \sigma_{ij}^e + \beta_1^2 \nabla C_1 + \beta_2^2 \nabla C_2 ,$$

where

$$\beta_j^k = \left(\frac{\partial g_k}{\partial C_j}\right)_{T,\sigma_{il}} = \frac{RTg_{kj}}{m_k C_k} \quad \text{and} \quad \beta_j^k = \beta_k^j . \qquad (1.35)$$

g_{kj} -are thermodynamical factors, depending on the composition and structure,

$$g_{jk} = \delta_{jk} + \frac{C_j}{C_k}\frac{\partial \ln \gamma_j}{\partial \ln C_k} , \qquad (1.36)$$

γ_j are activity coefficients, m_k are molar masses of species.

Taking into account the relation $\nabla C_1 = -\nabla C_2$,we shall find the thermodynamical diffusion force:

$$\mathbf{X}_D = \left[\mathbf{F}_1 - \mathbf{F}_2 + \frac{\alpha_{ij}^1 - \alpha_{ij}^2}{\rho}\nabla \sigma_{ij}^e - \left(\beta_1^1 - \beta_2^1 - \beta_1^2 + \beta_2^2\right)\nabla C_1\right]\frac{1}{T} . \qquad (1.37)$$

Thermodynamical force conjugate to the heat flux does not change.

For isotropic medium, tensor of concentration expansion coefficients α_{ij}^k has a simple form

$$\alpha_{ij}^k = \alpha_k \delta_{ij} .$$

Because the coefficients β_j^k are symmetrical, we shall find

$$\frac{g_{12}}{m_1 C_1} = \frac{g_{21}}{m_2 C_2}$$

or

$$\frac{C_1}{C_2}\frac{\partial \ln \gamma_1}{\partial \ln C_2} = \frac{C_2}{C_1}\frac{\partial \ln \gamma_2}{\partial \ln C_1} .$$

Hence,

$$\mathbf{X}_D = \left[\mathbf{F}_1 - \mathbf{F}_2 + \frac{\alpha_1 - \alpha_2}{\rho}\nabla \sigma_{ij}^e - \frac{RT}{m_1 C_1} \times \left(g_{11} - 2g_{12} + \frac{m_1 C_1}{m_2 C_2} g_{22}\right)\nabla C_1\right]\frac{1}{T} . \qquad (1.38)$$

In the particular case of ideal solution (this approximation works well for small concentrations of admixtures), we can assume

$$g_{11} = g_{22} = 1; \quad g_{12} = g_{21} = 0 .$$

Corresponding to diffusion theory [40, 41], phenomenological coefficient L_{11} is determined through self-diffusion coefficient:

$$L_{11} = \frac{\rho D_{11}^0 m_1 C_1}{R} \tag{1.39}$$

Comparing the formulae for the heat flux with experimental Fourier law, we obtain

$$\frac{L_{qq}}{T^2} = \lambda_T .$$

Then, in the approximation of ideal solution we shall find

$$\mathbf{J}_1 = \frac{\rho D_{11}^0 m_1 C_1}{RT}\left(\mathbf{F}_1 - \mathbf{F}_2 + \frac{\alpha_1 - \alpha_2}{\rho}\nabla\sigma_{kk}^e - \frac{RT}{m_1 C_1}\left(1 + \frac{m_1 C_1}{m_2 C_2}\right)\nabla C_1\right) + L_{1q}\frac{\nabla T}{T^2} + t_M\frac{d\mathbf{J}_1}{dt},$$

$$\mathbf{J}_q = \frac{L_{q1}}{T}\left(\mathbf{F}_1 - \mathbf{F}_2 + \frac{\alpha_1 - \alpha_2}{\rho}\nabla\sigma_{kk}^e - \frac{RT}{m_1 C_1}\left(1 + \frac{m_1 C_1}{m_2 C_2}\right)\nabla C_1\right) - \lambda_T\nabla T + t_R\frac{d\mathbf{J}_q}{dt} .$$

We introduce the designation for transfer coefficient under stress action

$$B_1 = \frac{D_{11}^0 m_1}{RT}\left(\alpha_1 - \alpha_2\right) . \tag{1.40}$$

This coefficient is derivative from other parameters.

Diffusion coefficient in the approximation of ideal solution is:

$$D_1 = D_{11}^0\left(1 + \frac{m_1 C_1}{m_2 C_2}\right) . \tag{1.41}$$

Coefficient L_{1q} is assumed usually as [42]

$$\frac{L_{1q}}{T^2} = C_1 D_T \rho ,$$

where D_T is thermal diffusion coefficient. Sometimes, the Sore coefficient is a more suitable for applications (it is measured in K^{-1})

$$S_T = \frac{D_T}{D_1} .$$

Hence,

$$L_{q1} = T^2 C_1 D_T \rho = T^2 C_1 D_1 S_T \rho .$$

As a result, we obtain the formulae

$$\mathbf{J}_1 = -\rho D_1 \nabla C_1 + B_1 C_1 \nabla\sigma_{kk}^e - C_1 D_1 S_T \rho \nabla T + \frac{\rho D_{11}^0 m_1 C_1}{RT}\left(\mathbf{F}_1 - \mathbf{F}_2\right) + t_M\frac{d\mathbf{J}_1}{dt} , \tag{1.42}$$

$$\mathbf{J}_q = -\lambda_T \nabla T - D_1 Q_1^* \nabla C_1 + C_1 D_1 T S_T\left[\left(\alpha_1 - \alpha_2\right)\nabla\sigma_{kk}^e + \rho\left(\mathbf{F}_1 - \mathbf{F}_2\right)\right] + t_R\frac{d\mathbf{J}_q}{dt} , \tag{1.43}$$

where

$$Q_1^* = \frac{\rho R T^2}{m_1} S_T\left(1 + \frac{m_1 C_1}{m_2 C_2}\right) -$$

is the transfer heat (J/kg).

If we have non ideal solutions, the form of the equations does not change. However, some concentration function appears in the coefficients [43]:

$$D_1 = D_{11}^0 f(C_1); \quad Q_1^* = \frac{\rho R T^2}{m_1} S_T f(C_1),$$

$$f(C_1) = g_{11} - 2g_{12} + \frac{m_1 C_1}{m_2(1 - C_1)} g_{22}.$$

We see that, only three from six transfer coefficients are independent.
No all physical effects are taken into account in modern theories of thermal elastic diffusion.

We mark, that non classical theories known as generalized thermo elasticity were introduced into the literature in an attempt to eliminate the shortcomings of the classical dynamical thermo elasticity [44, 18]. The problem of half space subjected of thermal shock, known as the theory of uncoupled thermo elasticity. In this theory, the temperature is governed by a parabolic partial differential equation that does not contain any elastic terms, unlike the conventional thermo elasticity theory [18], based on a parabolic heat equation, which predicts an infinite speed for the propagation of heat, generalized and modified into various thermo elastic models based on hyperbolic thermo elasticity [45]. These theories, referred to as generalized thermo elasticity, were introduced in the literature in an attempt to eliminate the shortcomings of the classical dynamical thermo elasticity. For example, Lord and Shulman [20], incorporated a flux rate term into Fourier’s law of heat conduction and formulated a generalized theory involving a hyperbolic heat transport equation, admitting finite speed for thermal signals.

Lately, Sherief and Saleh [32] investigated the problem of a thermo elastic half space in the context of the theory of generalized thermo elastic diffusion with one relaxation time. Singh discussed the reflection phenomena of waves from free surface of a thermo elastic diffusion elastic solid with one relaxation time in [46] and with two relaxation times in [47]. It does not violate Fourier's law of heat conduction when the body under consideration has a centre of symmetry, and it is valid for both isotropic and anisotropic bodies. Aouadi studied in [48] the generalized thermo elastic diffusion problem with variable electrical and thermal conductivity. Aouadi [49] also studied the interaction between the processes of elasticity, heat and diffusion in an infinitely long solid cylinder [50] and in an infinite elastic body with spherical cavity. Uniqueness and reciprocity theorems for the equations of generalized thermo elastic diffusion problem, in isotropic media, was proved by Sherief et al. [44] on the basis of the variation principle equations, under restrictive assumptions on the elastic coefficients. Due to the inherit complexity of the derivation of the variational principle equations, and by Aouadi [51] proved this theorem in the Laplace transform domain, under the assumption that the functions of the problem are continuous and the inverse Laplace transform of each is also unique. Aouadi [52] derived the uniqueness and reciprocity theorems for the generalized problem in anisotropic media, under the restriction that the elastic, thermal conductivity and diffusion tensors are positive definite. For the coupled problem, the existence of a generalized, regular and unique solution has been proved by Aouadi [53] by means of some results of semigroup of linear operator’s theory. Recently, Aouadi derived the general equations of motion and constitutive equations of the linear micro polar thermo elastic diffusion theory in both classic [54] and generalized [55] context, with uniqueness and existence theorems. Iesan [56, 57] has developed a linear theory of thermoelastic materials with voids. Aouadi [53, 55] has extended the thermoelastic theory with voids to include diffusion effects.

Elhagary [58] has discussed the one dimensional problem of generalized thermo elastic diffusion for a long hollow cylinder. Aouadi [50] studied the one dimensional problem of generalized thermo elastic diffusion for an infinitely long solid cylinder. Recently, Tripathi et al [59] discussed a two dimensional dynamic problem of generalized thermo elasticity in Lord-Shulman theory for a thick circular cylinder with hear sources. The work of Aouadi [50] is extended by [60] considering a two-dimensional generalized thermo elastic diffusion problem in a thick circular plate of infinite extent and finite length subjected to an axisymmetric heat supply with one relaxation parameter and discussed the effects of thermo elastic diffusion. The classical couple thermo elasticity is recovered as a special case. This is a new and novel contribution to the field.

Serious attention has been paid to the generalized thermo elasticity theories in solving thermo elastic problems in place of the classical uncoupled/coupled theory of thermo elasticity.

At present mainly two different models of generalized thermo elasticity are being extensively used one proposed by Lord and Shulman [20] and the other proposed by Green and Lindsay [61]. Lord and Shulman theory suggests one relaxation time and according to this theory, only Fourier’s heat conduction equation is modified; while Green and Lindsay theory suggests two relaxation times and both the energy equation and the equation of motion are modified.

In this work we generalize the thermal elastic diffusion for constant temperature to the body with chemical reactions.

1.8. Body with chemical reactions

In multi component body, the chemical reactions happen. It could be taken into account in the equations used for the description of applied problems.

Theory of kinetics of chemical reactions for homogeneous media is very well developed. For moving gas and liquid phases we can use the known theories without special restrictions.

Above we introduce two types of concentrations: mass concentration C_k (1.25) and relative molar concentrations y_k (1.27). The values ρ_k / m_k determine the number of mole of k-components in the unite volume:

$$n_k = \frac{\rho_k}{m_k},$$

and

$$N_k = \frac{M_k}{m_k}$$

is the number of moles in the volume V.

Then additionally to (1.27) we can write

$$y_i = \frac{N_i}{N} = \frac{M_i / m_i}{\sum\limits_{k=1}^{n} M_k / m_k} = \frac{C_i / m_i}{\sum\limits_{k=1}^{n} C_k / m_k}$$

where

$$N = \sum_{i=1}^{n} N_i \quad \text{and} \quad \sum_{i=1}^{n} y_i = 1 .$$

The change of the i-particles number in the reaction *j* follows from the equality [62]

$$d_j n_i = \nu_{ij} \Phi_j dt,$$

where Φ_j - is the *j*-reaction rate, mol/(m^3sec), ν_{ij} are stoichiometric coefficients for *i* – component in *j*- reaction. We can find the reaction rate through the concentration change of any component and introduce the new values:

$$\Phi_j = \frac{1}{\nu_{1j}} \frac{d_j n_1}{dt} = \frac{1}{\nu_{2j}} \frac{d_j n_2}{dt} = \ldots = \frac{1}{\nu_{ij}} \frac{d_j n_i}{dt} = \frac{d\xi_j}{dt},$$

where ξ_j is the reaction coordinate, $\lfloor \xi_j \rfloor =$ mol/m^3. It can be called as conversion degree for the reaction. So, for any i, j, we have

$$d\xi_j = \frac{d_j n_i}{\nu_{ij}} .$$

These values are state variables together with the temperature, pressure or together with temperature and volume, and etc. If r is number of the reactions, so change of the i-component in all reactions is (in the unit volume)

$$dn_i = \sum_{j=1}^{r} d_j n_i = \sum_{j=1}^{r} \nu_{ij} \Phi_j dt = \sum_{j=1}^{r} \nu_{ij} d\xi_j .$$

Gibbs equation for internal energy:

$$du = Tds + \rho^{-1} \sigma_{ij} d\varepsilon_{ij} + \sum_{k=1}^{n} g_k dC_k$$

gives

$$\rho \frac{dS}{dt} = \frac{1}{T} \rho \frac{du}{dt} - \frac{\sigma_{ij}}{T} \frac{d\varepsilon_{ij}}{dt} - \sum_{(i)} \frac{g_i}{T} \rho \frac{dC_i}{dt} = -\sum_{(i)} \frac{g_i}{T} \rho \frac{dC_i}{dt} .$$

Hence, for closed thermodynamical system, we have

$$\rho \frac{dS}{dt} = -\frac{1}{T} \sum_{i=1}^{n} g_i m_i \sum_{j=1}^{r} \nu_{ij} \frac{d\xi_j}{dt} = \frac{1}{T} \sum_{j=1}^{r} A_j \frac{d\xi_j}{dt} = \frac{1}{T} \sum_{j=1}^{r} A_j \Phi_j , \qquad (1.44)$$

where

$$A_j = -\sum_{i=1}^{n} g_i m_i \nu_{ij} \; – \qquad (1.45)$$

is chemical affinity for *j*-reaction.

Hence, entropy production due to chemical reactions is

$$\sigma_S = \sum_{j=1}^{r} \frac{\Phi_j A_j}{T} \geq 0 .$$

Corresponding to irreversible thermodynamics, the rate of chemical reaction is generalized flux, and chemical affinity is generalized force conjugate to reaction rate. Then Onsager theory gives

$$J_i = \Phi_i = \sum_{m=1}^{r} l_{im} \frac{A_m}{T} .$$

Chemical affinity is the function of composition and thermodynamical parameters determining the state of the system.

At the practical description of concentration change in chemical reactions various authors use experimental laws, however thermodynamics give some restrictions for the reactions [42, 43].

If only one reaction goes in the system, we can write its equation in the form

$$\sum_{k=1}^{n} \nu_k m_k = 0 . \qquad (1.46)$$

Mass concentrations of species change due to the kinetical equations or balance equations:

$$\rho \frac{dC_i}{dt} = \omega_i , \qquad (1.47)$$

$$\rho \frac{dC_i}{dt} = -\nabla \cdot \mathbf{J}_i + \omega_i , \qquad (1.48)$$

where $\omega_i = \nu_i m_i \Phi$, with $[\omega_i]$=Kg/(m^{3}sec); $[\Phi]=$ mol /(m$_2^3$sec);

$$\sigma_S = \frac{\Phi A}{T} = l \left(\frac{A}{T} \right) ,$$

where $A = -\sum_{k=1}^{n} m_k \nu_k g_k$, $[A]=$ J/mol; $[g_k]=$ J/kg; $[\sigma_S]=$ J /(K m^{3}sec).

For example for closed system, we have

$$X + Y = 2Z,$$

then

$$\frac{dn_X}{-1} = \frac{dn_Y}{-1} = \frac{dn_Z}{2} = d\xi$$

and

$$A = -[m_X \nu_X g_X + m_Y \nu_Y g_Y + m_Z \nu_Z g_Z] = m_X g_X + m_Y g_Y - 2m_Z g_Z .$$

Entropy production in the reaction is:

$$dS_i = \sigma_S dt = \frac{1}{T} [m_X g_X + m_Y g_Y - 2m_Z g_Z] d\xi \geq 0 .$$

Gibbs energy in the reaction

$$G_{XYZ} = m_X g_X + m_Y g_Y - 2m_Z g_Z \, \_$$

is the function of the composition and conditions.

If $G_{XYZ} > 0,$ so ξ grows, and the reaction goes in the forward direction.

If $G_{XYZ} < 0,$ so ξ diminishes.

If concentrations, temperature or stresses field are not uniform, the reaction rate depend on transfer processes.

It is necessary to refine this theory for solid substances and for irreversible conditions.

Conclusion

Elasticity is an elegant and fascinating subject that deals with determination of the stress, strain, and displacement distribution in an elastic solid under the influence of external forces. Hooks and Poisson laws play a significant role in the theory of elasticity, based on these two experimental laws, which speak about the stresses, strain and the relation between them. In general the hooks law and the Cauchy relation are the theory of thermal elasticity.

The theory of thermal elasticity is usually studying in two approaches: Coupled and uncoupled thermal elasticity. Coupled problem of thermal elasticity take into account the time rate of change of the first invariant of the strain tensor in the first law of thermodynamics causing the dependence between the temperature and strain fields, and thus creating the coupling between elastic and thermal fields. The uncoupled thermal elasticity approach is characterized by absence of the coupling term in the equation of heat conductivity. Using the coupled thermal elastic model, Nowacki developed the theory of thermal elastic diffusion. Sherief et al. introduced the theory of thermoelastic diffusion in the framework of Lord-Shulman theory by introducing thermal relaxation time parameter and diffusion relaxation parameters governing the field equations. Many researchers studied various types of problems in thermoelastic diffusion.

Serious attention has been paid to the generalized thermo elasticity theories in solving thermo elastic problems in place of the classical uncoupled/coupled theory of thermo elasticity.

In our work we generalize the thermal elastic diffusion for constant temperature to the body with chemical reactions. Theory of kinetics of chemical reactions for homogeneous media is very well developed. We have introduced two types of concentrations: mass concentration and relative molar concentrations.

Chapter 2

Thermal elastic diffusion theory for the multicomponent body with chemical reactions

2.1. Physical phenomena

Ion implantation technique initially developed for microelectronic applications. This is a process in which ions are accelerated in the material and the electric field effect in the rigid body. The technique dates back to the 1940's when it was developed at Oak Ridge National Laboratory as part of the Manhattan Project.2 Since then the technique has found a variety of applications in materials processing. In the 1970's the use of ion implantation to modify the electrical properties of semiconductors, metals, insulators and ceramics became extremely popular. Usually, the Monte Carlo and molecular dynamics methods are used for particle redistribution during plasma treatment or ion implantation. This process is used to alter the physical, chemical or electrical properties of the solid. Ion implantation is used in the manufacture of semiconductor devices and iron finishes and even for different applications in materials science studies. The method allows to obtain a very large range of concentrations ranging from less than 10^{14} to some amount of time $10^{22}/cm^3$. The process can be carried out at any temperature. Different regions of semiconductor devices conduct via electrons or positive holes, with the dominant conducting species being termed the majority carrier and the lesser the minority carrier. In order to make a region of a semiconductor electron or hole rich, impurity atoms have to be introduced into the semiconductor lattice. These impurities can either donate electrons (e.g., arsenic (As), phosphorous (P), or antimony (Sb) in silicon (Si)) or accept electrons and thereby create positive holes (e.g., boron (B) in silicon (Si)). These impurity atoms are called dopants.

Ion implantation is a low-temperature technique for the introduction of impurities (dopants) into semiconductors and offers more flexibility than diffusion. For example, in MOS transistors, ion implantation can be used to accurately adjust the threshold voltage. In ion implantation, dopant atoms are volatilized, ionized, accelerated, separated by the mass-to-charge ratios, and directed at a target that is typically a silicon substrate. The atoms enter the crystal lattice, collide with the host atoms, lose energy, and finally come to rest at some depth within the solid. The average penetration depth is determined by the dopant, substrate materials, and acceleration energy. Ion implantation energies range from several hundred to several million electron volts, resulting in ion distributions with average depths from <10 nm to 10μ Doses range from $10^{11}\, atoms/cm^2$ for threshold adjustment to $10^{18}\, atoms/cm^2$ for buried dielectric formation. Ion implantation represents a particularly useful means by which to modify the surface properties of a variety of materials. This prosaic statement, however, does not convey the depth of basic understanding which has been developed to fully utilize the advantages of ion implantation. The interaction of a host lattice with the energetic beams produces metastable states and structures which cannot be achieved by other means. However, ion implantation also requires an understanding of the fundamental physics and chemistry that dictate the interaction of the ion beam and the target. In addition to the fundamental nature of the process, ion implantation is important to a wide variety of technologies. While ion implantation has indeed become a technologically important processing component of the semiconductor fabrication and other industries, new developments demonstrate that ion implantation is an important tool for basic research and for future applications, with nanoclustered materials as an intriguing example.

Ion implantation allows low temperature forming of any thermodynamically stable or metastable Matrix-impurity combination that can be annealed in a wide range of temperatures in the movement afterward implantation thermal treatments. As a consequence, this method offers the perfect tool to study phase transformations and atomic transport in solids. Incoming ion piercing into a solid goal, losing their own energy with the support of two independent processes: inelastic collisions with the target electrons and elastic collisions with nuclei of the target [62-65]. First leads to ionized states, which in alloys rapidly target electrons recombine. In most cases, when the target material alloy (withdrawal compose only irradiation spectrum GeV energy) inelastic collisions lead only to the target heating .Elastic collisions between ions and target nuclei may lead to the highest accomplishment hundred keV energy is transmitted, that is, the main exceeding the binding energy of atoms in rigid bodies. These actions lead to collision cascades. Thorough description of the evolution of collision cascades allowed collision may be finding in numerous review articles [63-66].

Ion implantation also allows the reaction between two different atomic species implanted in the inert matrix. Pattern such experiment is described in [67]. The Previous research works for application of ion implantation in the transformation of the surface [65, 66] and were divided into two groups. Most studies of heavy ion implantation are focused on studying the effects of radiation damage or intense ion beams solid interactions. On the other hand, the light element of the ion implantation may well be advantageous to modify the physical structure of the materials near the surface. Being from excessive damage solids free, easy element of physical modification is effective in curing and strengthening solid through ion implantation.

Using implantation to advance processing for a variety of device structures is also becoming more important. Ion beams are used to modify optical properties of dielectric materials to fabricate optical waveguides, other related photonic devices, and novel crystal hosts. Focused ion beams represent another means to produce three-dimensional structures, including those for piezoelectric nanostructures. Likewise the formation of plasmonic nanocomposites using metallic species to form core-shell geometries can be controlled through implantation. In particular, the ion implantation can be used as a simulator to investigate the role of alloying elements or species in the design of coatings, various studies have been reported in the surface modification of the films of metal and clay coatings.

One of the major advantage of ion implantation is the fact that almost all of the process parameters (concentration of contaminants, the temperature, the types of atoms, the defect concentration, etc.) can be controlled independently. Thus, it is possible to study in detail the role of a particular parameter, keeping all other factors constant. This, along with the ability to modify the characteristics of the process in an extremely wide spectrum, makes ion implantation powerful machine in the formation phase and nuclear studies of movement [68]. Nitrogen implanted iron is one of the most well-studied systems in ion implantation metallurgy [69–72]. Detailed phase diagram of nitrogen implanted iron was published in [73].

The remixing of the particles in molecular level, we could use for chemical conversion description the traditional laws of chemical kinetics and diffusion kinetic models. Examples of enough complex similar models one can find in [68].

It is a powerful technique to introduce desired impurities irrespective of chemical and other limitations in and near the surface region of any substrate. It has both accelerator and plasma versions. The latter is cheaper and thus friendly for industry. Ion implantation service is available for partners from industry and can be used for basic and applied research to modify surface-sensitive properties like adhesion, wear, roughness, hardness, corrosion of metal or other materials.

Ion implantation is used in a number of applications, namely,

- Semiconductor doping,
- Synthesis of compound layers,
- Materials modification,
- Understanding the effects of radiation on living tissue.
- Low-temp. Process (can use photoresist as mask)
- Wide selection of masking materials e.g. photoresist, oxide, poly-Si, metal
- Less sensitive to surface cleaning procedures

Ion-implantation represents one method to modify materials, the range of implant conditions provides for some very creative approaches. The ability to optimize the properties of silicon nanoclusters in SiO2 through implantation using a combination of properly chosen annealing and irradiation conditions shows promise. Modification of phase change materials, crystallization rates and phase stability, for example with readily and controllably achieved through implantation of nitrogen or oxygen. Implantation of low energy nitrogen in GaAs also modifies the surface to produce quantum dot structures, alloyed semiconductors or GaN structures, depending on the conditions. Implantation into III-nitrides and ZnO to modify electrical properties has important technological applications as well as the study of interesting physical interactions in these systems.

Alumina, one of the most widely used wear, heat and electrical resistant materials, has a high hardness and excellent chemical stability even at high temperatures. At high contact stresses significant amounts of cracking can occur around scratches in brittle materials. Surface modification by energetic particles leads to surface damage, even though a new functional layer is generated on the materials with improved physical and chemical properties, such as adhesion, surface hardness, corrosion resistance and wear resistance. Implantation-induced changes in the surface charge state may also affect the adhesion of lubricant molecules. An increase of mechanical strength by high energy ion implantation has been attributed to compressive surface residual stress upon volume expansion in the implanted region by introduction of defects. For example the ion implantation of an Al2O3 surface leads to significant modifications of mechanical properties such as hardness, fracture toughness and friction. The properties are very sensitive to the presence of ion species induced by implantation and to modification of the surface composition. The implantation reaction produces Al, AlN or AlON with nitrogen whereas carbon film, Al, Al4C3 or Al4O4C are obtained with carbon, which lead to different physical properties of the resulting samples. The possibility of forming solid-lubricant films, new self-lubricating ceramic-matrix composites, or other reaction layers using ion implantation at low temperatures.

The field of ion implantation is not static. Improvements in equipment, understanding of beam-solid interactions, applications to new materials, and the recent developments to use implantation for nanostructure formation point to new directions for ion implantation.

2.2. General equations

To describe the new phase formation during ion implantation we use isothermal theory of thermal elastic diffusion. It includes the following equations:

Balance equation:

$$\frac{\partial Y_1}{\partial t} = -\frac{\partial J_1}{\partial x} - k_1 Y_1 \;;$$

Where $Y_1 (mol/m^3)$ is molar concentration, $k_1 = \nu_i k \;\; i = 1,2,3-$ is the rate constant for chemical reaction and $\nu_1 = \nu_2 = \nu_3 = 1$.

Generalized diffusion flux equation:

$$J_i = -D_i \frac{\partial Y_i}{\partial x} - t_i \frac{\partial J_i}{\partial t} \;;\; i = 1,2$$

Where $J_i \;\; (mol/m^3 \sec)$ is the $i-$ substance flux, t_i is the relaxation time, $D_i \;\; (m^2/\sec)$ is the diffusion coefficients.

Balance equation for concentration:

$$\frac{\partial Y_1}{\partial t} = -\nabla \cdot \mathbf{J}_1 + \omega_k \;\;;$$

$$\frac{\partial Y_2}{\partial t} = -\nabla \cdot \mathbf{J}_2 + \omega_k \;\;;$$

Where

$$\omega_k = \sum_{i=1}^{r} \nu_{ki} \varphi_i$$

φ_i - ith chemical reaction rate ν_{ki} - stochiometric coefficient of k-component in t-th reaction; r – number of reactions.

Diffusion fluxes:

$$\mathbf{J}_i = -D_i \frac{\partial Y_i}{\partial x} - t_i \frac{\partial J_i}{\partial t} \;;\; i = 1,2$$

where t_i are the relaxation times, D_i are diffusion coefficients of elements in the mixture, $\left(m^2/\sec\right)$.

2.3. General Problem formulation

When particle beam acts on the material surface, and the particle rate is uniform along it, we can restrict the particles redistribution by one-dimensional problem (Fig.1). The form of impulse can be various (Fig.2). When the chemical reaction is possible in the surface layer, the particles (atoms, ions) are consume for new phase formation.

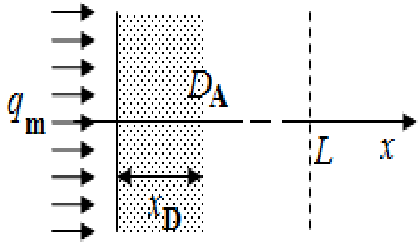


Fig.2.1.Illustration to problem formulation

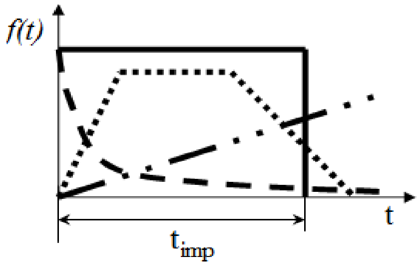


Fig.2.2.Various form of impulses

2.4 Qualitative results

2.4.1. Simple problem without chemical reaction

We can come to irreversible process description step by step starting from simple problems. When particle beam acts on the material surface, chemical reactions are absent, and the particle rate is uniform along it. The simple and known problem without chemical reaction is stated as

The diffusion equation has the form

$$\frac{\partial y_A}{\partial t} = D_A \frac{\partial^2 y_A}{\partial x^2} \tag{2.1}$$

With boundary and initial condition

$$x = 0\,; \quad \mathbf{J}_A = -D_A \frac{\partial y_A}{\partial x} = q_m$$

$$x \to \infty : \ \mathbf{J}_A = 0$$

$$t \to 0 : \ y_A = 0,$$

where y_A is molar concentration of the particles, t is the time, x is the space coordinate in the direction of particle beam action, D_A - is diffusion coefficient, q_m - is particle beam density.

The analytical solution of the known problem can be found by using any integral transform methods and has the form (it is contained in many reference books):

$$y_A = 2\frac{q_m}{\sqrt{D_A}}\sqrt{\frac{t}{\pi}}\left[\exp\left(-\frac{x^2}{4D_A t}\right) - \frac{x}{\sqrt{D_A}} erfc\left(\frac{x}{2\sqrt{D_A t}}\right)\right] \tag{2.2}$$

That is the particle concentration distribution along the coordinate perpendicular to treated surface is monotonic singularity-free function. It is shown on the Fig.3.

Concentration y_A changes in the point $x = 0$ as $\sqrt{t}$. $q_m = 1.5 \ \ mol/(m^2 s)$; $D_A = 10^{-7}$ cm^2/sec

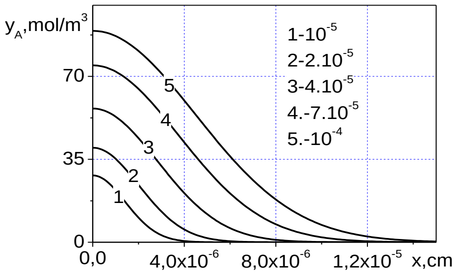


Fig 2.3

2.4.2. Simple problem with chemical reaction

When the chemical reaction is possible in surface layer [74], the particles are consume for new phase formation. Assume the chemical reaction occurs by the simplest scheme

$$A + B \rightarrow C,$$

where the letter B correspond to the substance contained in initial specimen, C – to the reaction product.

The additional term appears in this case in diffusion equation, and we come to the second simple problem.

$$\frac{\partial y_A}{\partial t} = D_A \frac{\partial^2 y_A}{\partial x^2} - k_A y_A \tag{2.3}$$

$$x = 0 : \mathbf{J}_A = -D_A \frac{\partial y_A}{\partial x} = q_m$$

$$x \to \infty : \ \mathbf{J}_A = 0,$$

$$t \to 0 : \ y_A = 0,$$

The exact solution of (2.3) can be calculated by Laplace transformation method and has the form:

$$y_A = \frac{q_m}{2\sqrt{D_A k_A}}\left[\exp\left(-x\sqrt{\frac{k_A}{D_A}}\right)erfc\left(\frac{x}{2\sqrt{D_A t}}-\sqrt{k_A t}\right)-\right.$$
$$\left.-\exp\left(x\sqrt{\frac{k_A}{D_A}}\right)erfc\left(\frac{x}{2\sqrt{D_A t}}+\sqrt{k_A t}\right)\right] \tag{2.4}$$

The formula (2.2) is limit of this solution for $k_A \to 0$.

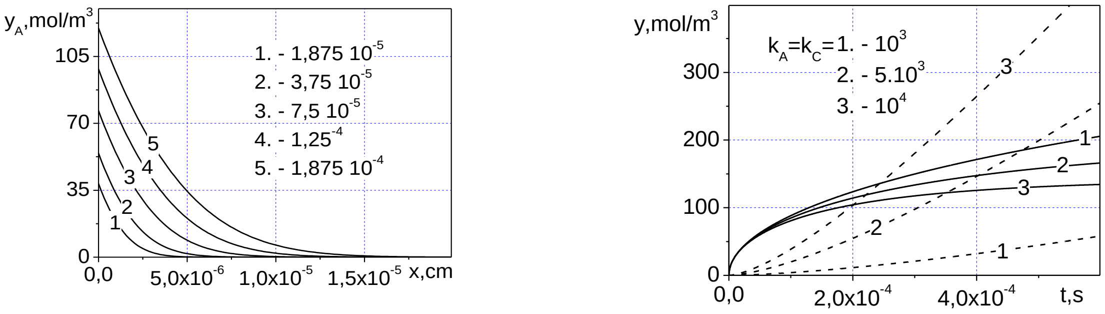
Because the entered particles are consumed for new phase formation, the diffusion concentration decreases in the volume. The product concentration changes by equation

$$\frac{\partial y_C}{\partial t} = \omega_C\ ,\quad \omega_C = k_C y_A \tag{2.5}$$

For simple reaction of first order we can evaluate the product concentration. Using Laplace integral transform method, we shall find

$$y_C = \frac{q_m}{2\sqrt{D_A k_A}} k_C \left[\exp\left(-x\sqrt{\frac{k_A}{D_A}}\right)\int_0^t (t-\tau) erfc\left(\frac{x}{2\sqrt{D_A \tau}}-\sqrt{k_A \tau}\right)d\tau-\right.$$
$$\left.-\exp\left(x\sqrt{\frac{k_A}{D_A}}\right)\int_0^t (t-\tau) erfc\left(\frac{x}{2\sqrt{D_A \tau}}+\sqrt{k_A \tau}\right)d\tau\right] \tag{2.6}$$

The reagent and product concentrations behavior with time is shown on the Fig.(2.4, a, b) in the point $x = 0$. Since the substance A is consumed for new phase formation, the reagent concentration grows slowly.



(a) (b)

Fig.2.4. The dynamics of concentration change. $q_m = 2.5\ \ mol/\left(m^2 s\right)$/; $D_A = 10^{-7}$ cm²/sec ; (a) $k_C = k_A = 10^3$ 1/s; (b) Solid line - y_A; dotted line y_C .

For the analytical solution of the known problem we assume that

$$\mathbf{J}_A = -D_A \frac{\partial y_A}{\partial x} = q_m f(t)$$

We have (2.3)

$$\frac{\partial y_A}{\partial t} = D_A \frac{\partial^2 y_A}{\partial x^2} - k_A y_A$$

Taking Laplace transformation
That is

$$t \to s, \quad Y_A(t) \to Y_A(s)$$

And using the Initial condition, we get $\frac{\partial Y_A}{\partial t} \to \mathrm{sY_A}$

Put these values and simplifying (2.3), we get

$$\mathrm{sY_A} = D_A \frac{d^2 Y_A}{dx^2} - k_A Y_A$$

Or

$$\frac{d^2 Y_A}{dx^2} - \left(\frac{s + k_A}{D_A}\right) Y_A = 0$$

Let $Y_A = ce^{\lambda x}$, be the solution , then

$$\lambda^2 ce^{\lambda x} - \left(\frac{s + k_A}{D_A}\right) ce^{\lambda x} = 0$$

Or

$$\lambda = \pm \sqrt{\frac{s + k_A}{D_A}}$$

So the solution is of the form

$$Y_A = A_1 e^{\lambda x} + A_2 e^{-\lambda x} \tag{2.7}$$

Where A_1 and A_2 are constant to be determined
So for $x = 0$

$$J_A = -D_A \frac{\partial Y_A}{\partial x} \quad \text{where } J_A = q_m f(t)$$

Let $f(t) = e^{-At} \; so \; J_A = q_m f(t) = q_m e^{-At}$

$$\frac{\partial J_A}{\partial t} = -A q_m e^{-At}$$

$$J_A = -D_A \frac{\partial Y_A}{\partial x}$$

$$q_m e^{-At} = -D_A \frac{\partial Y_A}{\partial x}$$

Or

$$-D_A \frac{\partial Y_A}{\partial x} = q_m e^{-At}$$

Again using Laplace transformation

$$-D_A \frac{dY_A(s)}{dx} \to q_m \frac{1}{s+A}$$

Also at $x \to \infty$

$$Y_A = A_2 e^{-\lambda x}$$

So

$$\frac{dY_A}{dx} = -A_2 \lambda e^{-\lambda x} \text{ or } -D_A \frac{dY_A(s)}{dx} = A_2 \lambda D_A e^{-\lambda x}$$

Implies

$$A_2 = \frac{q_m}{D_A \lambda (s+A)}$$

Hence $A_2 = \frac{q_m}{D_A \lambda (s+A)}$, $A_1 = 0$ put in (2.7), gives

$$Y_A = \frac{q_m}{D_A (s+A) \sqrt{\frac{s+k_A}{D_A}}} \exp\left[-\sqrt{\frac{s+k_A}{D_A}}\, x\right]$$

$$y_A = \frac{q_m}{(s+A)\sqrt{s+k_A}} \frac{1}{\sqrt{D_A}} \exp\left[-\sqrt{\frac{s+k_A}{D_A}}\, x\right] \equiv Y_A^0$$

$$Y_A = \frac{q_m}{\sqrt{D_A}} \left[\left(\frac{s}{(s+A)(s+k_A)}\right)\left(\frac{\sqrt{s+k_A}}{s} \exp\left[-\sqrt{\frac{s+k_A}{D_A}}\, x\right]\right)\right] \equiv$$

$$\equiv Y_A^0 = F_1(s) \cdot F_2(s)$$

$$F_1(s) = \frac{s}{s+A} \frac{1}{s+k_A} \div \frac{1}{A-k_A}\left[A \exp(-At) - k_A \exp(-k_A t)\right]$$

,

$$F_2(s) = \frac{\sqrt{s+k_A}}{s} \exp\left[-\sqrt{\frac{s+k_A}{D_A}}\, x\right] \div \frac{1}{\sqrt{\pi t}} \exp\left[-\left(\frac{x^2}{4D_A t} + k_A t\right)\right] +$$

$$+ \frac{\sqrt{k_A}}{2}\left[\exp\left(-x\sqrt{\frac{k_A}{D_A}}\right) erfc\left(\frac{x}{2\sqrt{D_A t}} - \sqrt{k_A t}\right) - \exp\left(x\sqrt{\frac{k_A}{D_A}}\right) erfc\left(\frac{x}{2\sqrt{D_A t}} + \sqrt{k_A t}\right)\right]$$

Therefore, the solution gets the form

$$\begin{aligned} Y_A^0 = \frac{q_m}{\sqrt{D_A}} \int_0^t &\left\{ \frac{A \exp(-A(t-\tau)) - k_A \exp(-k_A(t-\tau))}{A-k} \left\{ \frac{1}{\sqrt{\pi\tau}} \exp\left[-\left(\frac{x^2}{4D_A \tau} + k_A \tau\right)\right] + \right.\right. \\ &\left.\left. + \frac{\sqrt{k_A}}{2}\left[\exp\left(-x\sqrt{\frac{k_A}{D_A}}\right) erfc\left(\frac{x}{2\sqrt{D_A \tau}} - \sqrt{k_A \tau}\right) - \exp\left(x\sqrt{\frac{k_A}{D_A}}\right) erfc\left(\frac{x}{2\sqrt{D_A \tau}} + \sqrt{k_A \tau}\right)\right]\right\}\right\} d\tau \end{aligned}$$

(2.8)

In this case the concentration distribution depends essential on relations between different physical scales: diffusion rate, reaction rate, and reactant intake. Because the mass flux diminishes quickly with time, it is necessary to large reaction rate constant to product appearance would appreciably.

The form of ions source could be different in time. For example, we can write

$$\mathbf{J}_A = -D_A \frac{\partial y_A}{\partial x} = q_m(\alpha + \beta t) \quad \text{or} \quad \mathbf{J}_A = -D_A \frac{\partial y_A}{\partial x} = q_m(1 - \cos(\gamma t))$$

Or

$$\mathbf{J}_A = -D_A \frac{\partial y_A}{\partial x} = \frac{q_m}{1 + \delta t}$$

For these cases, analytical solutions are not possible or are obtained very cumbersome and do not handy for using. Hence, we will use numerical methods.

Conclusions

We have tried to construct some models of thermal elastic diffusion with chemical reaction, for which we need some basic concept that is, ion implantation which is a technique for introducing foreign atoms into materials by bombarding it with energetic ions of the desired species. The process can be carried out at any temperature. One of the major advantage of ion implantation is the fact that almost all of the process parameters (concentration of contaminants, the temperature, the types of atoms, the defect concentration, etc.) can be controlled independently. For mathematical purpose we have designate in detail the equation of motion, the relation between strain and displacement and the compatibility equation which has a key role in the theory of thermal elastic diffusion. The governing equations of generalized thermal elastic diffusion are also demarcated. Regarding to the problem formulation, we have started from the basic and known problem. The solution of the known problem is present in many books in detail. But when the chemical reaction is possible in surface layer, the particles are consume for new phase formation and, the additional term appears in this case in diffusion equation, and hence we come to the second simple problem, where the chemical reaction occurs corresponding to reaction scheme having unit stoichiometric coefficients. In the next problem we take into account three chemical reaction with the molar concentration distribution of $Ni, Al, NiAl$, Ni_3Al. The same problem will correct for other systems, for example $Ti + Al$, $Ni + Ti$.

Finally, we analytically solve the problems by Laplace transformation method, but sometime it is complicated to solve analytically in that case we are trying to approach numerically with different methods, and that’s what we are doing in the next chapter.

Chapter 3

The nonlinear models with chemical reactions

3.1. Description of physical situation

When we have the body, the surface of which is treated uniformly by particle beam with given intensity and given time structure.The isothermal problem describes the composition of surface layer change during particle beam action [75]. The finiteness of relaxation time for mass flux is taken into account. While the concentration distributions for reactants and reaction product depend on relation between various physical scales. We have carried out the analytical solutions and Numerical solution of total problem.

3.2. The problem with summary reaction

Let the chemical reaction occurs correspondingly to reaction scheme

$$\nu_A A + \nu_B B \rightarrow \nu_C C$$

where ν_A, ν_B, ν_C are stoichiometric coefficients. For example, for the systems Ti + Ni, Ti + Al, Ni + Al we can suggest the simplified reaction schemes: $Ti + Ni \rightarrow TiNi$, $Ti + Al \rightarrow TiAl$, $Ni + Al \rightarrow NiAl$, respectively. In this case, the absolute values of stoichiometric coefficients equal to unity $\nu_A = \nu_B = \nu_C = 1$.

In this case, the reaction rate is

$$\varphi = k(T) y_A y_B .$$

When $y_A << y_B$, one can assume

$$\varphi = k'(T) y_A ,$$

where

$$k'(T) = k y_B .$$

In general case, correspondingly to mass action law, the chemical reaction rate could be written as

$$\omega = k {y_A}^{\nu_A} {y_B}^{\nu_B} ,$$

where y_B - is concentration of basic substance. But, in many situations we can assume then the substance is in excess supply, and its concentration does not change practically. Then

$$\omega = k' y_A .$$

This linearization was allowed above using analytical methods.

3.2.1. Mathematical problem formulation

The implanted particles concentration in surface layer can change due to the diffusion and due to the reaction (the particles are consumed in reaction), that the balance equation reproduces

$$\frac{\partial y_A}{\partial t} = -\frac{\partial}{\partial x} \mathbf{J}_A - \omega_A ; \tag{3.1}$$

The implantation process is irreversible, the specific time is very small, and hence we could use for diffusion flux the generalized equation

$$\mathbf{J}_A = -D_A \frac{\partial y_A}{\partial x} - t_A \frac{\partial \mathbf{J}_A}{\partial t} ; \tag{3.2}$$

The boundary and initial conditions take the form

$$x = 0 : \mathbf{J}_A = q_m f(t);$$

$$x \to \infty : y_A = 0 \text{ or } \mathbf{J}_A = 0$$

$$t \to 0 : y_A = 0, \quad \frac{\partial \mathbf{J}_A}{\partial t} = 0$$

Here: y_A - concentration of A-substance (implanted particles, mol/m^3), $\mathbf{J}_A$ is the A-substance flux $(mol/m^3 \sec)$); $\omega_A = k_A y_A = \omega \nu_A$ $(1/\sec)$; $k_A = \nu_A k$ - rate constant for chemical reaction, t_A is the relaxation time , D_A is the diffusion coefficient $(m^2/\sec)$.

3.2.2. Simplification and analytical estimations.

In order to solve the problem analytically we will use the Laplace transformation method. Therefore from equation (3.2) we have

$$\frac{\partial \mathbf{J}_A}{\partial x} = -D_A \frac{\partial^2 y_A}{\partial x^2} - t_A \frac{\partial}{\partial x}\frac{\partial \mathbf{J}_A}{\partial t},$$

and from (3.1)

$$\frac{\partial^2 y_A}{\partial t^2} = -\frac{\partial}{\partial t}\frac{\partial}{\partial x}\mathbf{J}_A + \frac{\partial \omega_A}{\partial t}.$$

Hence

$$\frac{\partial \mathbf{J}_A}{\partial x} = -D_A \frac{\partial^2 y_A}{\partial x^2} + t_A\left(\frac{\partial^2 y_A}{\partial t^2} - \frac{\partial \omega_A}{\partial t}\right)$$

Using the flux derivative from (3.1), we shall find

$$\omega_A - \frac{\partial y_A}{\partial t} = -D_A \frac{\partial^2 y_A}{\partial x^2} + t_A\left(\frac{\partial^2 y_A}{\partial t^2} - \frac{\partial \omega_A}{\partial t}\right) \tag{3.3}$$

Where t_A is the relaxation time, for which we are discussing two cases.

Case-I. *When relaxation time is not equal to zero,* $t_A \neq 0$, we have

$$t_A \frac{\partial^2 Y_A}{\partial t^2} + \frac{\partial Y_A}{\partial t} = D_A \frac{\partial^2 Y_A}{\partial x^2} - k_A y_A \tag{3.4}$$

Taking Laplace transformation

That is

$$t \to s, \; Y_A(t) \to Y_A(s)$$

And using the Initial condition, we get

$$\frac{\partial^2 Y_A}{\partial t^2} \to s^2 Y_A \;, \quad \frac{\partial Y_A}{\partial t} \to s Y_A$$

Put these values and simplifying (3.4), we get

$$t_A s^2 Y_A + s Y_A = D_A \frac{d^2 Y_A}{dx^2} - k_A Y_A$$

Or

$$\frac{d^2Y_A}{dx^2}-\left(\frac{t_As^2+s+k_A}{D_A}\right)Y_A=0$$

Let $Y_A=ce^{\lambda x}$, be the solution , then

$$\lambda^2ce^{\lambda x}-\left(\frac{t_As^2+s+k_A}{D_A}\right)ce^{\lambda x}=0$$

Or

$$\lambda=\pm\sqrt{\frac{t_As^2+s+k_A}{D_A}}$$

So the solution is of the form

$$Y_A=A_1e^{\lambda x}+A_2e^{-\lambda x} \tag{3.5}$$

Where A_1 and A_2 are constant to be determined

So for $x=0$

$$J_A=-D_A\frac{\partial Y_A}{\partial x}-t_A\frac{\partial J_A}{\partial t} \quad \text{where} \quad J_A=q_mf(t)$$

Let $f(t)=e^{-At}\; so\; J_A=q_mf(t)=q_me^{-At}$

$$\frac{\partial J_A}{\partial t}=-Aq_me^{-At}$$

$$J_A=-D_A\frac{\partial Y_A}{\partial x}+At_Aq_me^{-At}$$

$$q_me^{-At}-At_Aq_me^{-At}=-D_A\frac{\partial Y_A}{\partial x}$$

Or

$$-D_A\frac{\partial Y_A}{\partial x}=q_m(1-At_A)e^{-At}$$

Again using Laplace transformation

$$-D_A\frac{dY_A(s)}{dx}\rightarrow q_mq_m(1-At_A)\frac{1}{s+A}$$

Also at $x\rightarrow\infty$

$$Y_A=A_2e^{-\lambda x}$$

So

$$\frac{dY_A}{dx}=-A_2\lambda e^{-\lambda x}\; or\; -D_A\frac{dY_A(s)}{dx}=A_2\lambda D_Ae^{-\lambda x}$$

Implies

$$A_2=\frac{q_m(1-At_A)}{D_A\lambda(s+A)},$$

Hence $A_2=\dfrac{q_m(1-At_A)}{D_A\lambda(s+A)},\; A_1=0$ put in (3.5), gives

$$Y_A = \frac{q_m\left(1-At_A\right)}{D_A\left(s+A\right)\sqrt{\frac{t_A s^2+s+k_A}{D_A}}}\exp\left[-\sqrt{\frac{t_A s^2+s+k_A}{D_A}}x\right]$$

Using Lorient series and taking t_A small, we have

$$Y_A \approx Y_A^0\Big|_{t_A=0} + \left(\frac{\partial Y_A}{\partial t_A}\right)\Big|_{t_A=0} t_A + O\left(t_A{}^2\right)$$

$$Y_A^0\Big|_{t_A=0} = \frac{q_m}{D_A\left(s+A\right)\sqrt{\frac{s+k_A}{D_A}}}\exp\left[-\sqrt{\frac{s+k_A}{D_A}}x\right]$$

$$\left(\frac{\partial Y_A}{\partial t_A}\right)\Big|_{t_A=0} = -\frac{q_m A}{D_A\left(s+A\right)\sqrt{\frac{s+k_A}{D_A}}}\exp\left[-\sqrt{\frac{s+k_A}{D_A}}x\right]-$$

$$-\frac{q_m\, x\, s^2}{2D_A\left(s+A\right)\left(s+k_A\right)}\exp\left[-\sqrt{\frac{s+k_A}{D_A}}x\right]-\frac{q_m\, s^2}{2D_A\left(s+A\right)\left(\frac{s+k_A}{D_A}\right)^{\frac{3}{2}}}\exp\left[-\sqrt{\frac{s+k_A}{D_A}}x\right]$$

$$Y_A^0 = \frac{q_m}{D_A}F_1(s)\cdot F_2(s) = \frac{q_m}{D_A}\left(\frac{s}{s+A}\,\frac{\sqrt{D_A}}{s+k_A}\right)\frac{\sqrt{s+k_A}}{s}\exp\left[-\sqrt{\frac{s+k_A}{D_A}}x\right]$$

$$F_1(s) = \frac{s}{s+A}\,\frac{\sqrt{D_A}}{s+k_A} = \sqrt{D_A}\left[\frac{A}{A-k_A}\,\frac{1}{s+A}-\frac{k_A}{A-k_A}\,\frac{1}{s+k_A}\right] \to \frac{\sqrt{D_A}}{A-k_A}\left(Ae^{-At}-k_A e^{-k_A t}\right)$$

$$F_2(s) = \frac{\sqrt{s+k_A}}{s}\exp\left[-\sqrt{\frac{s+k_A}{D_A}}x\right] \to \frac{1}{\sqrt{\pi t}}\exp\left[-\left(\frac{x^2}{4D_A t}+k_A t\right)\right]+$$

$$+\frac{\sqrt{k_A}}{2}\left(\exp\left[-x\sqrt{\frac{k_A}{D_A}}\right]erfc\left(\frac{x}{2\sqrt{D_A t}}-\sqrt{k_A t}\right)-\exp\left[-x\sqrt{\frac{k_A}{D_A}}\right]erfc\left(\frac{x}{2\sqrt{D_A t}}+\sqrt{k_A t}\right)\right)$$

$$Y_A^0 \to Y_A^0 = \frac{q_m}{D_A}\int_0^t F_1(t-\tau)\cdot F_2(\tau)\,d\tau$$

$$Y_A^0 \to Y_A^0 = \frac{q_m}{D_A}\,\frac{1}{A-k}\int_0^t\left(Ae^{-A(t-\tau)}-k_A e^{-k_A(t-\tau)}\right)\left\{\frac{1}{\sqrt{\pi t}}\exp\left[-\left(\frac{x^2}{4D_A\tau}+k_A\tau\right)\right]+\right.$$

$$\left.+\frac{\sqrt{k_A}}{2}\left(\exp\left[-x\sqrt{\frac{k_A}{D_A}}\right]erfc\left(\frac{x}{2\sqrt{D_A\tau}}-\sqrt{k_A\tau}\right)-\exp\left[-x\sqrt{\frac{k_A}{D_A}}\right]erfc\left(\frac{x}{2\sqrt{D_A\tau}}+\sqrt{k_A\tau}\right)\right)\right\}d\tau$$

Now

$$Y_A^{(1)} = I_1+I_2+I_3$$

$$I_1 = -\frac{q_m A}{D_A}\frac{1}{s+A}\frac{1}{\sqrt{\frac{s+k_A}{D_A}}}\exp\left[-\sqrt{\frac{s+k_A}{D_A}}x\right] =$$

$$= -\frac{q_m A}{\sqrt{D_A}}\left(\frac{1}{s+A}\frac{s}{s+k_A}\right)\left(\frac{\sqrt{s+k_A}}{s}\exp\left[-\sqrt{\frac{s+k_A}{D_A}}x\right]\right)$$

$$= -\frac{q_m A}{\sqrt{D_A}}\left[\frac{A}{A-k_A}\frac{1}{s+A}-\frac{k_A}{A-k_A}\frac{1}{s+k_A}\right]F_2(s)$$

$$= -\frac{q_m A}{\sqrt{D_A}}\frac{1}{A-k_A}\left[\frac{A}{s+A}-\frac{k_A}{s+k_A}\right]F_2(s)$$

$$= -\frac{q_m A}{\sqrt{D_A}}\frac{1}{A-k_A}F_1(s)F_2(s)$$

$$I_1 \to I_1 = -\frac{q_m A}{\sqrt{D_A}}\frac{1}{A-k}\int_0^t\left(Ae^{-A(t-\tau)}-k_A e^{-k_A(t-\tau)}\right)\left\{\frac{1}{\sqrt{\pi t}}\exp\left[-\left(\frac{x^2}{4D_A\tau}+k_A\tau\right)\right]+\right.$$

$$\left.+\frac{\sqrt{k_A}}{2}\left(\exp\left[-x\sqrt{\frac{k_A}{D_A}}\right]erfc\left(\frac{x}{2\sqrt{D_A\tau}}-\sqrt{k_A\tau}\right)-\exp\left[-x\sqrt{\frac{k_A}{D_A}}\right]erfc\left(\frac{x}{2\sqrt{D_A\tau}}+\sqrt{k_A\tau}\right)\right)\right\}d\tau$$

$$I_2 = -\frac{q_m x}{2D_A}\frac{s^2}{(s+A)(s+k_A)}\exp\left[-\sqrt{\frac{s+k_A}{D_A}}x\right] =$$

$$= -\frac{q_m x}{2D_A}\left(\frac{s^2}{(s+A)(s+k_A)}\right)\exp\left[-\frac{x}{\sqrt{D_A}}\sqrt{s}\right]\exp\left[-\frac{k_A x}{2\sqrt{D_A}}\frac{1}{\sqrt{s}}\right]$$

$$= -\frac{q_m x}{2D_A}\left(1+\frac{k_A^2}{A-k_A}\frac{1}{s+k_A}-\frac{A^2}{A-k_A}\frac{1}{s+A}\right)\exp\left[-\frac{x}{\sqrt{D_A}}\sqrt{s}\right]\left(1-\frac{k_A x}{2\sqrt{D_A}}\frac{1}{\sqrt{s}}\right)$$

$$where\ \left|\frac{k_A x}{2\sqrt{D_A}}\frac{1}{\sqrt{\pi t}}\right| << 1$$

$$= -\frac{q_m x}{2D_A}\left(1+\frac{k_A^2}{A-k_A}\frac{1}{s+k_A}-\frac{A^2}{A-k_A}\frac{1}{s+A}\right)\left(\exp\left[-\frac{x}{\sqrt{D_A}}\sqrt{s}\right]-\frac{k_A x}{2\sqrt{D_A}}\frac{\exp\left[-\frac{x}{\sqrt{D_A}}\sqrt{s}\right]}{\sqrt{s}}\right)$$

$$where\ \left|\frac{k_A x}{2\sqrt{D_A}}\frac{1}{\sqrt{\pi t}}\right| << 1$$

$$= -\frac{q_m x}{2D_A}\left(\exp\left[-\frac{x}{\sqrt{D_A}}\sqrt{s}\right]-\frac{k_A x}{2\sqrt{D_A}}\frac{\exp\left[-\frac{x}{\sqrt{D_A}}\sqrt{s}\right]}{\sqrt{s}}\right)-$$

$$-\frac{q_m x}{2D_A}\frac{1}{A-k_A}\left(\frac{k_A^2}{s+k_A}-\frac{A^2}{s+A}\right)\left(\exp\left[-\frac{x}{\sqrt{D_A}}\sqrt{s}\right]-\frac{k_A x}{2\sqrt{D_A}}\frac{\exp\left[-\frac{x}{\sqrt{D_A}}\sqrt{s}\right]}{\sqrt{s}}\right)$$

$$where\ \left|\frac{k_A x}{2\sqrt{D_A}}\frac{1}{\sqrt{\pi t}}\right|<<1$$

$$I_2=-\frac{q_m x}{2D_A}F_4-\frac{q_m x}{2D_A}\frac{1}{A-k_A}F_3(s)\cdot F_4(s)\quad where\ \left|\frac{k_A x}{2\sqrt{D_A}}\frac{1}{\sqrt{\pi t}}\right|<<1$$

$$F_4(s)=\left(\exp\left[-\frac{x}{\sqrt{D_A}}\sqrt{s}\right]-\frac{k_A x}{2\sqrt{D_A}}\frac{\exp\left[-\frac{x}{\sqrt{D_A}}\sqrt{s}\right]}{\sqrt{s}}\right)\rightarrow$$

$$\rightarrow\frac{x}{2\sqrt{D_A}}\frac{\exp\left[-\frac{x^2}{4D_A t}\right]}{\sqrt{\pi t^3}}-\frac{k_A x}{\sqrt{D_A}}\frac{\exp\left[-\frac{x^2}{4D_A t}\right]}{\sqrt{\pi t}}$$

$$F_3(s)=\left[\frac{k_A^2}{s+k_A}-\frac{A^2}{s+A}\right]\rightarrow\left(k_A^2 e^{-k_A t}-A^2 e^{-At}\right)$$

$$I_2\rightarrow I_2=-\frac{q_m x}{2D_A}\left(\frac{x}{2\sqrt{D_A}}\frac{\exp\left[-\frac{x^2}{4D_A t}\right]}{\sqrt{\pi t^3}}-\frac{k_A x}{\sqrt{D_A}}\frac{\exp\left[-\frac{x^2}{4D_A t}\right]}{\sqrt{\pi t}}\right)-$$

$$-\frac{q_m x}{2D_A}\frac{1}{A-k_A}\int_0^t\left(k_A^2 e^{-k_A(t-\tau)}-A^2 e^{-A(t-\tau)}\right)\cdot\left(\frac{x}{2\sqrt{D_A}}\frac{\exp\left[-\frac{x^2}{4D_A\tau}\right]}{\sqrt{\pi\tau^3}}-\frac{k_A x}{\sqrt{D_A}}\frac{\exp\left[-\frac{x^2}{4D_A\tau}\right]}{\sqrt{\pi\tau}}\right)\text{where}$$

$$t>>\frac{k_A^2 x^2}{4D_A\pi}$$

$$I_3=-\frac{q_m D_A^{\frac{3}{2}}}{2D_A}\frac{s^2}{(s+A)(s+k_A)^{\frac{3}{2}}}\exp\left[-\sqrt{\frac{s+k_A}{D_A}}x\right]=$$

$$=-\frac{q_m}{2\sqrt{D_A}}\left(\frac{s^3}{(s+A)(s+k_A)^2}\right)\left(\frac{\sqrt{s+k_A}}{s}\exp\left[-\sqrt{\frac{s+k_A}{D_A}}x\right]\right)$$

$$=-\frac{q_m}{2\sqrt{D_A}}\left(1-\frac{A^3}{(A-k_A)^2}\frac{1}{s+A}+\frac{k_A^2(3A-2k_A)}{(A-k_A)^2}\frac{1}{s+k_A}-\frac{k_A^3}{A-k_A}\frac{1}{(s+k_A)^2}\right)F_2(s)$$

$$= -\frac{q_m}{2\sqrt{D_A}} F_2(s) + \frac{q_m}{2\sqrt{D_A}} \left(\frac{A^3}{(A-k_A)^2} \frac{1}{s+A} - \frac{k_A^2(3A-2k_A)}{(A-k_A)^2} \frac{1}{s+k_A} + \frac{k_A^3}{A-k_A} \frac{1}{(s+k_A)^2} \right) F_2(s)$$

$$F_6(s) = \left(\frac{A^3}{(A-k_A)^2} \frac{1}{s+A} - \frac{k_A^2(3A-2k_A)}{(A-k_A)^2} \frac{1}{s+k_A} + \frac{k_A^3}{A-k_A} \frac{1}{(s+k_A)^2} \right)$$

$$= \frac{A^3}{(A-k_A)^2} e^{-At} - \frac{k_A^2(3A-2k_A)}{(A-k_A)^2} e^{-k_A t} + \frac{k_A^3}{A-k_A} t\, e^{-k_A t}$$

$$I_3 \to I_3 = -\frac{q_m}{2\sqrt{D_A}} \frac{1}{\sqrt{\pi t}} \exp\left[-\left(\frac{x^2}{4D_A t} + k_A t \right) \right] +$$

$$+ \frac{\sqrt{k_A}}{2} \left(\exp\left[-x\sqrt{\frac{k_A}{D_A}} \right] erfc\left(\frac{x}{2\sqrt{D_A t}} - \sqrt{k_A t} \right) - \exp\left[-x\sqrt{\frac{k_A}{D_A}} \right] erfc\left(\frac{x}{2\sqrt{D_A t}} + \sqrt{k_A t} \right) \right) +$$

$$+ \frac{q_m}{2\sqrt{D_A}} \int_0^t \left(\frac{A^3}{(A-k_A)^2} e^{-A(t-\tau)} - \frac{k_A^2(3A-2k_A)}{(A-k_A)^2} e^{-k_A(t-\tau)} + \frac{k_A^3}{A-k_A} t\, e^{-k_A(t-\tau)} \right) \cdot$$

$$\cdot \left(\frac{1}{\sqrt{\pi t}} \exp\left[-\left(\frac{x^2}{4D_A \tau} + k_A \tau \right) \right] \right) +$$

$$+ \frac{\sqrt{k_A}}{2} \left(\exp\left[-x\sqrt{\frac{k_A}{D_A}} \right] erfc\left(\frac{x}{2\sqrt{D_A \tau}} - \sqrt{k_A \tau} \right) - \exp\left[-x\sqrt{\frac{k_A}{D_A}} \right] erfc\left(\frac{x}{2\sqrt{D_A \tau}} + \sqrt{k_A \tau} \right) \right) d\tau$$

Thus

$$Y_A^{(1)} = I_1 + I_2 + I_3$$

$$Y_A^{(1)} = \left\{ -\frac{q_m A}{\sqrt{D_A}} \frac{1}{A-k} \int_0^t \left(Ae^{-A(t-\tau)} - k_A e^{-k_A(t-\tau)} \right) \left\{ \frac{1}{\sqrt{\pi t}} \exp\left[-\left(\frac{x^2}{4D_A \tau} + k_A \tau \right) \right] + \right.\right.$$

$$\left.\left. + \frac{\sqrt{k_A}}{2} \left(\exp\left[-x\sqrt{\frac{k_A}{D_A}} \right] erfc\left(\frac{x}{2\sqrt{D_A \tau}} - \sqrt{k_A \tau} \right) - \exp\left[-x\sqrt{\frac{k_A}{D_A}} \right] erfc\left(\frac{x}{2\sqrt{D_A \tau}} + \sqrt{k_A \tau} \right) \right) \right\} d\tau \right\} +$$

$$+ \left\{ -\frac{q_m x}{2D_A} \left(\frac{x}{2\sqrt{D_A}} \frac{\exp\left[-\frac{x^2}{4D_A t} \right]}{\sqrt{\pi t^3}} - \frac{k_A x}{\sqrt{D_A}} \frac{\exp\left[-\frac{x^2}{4D_A t} \right]}{\sqrt{\pi t}} \right) - \right.$$

$$\left. -\frac{q_m x}{2D_A} \frac{1}{A-k_A} \int_0^t \left(k_A^2 e^{-k_A(t-\tau)} - A^2 e^{-A(t-\tau)} \right) \cdot \left(\frac{x}{2\sqrt{D_A}} \frac{\exp\left[-\frac{x^2}{4D_A \tau} \right]}{\sqrt{\pi \tau^3}} - \frac{k_A x}{\sqrt{D_A}} \frac{\exp\left[-\frac{x^2}{4D_A \tau} \right]}{\sqrt{\pi \tau}} \right) \right\} +$$

$$+ \left\{ -\frac{q_m}{2\sqrt{D_A}} \frac{1}{\sqrt{\pi t}} \exp\left[-\left(\frac{x^2}{4D_A t} + k_A t \right) \right] + \right.$$

$$+\frac{\sqrt{k_A}}{2}\Bigg(\exp\left[-x\sqrt{\frac{k_A}{D_A}}\right]erfc\left(\frac{x}{2\sqrt{D_A t}}-\sqrt{k_A t}\right)-\exp\left[-x\sqrt{\frac{k_A}{D_A}}\right]erfc\left(\frac{x}{2\sqrt{D_A t}}+\sqrt{k_A t}\right)\Bigg)\Bigg)+$$

$$+\frac{q_m}{2\sqrt{D_A}}\int_0^t\left(\frac{A^3}{(A-k_A)^2}e^{-A(t-\tau)}-\frac{k_A^2(3A-2k_A)}{(A-k_A)^2}e^{-k_A(t-\tau)}+\frac{k_A^3}{A-k_A}t\,e^{-k_A(t-\tau)}\right)\cdot$$

$$\frac{1}{\sqrt{\pi t}}\exp\left[-\left(\frac{x^2}{4D_A\tau}+k_A\tau\right)\right]+$$

$$+\frac{\sqrt{k_A}}{2}\left(\exp\left[-x\sqrt{\frac{k_A}{D_A}}\right]erfc\left(\frac{x}{2\sqrt{D_A\tau}}-\sqrt{k_A\tau}\right)-\exp\left[-x\sqrt{\frac{k_A}{D_A}}\right]erfc\left(\frac{x}{2\sqrt{D_A\tau}}+\sqrt{k_A\tau}\right)\right)d\tau\Bigg\}$$

$$where\ \ t >> \frac{k_A^2x^2}{4D_A\pi}$$

$$Y_A^{(1)}=-\frac{q_m A}{\sqrt{D_A}}\Bigg\{\frac{1}{\sqrt{\pi t}}\exp\left[-\left(\frac{x^2}{4D_A\tau}+k_A\tau\right)\right]+$$

$$+\frac{\sqrt{k_A}}{2}\left(\exp\left[-x\sqrt{\frac{k_A}{D_A}}\right]erfc\left(\frac{x}{2\sqrt{D_A\tau}}-\sqrt{k_A\tau}\right)-\exp\left[-x\sqrt{\frac{k_A}{D_A}}\right]erfc\left(\frac{x}{2\sqrt{D_A\tau}}+\sqrt{k_A\tau}\right)\right)\Bigg\}-$$

$$-\frac{q_m x^2}{2D^{\frac{3}{2}}{}_A}\left(\frac{\exp\left[-\frac{x^2}{4D_A t}\right]}{2\sqrt{\pi t^3}}-k_A\frac{\exp\left[-\frac{x^2}{4D_A t}\right]}{\sqrt{\pi t}}\right)$$

$$-\frac{q_m x^2}{2D^{\frac{3}{2}}{}_A}\frac{1}{A-k_A}\int_0^t\left(k_A^2e^{-k_A(t-\tau)}-A^2e^{-A(t-\tau)}\right)\cdot\left(\frac{\exp\left[-\frac{x^2}{4D_A\tau}\right]}{\sqrt{\pi\tau^3}}-k_A\frac{\exp\left[-\frac{x^2}{4D_A\tau}\right]}{\sqrt{\pi\tau}}\right)d\tau+$$

$$+\left(\frac{-q_m A}{\sqrt{D_A}(A-k_A)}+\frac{q_m}{2\sqrt{D_A}}\right)\int_0^t\Bigg(\left(A+\frac{A^3}{(A-k_A)^2}\right)e^{-A(t-\tau)}-$$

$$-\left(k+\frac{k_A^2(3A-2k_A)}{(A-k_A)^2}+\frac{k_A^3(t-\tau)}{A-k_A}\right)e^{-k_A(t-\tau)}\Bigg)\cdot\left(\frac{1}{\sqrt{\pi t}}\exp\left[-\left(\frac{x^2}{4D_A\tau}+k_A\tau\right)\right]\right)+$$

$$+\frac{\sqrt{k_A}}{2}\left(\exp\left[-x\sqrt{\frac{k_A}{D_A}}\right]erfc\left(\frac{x}{2\sqrt{D_A\tau}}-\sqrt{k_A\tau}\right)-\exp\left[-x\sqrt{\frac{k_A}{D_A}}\right]erfc\left(\frac{x}{2\sqrt{D_A\tau}}+\sqrt{k_A\tau}\right)\right)d\tau\Bigg\}$$

$$where\ \ t >> \frac{k_A^2x^2}{4D_A\pi}$$

Now

$$Y_A \approx Y_A^0\Big|_{t_A=0} + \left(\frac{\partial Y_A}{\partial t_A}\right)\Bigg|_{t_A=0} t_A$$

That is

$$Y_A \to Y_A = Y_A^0 + Y_A^{(1)}\, t_A$$

Implies that when $t_A \neq 0$

$$t >> \frac{k_A^2 x^2}{4D_A\pi}$$

$$Y_A^{(1)} = -\frac{q_m\, t_A}{\sqrt{D_A}}\left\{\frac{1}{\sqrt{\pi t}}\exp\left[-\left(\frac{x^2}{4D_A\tau}+k_A\tau\right)\right]+\right.$$

$$\left.+\frac{\sqrt{k_A}}{2}\left(\exp\left[-x\sqrt{\frac{k_A}{D_A}}\right]erfc\left(\frac{x}{2\sqrt{D_A\tau}}-\sqrt{k_A\tau}\right)-\exp\left[-x\sqrt{\frac{k_A}{D_A}}\right]erfc\left(\frac{x}{2\sqrt{D_A\tau}}+\sqrt{k_A\tau}\right)\right)\right\}-$$

$$-\frac{q_m\, x^2}{2D^{\frac{3}{2}}{}_A}\left(\frac{1}{2\sqrt{\pi t^3}}-\frac{k_A}{\sqrt{\pi t}}\right)\exp\left[-\frac{x^2}{4D_A t}\right]$$

$$-\frac{q_m\, x^2}{2D^{\frac{3}{2}}{}_A}\frac{1}{A-k_A}\int_0^t\left(k_A^2 e^{-k_A(t-\tau)}-A^2 e^{-A(t-\tau)}\right)\cdot\left(\frac{\exp\left[-\dfrac{x^2}{4D_A\tau}\right]}{\sqrt{\pi\tau^3}}-k_A\frac{\exp\left[-\dfrac{x^2}{4D_A\tau}\right]}{\sqrt{\pi\tau}}\right)d\tau+$$

$$+\left(\frac{q_m(1-At_A)}{\sqrt{D_A}(A-k_A)}+\frac{q_m}{2\sqrt{D_A}}\right)\int_0^t\left(\left(2A+\frac{A^3}{(A-k_A)^2}\right)e^{-A(t-\tau)}-\right.$$

$$\left(2k+\frac{k_A^2(3A-2k_A)}{(A-k_A)^2}+\frac{k_A^3(t-\tau)}{A-k_A}\right)e^{-k_A(t-\tau)}\Bigg)\cdot\left(\frac{1}{\sqrt{\pi t}}\exp\left[-\left(\frac{x^2}{4D_A\tau}+k_A\tau\right)\right]\right)+$$

$$+\frac{\sqrt{k_A}}{2}\left(\exp\left[-x\sqrt{\frac{k_A}{D_A}}\right]erfc\left(\frac{x}{2\sqrt{D_A\tau}}-\sqrt{k_A\tau}\right)-\exp\left[-x\sqrt{\frac{k_A}{D_A}}\right]erfc\left(\frac{x}{2\sqrt{D_A\tau}}+\sqrt{k_A\tau}\right)\right)d\tau\Bigg\}$$

$$where\ \ t >> \frac{k_A^2 x^2}{4D_A\pi}$$

The exact analytical solution can be obtained for some other functions $f(t)$.

Case-II. When the relaxation time is equal to zero

When, $t_A = 0$ the analytical solutions can be found without any complexity using Laplace integral transform method, for $f(t) = 1$, we shall obtain (2.4).

3.2.3. Numerical algorithm

The difference between two neighboring values of the function y_A in neighboring mesh points is finite difference of first order Backward difference scheme $\nabla y_{A.j}$, Forward difference scheme $\Delta y_{A.j}$ and Central difference $\delta y_{A,j} = \frac{1}{2}\left(\Delta y_{A,j} + \nabla y_{A,j}\right)$. The finite difference of second order can be present as

$$\Delta^2 y_{A,j} = \Delta\left(\Delta y_{A,j}\right) = \Delta\left(y_{A,j+1} - y_{A,j}\right) = y_{A,j+2} - 2y_{A,j+1} + y_{A,j}$$

$$\Delta\nabla y_{A,j} = \Delta\left(y_{A,j} - y_{A,j-1}\right) = y_{A,j+1} - 2y_{A,j} + y_{A,j-1}$$

or

$$\Delta^2 y_{A,j} = \Delta\nabla y_{A,j+1} .$$

Here the symbol Δ is used for difference designation.
Then the difference of m-order can be written as

$$\Delta^m y_{A,j} = \Delta\left(\Delta^{m-1} y_{A,j}\right)$$

For first and second space derivatives we can write the difference approximation as

$$\frac{\partial y_A}{\partial x} \to \frac{y_{A,j} - y_{A,j-1}}{h} ; \frac{y_{A,j+1} - y_{A,j}}{h} ; \frac{y_{A,j+1} - y_{A,j-1}}{2h}$$

$$\frac{\partial^2 y_A}{\partial x^2} \approx \frac{y_{A,j+1} - 2y_{A,j} + y_{A,j-1}}{h^2}$$

We introduce the discrete time points

$$\Delta t = \tau ,\ t_k = \tau \cdot k ,\ k = 0,1,2,...$$

For time derivatives we have

$$\frac{\partial y_A}{\partial t} \approx \frac{y_{A,j}^{k+1} - y_{A,j}^{k-1}}{2\tau} \quad \text{or} \quad \frac{\partial y_A}{\partial t} \approx \frac{y_{A,j}^{k+1} - y_{A,j}^{k}}{\tau} \quad \text{or} \quad \frac{\partial y_A}{\partial t} \approx \frac{y_{A,j}^{k} - y_{A,j}^{k-1}}{\tau}$$

$$\frac{\partial^2 y_A}{\partial t^2} \approx \frac{y_{A,j}^{k+1} - 2y_{A,j}^{k} + y_{A,j}^{k-1}}{\tau^2}$$

We call time point as time layer. And we can calculate the space derivative in any time layer. We will use the designations:

$$y_{A,j}^{k+1} = \hat{y}_{A,j} ; y_{A,j}^{k} = y_{A,j} ; y_{A,j}^{k-1} = \breve{y}_{A,j}$$

Now we come to our problem. In order to solve the problem numerically, from equation (3.2) we have

$$\frac{\partial \mathbf{J}_A}{\partial x} = -D_A \frac{\partial^2 y_A}{\partial x^2} - t_A \frac{\partial}{\partial x}\frac{\partial \mathbf{J}_A}{\partial t} ,$$

and from (3.1)

$$\frac{\partial^2 y_A}{\partial t^2} = -\frac{\partial}{\partial t}\frac{\partial}{\partial x}\mathbf{J}_A + \frac{\partial \omega_A}{\partial t}.$$

Hence

$$\frac{\partial \mathbf{J}_A}{\partial x} = -D_A \frac{\partial^2 y_A}{\partial x^2} + t_A\left(\frac{\partial^2 y_A}{\partial t^2} - \frac{\partial \omega_A}{\partial t}\right)$$

Using the flux derivative from (3.1), we shall find

$$\omega_A - \frac{\partial y_A}{\partial t} = -D_A \frac{\partial^2 y_A}{\partial x^2} + t_A\left(\frac{\partial^2 y_A}{\partial t^2} - \frac{\partial \omega_A}{\partial t}\right) \qquad (3.6)$$

Or for given kinetics

$$\frac{t_A}{1+t_A k_A}\frac{\partial^2 y_A}{\partial t^2} + \frac{\partial y_A}{\partial t} = \frac{D_A}{1+t_A k_A}\frac{\partial^2 y_A}{\partial x^2} - \frac{k_A}{1+t_A k_A} y_A \qquad (3.7)$$

We have several specific physical scales. For example time scales are k_A^{-1}; A^{-1}; t_A and space scale are $\sqrt{D_A t_A}$; $\sqrt{D_A A^{-1}}$; $\sqrt{D_A k_A^{-1}}$ .The result of the solution depends on proportions between scales. We solve the problem (3.7) numerically with initial and boundary condition below

$$x = 0: \quad -D_A \frac{\partial y_A}{\partial x} = q_m (1 - t_A A)\exp(-At);$$

$$x \to \infty: \; y_A = 0 \text{ or } \mathbf{J}_A = 0;$$

$$t = 0: \; y_A = 0; \quad \frac{\partial \mathbf{J}_A}{\partial t} = 0;$$

The numerical solution of the problem carried out by using implicit difference scheme, which leads from differential equation (3.7) to the equation in finite differences.

$$\frac{t_A}{1+t_A k_A}\frac{\hat{y}_{Ai} - 2y_{Ai} + \check{y}_{Ai}}{\tau^2} + \frac{\hat{y}_{Ai} - y_{Ai}}{\tau} = \frac{D_A}{1+t_A k_A}\frac{\hat{y}_{Ai+1} - 2\hat{y}_{Ai} + \hat{y}_{Ai-1}}{\tau^2} - \frac{k_A}{1+t_A k_A}\hat{y}_A$$

The implicit difference scheme of (3.7) takes the form

$$\frac{t_A}{1+t_A k_A}\frac{{y_{Ai}}^{j+1} - 2{y_{Ai}}^{j} + {y_{Ai}}^{j-1}}{\tau^2} + \frac{{y_{Ai}}^{j+1} - {y_{Ai}}^{j}}{\tau} =$$

$$= \frac{D_A}{1+t_A k_A}\frac{{y_{Ai+1}}^{j+1} - 2{y_{Ai}}^{j+1} + {y_{Ai-1}}^{j+1}}{h^2} - \frac{k_A}{1+t_A k_A}{y_{Ai}}^{j+1}$$

In this case we obtain the linear equations system which could be solved by double-sweep method. In computation area we introduce the difference mesh. Let h - mesh step. Then instead of continuous space coordinate we come to discrete space points

$$x_i = j \cdot h, \quad j = 0,1,2,\dots,n$$

where n is point number in integration interval.

In cases of implicit difference schemes and in some stationary problems, we have obtain the algebraic equation system of the form

$$a_j u_{j-1} - c_j u_j + b_j u_{j+1} = -f_j \qquad (3.8)$$
$$a_j \neq 0, b_j \neq 0;\ j = 1,2,\ldots, N-1$$

Let us Assume that the equality

$$u_j = \alpha_{j+1} u_{j+1} + \beta_{j+1}$$

takes a place. Here α_{j+1}, β_{j+1} are double-sweep coefficients which are undefined now. Hence

$$u_{j-1} = \alpha_j u_j + \beta_j \qquad (3.9)$$

Substituting (3.9) in the equation (3.8), we obtain

$$a_j \left(\alpha_j u_j + \beta_j\right) - c_j u_j + b_j u_{j+1} = -f_j$$

Or

$$u_j \left(a_j \alpha_j - c_j\right) + b_j u_{j+1} = -\left(f_j + a_j \beta_j\right).$$

Hence, we come to correlations

$$\alpha_{j+1} = \frac{b_j}{c_j - a_j \alpha_j}, \qquad \beta_{j+1} = \frac{a_j \beta_j + f_j}{c_j - a_j \alpha_j}$$

We use the condition in zero-point and equation (3.9) for $j = 1$.

$$\left.\begin{aligned} u_0 &= \kappa_1 u_1 + \mu_1 \\ u_0 &= \alpha_1 u_1 + \beta_1 \end{aligned}\right\} \Rightarrow \alpha_1 = \kappa_1,\ \beta_1 = \mu_1$$

Because α_1, β_1 are known, we can determine sequentially all coefficients α_j, β_j to point N. Now we use the condition in point N and equation (3.9) for $j = 1$.

$$\left.\begin{aligned} u_N &= \kappa_2 u_{N-1} + \mu_2 \\ u_{N-1} &= \alpha_N u_N + \beta_N \end{aligned}\right\}$$

Implies that

$$u_N = \frac{\mu_2 + \kappa_2 \beta_N}{1 - \kappa_2 \alpha_N} \qquad (3.10)$$

Here straight marching stops.

Backward marching uses the equation (3.9) for points $j = N-1, N-2, \ldots .1, 0$.

For our differential equation (3.7) we can suggest the family of difference schemes corresponding in general case to nine -point template

$$\frac{t_A}{1 + t_A k_A} \frac{\hat{y}_{A,j} - 2y_{A,j} + \breve{y}_{A,j}}{\tau^2} + \sigma_1 \frac{\hat{y}_{A,j} - y_{A,j}}{\tau} + \left(1 - \sigma_1\right) \frac{y_{A,j} - \breve{y}_{A,j}}{\tau} =$$
$$= \frac{D_A}{1 + t_A k_A} \left[\sigma_2 \frac{y_{A,j+1} - 2y_{A,j} + y_{A,j-1}}{h^2} + \sigma_3 \frac{y_{A,j+1} - 2y_{A,j} + y_{A,j-1}}{h^2} + \right.$$
$$\left. + \left(1 - \sigma_2 - \sigma_3\right) \frac{\breve{y}_{A,j+1} - 2\breve{y}_{A,j} + \breve{y}_{A,j-1}}{h^2}\right] - \frac{k_A}{1 + t_A k_A} \left(\frac{\breve{y}_{A,j} + y_{A,j}}{2}\right) \qquad (3.11)$$

Comparing coefficients of (3.8) and (3.11) we can get

$$a_j = \sigma_2 \frac{D_A \tau}{(1+t_A k_A)h^2}; \; b_j = \sigma_2 \frac{D_A \tau}{(1+t_A k_A)h^2}$$

$$c_j = \frac{t_A}{(1+t_A k_A)\tau} + \sigma_1 + 2\sigma_2 \frac{D_A \tau}{(1+t_A k_A)h^2};$$

$$f_j = \frac{D_A \tau}{(1+t_A k_A)h^2}\left[\sigma_3\left(y_{A,i+1} - 2y_{A,j} + y_{A,i-1}\right) + (1-\sigma_2-\sigma_3)\left(\breve{y}_{A,j+1} - 2\breve{y}_{A,j} + \breve{y}_{A,j-1}\right)\right] -$$
$$-\frac{\tau k_A}{1+t_A k_A}\left(\frac{\breve{y}_{A,j} + y_{A,j}}{2}\right) + \frac{t_A}{\tau(1+t_A k_A)}\left(2y_{A,j} - \breve{y}_{A,j}\right) + \sigma_1 y_{A,j} + (1-\sigma_1)\left(y_{A,j} - \breve{y}_{A,j}\right) \quad (3.12)$$

where $\sigma_1, \sigma_2, \sigma_3$ are the weights of difference schemes, $\sigma_1 < 1$; $\sigma_2 + \sigma_3 < 1$.

To complete the problem formulation, we add to the equation (3.3) and with the boundary and initial condition, the kinetic equation for reaction product:

$$\frac{\partial y_C}{\partial t} = \omega_C \quad (3.13)$$

where $\omega_C = k_C \omega$, and equation for basic material (because the moles are not conserved during the reaction). When the species B is mobile and could diffuse also in the mixture from three component $A+B+C$, we could assume that relaxation time for this element t_B is not equal to t_A. Hence, we obtain the equations

$$\mathbf{J}_B = -D_B \frac{\partial y_B}{\partial z} - t_B \frac{\partial \mathbf{J}_B}{\partial t}$$

And

$$t_B\left(\frac{\partial^2 y_B}{\partial t^2} - \frac{\partial \omega_B}{\partial t}\right) + \frac{\partial y_B}{\partial t} = D_B \frac{\partial^2 y_B}{\partial x^2} + \omega_B$$

For example, for reactions

$$Ti + Ni \rightarrow TiNi, \; Ti + Al \rightarrow TiAl, \; Ni + Al \rightarrow NiAl$$

absolute values of stoichiometric coefficients equal to unity:

$$\nu_A = \nu_B = \nu_C = 1,$$

and we have

$$\omega = k y_A y_B.$$

Then the diffusion equations take the form

$$t_A \frac{\partial^2 y_A}{\partial t^2} + (1 + t_A k y_B)\frac{\partial y_A}{\partial t} = D_A \frac{\partial^2 y_A}{\partial x^2} - k y_A\left[y_B + t_A \frac{\partial y_B}{\partial t}\right]; \quad (3.14)$$

$$t_B \frac{\partial^2 y_B}{\partial t^2} + (1 + t_B k y_A)\frac{\partial y_B}{\partial t} = D_B \frac{\partial^2 y_B}{\partial x^2} - k y_B\left[y_A + t_B \frac{\partial y_A}{\partial t}\right]; \quad (3.15)$$

Kinetic equation does not change.

Assuming $f(t)=\exp(-At)$, from (3.1) and from boundary and initial conditions we shall find

$$q_m(1-t_A A)\exp(-At)=-D_A\frac{\partial y_A}{\partial x}\ ,\ x=0 \tag{3.16}$$

In this point $\mathbf{J}_B=0$.

The last boundary and initial conditions:

$$x\to\infty: y_A=0 \text{ or } \mathbf{J}_A=0\,;\ \mathbf{J}_B=0 \tag{3.17}$$

$$t=0: y_A=0;\ \frac{\partial \mathbf{J}_A}{\partial t}=0\ ;\ y_B=y_{B0}\ ;\ \frac{\partial \mathbf{J}_B}{\partial t}=0\ ;\ y_C=0 \tag{3.18}$$

The problem (3.13), (3.14)- (3.18) was solved numerically. The implicit difference scheme for diffusion equations was used.

3.2.4. Results and analysis

Parameters evaluation

According to periodic table, for the $Ti-Ni$ -system we have

$$m_A=48;\ m_B=59;\ m_C=m_A+m_B=107 \text{ g/mol.}$$

We can determine partial densities of species

$$\rho_i=y_i m_i\ ,\ i=A,B,C$$

and calculate the density change

$$\rho=\rho_A+\rho_B+\rho_C$$

during implantation accompanied by chemical reaction.
Assuming $\rho_B=8.9$ g/cm^3, we shall find $y_{B0}\approx 0.151$ mol/cm^3. Impulse source could be characterized by impulse duration $t_i=(2\div 4)\cdot 10^{-4}$ sec; $q_m=(0.1\div 2)\cdot 10^{-8}$ mol/(cm^{2}sec).

Relaxation time depends on material structure, but for majority of substances it is unknown. It is interested for investigation the parameters region, when various physical processes could effect on each other. In this model there are several specific times. Relaxation times t_A, t_B impulse duration t_i, chemical reaction time t_{ch}, specific diffusion time. The correlations between these times will determine the concentration distributions.

Analysis of dimensionality allows writing

$$t_{ch}=y_{B0}/k\ .$$

Taking $k=k_0\exp\left(-\frac{E_R}{RT}\right)$; $k_0/y_{B0}=2\cdot 10^{16}$ 1/sec; $E_R=1.181\cdot 10^5$ J/mol [76], we find $t_{ch}=0.135;\ 1.1\cdot 10^{-4};\ 9.7\cdot 10^{-7}$ sec for temperature $T=400,500,600$ K. Really, the reaction constant could differ from pure thermo dynamical evaluation due to activation phenomena [77], but it changes in wide limits when the temperature varies.

Diffusion coefficients depend on temperature in accordance with Arrhenius's law also

$$D_k = D_{k0} \exp\left(-\frac{E_{Dk}}{RT} \right), \quad k = A, B .$$

It is not difficult to find in the literature the data concerning self-diffusion. The diffusion coefficients in complex media are proportional to self-diffusion coefficients. Diffusion data depend essential on structure material, impurity presence, and conditions of measurement.

Since [78] for nickel and titanium we have

$$D_{Ni} = 1.9 \exp\left[-\frac{279700}{RT} \right] \text{ and } D_{Ti} = 1.09 \cdot \exp\left[-\frac{251200}{RT} \right] + 3.58 \cdot 10^{-4} \exp\left[-\frac{130600}{RT} \right] \text{ cm}^2\text{/sec},$$

so for temperature $T = 500, 600$ K we obtain $D_A = 1.39 \cdot 10^{-16}; 1.51 \cdot 10^{-15}$ and $D_B = 5.03 \cdot 10^{-27}; 8.2 \cdot 10^{-25}$ cm^2/sec respectively. Hence it is impossible to expect diffusion zone formation during times t_A, t_B and t_i without additional acceleration of diffusion.

Experimental data indicate that the materials activation happens under irreversible conditions of particle beam action. It leads to diffusion acceleration and changes many physical properties [77]. Diffusion acceleration could be connected with activation energy reduction. Kinetics of this physical process would be investigated especially. Here we assume that the activation energies reduction in four times. That gives for $T = 500, 600$ K the diffusion coefficients respectively are $D_A = 1.46 \cdot 10^{-6}; 4.21 \cdot 10^{-6}$ and $D_B = 4.31 \cdot 10^{-7}; 1.54 \cdot 10^{-6}$ cm^2/sec.

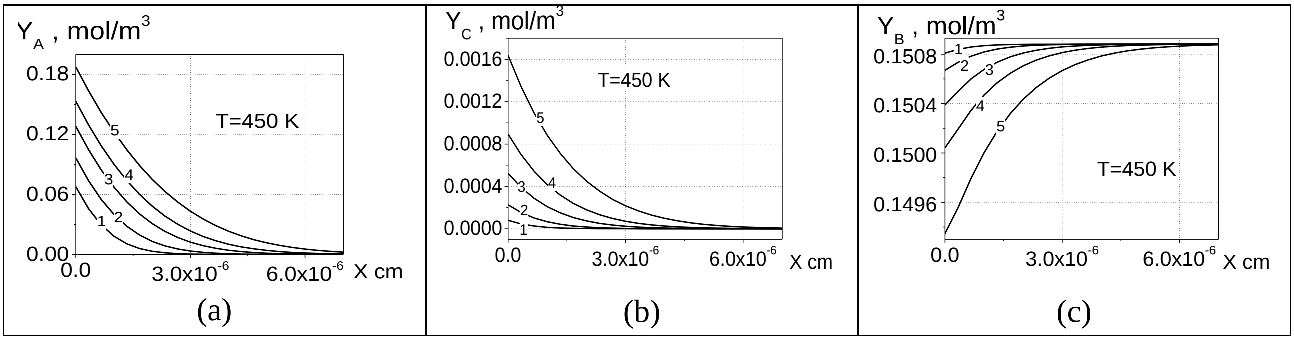
The concentration distributions for $t_A = t_B = 0$ is presented in the Fig. (3.1-3.3) for $q_m = 2.5 \cdot 10^{-4}\ mol/cm^2 \sec$; $T = 550\ K$, $T = 600\ K$, $T = 650\ K$ and $A = 0$. In this case we have $t_{ch} = 8.36 \cdot 10^{-6}$ sec, $9.67 \cdot 10^{-7}$ sec, $1.56 \cdot 10^{-7}$ sec, respectively. While, when we increase the temperature the reaction time decreases as showed in the table and the concentration change for B-substance is more visible Fig. (3.1-3.3). The temperature leads to diffusion acceleration and diffusion zone increase gradually.

Table 1

S#	Temperature	t_{ch} sec	D_A cm^2/sec	D_B cm^2/sec	Reaction rate mol/m^{3}sec
1	450	$2.59 \cdot 10^{-3}$	$3.35 \cdot 10^{-9}$	$2.82 \cdot 10^{-11}$	58.06
1	500	$1.1 \cdot 10^{-4}$	$1.201 \cdot 10^{-8}$	$3.41 \cdot 10^{-10}$	$1.36 \cdot 10^{3}$
2	550	$8.36 \cdot 10^{-6}$	$3.81 \cdot 10^{-8}$	$2.62 \cdot 10^{-9}$	$1.80 \cdot 10^{4}$
3	600	$9.67 \cdot 10^{-7}$	$1.13 \cdot 10^{-7}$	$1.43 \cdot 10^{-8}$	$1.55 \cdot 10^{5}$
4	650	$1.56 \cdot 10^{-7}$	$3.15 \cdot 10^{-7}$	$6.06 \cdot 10^{-8}$	$9.64 \cdot 10^{5}$
5	700	$3.28 \cdot 10^{-8}$	$8.12 \cdot 10^{-7}$	$2.07 \cdot 10^{-7}$	$4.59 \cdot 10^{6}$
6	750	$8.48 \cdot 10^{-9}$	$1.92 \cdot 10^{-6}$	$6.05 \cdot 10^{-7}$	$1.77 \cdot 10^{7}$
7	800	$2.59 \cdot 10^{-9}$	$4.20 \cdot 10^{-6}$	$1.54 \cdot 10^{-6}$	$5.81 \cdot 10^{7}$
8	850	$9.12 \cdot 10^{-10}$	$8.50 \cdot 10^{-6}$	$3.51 \cdot 10^{-6}$	$1.65 \cdot 10^{8}$
9	900	$3.60 \cdot 10^{-10}$	$1.60 \cdot 10^{-5}$	$7.32 \cdot 10^{-6}$	$4.18 \cdot 10^{8}$

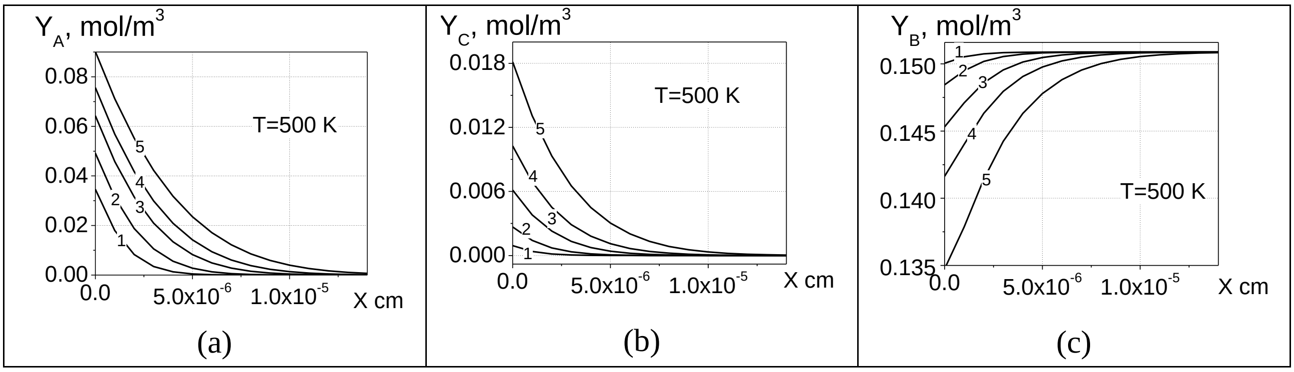
10	950	$1.57\cdot10^{-10}$	$2.84\cdot10^{-5}$	$1.41\cdot10^{-5}$	$9.60\cdot10^{8}$
11	1000	$7.43\cdot10^{-11}$	$4.77\cdot10^{-5}$	$2.54\cdot10^{-5}$	$2.03\cdot10^{9}$

In the absence of relaxation time the concentration distributions are presented in Fig. (3.1-3.3) for $q_m = 2.5\cdot10^{-4}$ $mol/(cm^2\sec)$; $A=0$ and $T=450\,K, T=500\,K$ and $T=550\,K$ respectivelly. We can actually neglect the initial substance concentration change for small times, less than specific reaction time. In this case we have the reaction time $2.59\cdot10^{-3}$ sec for $T=450\,K$, while, when we increase the temperature the reaction time decreases see Table 1 and hence the concentration changes for B-substance is more visible showed in Fig. (3.1-3.3, c). The temperature leads to diffusion acceleration and diffusion zone increase gradually.



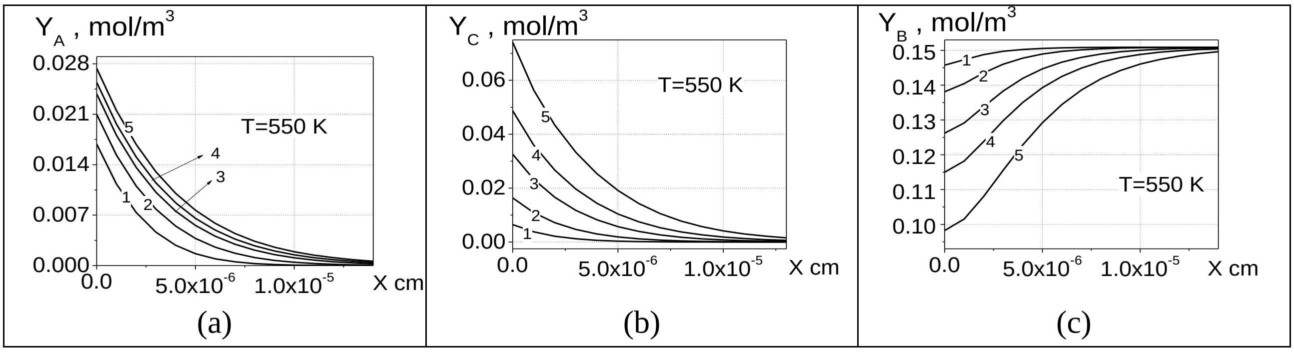
(a) (b) (c)

Fig.3.1. (a): The concentration distribution in specimen for implanted element, (b): Reaction product (c): Initial substance for different time moment; t=(1). $1.99\cdot10^{-4}$; (2). $3.99\cdot10^{-4}$; (3). $6.99\cdot10^{-4}$; (4). $9.99\cdot10^{-4}$; (5). $1.5\cdot10^{-3}$ sec with $t_A = t_B = 0$; $T = 450\ K$ and $A=0$.



(a) (b) (c)

Fig.3.2. (a): The concentration distribution in specimen for implanted element, (b): Reaction product (c): Initial substance for different time moment; t=(1). $1.99\cdot10^{-4}$; (2). $3.99\cdot10^{-4}$; (3). $6.99\cdot10^{-4}$; (4). $9.99\cdot10^{-4}$; (5). $1.5\cdot10^{-3}$ sec with $t_A = t_B = 0$; $T = 500\ K$ and $A=0$.

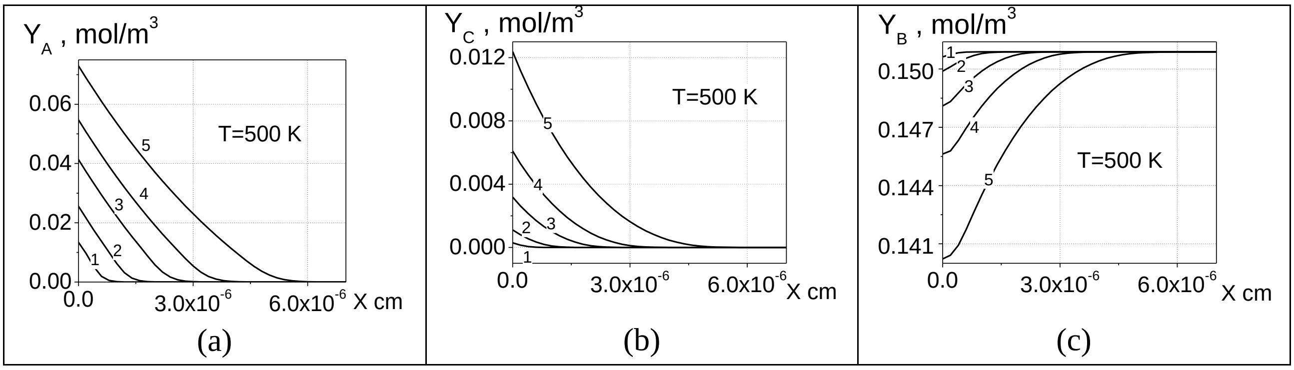


(a) (b) (c)

Fig.3.3. (a): The concentration distribution in specimen for implanted element, (b): Reaction product (c): Initial substance for different time moment; t =(1). $1.99\cdot10^{-4}$; (2). $3.99\cdot10^{-4}$; (3). $6.99\cdot10^{-4}$; (4). $9.99\cdot10^{-4}$; (5). $1.5\cdot10^{-3}$ sec with $t_A = t_B = 0$; $T = 550\ K$ and $A = 0$.

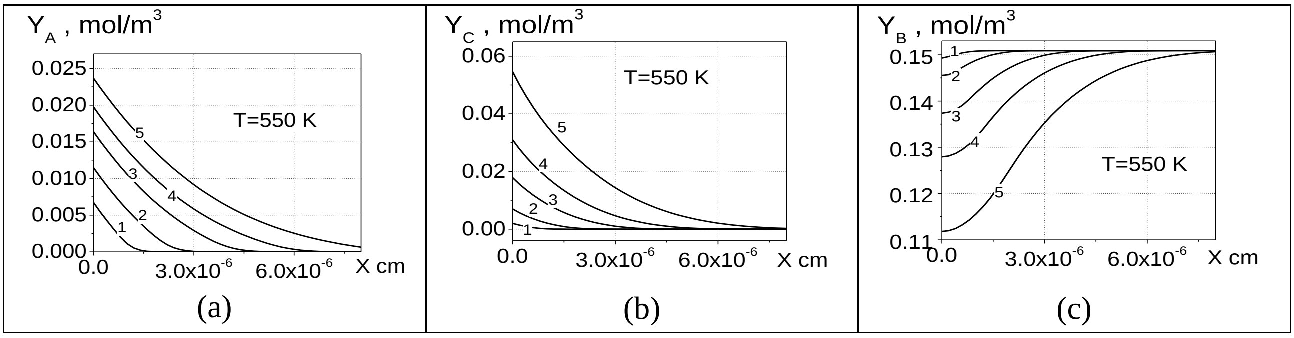
When we take into account the finiteness of relaxation time we shall obtain some interested result for T=600K and T=650 respectively. In this case we can discuss two main cases.

Case-*I*: When the releaxiation times are less than the time impulse that is for $t_A = 10^{-3}$ sec and $t_A = 1.5\cdot10^{-3}$ sec along with $t < t_i = 2\cdot10^{-3}$, the implanted particles are distributed monotonically and almost linearly Fig.(3.4-3.7, a). The concentration curves for reaction product do not change Fig. (3.4-3.7, b). Redistribution of initial substance is observed in diffusion zone Fig. (3.4-3.7, c), that leads to density evaluation.



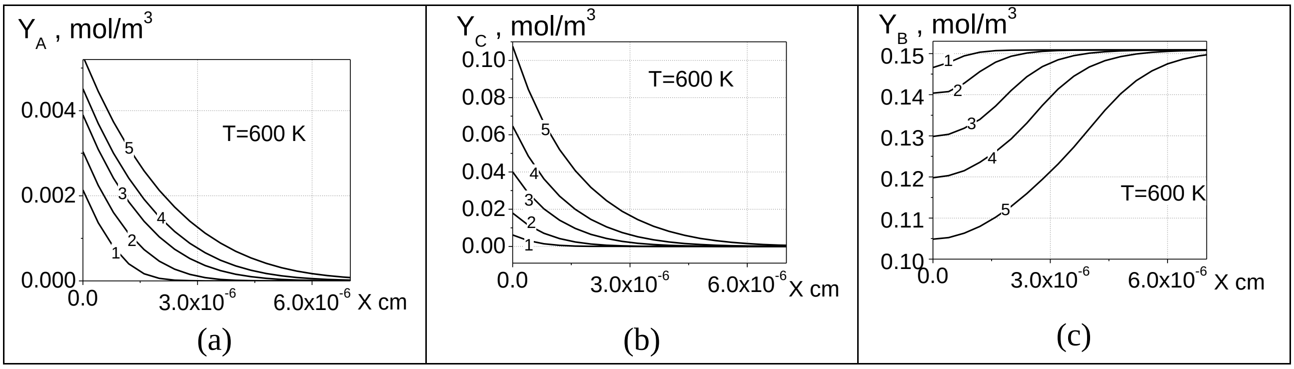
(a) (b) (c)

Fig.3.4. (a): The concentration distribution in specimen for implanted element, (b): Reaction product (c): Initial substance for different time moment; t =(1). $1.99\cdot10^{-4}$; (2). $3.99\cdot10^{-4}$; (3). $6.99\cdot10^{-4}$; (4). $9.99\cdot10^{-4}$; (5). $1.5\cdot10^{-3}$ sec with $t_A = 10^{-3}$;$t_A = 1.5\cdot10^{-3}$; $T = 500\,K$ and $A = 0$.



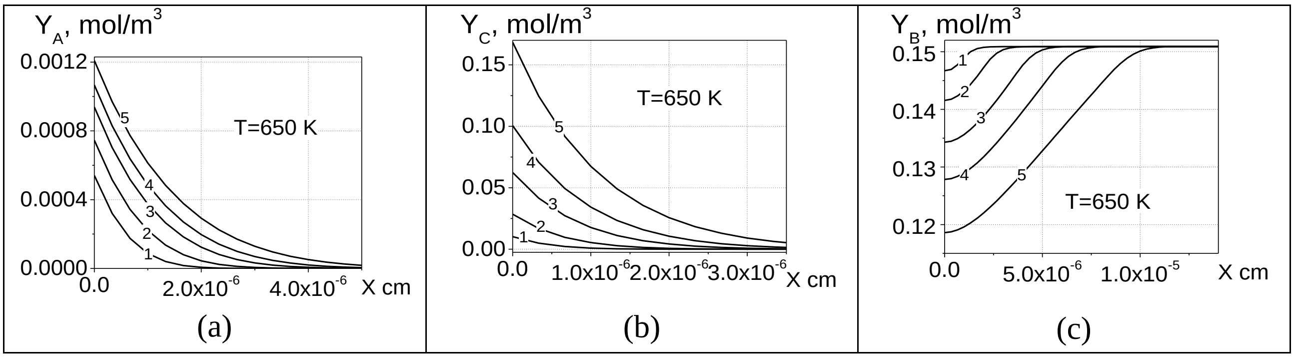
(a) (b) (c)

Fig.3.5. (a): The concentration distribution in specimen for implanted element, (b): Reaction product (c): Initial substance for different time moment; t =(1). $1.99\cdot10^{-4}$; (2). $3.99\cdot10^{-4}$; (3). $6.99\cdot10^{-4}$; (4). $9.99\cdot10^{-4}$; (5). $1.5\cdot10^{-3}$ sec with $t_A=10^{-3}$;$t_A=1.5\cdot10^{-3}$; $T=550\,K$ and $A=0$.



(a) (b) (c)

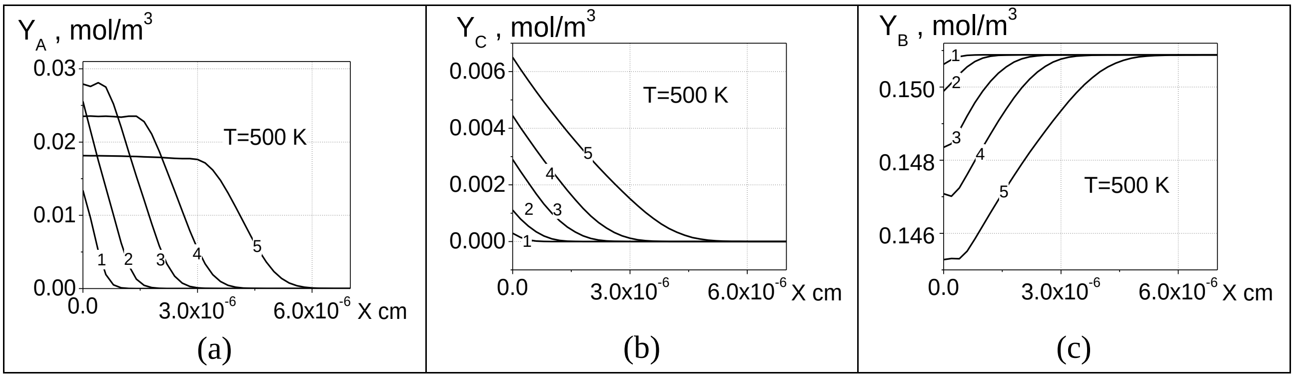
Fig.3.6. (a): The concentration distribution in specimen for implanted element, (b): Reaction product (c): Initial substance for different time moment; t =(1). $1.99\cdot10^{-4}$; (2). $3.99\cdot10^{-4}$; (3). $6.99\cdot10^{-4}$; (4). $9.99\cdot10^{-4}$; (5). $1.5\cdot10^{-3}$ sec with $t_A=10^{-3}$;$t_A=1.5\cdot10^{-3}$; $T=600\,K$ and $A=0$.



(a) (b) (c)

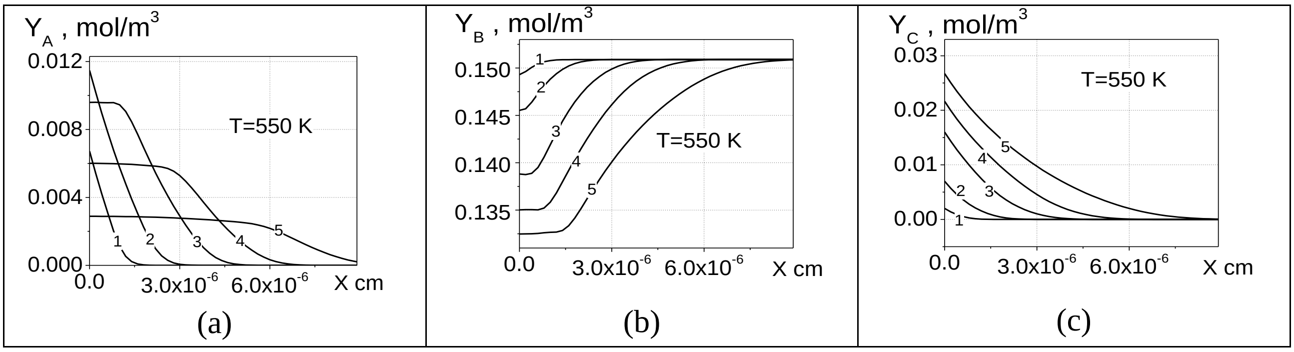
Fig.3.7. (a): The concentration distribution in specimen for implanted element, (b): Reaction product (c): Initial substance for different time moment; t =(1). $1.99\cdot10^{-4}$; (2). $3.99\cdot10^{-4}$; (3). $6.99\cdot10^{-4}$; (4). $9.99\cdot10^{-4}$; (5). $1.5\cdot10^{-3}$ sec with $t_A=10^{-3}$;$t_A=1.5\cdot10^{-3}$; $T=650\,K$ and $A=0$.

Case-*II*: While in opposite case, when the releaxiation times are greater than that the time impulse that is for, for $t_A = 10^{-3}\,\sec$ and $t_B = 1.5\cdot 10^{-3}$ along with $t_i = 5\cdot 10^{-4}\,\sec$, that is when mass source acts, no monotonic concentration curves appear for implanted particles after t_i (Fig.3.8-3.11.a) that propagates into the depth and leads to new phase formation acceleration (Fig. 3.8-3.11,b). In this case, the extreme is observed in initial substance concentration (Fig. 3.8-3.11, c). The evaluation of mass flux density allows seeing the stepped concentration curves for small times and thus After t_i step-by-step concentration of implanted material is visible (Fig. 3.8-3.11.a).



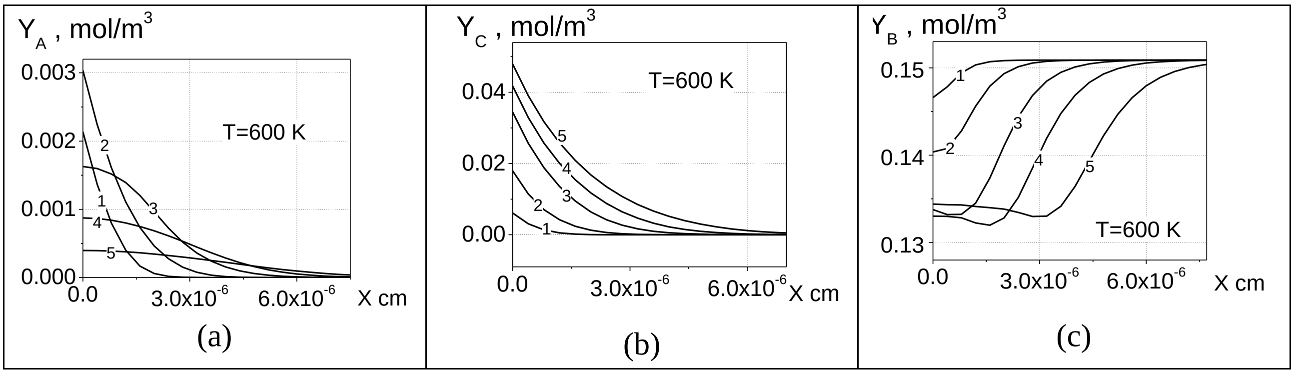
(a) (b) (c)

Fig.3.8. (a): The concentration distribution in specimen for implanted element, (b): Reaction product (c): Initial substance for different time moment; t =(1). $1.99\cdot 10^{-4}$; (2). $3.99\cdot 10^{-4}$; (3). $6.99\cdot 10^{-4}$; (4). $9.99\cdot 10^{-4}$; (5). $1.5\cdot 10^{-3}$ sec with $t_A = 10^{-3}$;$t_B = 1.5\cdot 10^{-3}$; $T = 500\,K$ and $A = 0$.



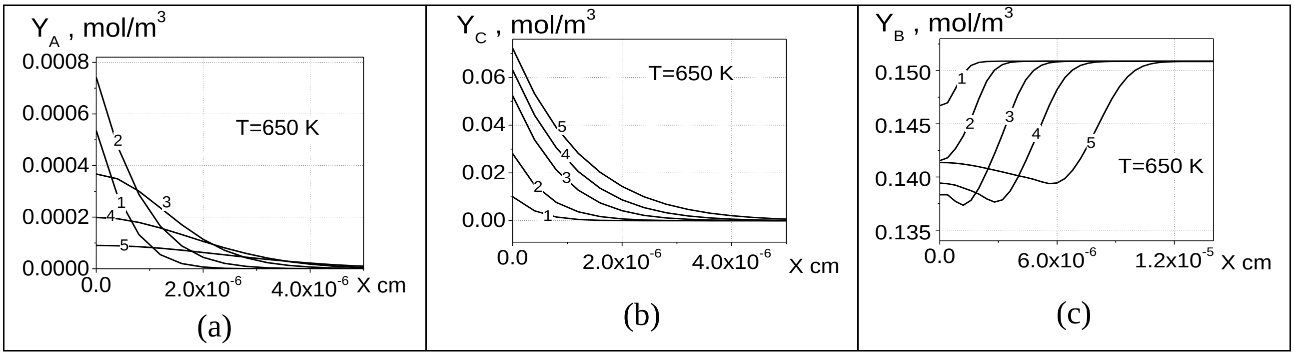
(a) (b) (c)

Fig.3.9. (a): The concentration distribution in specimen for implanted element, (b): Reaction product (c): Initial substance for different time moment; t =(1). $1.99\cdot 10^{-4}$; (2). $3.99\cdot 10^{-4}$; (3). $6.99\cdot 10^{-4}$; (4). $9.99\cdot 10^{-4}$; (5). $1.5\cdot 10^{-3}$ sec with $t_A = 10^{-3}$;$t_B = 1.5\cdot 10^{-3}$; $T = 550\,K$ and $A = 0$.



(a) (b) (c)

Fig.3.10. (a): The concentration distribution in specimen for implanted element, (b): Reaction product (c): Initial substance for different time moment; t =(1). $1.99\cdot10^{-4}$; (2). $3.99\cdot10^{-4}$; (3). $6.99\cdot10^{-4}$; (4). $9.99\cdot10^{-4}$; (5). $1.5\cdot10^{-3}$ sec with $t_A=10^{-3}$;$t_B=1.5\cdot10^{-3}$; $T=600\,K$ and $A=0$.



(a) (b) (c)

Fig.3.11. (a): The concentration distribution in specimen for implanted element, (b): Reaction product (c): Initial substance for different time moment; t =(1). $1.99\cdot10^{-4}$; (2). $3.99\cdot10^{-4}$; (3). $6.99\cdot10^{-4}$; (4). $9.99\cdot10^{-4}$; (5). $1.5\cdot10^{-3}$ sec with $t_A=10^{-3}$;$t_B=1.5\cdot10^{-3}$; $T=650\,K$ and $A=0$.

3.3. The problem with detailed reaction scheme

This problem is actually the continuation of the above model by adding new chemical reactions. We consider a model for non-equilibrium conditions of three stage reactions for the formation of intermetallic compounds. Consider the plane layer of nickel. The flow of aluminum particles distributed uniformly along the surface to be treated. Assume the implantation of aluminum ions in the surface layer of nickel may occurs the chemical reactions. In general, the problem is conjugate (there is the interface), coupling (there are the interrelation between various physical phenomena) and demands the large calculating resources. That connects with the difference between scales of various physical and chemical phenomena.

3.3.1. Mathematical problem formulation

We use the model [75] and add it by new chemical reactions. We assume that three reactions are possible in the surface layer.

(a) $Ni + Al \to NiAl$

(b) $3Ni + Al \to Ni_3Al$

(c) $Ni_3Al + 2Al \to 3NiAl$

The molar concentration distribution of $Ni, Al, NiAl$ and Ni_3Al follows from equations

$$\frac{\partial[Al]}{\partial t} = -\nabla \cdot \mathbf{J}_{Al} + \omega_{Al} + q_m F(x,t)$$

$$\frac{\partial[Ni]}{\partial t} = -\nabla \cdot \mathbf{J}_{Ni} + \omega_{Ni}$$

$$\frac{\partial[NiAl]}{\partial t} = \omega_{NiAl}$$

$$\frac{\partial[Ni_3Al]}{\partial t} = \omega_{Ni_3Al}$$

where ω_k , $k = Ni, Al, NiAl, Ni_3Al$ the summary sources and/or sinks of substances due to the reactions,

$$\omega_k = \sum_{\mathrm{i}=1}^{4} \nu_{ki}\varphi_i ,$$

φ_i - are the reaction rates $\left(mol/\left(m^3 \sec\right)\right)$, ν_{ki} are stoichiometric coefficients. For our reaction scheme, we have

$$\omega_{Al} = -(\varphi_1 + \varphi_2 + 2\varphi_3) \text{ , } \omega_{Ni} = -(\varphi_1 + 3\varphi_2)$$

$$\omega_{NiAl} = \varphi_1 + 3\varphi_3 \text{ , } \omega_{Ni_3Al} = \varphi_2 - \varphi_3$$

The reaction rates depend on concentrations and temperature:

$$\varphi_1 = k_{10} \exp\left[-\frac{E_1}{RT}\right] \cdot [Ni] \cdot [Al] = k_1 \cdot [Ni] \cdot [Al]$$

$$\varphi_2 = k_{20} \exp\left[-\frac{E_2}{RT}\right] \cdot [Ni]^3 \cdot [Al] = k_2 \cdot [Ni]^3 \cdot [Al]$$

$$\varphi_3 = k_{30} \exp\left[-\frac{E_3}{RT}\right] \cdot [Ni_3Al] \cdot [Al]^2 = k_3 \cdot [Ni_3Al] \cdot [Al]^2$$

where E_1, E_2, E_3 are the activation energies, R is universal gas constant, k_{10}, k_{20}, k_{30} - pre-exponential factors.

The diffusion fluxes $\left(mol/\left(m^2 \sec\right)\right)$ follows from relations

$$\mathbf{J}_{Al} = -D_{Al}\frac{\partial[Al]}{\partial x} - t_{Al}\frac{\partial J_{Al}}{\partial t}$$

$$\mathbf{J}_{Ni} = -D_{Ni}\frac{\partial[Ni]}{\partial x} - t_{Ni}\frac{\partial J_{Ni}}{\partial t}$$

where t_{Al}, t_{Ni} are the relaxation times, D_{Al}, D_{Ni} are diffusion coefficients of elements in the mixture, $\left(m^2/\sec\right)$.

The Initial conditions, $t = 0$, are

$$[Al] = [NiAl] = [Ni_3Al] = 0, \; [Ni] = [N_{i0}].$$

The boundary conditions are

$$x = 0: \qquad J_{AL} = J_{Ni} = 0$$

$$x = \infty: \qquad J_{AL} = J_{Ni} = 0$$

Note, that the same problem will correct for other systems, for example $Ti + Al$, $Ni + Ti$. The problem is solved numerically.

In the simplest case, we can restrict the chemical reaction by one stage and take $F = 0$ in diffusion equation. That corresponds to the condition $x = 0: J_{Al} = q_m \; f(t)$ when ions enter from the surface.

For simplicity we assume that $Y_1 = [AL], Y_2 = [Ni], Y_3 = [NiAL], Y_4 = [Ni_3AL]$ so that the above problem statement can be respectively written as

$$\frac{\partial Y_1}{\partial t} = -\nabla \cdot \mathbf{J}_1 + \omega_1 + q_m F(x,t)$$

Where

$$F = F_1(x)F_2(x)$$

$$\frac{\partial Y_2}{\partial t} = -\nabla \cdot \mathbf{J}_2 + \omega_2$$

$$\frac{\partial Y_3}{\partial t} = \omega_3$$

$$\frac{\partial Y_4}{\partial t} = \omega_4$$

$$\mathbf{J}_1 = -D_1 \frac{\partial Y_1}{\partial x} - t_1 \frac{\partial J_1}{\partial t}$$

$$\mathbf{J}_2 = -D_2 \frac{\partial Y_2}{\partial x} - t_2 \frac{\partial J_2}{\partial t}$$

$$\omega_k = \sum_{i=1}^{r} \nu_{ki} \varphi_i \qquad (3.19)$$

φ_i - ith chemical reaction rate ν_{ki} - stochiometric coefficient of k -component in t-th reaction; r – number of reactions.

3.3.2. Numerical algorithm

The system (3.19) can be written as

$$t_1\left(\frac{\partial^2 Y_1}{\partial t^2} - \frac{\partial \omega_1}{\partial t} - q_m \frac{\partial F(x,t)}{\partial t}\right) + \frac{\partial Y_1}{\partial t} = D_1 \frac{\partial^2 Y_1}{\partial x^2} + \omega_1 + q_m F(x,t) \qquad (3.20)$$

$$t_2\left(\frac{\partial^2 Y_2}{\partial t^2} - \frac{\partial \omega_2}{\partial t}\right) + \frac{\partial Y_2}{\partial t} = D_2 \frac{\partial^2 Y_2}{\partial x^2} + \omega_2 \qquad (3.21)$$

$$\frac{\partial Y_3}{\partial t} = \omega_3 \qquad (3.22)$$

$$\frac{\partial Y_4}{\partial t} = \omega_4 \qquad (3.23)$$

The boundary conditions are

$$x = 0: \qquad J_1 = J_2 = 0$$

$$x = L: \qquad J_1 = J_2 = 0$$

The initial conditions, $t = 0$, are

$$Y_1 = Y_3 = Y_4 = 0\,, \;\; Y_2 = Y_{20}.$$

To solve this problem we must write down the sources ω_k explicitly.
For system $Ni - Al$ we have reactions (a)-(c)
The reaction rates are

$$\varphi_1 = k_1 Y_1 Y_2 \;\; , \;\; \varphi_2 = k_2 Y_1 Y_2^3 \quad , \quad \varphi_3 = k_3 Y_4 Y_1^2$$

Hence, for sources in the diffusion and kinetic equations we shall find

$$\omega_1 = -(\varphi_1 + \varphi_2 + 2\varphi_3) = -k_1 Y_1 Y_2 - k_2 Y_1 Y_2^3 - 2k_3 Y_4 Y_1^2 \quad \text{; Al}$$

$$\omega_2 = -(\varphi_1 + 3\varphi_2) = -k_1 Y_1 Y_2 - 3k_2 Y_1 Y_2^3 \quad \text{; Ni}$$

$$\omega_3 = \varphi_1 + 3\varphi_3 = k_1 Y_1 Y_2 + 3k_3 Y_4 Y_1^2 \quad \text{; NiAl}$$

$$\omega_4 = \varphi_2 - \varphi_3 = k_2 Y_1 Y_2^3 - k_3 Y_4 Y_1^2 \quad \text{. Ni}_3\text{Al}$$

Determining the derivative

$$\frac{\partial \omega_1}{\partial t} = \frac{\partial}{\partial t}(-k_1 Y_1 Y_2 - k_2 Y_1 Y_2^3 - 2k_3 Y_4 Y_1^2) =$$

$$= -k_1 \frac{\partial}{\partial t}(Y_1 Y_2) - k_2 \frac{\partial}{\partial t}(Y_1 Y_2^3) - 2k_3 \frac{\partial}{\partial t}(Y_4 Y_1^2)$$

$$= -k_1 (Y_1 \frac{\partial}{\partial t} Y_2 + Y_2 \frac{\partial}{\partial t} Y_1) - k_2 (3Y_1 Y_2^2 \frac{\partial}{\partial t} Y_2 + Y_2^3 \frac{\partial}{\partial t} Y_1) - 2k_3 (Y_1^2 \frac{\partial}{\partial t} Y_4 + 2Y_1 Y_4 \frac{\partial}{\partial t} Y_1)$$

and substituting it in equation (3.20) we obtain

$$t_1 \left[\frac{\partial^2 Y_1}{\partial t^2} + k_1 \left(Y_1 \frac{\partial}{\partial t} Y_2 + Y_2 \frac{\partial}{\partial t} Y_1 \right) + k_2 \left(3Y_1 Y_2^2 \frac{\partial}{\partial t} Y_2 + Y_2^3 \frac{\partial}{\partial t} Y_1 \right) + \right.$$

$$\left. + 2k_3 \left(Y_1^2 \frac{\partial}{\partial t} Y_4 + 2Y_1 Y_4 \frac{\partial}{\partial t} Y_1 \right) \right] - q_m t_1 \frac{\partial F(x,t)}{\partial t} + \frac{\partial Y_1}{\partial t} = D_1 \frac{\partial^2 Y_1}{\partial x^2} + \omega_1 + q_m F(x,t)$$

or

$$t_1 \frac{\partial^2 Y_1}{\partial t^2} + \left(k_1 t_1 Y_2 + k_2 t_1 Y_2^3 + 4k_3 t_1 Y_1 Y_4 + 1 \right) \frac{\partial}{\partial t} Y_1 + \left(k_1 t_1 Y_1 + 3k_2 t_1 Y_1 Y_2^2 \right) \frac{\partial}{\partial t} Y_2 +$$

$$+ 2k_3 t_1 Y_1^2 \frac{\partial}{\partial t} Y_4 - t_1 q_m \frac{\partial F(x,t)}{\partial t} = D_1 \frac{\partial^2 Y_1}{\partial x^2} + \omega_1 + q_m F(x,t)$$

or

$$t_1 \frac{\partial^2 Y_1}{\partial t^2} + G_1 \frac{\partial}{\partial t} Y_1 + H_1 \frac{\partial}{\partial t} Y_2 + 2k_3 t_1 Y_1^2 \left(k_2 Y_1 Y_2^3 - k_3 Y_4 Y_1^2 \right) - t_1 q_m \frac{\partial F(x,t)}{\partial t} =$$

$$= D_1 \frac{\partial^2 Y_1}{\partial x^2} - \left(k_1 Y_1 Y_2 + k_2 Y_1 Y_2^3 + 2k_3 Y_4 Y_1^2 \right) + q_m F(x,t)$$

or

$$t_1 \frac{\partial^2 Y_1}{\partial t^2} + G_1 \frac{\partial}{\partial t} Y_1 + H_1 \frac{\partial}{\partial t} Y_2 - t_1 q_m \frac{\partial F(x,t)}{\partial t} = D_1 \frac{\partial^2 Y_1}{\partial x^2} -$$

$$- Y_1 S_1 + 2k_3^2 t_1 Y_1^4 Y_4 + q_m F(x,t) \tag{3.24}$$

Here

$$G_1(Y_k, t_1) = k_1 t_1 Y_2 + k_2 t_1 Y_2^3 + 4k_3 t_1 Y_1 Y_4 + 1, \; k = 1,2,3,4$$

$$H_1(Y_k, t_1) = k_1 t_1 Y_1 + 3k_2 t_1 Y_1 Y_2^2$$

$$S_1(Y_k, t_1) = k_1 Y_2 + k_2 Y_2^3 + 2k_3 Y_4 Y_1 + 2k_3 k_2 t_1 Y_1^2 Y_2^3$$

Differentiating the source for second component (Ni), we come to the equation

$$\frac{\partial \omega_2}{\partial t} = \frac{\partial}{\partial t}(-k_1 Y_1 Y_2 - 3k_2 Y_1 Y_2{}^3) = -k_1 \frac{\partial}{\partial t}(Y_1 Y_2) - 3k_2 \frac{\partial}{\partial t}(Y_1 Y_2{}^3)$$

$$= -k_1 (Y_1 \frac{\partial}{\partial t} Y_2 + Y_2 \frac{\partial}{\partial t} Y_1) - 3k_2 (3Y_1 Y_2{}^2 \frac{\partial}{\partial t} Y_2 + Y_2{}^3 \frac{\partial}{\partial t} Y_1)$$

From equation (3.21), we obtain

$$t_2 \left[\frac{\partial^2 Y_2}{\partial t^2} + k_1 \left(Y_1 \frac{\partial}{\partial t} Y_2 + Y_2 \frac{\partial}{\partial t} Y_1 \right) + 3k_2 \left(3Y_1 Y_2{}^2 \frac{\partial}{\partial t} Y_2 + Y_2{}^3 \frac{\partial}{\partial t} Y_1 \right) \right] + \frac{\partial Y_2}{\partial t} = D_2 \frac{\partial^2 Y_2}{\partial x^2} + \omega_2$$

or

$$t_2 \frac{\partial^2 Y_2}{\partial t^2} + \left(k_1 t_2 Y_1 + 9k_2 t_2 Y_1 Y_2{}^2 + 1 \right) \frac{\partial}{\partial t} Y_2 + \left(k_1 t_2 Y_2 + 3k_2 t_2 Y_2{}^3 \right) \frac{\partial}{\partial t} Y_1 = D_2 \frac{\partial^2 Y_2}{\partial x^2} + \omega_2$$

or

$$t_2 \frac{\partial^2 Y_2}{\partial t^2} + H_2 \frac{\partial}{\partial t} Y_2 + G_2 \frac{\partial}{\partial t} Y_1 = D_2 \frac{\partial^2 Y_2}{\partial x^2} - Y_2 S_2 \qquad (3.25)$$

where

$$H_2(Y_k, t_1) = k_1 t_2 Y_1 + 9k_2 t_2 Y_1 Y_2{}^2 + 1 \quad k = 1,2,3,4;$$

$$G_2(Y_k, t_1) = k_1 t_2 Y_2 + 3k_2 t_2 Y_2{}^3 \; ;$$

$$S_2(Y_k, t_1) = k_1 Y_1 + 3k_2 Y_1 Y_2{}^2 \; ;$$

Other equations do not change.

To solve this problem (3.24), (3.25), (3.22) and (3.23) with initial and boundary conditions we can use various methods [79].

First Concentration:

Fist concentration (3.24)

$$= t_1 \left(\frac{Y_{1i} - 2\tilde{Y}_{1i} + \check{Y}_{1i}}{\Delta t^2} \right) + \check{G}_{1i} \left(\frac{Y_{1i} - \tilde{Y}_{1i}}{\Delta t} \right) + \check{H}_{1i} \left(\frac{\tilde{Y}_{2i} - \check{Y}_{2i}}{\Delta t} \right) -$$

$$- t_1 q_m \frac{\partial F(x,t)}{\partial t} - q_m F(x,t) = D_1 \left(\frac{Y_{1i+1} - 2Y_{1i} + Y_{1i-1}}{\Delta x^2} \right) - Y_{1i} S_1 + 2k_3{}^2 \check{Y}_{4i} \check{Y}_{1i}{}^4$$

or

$$\frac{D_1 \Delta t}{\Delta x^2} Y_{1i-1} - \left(\frac{t_1}{\Delta t} + \check{G}_{1i} + 2 \frac{D_1 \Delta t}{\Delta x^2} + \Delta t S_{1i} \right) Y_{1i} + \frac{D_1 \Delta t}{\Delta x^2} Y_{1i+1};$$

$$= - \left[2\Delta t k_3{}^2 t_1 \check{Y}_{4i} \check{Y}_{1i}{}^4 + \check{G}_{1i} \tilde{Y}_{1i} - \check{H}_{1i} \left(\tilde{Y}_{2i} - \check{Y}_{2i} \right) + \right.$$

$$\left. + \Delta t q_m \left(t_1 \frac{\partial F(x,t)}{\partial t} + F(x,t) \right) - \frac{t_1}{\Delta t} \left(\check{Y}_{1i} - 2\tilde{Y}_{1i} \right) \right]$$

By comparison with

$$A_{1i} Y_{1,i-1} - C_{1i} Y_{1,i} + B_{1i} Y_{i1,+1} + F_{1i} = 0 \,,$$

We can get the Double sweep coefficients

$$A_{1i} = \frac{D_1 \Delta t}{\Delta x^2} \ ; \quad B_{1i} = \frac{D_1 \Delta t}{\Delta x^2} \quad ; \quad C_{1i} = \frac{t_1}{\Delta t} + \check{G}_{1i} + 2\frac{D_1 \Delta t}{\Delta x^2} + \Delta t S_{1i} \ ;$$

$$f_{1i} = 2\Delta t {k_3}^2 t_1 \check{Y}_{4i} {\check{Y}_{1i}}^4 + \check{G}_{1i} \tilde{Y}_{1i} - \check{H}_{1i}\left(\tilde{Y}_{2i} - \check{Y}_{2i} \right) +$$

$$+ \Delta t q_m \left(t_1 \frac{\partial F(x,t)}{\partial t} + F(x,t) \right) - \frac{t_1}{\Delta t}\left(\check{Y}_{1i} - 2\tilde{Y}_{1i} \right)$$

(3.26)

Boundary condition in the point

$$at \ \ x = 0\,, \ \mathbf{J}_1 = 0 \ , \ \mathbf{J}_1 = -D_1 \frac{\partial Y_1}{\partial x} - t_1 \frac{\partial J_1}{\partial t} \ \Rightarrow - D_1 \frac{\partial Y_1}{\partial x} - t_1 \frac{\partial J_1}{\partial t} = 0$$

Present concentration in the point $x = 0 + dx$ (or in the point $i = 1$) in form of series relatively to point $x = 0$ for small Δx

$$Y_{11} = Y_{10} + \left(\frac{\partial Y_1}{\partial x} \right) \Delta x + \left(\frac{\partial^2 Y_1}{\partial x^2} \right) \frac{\Delta x^2}{2} + O\left(\Delta x^3 \right)$$

Hence,

$$\left(\frac{\partial Y_1}{\partial x} \right)_0 = \frac{Y_{11} - Y_{10}}{\Delta x} - \left(\frac{\partial^2 Y_1}{\partial x^2} \right)_0 \frac{\Delta x}{2} \ ,$$

To find the second derivative we use equation (3.24)

$$D_1 \frac{\partial^2 Y_1}{\partial x^2} = t_1 \frac{\partial^2 Y_1}{\partial t^2} + G_1 \frac{\partial}{\partial t} Y_1 + H_1 \frac{\partial}{\partial t} Y_2 -$$

$$- t_1 q_m \frac{\partial F(x,t)}{\partial t} + Y_1 S_1 - 2{k_3}^2 t_1 {Y_1}^4 Y_4 - q_m F(x,t)$$
.

Hence we write for this point

$$\frac{Y_{11} - Y_{10}}{\Delta x} - \frac{1}{D_1} \frac{\Delta x}{2} \left[D_1 \frac{Y_{10} - 2\tilde{Y}_{10} + \check{Y}_{10}}{\Delta t^2} + \check{G}_{10} \frac{Y_{10} - \tilde{Y}_{10}}{\Delta t} + \check{H}_{10} \frac{\tilde{Y}_{20} - \check{Y}_{20}}{\Delta t} - . \right.$$

$$\left. - q_m F - t_1 q_m \frac{\partial F(x,t)}{\partial t} - Y_1 \check{S}_{10} + 2 k_3 t_1 {\check{Y}_{10}}^4 \check{Y}_{40} \right] = 0$$

We obtain:

$$Y_{10} = \alpha_1 Y_{11} + \beta_1 \ ,$$

where

$$\alpha_1 = \frac{2 D_1 \Delta t}{\Delta x^2} \frac{1}{Z} \ ;$$

$$\beta_1 = \left[\Delta t q_m F(x,t) + t_1 \Delta t q_m \frac{\partial F(x,t)}{\partial t} + 2\Delta t {k_3}^2 t_1 {\check{Y}_{10}}^4 \check{Y}_{40} + \right.$$

$$\left. + \check{G}_{10} \tilde{Y}_{10} - \check{H}_{10}\left(\tilde{Y}_{20} - \check{Y}_{20} \right) + \frac{t_1}{\Delta t}\left(2\tilde{Y}_{10} - \check{Y}_{10} \right) \right] \frac{1}{Z},$$

(3.27)

where

$$Z = \check{G}_{10} + \frac{t_1}{\Delta t} + \frac{2D_1 \Delta t}{\Delta x^2} + \Delta t\, \check{S}_{10}.$$

The formulae of double sweep method are usual:

$$Y_{1i} = \alpha_{i+1} Y_{1i+1} + \beta_{i+1} \tag{3.28}$$

Here α_{i+1}, β_{i+1} are double-sweep coefficients

$$\alpha_{i+1} = \frac{B_i}{C_i - A_i \alpha_i}, \quad \beta_{i+1} = \frac{A_i \beta_i + f_i}{C_i - A_i \alpha_i}. \tag{3.29}$$

Second boundary condition is written in difference form by similarly way. However, the series is constructed for Y_{1N-1} relatively to the point $i = N$. As a result we present the boundary condition in the form

$$Y_{1N} = \kappa_1 Y_{1N-1} + \mu_1.$$

This equality together with

$$Y_{1N-1} = \alpha_N Y_{1N} + \beta_N$$

gives

$$Y_{1N} = \frac{\mu_1 + \kappa_1 \beta_N}{1 - \kappa_1 \alpha_N}. \tag{3.30}$$

Here

$$\kappa_1 = \frac{2D_1 \Delta t}{\Delta x^2} \frac{1}{Z}; \quad \mu_1 = \left[\Delta t q_m F(x,t) + t_1 \Delta t q_m \frac{\partial F(x,t)}{\partial t} + 2\Delta t k_3{}^2 t_1 \check{Y}_{1N}{}^4 \check{Y}_{4N} + \right.$$
$$\left. + \check{G}_{1N} \tilde{Y}_{1N} - \check{H}_{1N} \left(\tilde{Y}_{2N} - \check{Y}_{2N} \right) + \frac{t_1}{\Delta t} \left(2\tilde{Y}_{1N} - \check{Y}_{1N} \right) \right] \frac{1}{Z}, \tag{3.31}$$

$$Z = \check{G}_{1N} + \frac{t_1}{\Delta t} + \frac{2D_1 \Delta t}{\Delta x^2} + \Delta t\, \check{S}_{1N}$$

The conditions of stability for double sweep method are right always:

$$|b_i| \ge |a_i| + |b_i|, \quad i = 1, 2, \ldots, N-1$$
$$|\kappa_1| \le 1; \ |\alpha_1| \le 1; \ |\kappa_1 + \alpha_1| < 2$$

Second concentration:

Difference equation for the second concentration (3.25):

$$t_2 \left(\frac{Y_{2i} - 2\tilde{Y}_{2i} + \check{Y}_{2i}}{\Delta t^2} \right) + \check{H}_{2i} \left(\frac{Y_{2i} - \tilde{Y}_{2i}}{\Delta t} \right) + \check{G}_{2i} \left(\frac{\tilde{Y}_{1i} - \check{Y}_{1i}}{\Delta t} \right) =$$

$$= D_2 \left(\frac{Y_{2i+1} - 2Y_{2i} + Y_{2i-1}}{\Delta x^2} \right) - \left(k_1 \check{Y}_{1i} + 3k_2 \check{Y}_{1i} \check{Y}_{2i}{}^2 \right) Y_{2i},$$

or

$$A_{2i}Y_{2,i-1} - C_{2i}Y_{1,i} + B_{2i}Y_{2,i+1} + F_{2i} = 0\ ,$$

where

$$A_{2i} = \frac{D_2\Delta t}{\Delta x^2}\ ;\quad B_{2i} = \frac{D_2\Delta t}{\Delta x^2}\ ;\quad C_{2i} = \frac{t_2}{\Delta t} + \check{H}_{2i} + 2\frac{D_2\Delta t}{\Delta x^2} + \Delta t S_{2i}\ ;$$

$$f_{2i} = \check{H}_{2i}\tilde{Y}_{2i} - \check{G}_{2i}\left(\tilde{Y}_{1i} - \check{Y}_{1i}\right) + \frac{t_2}{\Delta t}\left(2\tilde{Y}_{2i} - \check{Y}_{2i}\right). \tag{3.32}$$

Boundary condition

$$x = 0\ ,\ \mathbf{J}_2 = 0\ ,\ D_2\frac{\partial Y_2}{\partial x} = 0$$

$$\left(\frac{\partial Y_2}{\partial x}\right)_0 = \frac{Y_{21} - Y_{20}}{\Delta x} - \left(\frac{\partial^2 Y_2}{\partial x^2}\right)_0 \frac{\Delta x}{2}\ ,$$

To find the second derivative we use the equation (3.25) at the point $i = 0$. After transformations similar to previous ones, we come to equations:

$$Y_{20} = \alpha_1' Y_{21} + \beta_1'\ ,$$

where

$$\alpha_1' = \frac{2D_2\Delta t}{\Delta x^2}\frac{1}{Z}\ ;\quad \beta_1' = \left[\check{H}_{20}\tilde{Y}_{20} - \check{G}_{20}\left(\tilde{Y}_{10} - \check{Y}_{10}\right) + \frac{t_2}{\Delta t}\left(2\tilde{Y}_{20} - \check{Y}_{20}\right)\right]\frac{1}{Z}\ , \tag{3.33}$$

$$Z = \check{H}_{20} + \frac{t_2}{\Delta t} + \frac{2D_2\Delta t}{\Delta x^2} + \Delta t\,\check{S}_{20}\ .$$

General formulae for double sweep method are the same, that is

$$Y_{2i} = \alpha_{i+1}' Y_{2i+1} + \beta_{i+1}' \tag{3.34}$$

Here α_{i+1}' , β_{i+1}' are double-sweep coefficients

$$\alpha_{i+1}' = \frac{B_i}{C_i - A_i\alpha_i'}\ ,\quad \beta_{i+1}' = \frac{A_i\beta_i' + f_i}{C_i - A_i\alpha_i'}\ . \tag{3.35}$$

Second boundary condition is written in difference form by similarly way. However, the series is constructed for Y_{2N-1} relatively to the point $i = N$. As a result we present the boundary condition in the form

$$Y_{2N} = \kappa_2 Y_{2N-1} + \mu_2\ .$$

This equality together with

$$Y_{2N-1} = \alpha_N Y_{2N} + \beta_N$$

gives

$$Y_{2N} = \frac{\mu_2 + \kappa_2\beta_N}{1 - \kappa_2\alpha_N}\ . \tag{3.36}$$

Here

$$\kappa_2 = \frac{2D_2\Delta t}{\Delta x^2}\frac{1}{Z}\ ; \quad \mu_2 = \left[\check{H}_{2N}\tilde{Y}_{2N} - \check{G}_{2N}\left(\tilde{Y}_{1N} - \check{Y}_{1N}\right) + \frac{t_2}{\Delta t}\left(2\tilde{Y}_{2N} - \check{Y}_{2N}\right)\right]\frac{1}{Z}\ , \qquad (3.37)$$

$$Z = \check{H}_{1N} + \frac{t_2}{\Delta t} + \frac{2D_2\Delta t}{\Delta x^2} + \Delta t\,\check{S}_{2N}\ .$$

Kinetics equations (22) and (23)

$$\frac{\partial Y_3}{\partial t} = \omega_3$$

$$\omega_3 = \varphi_1 + 3\varphi_3 = k_1 Y_1 Y_2 + 3k_3 Y_4 Y_1^2\ ,$$

$$\frac{\partial Y_4}{\partial t} = \omega_4$$

$$\omega_4 = \varphi_2 - \varphi_3 = k_2 Y_1 Y_2^3 - k_3 Y_4 Y_1^2\ ,$$

can be realized numerically using Euler method.

3.3.3. Results and analysis

Parameters Evaluation

In order to discuss the analysis of the result the following parameters must be used. The reaction rates and diffusion coefficients depend on temperature by Arrhenius law. The activation energy of reactions are

$$E_{a1} = 86128\ ;\ E_{a2} = 169149\ ;\ E_{a3} = 48715\ \text{J/mol;}$$

$$k_{01} = 8.994 * 10^4\ ,\ k_{02} = 1.517 * 10^9\ ,\ k_{03} = 0.853 * 10^2$$

While the diffusion coefficient are:

$$D_1 = D_{10}\exp\left(-\frac{E_{D1}}{RT}\right)\ ;\quad D_2 = D_{2A}\exp\left(-\frac{E_{DA}}{RT}\right) + D_{2B}\exp\left(-\frac{E_{DB}}{RT}\right)\ ,$$

$$D_{10} = 1.09\ cm^2/\sec\ ;\ E_{D1} = 2.512\times10^5\ \text{J/mol;}$$

$$D_{2A} = 3.58\times10^{-4}\ ;\ E_{DA} = 1.306\times10^5\ ;$$

$$D_{2B} = 1.19\ ;\ E_{DA} = 2.797\times10^5\ ;\ T = 700\ \text{K}$$

Here we employment mixture measurement unit that is convenient for calculation and for results presentation. Here we also discuss two cases.

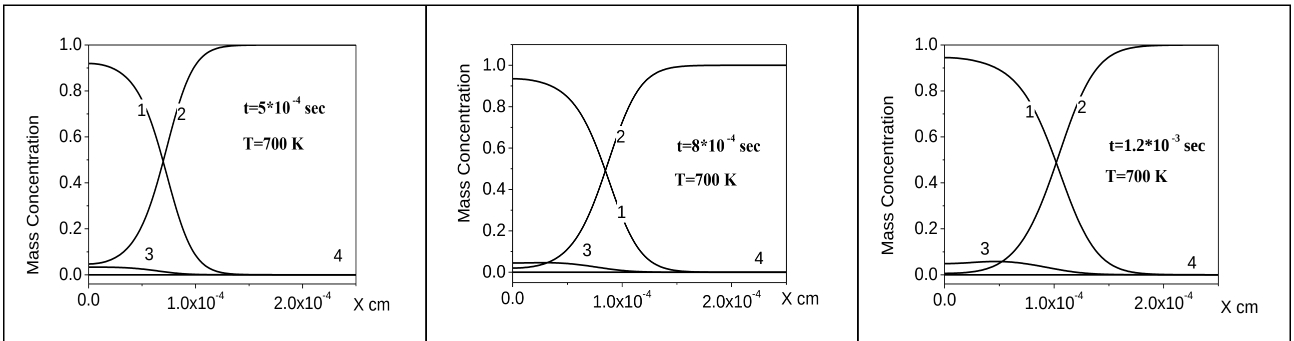
Case-I

When $t_1 = 0,\ t_2 = 0$, this model is interested for slow processes only, when reaction rates are determined by slow diffusion. Pre-exponential factors treating the corresponding "ideal" conditions for chemical reactions when there are no kinetic difficulties. Mass concentration can be calculated by formula.

$$C_k = \frac{Y_k m_k}{\sum_{i=1}^{4} Y_i m_i}$$

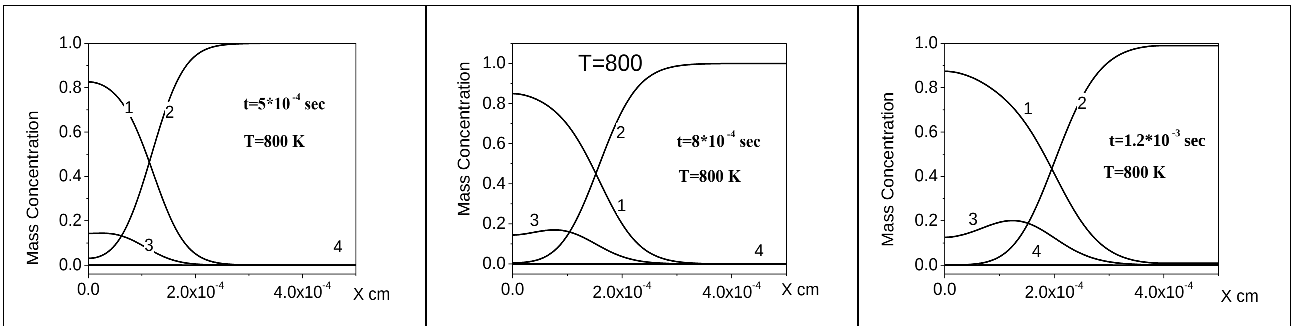
Where m_k - molar masses of substances.

Fig. 3.12-15 shows that, at a temperature T=700 K the phase Ni_3Al is absent, while the phase *NiAl* appearing as gradually by increasing the time which show that the process is slow and the diffusion is absent. On the other side *Ni* and *Al* is transfer to each other for reaction continuation and trace more large distance. The rate of new phase formation in this case is slow. Whereas at temperature T=800 K, T=900 K and T=1000 K the ratio between the reaction rate are changed, and hence, there is a region where we have a finite fraction of phase *NiAl* and *Ni*3*Al.*



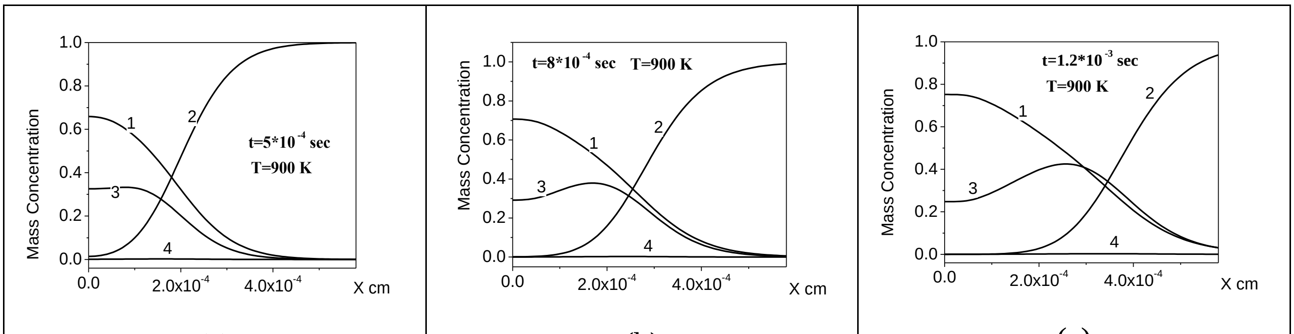
(a) (b) (c)

Fig. 3.12. Distribution of elements and phases in surface layer for (a) $t = 5\cdot10^{-4}\sec$ (b) $8\cdot10^{-4}\sec$ (c) $1.2\cdot10^{-4}\sec$ at temperature T=700 K with mass flux $q_m = 12\cdot10^3\ mol/cm^2\sec$, $t_{imp} = 3\cdot10^{-3}\sec$ and $\Delta t = 10^{-5}\sec$. Where 1.-*Al* , 2.- *Ni* , 3.-*NiAl* , 4.-Ni_3Al



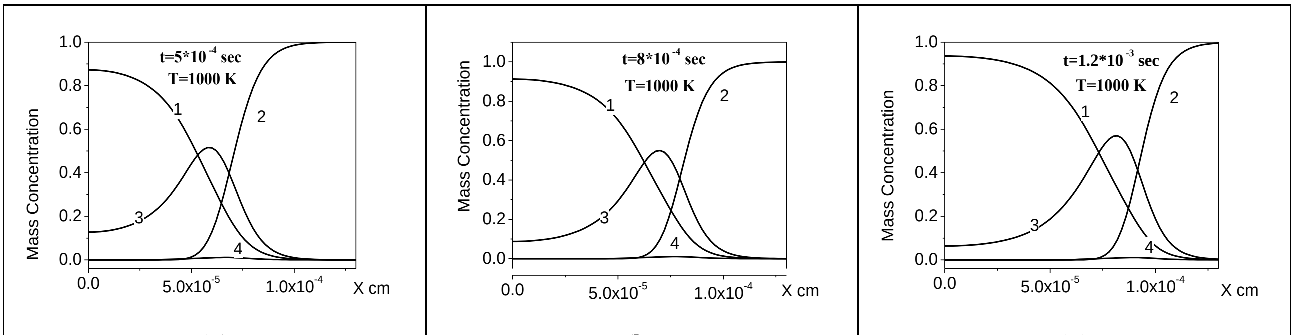
(a) (b) (c)

Fig. 3.13. Distribution of elements and phases in surface layer for (a) $t = 5\cdot10^{-4}\sec$ (b) $8\cdot10^{-4}\sec$ (c) $1.2\cdot10^{-4}\sec$ at temperature T=800 K with mass flux $q_m = 12\cdot10^3\ mol/cm^2\sec$, $t_{imp} = 3\cdot10^{-3}\sec$ and $\Delta t = 10^{-5}\sec$. Where 1.-*Al* , 2.- *Ni* , 3.-*NiAl* , 4.-Ni_3Al



(a) (b) (c)

Fig. 3.14. Distribution of elements and phases in surface layer for (a) $t = 5 \cdot 10^{-4}\sec$ (b) $8 \cdot 10^{-4}\sec$ (c) $1.2 \cdot 10^{-4}\sec$ at temperature T=900 K with mass flux $q_m = 12 \cdot 10^3\ mol/cm^2\sec$, $t_{imp} = 3 \cdot 10^{-3}\sec$ and $\Delta t = 10^{-5}\sec$. Where 1.-*Al* , 2.- *Ni* , 3.-*NiAl* , 4.-Ni_3Al.



(a) (b) (c)

Fig. 3.15. Distribution of elements and phases in surface layer for (a) $t = 5 \cdot 10^{-4}\sec$ (b) $8 \cdot 10^{-4}\sec$ (c) $1.2 \cdot 10^{-4}\sec$ at temperature T=1000 K with mass flux $q_m = 12 \cdot 10^3\ mol/cm^2\sec$, $t_{imp} = 3 \cdot 10^{-3}\sec$ and $\Delta t = 10^{-5}\sec$. Where 1.-*Al* , 2.- *Ni* , 3.-*NiAl* , 4.-Ni_3Al.

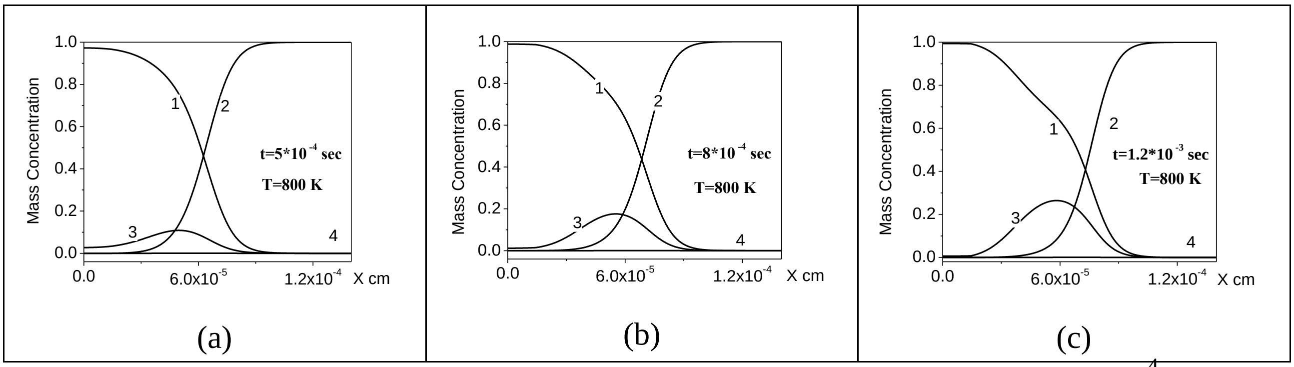
We observed that by increasing temperature the diffusion and reactions accelerated, and we come to the treated zone. In the processing zone one can clearly find where the phase is preferably *NiAl* . This is followed by a zone containing main part of phase Ni_3Al . Zone sizes depend on the temperature of the mass flux density.

Case-II

When $t_1 \neq 0$ and $t_2 \neq 0$, the model corresponds to irreversible conditions and in this case diffusion zone forms more quickly. The model is also interested for treating conditions of short pulses with a high particle density.

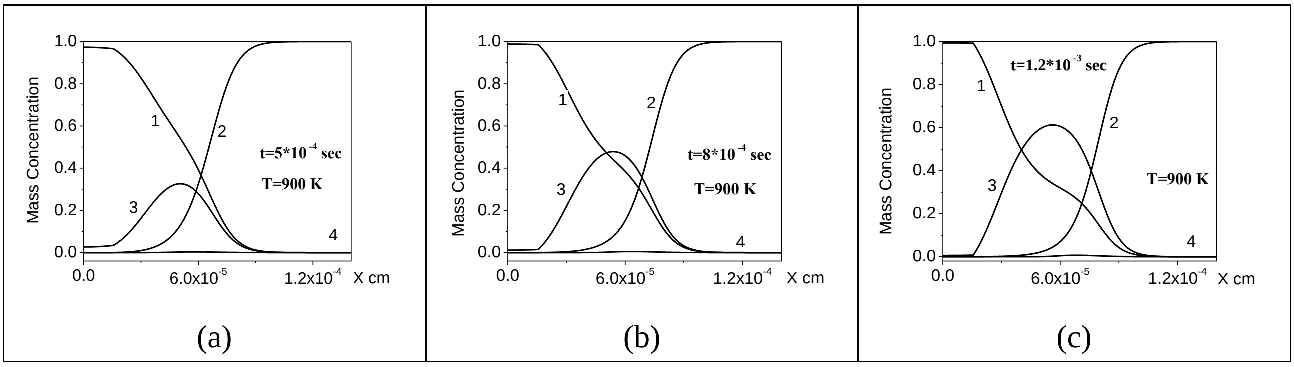
Here we assume $t_1 = 10^{-3}\sec, t_2 = 1.5 \cdot 10^{-3}\sec$, $Y_{20} = 1.8, t_{imp} = 2 \cdot 10^{-3}\sec$ and $q_m = 1.5 \cdot 10^5\ mol/cm^2\sec$, the chemical reaction occur if the heat flux increase in the range $10^4 \div 10^8$ times.

Distribution of elements and phases of different times (given below) for temperature *T*=800 K *T*=900 K and *T*=1000 K are given. Fig. 3.16-3.18 shows a gradual increase in the area occupied by phase *NiAl* and a mixture of the two phases *NiAl*+Ni_3Al. Features are only for the clearer separation of two zones.



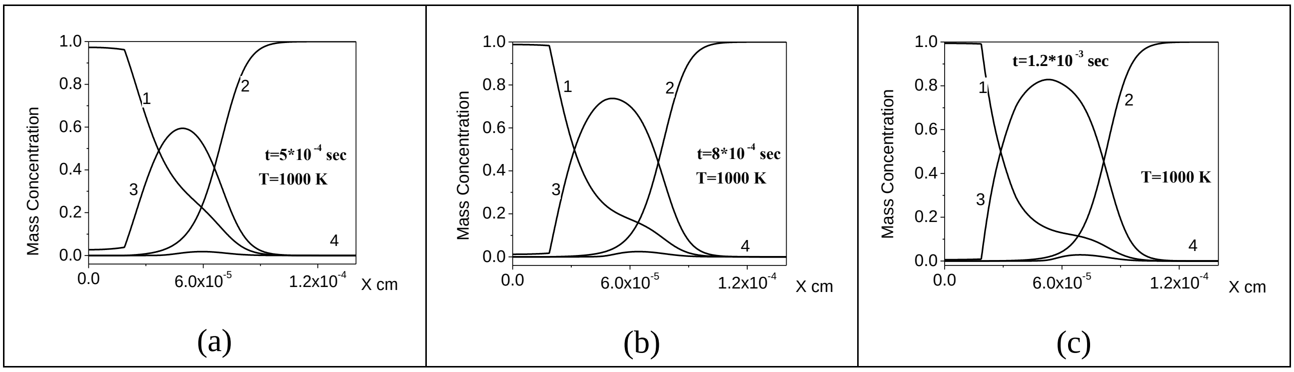
(a) (b) (c)

Fig. 3.16. Distribution of elements and phases in surface layer for (a) $t = 5\cdot 10^{-4}\sec$ (b) $8\cdot 10^{-4}\sec$ (c) $1.2\cdot 10^{-4}\sec$ at temperature T=800 K with $t_1 = 10^{-3}\sec, t_2 = 1.5\cdot 10^{-3}\sec$ mass flux $q_m = 1.5\cdot 10^5\ mol/cm^2\sec$, $t_{imp} = 2\cdot 10^{-3}\sec$ and $\Delta t = 10^{-5}\sec$. Where 1. - *Al*, 2.- *Ni* , 3.- *NiAl* , 4.- Ni_3Al.



(a) (b) (c)

Fig. 3.17. Distribution of elements and phases in surface layer for (a) $t = 5\cdot 10^{-4}\sec$ (b) $8\cdot 10^{-4}\sec$ (c) $1.2\cdot 10^{-4}\sec$ at temperature T=900 K with $t_1 = 10^{-3}\sec, t_2 = 1.5\cdot 10^{-3}\sec$ mass flux $q_m = 1.5\cdot 10^5\ mol/cm^2\sec$, $t_{imp} = 2\cdot 10^{-3}\sec$ and $\Delta t = 10^{-5}\sec$. Where 1. - *Al*, 2.- *Ni* , 3.- *NiAl* , 4.- Ni_3Al.

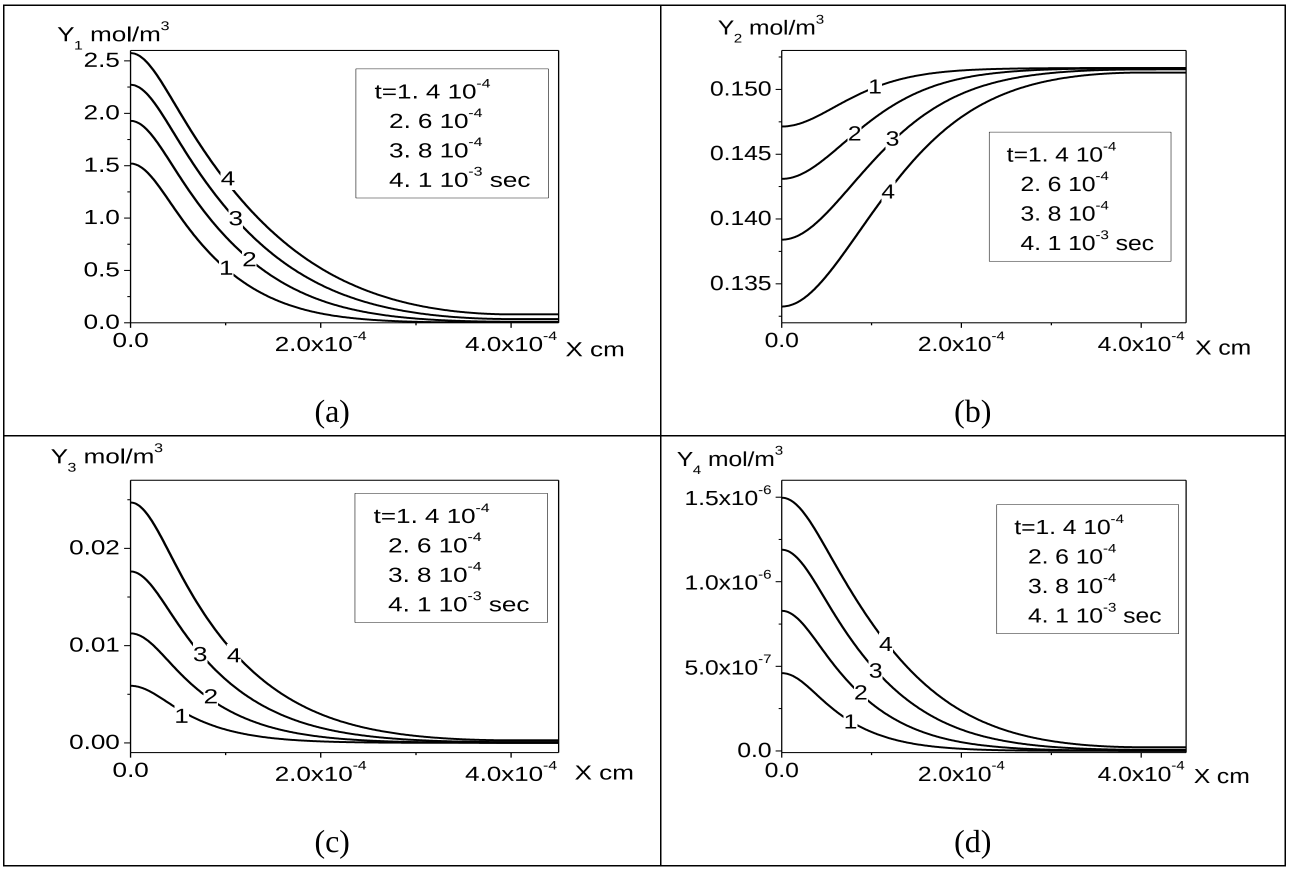


(a) (b) (c)

Fig. 3.18. Distribution of elements and phases in surface layer for (a) $t=5\cdot10^{-4}\sec$ (b) $8\cdot10^{-4}\sec$ (c) $1.2\cdot10^{-4}\sec$ at temperature T=1000 K with $t_1=10^{-3}\sec, t_2=1.5\cdot10^{-3}\sec$ mass flux $q_m=1.5\cdot10^5\ mol/cm^2\sec$, $t_{imp}=2\cdot10^{-3}\sec$ and $\Delta t=10^{-5}\sec$. Where 1. - *Al*, 2.- *Ni* , 3.- *NiAl* , 4.- Ni_3Al.

Molar concentration

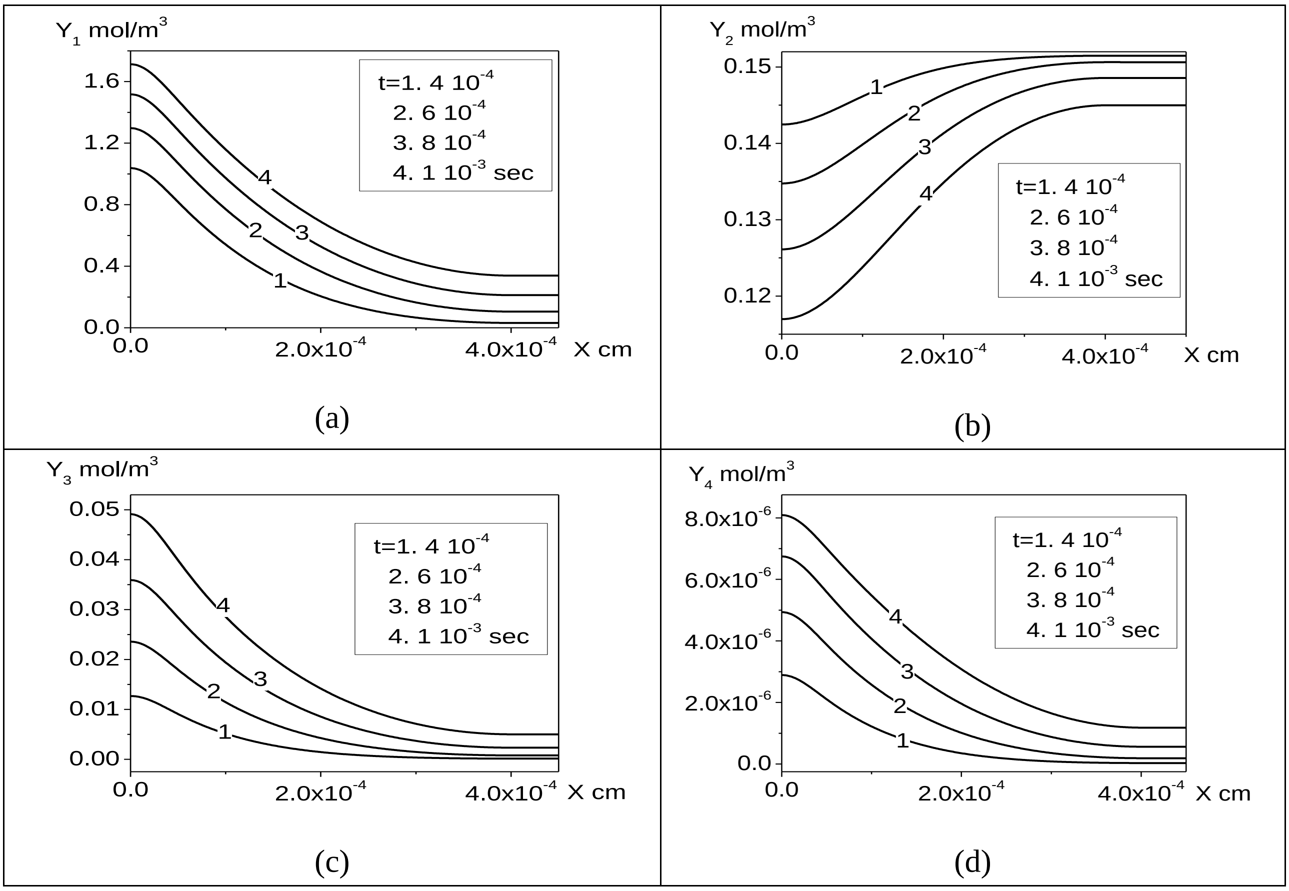
In the absence of relaxation time the molar concentration distribution of elements and chemical compounds are presented in the Fig.(3.19-3.20) for different time moments. In this case, when the temperature is low for reaction activation the distribution is almost near to the initial ion distribution after implantation, but when the temperature is increase gradually the values of concentration is decreases.



(a) (b)

(c) (d)

Fig. 3.19. Molar concentration distribution of elements and phases in surface layer for different time moments t= (1). $4\cdot10^{-4}$; (2). $6\cdot10^{-4}$; (3). $8\cdot10^{-4}$; (4). 10^{-3}sec with $t_1=t_2=0$; $T=650\ K$; $q_m=13\cdot10^3\ mol/cm^2\sec$; $\Delta t=10^{-5}\sec$ and $A=0$.



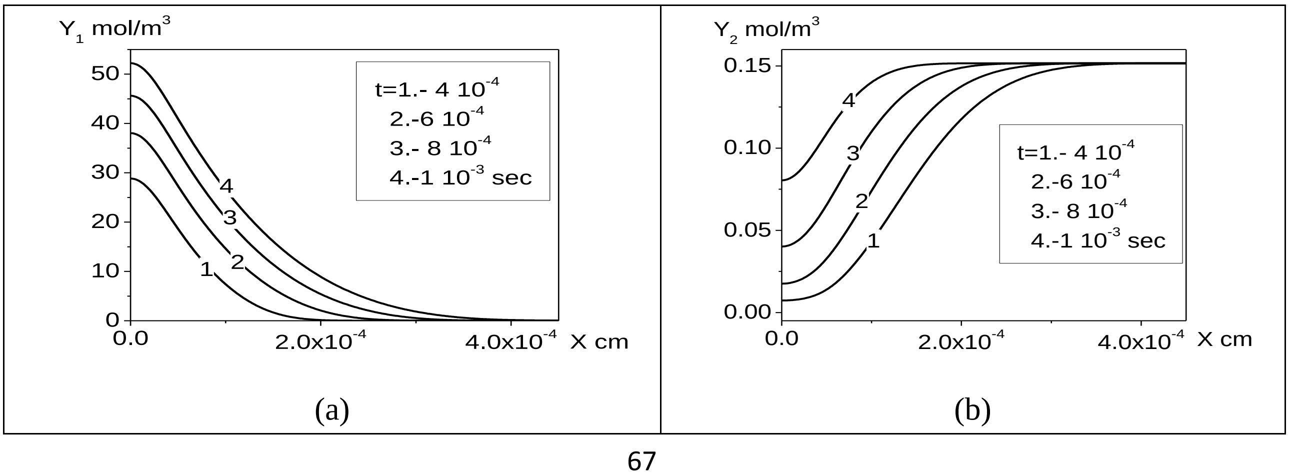
(a) (b)

(c) (d)

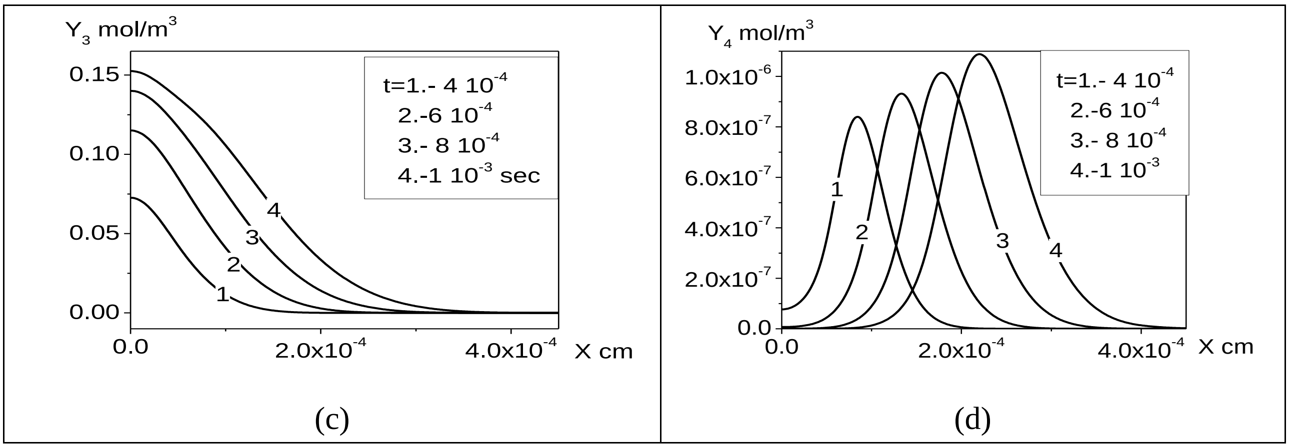
Fig. 3.20. Molar concentration distribution of elements and phases in surface layer for different time moments t = (1). $4\cdot10^{-4}$; (2). $6\cdot10^{-4}$; (3). $8\cdot10^{-4}$; (4). 10^{-3} sec with $t_1 = t_2 = 0$; $T = 700\ K$; $q_m = 13\cdot10^3\ mol/cm^2 \sec$; $\Delta t = 10^{-5} \sec$ and $A = 0$.

When we take into account the finiteness of relaxation time we obtain some attractive result. That is for $t_1 = 10^{-4} \sec, t_2 = 3\cdot10^{-3} \sec$ and when the temperature raises the diffusion and reaction zones are accelerated and we come to the treated zone Fig.(3.21-3.22). Hence we can obtain the composition of treated surface layer by varying the parameters include in the model

Where $Y_1 = AL\ , Y_2 = Ni\ , Y_3 = NiAL\ ,\ Y_4 = Ni_3AL\ \ mol/m^3$.

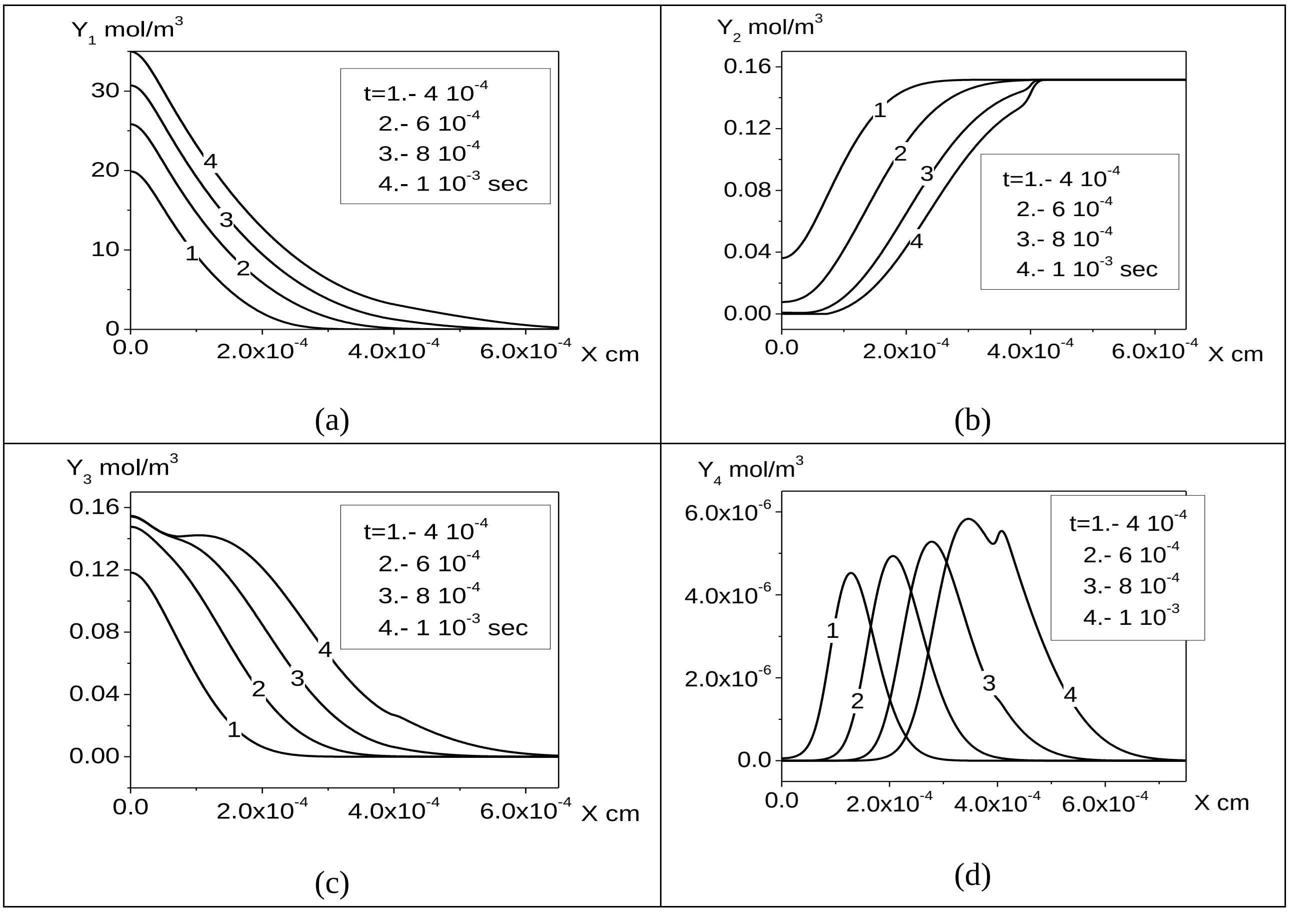


(a) (b)



(c) (d)

Fig. 3.21. Molar concentration distribution of elements and phases in surface layer for different time moments t = (1). $4\cdot10^{-4}$; (2). $6\cdot10^{-4}$; (3). $8\cdot10^{-4}$; (4). 10^{-3} sec with $q_m = 2.5\cdot10^5\, mol/cm^2 \sec$; $t_1 = 10^{-4}$, $t_2 = 3\cdot10^{-3}$, sec; $\Delta t = 10^{-5}$ sec; $t_{imp} = 2\cdot10^{-3}$ sec and with temperature T=650 K.



(a) (b)

(c) (d)

Fig. 3.22. Molar concentration distribution of elements and phases in surface layer for different time moments t = (1). $4\cdot10^{-4}$; (2). $6\cdot10^{-4}$; (3). $8\cdot10^{-4}$; (4). 10^{-3} sec with $q_m = 2.5\cdot10^5\, mol/cm^2 \sec$; $t_1 = 10^{-4}$, $t_2 = 3\cdot10^{-3}$, sec; $\Delta t = 10^{-5}$ sec; $t_{imp} = 2\cdot10^{-3}$ sec and with temperature T=700 K.

3.3.4. Generalization for other chemical systems

We can extend and generalize our problems to some more complicated problems: Thermal conductivity process is more fast than diffusion one, the heated zone is more extensive than specimen size. We believe that diffusion and chemical processes go in some narrow temperature interval and assume that temperature is constant which is given. Hence we come to thermal elastic diffusion for isothermal conditions with chemical reactions.

Assume that the n -chemical reactions are possible in the surface layer.

$$\nu_{ki}A+\nu_{ki}B\to\nu_{ki}AB, i=1,2,...,n\ ;\ k=1,2,...,m$$

The molar concentration distribution Y_k follows from the diffusion equations (1) for moving elements and kinitical equations (2) for immobile phases.

$$\frac{\partial Y_k}{\partial t}=-\nabla\cdot\mathbf{J}_k+\omega_k\ ,\ k=1,2,...,m-r$$

$$\frac{\partial Y_k}{\partial t}=\omega_k\ ,\ k=m-(r+1),...,m$$

where $\omega_k\ ,\ k=1,2,...,5$ is the sinks of substances due to the reactions,

$$\omega_k=\sum_{\mathrm{i=1}}^{\mathrm{n}}\nu_{ki}\varphi_i\ ,$$

Where φ_i - are the i-th chemical reaction rate $mol/m^3\sec$, ν_{ki} are the stoichiometric coefficient of k -component in m-th reaction; n is the number of reactions.

The reaction rates depend on concentrations and temperature:

$$\varphi_i=k_{i0}\exp\left[-\frac{E_i}{RT}\right]\cdot Y_{ki}\cdot Y_{kj}=k_i\cdot Y_{ki}\cdot Y_{kj}\ ;\ i\neq j=1,2,...,n$$

where E_i are the activation energies, R is the universal gas constant and k_{i0} is the pre-exponential factors.

The diffusion fluxes $mol/m^2\sec$ follows from relations

$$\mathbf{J}_k=-D_k\frac{\partial Y_k}{\partial x}-t_k\frac{\partial J_k}{\partial t}\ ,\ k=1,2$$

where t_k is the relaxation times, D_k is the diffusion coefficients of elements in the mixture, $\left(m^2/\sec\right)$.

The Initial conditions are

$$t = 0 \quad Y_k = 0$$

The boundary conditions are

$$x = 0: \qquad J_k = 0$$

$$x = \infty: \qquad J_k = 0$$

Note, that the same problem can be implemented on other systems, for example $Ti + Al$, $Ni + Ti$ etc. The problems can be solved numerically.

3.4. Stresses and strains in the reaction zone

Because the temperature is not too big, the stresses in diffusion zone are elastic and we can use known solutions of thermal elasticity theory, where some changing are permissible. According to Dugamel Neyman relations, we have connection between stress and strain tensor components and temperature in the form [80].

$$\sigma_{ij} = 2\mu\varepsilon_{ij} + \delta_{ij}\left[\lambda\varepsilon_{kk} - K\omega\right]$$

or

$$\sigma_{ij} = 2\frac{E}{2(1+\nu)}\varepsilon_{ij} + \delta_{ij}\left[\frac{E\nu}{(1-2\nu)(1+\nu)}\varepsilon_{kk} - \frac{E(\nu-1)}{3(1-2\nu)(1+\nu)}\omega\right],$$

where $i, j = x, y, z$; λ, μ - Lame coefficients, $K = \lambda + \frac{2}{3}\mu$ - is bulk module, connecting with technical values – elastic module and Poisson coefficient by relations

$$K = \frac{E}{3(1-2\nu)}, \; \lambda = \frac{E\nu}{(1+\nu)(1-2\nu)}, \; \mu = \frac{E}{2(1+\nu)}$$

and

$$\begin{cases} \delta_{ij} = 1, \text{if i = j;} \\ \delta_{ij} = 0, if \text{ i} \neq \text{j,} \end{cases}$$

$$\omega = 3\alpha_T\left(T - T_0\right)$$

α_T is thermal expansion coefficient, T_0 - initial temperature.

When the composition changes, we can write [81]

$$\omega = 3\left[\alpha_T\left(T - T_0\right) + \sum_{k=1}^{n}\alpha_k\left(C_k - C_{k0}\right)\right]$$

α_k - concentration expansion coefficients; C_k - are relative mass concentrations; index «0» relates to no deformed state; n - is species number (pure elements and chemical compounds).

Mass concentrations are determined by following way

$$C_k = \frac{\rho_k}{\rho} = \frac{m_k y_k}{\rho}, \; \rho = \sum_{k=1}^{n}\rho_k,$$

where m_k is molar mass of *k*-species.

Hence, we can write for $T = const$

$$\omega = 3\sum_{k=1}^{n} \frac{\alpha_k m_k}{\rho_0}\left(y_k \frac{\rho_0}{\rho} - y_{k0} \right).$$

For coefficients α_k the simple evaluation takes a place

$$\alpha_k = \frac{1}{3} \frac{\omega_k}{\sum_{i=1}^{n} \omega_i},$$

Where for pure substances ω_i - are atom volumes; for chemical compounds - molar volumes:

$$\omega_i = \frac{m_i}{\rho_{i0}},$$

ρ_{i0} is individual density of substance in standard state.

3.4.1. Problem on mechanical equilibrium

Taking the solution of the problem on mechanical equilibrium of thick plate free on external mechanical loading, but absorbing the admixture from environment [80], and taking into account the presented above formulae, we write the expressions for stress and strain tensor components in the form

$$\varepsilon_{xx} = \varepsilon_{xx}(x), \quad \varepsilon_{yy} = \varepsilon_{zz} = \varepsilon(x), \quad \varepsilon_{xy} = \varepsilon_{xz} = \varepsilon_{zy} = 0$$

$$\sigma_{yy} = \sigma_{zz} = \sigma(x), \quad \sigma_{xy} = \sigma_{xz} = \sigma_{zy} = 0$$

$$\varepsilon_{xx} = \frac{1}{3}\frac{1+\nu}{1-\nu}\omega - \frac{2\nu}{1-\nu}(F_1 x + F_2)$$

$$\sigma = \sigma_{yy} = \sigma_{zz} = -\frac{\omega}{3}\frac{E}{1-\nu} + \frac{E}{1-\nu}(F_1 x + F_2)$$

$$\varepsilon = F_1 x + F_2,$$

where

$$F_1 = \frac{N\beta - M\alpha}{\beta^2 - \gamma\alpha}, \quad F_2 = -\frac{N\gamma - M\beta}{\beta^2 - \gamma\alpha}$$

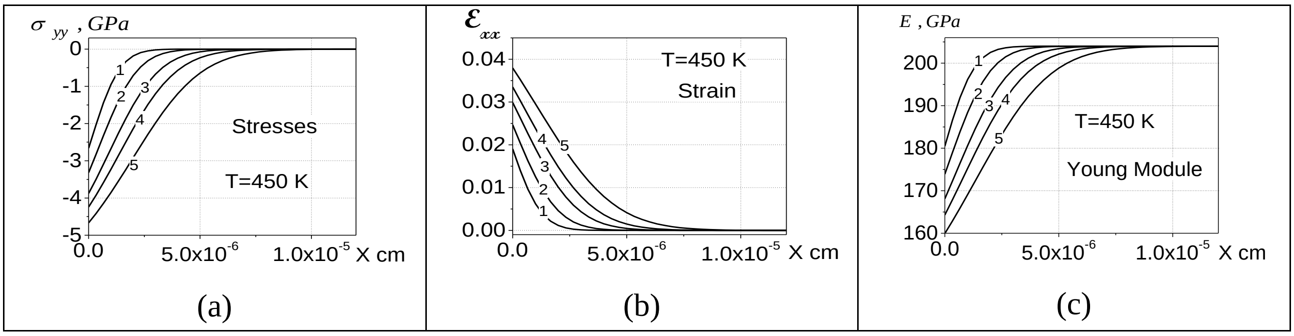
$$N = \frac{1}{3}\int_0^H \omega(z,t)\frac{E}{1-\nu}dz, \quad M = \frac{1}{3}\int_0^H \omega(z,t) z \frac{E}{1-\nu}dz$$

$$\alpha = \int_0^H \frac{E}{1-\nu}dz, \quad \beta = \int_0^H \frac{E}{1-\nu}zdz, \quad \gamma = \int_0^H \frac{E}{1-\nu}z^2 dz$$

The similar solution has been used in many publications, for example [82, 21]. Because function ω equal to zero far from diffusion zone, $x_D << H$, the integrals differ from zero only in diffusion zone, $x < x_D$. This value is determined numerically during solution of diffusion-kinetic problem. The mechanical properties (modulus of elasticity and Poisson's ratio) can depend on composition. We assume $E = E_A C_A + E_B C_B + E_C C_C$; $\nu = \nu_A C_A + \nu_B C_B + \nu_C C_C$. In accordance with literature data [83], we have $E_A = 116$; $E_B = 204$; $E_C = 200$ GPa; $\nu_A = 0.32$; $\nu_B = 0.28$; $\nu_C = 0.35$.

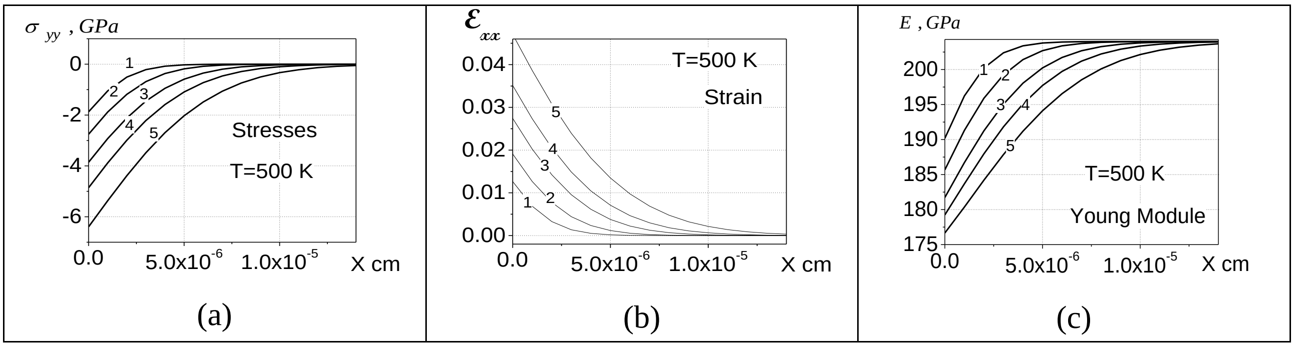
3.4.2. Stresses and strains calculation for the problem with summary reaction

In the absences of relaxation time and for small mass flux the stress and strains distributions are presented in Fig.(3.23-3.25). The strains are small for small $q_m = 2.5 \cdot 10^{-4}\, mol / cm^2 \sec$ but increase with temperature as shown in the Fig.(3.23-3.25, a), while the character of strains distribution is look like similar to the reaction product distribution Fig.(3.23-3.25, b).



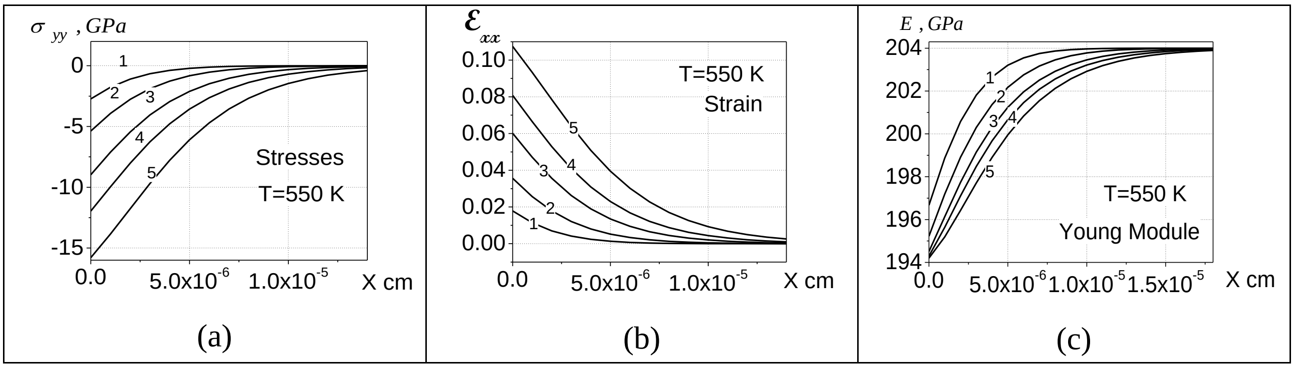
(a) (b) (c)

Fig. 3.23. (a): Stresses (b): Strains and (c): Young module in surface layer for different time moment; t =(1). $1.99 \cdot 10^{-4}$; (2). $3.99 \cdot 10^{-4}$; (3). $6.99 \cdot 10^{-4}$; (4). $9.99 \cdot 10^{-4}$; (5). $1.5 \cdot 10^{-3}$ sec with $t_A = 0$; $t_B = 0$; $T = 450\,K$ and $A = 0$.



(a) (b) (c)

Fig. 3.24. (a): Stresses (b): Strains and (c): Young module in surface layer for different time moment; t =(1). $1.99 \cdot 10^{-4}$; (2). $3.99 \cdot 10^{-4}$; (3). $6.99 \cdot 10^{-4}$; (4). $9.99 \cdot 10^{-4}$; (5). $1.5 \cdot 10^{-3}$ sec with $t_A = 0$; $t_B = 0$; $T = 500\,K$ and $A = 0$.



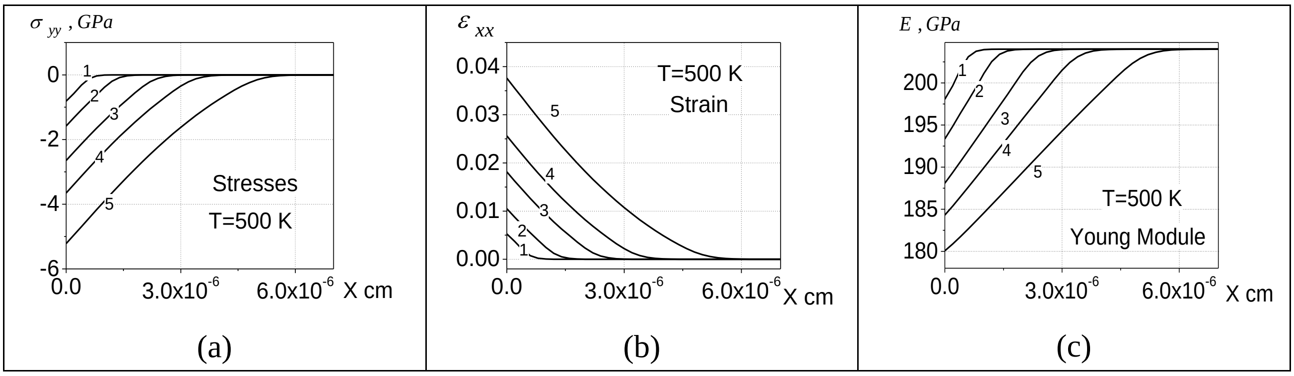
(a) (b) (c)

Fig. 3.25. (a): Stresses (b): Strains and (c): Young module in surface layer for different time moment; t=(1). $1.99\cdot10^{-4}$; (2). $3.99\cdot10^{-4}$; (3). $6.99\cdot10^{-4}$; (4). $9.99\cdot10^{-4}$; (5). $1.5\cdot10^{-3}$ sec with $t_A=0$; $t_B=0$; $T=550\,K$ and $A=0$.

When the relaxation time is takeing into account the stresses in the reaction zone in the direction perpendicular to particle beam action achieve the large values. Most of them correspond to the case with large mass fluxes q_m and short impulse time (Fig. 3.26-3.33, a, b). In this case the values of stress and strains are proportional to temperature .The Young module changes very quickly, because the properties of materials are near to each other. The E-curves repeat qualitatively the implanted particles curves (Fig. 3.26-3.33, c).

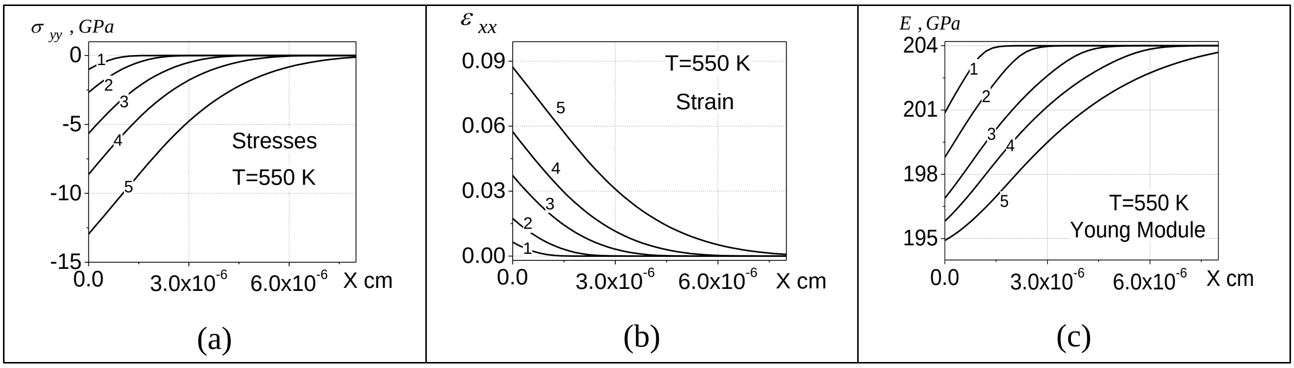
For non-zero relaxation time we have

$t_A < t_B < t_i = 2\cdot10^{-3}$



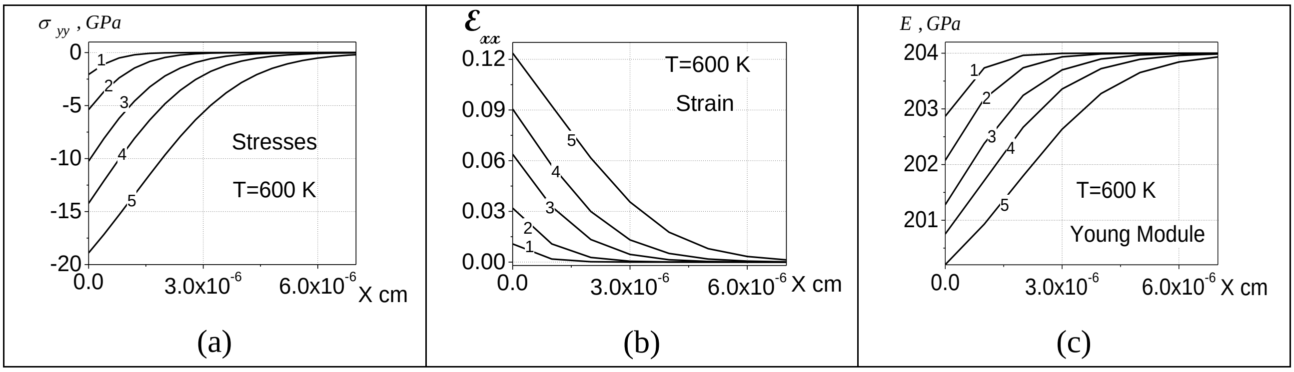
(a) (b) (c)

Fig. 3.26. (a): Stresses (b): Strains and (c): Young module in surface layer for different time moment; ; t=(1). $1.99\cdot10^{-4}$; (2). $3.99\cdot10^{-4}$; (3). $6.99\cdot10^{-4}$; (4). $9.99\cdot10^{-4}$; (5). $1.5\cdot10^{-3}$ sec with $t_A=10^{-3}$; $t_B=1.5\cdot10^{-3}$; $t_i=2\cdot10^{-3}$ $T=500\,K$ and $A=0$.



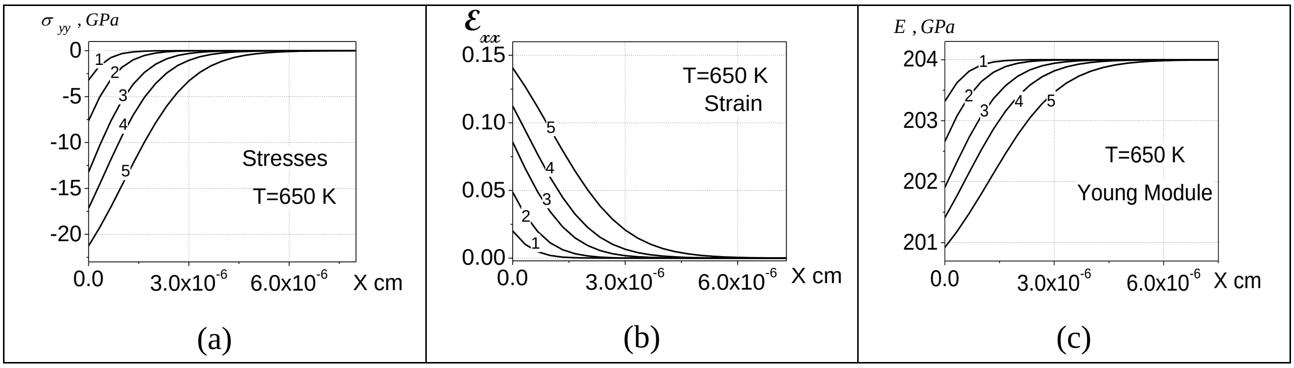
(a) (b) (c)

Fig. 3.27. (a): Stresses (b): Strains and (c): Young module in surface layer for different time moment; ; t=(1). $1.99\cdot10^{-4}$; (2). $3.99\cdot10^{-4}$; (3). $6.99\cdot10^{-4}$; (4). $9.99\cdot10^{-4}$; (5). $1.5\cdot10^{-3}$ sec with $t_A=10^{-3}$; $t_B=1.5\cdot10^{-3}$; $t_i=2\cdot10^{-3}$ $T=550\,K$ and $A=0$.



(a) (b) (c)

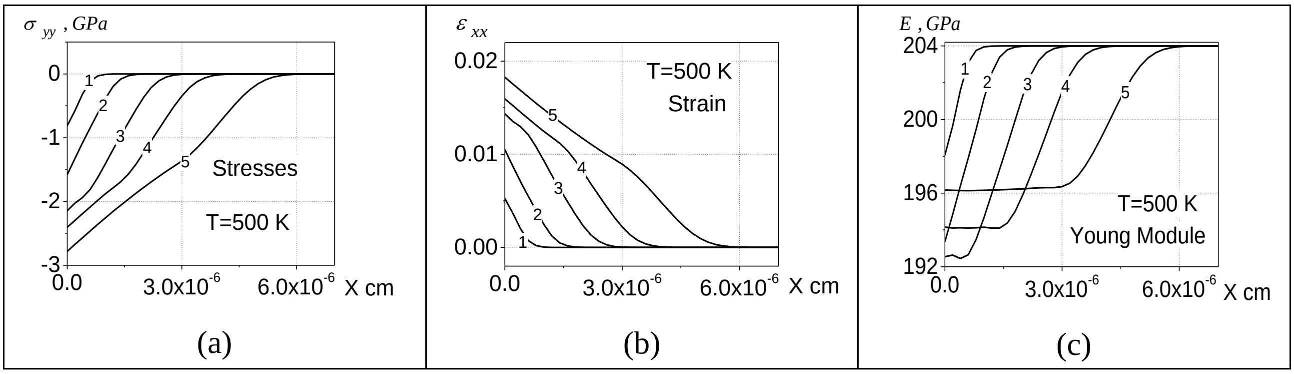
Fig. 3.28. (a): Stresses (b): Strains and (c): Young module in surface layer for different time moment; ; t=(1). $1.99\cdot10^{-4}$; (2). $3.99\cdot10^{-4}$; (3). $6.99\cdot10^{-4}$; (4). $9.99\cdot10^{-4}$; (5). $1.5\cdot10^{-3}$ sec with $t_A=10^{-3}$; $t_B=1.5\cdot10^{-3}$; $t_i=2\cdot10^{-3}$ $T=600\,K$ and $A=0$.



(a) (b) (c)

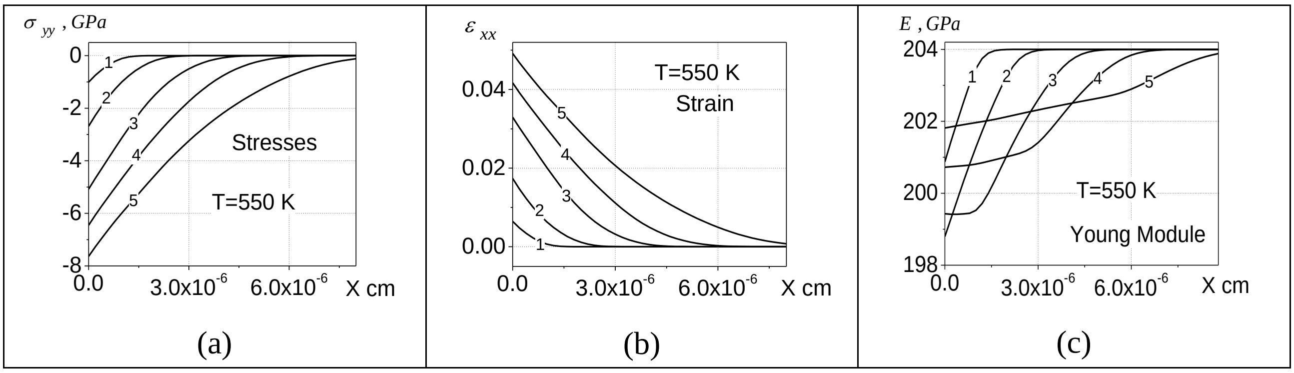
Fig. 3.29. (a): Stresses (b): Strains and (c): Young module in surface layer for different time moment; ; t=(1). $1.99\cdot10^{-4}$; (2). $3.99\cdot10^{-4}$; (3). $6.99\cdot10^{-4}$; (4). $9.99\cdot10^{-4}$; (5). $1.5\cdot10^{-3}$ sec with $t_A=10^{-3}$; $t_B=1.5\cdot10^{-3}$; $t_i=2\cdot10^{-3}$ $T=650\,K$ and $A=0$.

$t_i < t_A < t_B$



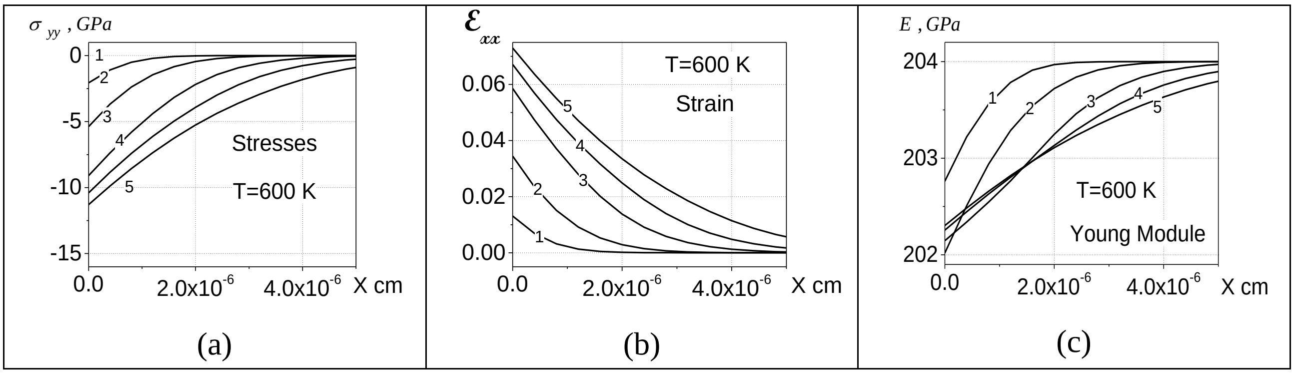
(a) (b) (c)

Fig. 3.30. (a): Stresses (b): Strains and (c): Young module in surface layer for different time moment; ; t =(1). $1.99\cdot10^{-4}$; (2). $3.99\cdot10^{-4}$; (3). $6.99\cdot10^{-4}$; (4). $9.99\cdot10^{-4}$; (5). $1.5\cdot10^{-3}$ sec with $t_A=10^{-3}$;$t_B=1.5\cdot10^{-3}$; $t_i=5\cdot10^{-4}$ $T=500\,K$ and $A=0$.



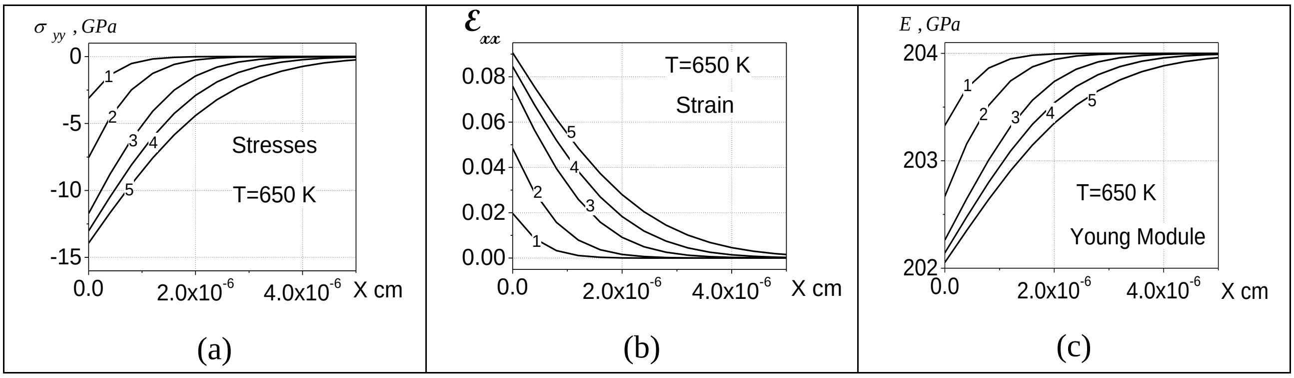
(a) (b) (c)

Fig. 3.31. (a): Stresses (b): Strains and (c): Young module in surface layer for different time moment; ; t =(1). $1.99\cdot10^{-4}$; (2). $3.99\cdot10^{-4}$; (3). $6.99\cdot10^{-4}$; (4). $9.99\cdot10^{-4}$; (5). $1.5\cdot10^{-3}$ sec with $t_A=10^{-3}$;$t_B=1.5\cdot10^{-3}$; $t_i=5\cdot10^{-4}$ $T=550\,K$ and $A=0$.



(a) (b) (c)

Fig. 3.32. (a): Stresses (b): Strains and (c): Young module in surface layer for different time moment; ; ; t =(1). $1.99\cdot10^{-4}$; (2). $3.99\cdot10^{-4}$; (3). $6.99\cdot10^{-4}$; (4). $9.99\cdot10^{-4}$; (5). $1.5\cdot10^{-3}$ sec with $t_A=10^{-3}$;$t_B=1.5\cdot10^{-3}$; $t_i=5\cdot10^{-4}$ $T=600\,K$ and $A=0$.

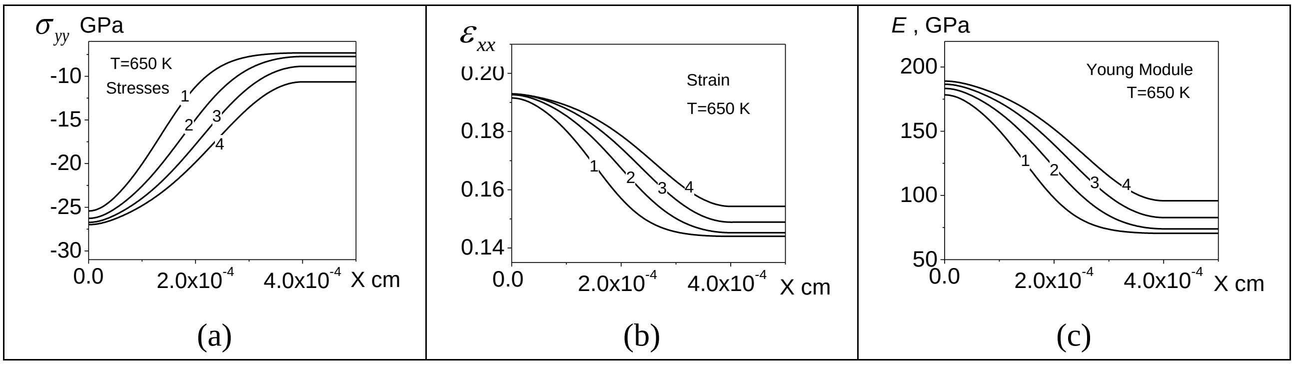


(a) (b) (c)

Fig. 3.33. (a): Stresses (b): Strains and (c): Young module in surface layer for different time moment; ; ; t=(1). $1.99\cdot10^{-4}$; (2). $3.99\cdot10^{-4}$; (3). $6.99\cdot10^{-4}$; (4). $9.99\cdot10^{-4}$; (5). $1.5\cdot10^{-3}$ sec with $t_A=10^{-3}$;$t_B=1.5\cdot10^{-3}$; $t_i=5\cdot10^{-4}$ $T=650\ K$ and $A=0$.

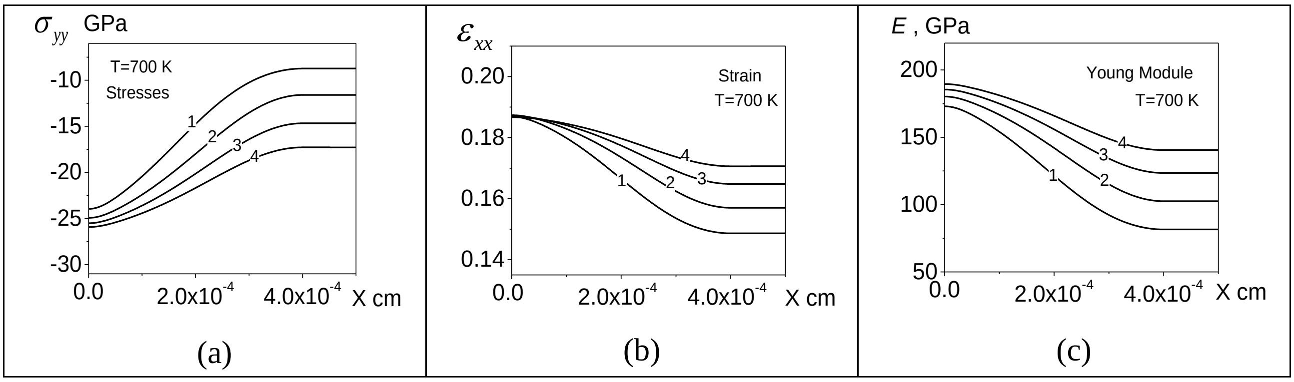
3.4.3. Stresses and strains calculation for the problem with detailed reaction scheme

In the absences of relaxation time and for small $q_m=13\cdot10^3\ mol/cm^2\sec$, the stress and strain distribution are presented in Fig.(3.34-3.35). In this case the stresses and strain Fig.(3.34-3.35, a,b) are decreases slowly by increasing the temperature.



(a) (b) (c)

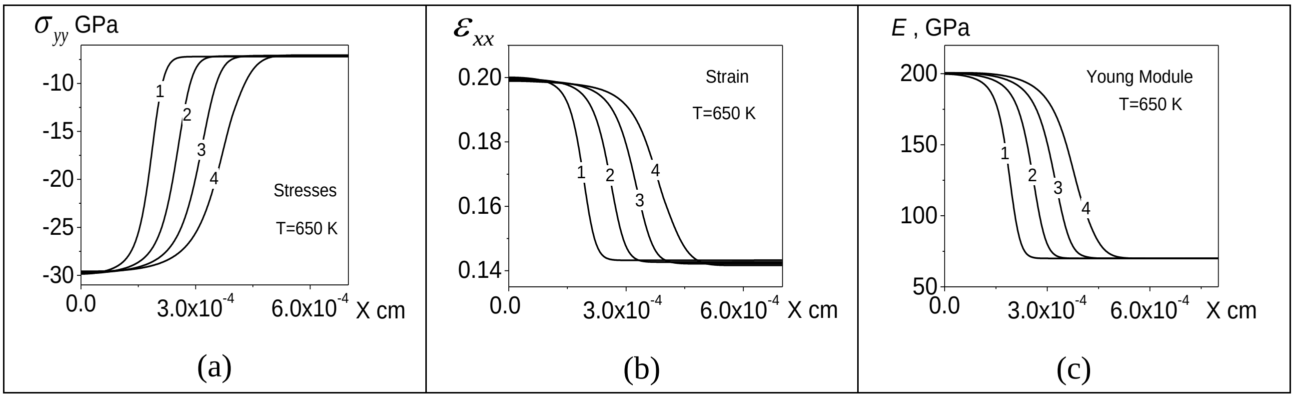
Fig.3.34 (a): Stresses (b): Strains and (c): Young module in surface layer for different time moment; t= (1). $4\cdot10^{-4}$; (2). $6\cdot10^{-4}$; (3). $8\cdot10^{-4}$; (4). 10^{-3}sec with $t_1=t_2=0$; $T=650\ K$; $q_m=13\cdot10^3\ mol/cm^2\sec,\Delta t=10^{-5}\sec$ and $A=0$.



(a) (b) (c)

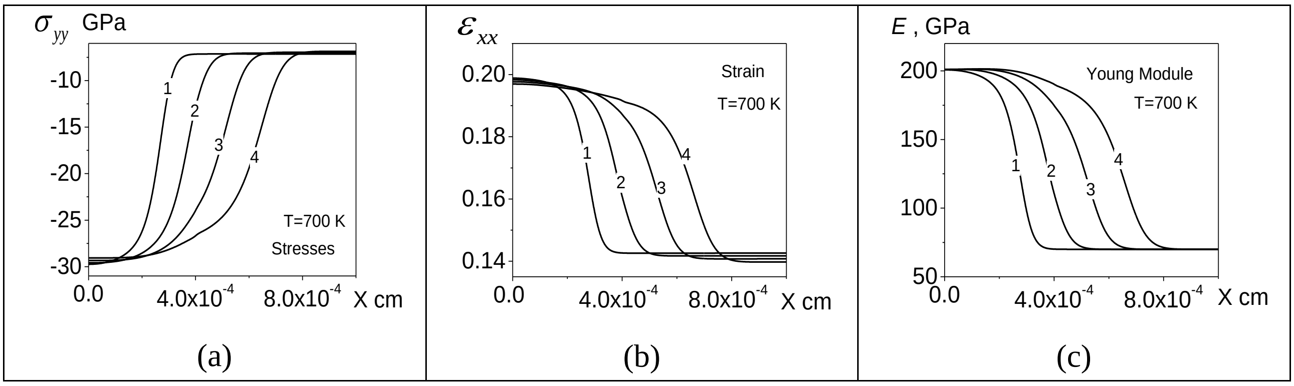
Fig.3.35 (a): Stresses (b): Strains and (c): Young module in surface layer for different time moment; $t =$ (1). $4\cdot 10^{-4}$; (2). $6\cdot 10^{-4}$; (3). $8\cdot 10^{-4}$; (4). 10^{-3} sec with $t_1 = t_2 = 0$; $T = 700\ K$; $q_m = 13\cdot 10^3\ mol/cm^2 \sec, \Delta t = 10^{-5} \sec$ and $A = 0$.

When we take into account the finiteness of relaxation time that is for $t_1 = 10^{-4} \sec,\ t_2 = 2\cdot 10^{-3} \sec,$ and when the temperature increases the stress and strain Fig. (3.36-3.37, a, b) in the reaction zone achieve large values with large q_m. The Young module Fig. (3.36-3.37, c) also change quickly by increasing temperature.



(a) (b) (c)

Fig. 3.36. (a): Stresses (b): Strains (c): Young Module in surface for different time moment $t =$ (1). $4\cdot 10^{-4}$; (2). $6\cdot 10^{-4}$; (3). $8\cdot 10^{-4}$; (4). 10^{-3} sec with $q_m = 2.5\cdot 10^5\ mol/cm^2 \sec$; $t_1 = 10^{-4},\ t_2 = 3\cdot 10^{-3}, \sec$; $\Delta t = 10^{-5}$ sec; $t_{imp} = 2\cdot 10^{-3}$ sec and with temperature T=650 K.



(a) (b) (c)

Fig. 3.37. (a): Stresses (b): Strains (c): Young Module in surface for different time moment $t =$ (1). $4\cdot 10^{-4}$; (2). $6\cdot 10^{-4}$; (3). $8\cdot 10^{-4}$; (4). 10^{-3} sec with $q_m = 2.5\cdot 10^5\ mol/cm^2 \sec$; $t_1 = 10^{-4},\ t_2 = 3\cdot 10^{-3}, \sec$; $\Delta t = 10^{-5}$ sec; $t_{imp} = 2\cdot 10^{-3}$ sec and with temperature T=700 K.

Conclusion

This chapter embraces some particular problem of generalized thermal elastic diffusion with chemical ration. We started from the known problem in literature and then added additional term in order to discuss the chemical aspect. The reactions are written for system Ni-Al based on state diagram. The first problem is on the equation system of Ni-Al having united stoichiometric coefficient, while the second one are little bit more complicated. We have described the generalized formulation as well as the particular problem formulation of the generalized thermal elastic diffusion with chemical reaction. We constructed the mathematical models. Since such problems are not easy to solve analytically so we have solved it numerically by using the implicit deference scheme. The linear difference equations are solved by double-sweep method. The numerical algorithm is suggested for all parameters region.

In the first problem we have disused simple model for new phase formation in surface layer during ion implantation, with and without relaxation time for mass flux are take into account.

It has been shown that finiteness of relaxation time changes the molar concentrations distribution in diffusion zone in comparison with usual diffusion problems. The stresses and strains can achieve large values. It has also been shown that the concentration distribution and stresses values depend on the relation between time scales of numerous physical processes. The model can be applied for different chemical system.

In the second problem simple model has been constructed in order to describe the intermetallic formation on surface layers during ion implantation, with the assumption of isothermal condition. The implicit difference scheme has been suggested for the solution of diffusion kinetic problem describing ion implantation by intermetallic phase formation. We actually suggest a model of the surface modification of nickel- aluminum ions with the relaxation of mass flows. The model corresponds to irreversible conditions and includes finiteness of relaxation times for mass fluxes. The finiteness of relaxation time is very important for the initial step of the process. Several specific times are used for example relaxation times, impulse duration, chemical reaction time and specific diffusion time. The results illustrate the convergence of difference scheme at variation of its parameters. Results analysis evolution in the surface layer is obtained different for problem with and without finite relaxation times. It has also been shown that the finiteness of relaxation time changes the concentrations distribution in diffusion zone in comparison with usual diffusion problems with high temperature. Stresses, Strain and Young Module also have been analyzed for the said problem.

Resultant Conclusion

Consequently, in our work we embraces some particular problem of generalized thermal elastic diffusion with chemical ration. We started from the known problem in literature and then added additional term in order to discuss the chemical aspect. The reactions are written for system Ni-Al based on state diagram. The first problem is on the equation system of Ni-Al having united stoichiometric coefficient, while the second one are little bit more complicated. We have described the generalized formulation as well as the particular problem formulation of the generalized thermal elastic diffusion with chemical reaction. We constructed the mathematical models. Since such problem is not easy to solve analytically so we have solved it numerically by using the implicit deference scheme. The linear difference equations are solved by double-sweep method. The numerical algorithm is suggested for all parameters region.

In the first problem we have disused simple model for new phase formation in surface layer during ion implantation, with and without relaxation time for mass flux are take into account. It has been shown that finiteness of relaxation time changes the molar concentrations distribution in diffusion zone in comparison with usual diffusion problems. The stresses and strains can achieve large values. It also has been shown that the concentration distribution and stresses values depend on the relation between time scales of numerous physical processes. The model can be applied for different chemical system.

In the second problem simple model has been constructed in order to describe the intermetallic formation on surface layers during ion implantation, with the assumption of isothermal condition. The implicit difference scheme has been suggested for the solution of diffusion kinetic problem describing ion implantation by intermetallic phase formation. We actually suggest a model of the surface modification of nickel- aluminum ions with the relaxation of mass flows. The model corresponds to irreversible conditions and includes finiteness of relaxation times for mass fluxes. The finiteness of relaxation time is very important for the initial step of the process. Several specific times are used for example relaxation times, impulse duration, chemical reaction time and specific diffusion time. The results illustrate the convergence of difference scheme at variation of its parameters. Results analysis evolution in the surface layer is obtained different for problem with and without finite relaxation times. It has also been shown that the finiteness of relaxation time changes the concentrations distribution in diffusion zone in comparison with usual diffusion problems with high temperature. Stresses, Strain and Young Module also have been analyzed for the said problem.

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Appendix

List of the main symbols

E Young's modulus;
ν Poisson's ratio;
ε is small strain tensor with components ε_{ij};
σ is stress tensor with components σ_{ij};
λ, μ are Lame coefficients;
δ is Kronecker delta;
$\mathbf{u}$ is displacement vector with components u_i
G is shear module
t is the time
$\mathbf{F}$ is vector of volume forces
T is the temperature
T_0 is the temperature of no deformed state
$\mathbf{q}$ - is the heat flux
λ_T is thermal conductivity coefficient;
c is heat capacity
c_ε is the heat capacity at the constant strains;
ρ is the density;
t_R, t_M, t_k are the relaxation times
α_T is linear thermal expansion coefficient;
K is the bulk modulus
U is the internal energy
S is the entropy
V is the Volume
G is the Gibbs energy
F - is free (Helmholtz) energy
H - is the enthalpy
p - is the pressure
C_{ijkl} is tensor of elastic modulus
D is diffusion coefficient
$\mathbf{J}$ is the diffusion flux
C_k are the mass concentrations
y_k are the relative molar concentrations
ρ_k are partial densities
α_C is concentration expansion coefficient
s_k, g_k, H_k are the partial densities, chemical potentials (partial Gibbs energies) , partial enthalpies for species (components)

L_{qq} - is the phenomenological coefficients;

D_T is thermal diffusion coefficient

ν_{ij} are stoichiometric coefficients

ξ_j is the reaction coordinate

x is the space coordinate

q_m - is particle beam density

ω_k is the chemical reaction rate

x, y, z are spatial coordinates of Cartesian coordinate system

$\nabla \cdot ... \equiv div...$; $\nabla \cdot ... \equiv grad...$

First problem programing

```
program problem_1
implicit none
integer, parameter:: n=1000,m=20
real, parameter:: RR=8.31
real:: YA(0:n),YAN(0:n),YANN(0:n),X(0:n),alp(1:n),bet(1:n)
real:: YC(0:n),YCN(0:n),YBNN(0:n)
real:: YB(0:n),YBN(0:n),YCNN(0:n)
real:: A,B,C,F,znam,YA0,m0,A0,k0,tA,DA,tB,DB,time,tau,h,time_end,h1,h2
real:: sig1,sig2,sig3,kappa,R,RA,XDA,XDB,tau_print,tt,kC,kA,kB,RB,YB0
real:: SZY(0:n),EXX(0:n),EZY(0:n),Eu(0:n),nyu(0:n),alpB,alpA,alpC
real:: EA,EB,EC,nyuA,nyuB,nyuC,mA,mB,mC,pL(0:n),pL0,pLA,pLB,pLC
real:: om(0:n),omA,omB,omC,kappaB,H_spes,H_spesD,kap0,myu0,Ft,Ftt,t_imp
real:: ALP_S,BET_S,GAM_S,N_S,M_S,F_1,F_2,CA,CB,CC,CB0
real:: ER,k00,TEMPER,tch,xxx
real:: DA01,DA02,EDA1,EDA2,DB0,EDB,DK
real:: xdif,ddd,YAS,YBS,YCS,YKR
integer:: i,j,jprint(1:m),j1,m1,m2,k,n0,kdif,kk
character*9 X_Y(m)
character*2 dn(m)
```

```
character*12 rez
data dn/'01','02','03','04','05','06','07','08','09','10',&
'11','12','13','14','15','16','17','18','19','20'/
open(1,file='dann.dat')
!Y - diffusant concentration; YN,YNN - the same, from lower layers
!DA,DB - diffusion coefficients
!tA,tA - relaxation times
!A - Ti
!B - Ni
!tau, h - time step and spatial step
!k00,ER - reaction parameters
!m0 - mass flux density
!Eu,EA,EB,EC - elastic modulus
!nyu,nyuA,nyuB,nyuC - Puisson's ratio
!alpB,alpA,alpC - concentration expansion coefficients
!mA,mB,mC - molar masses, kg/mol
!H_spes - thickness of spesimen
!nA,nB,nC - stoichiometric coefficients
read(1,*)tau,n0
read(1,*)YA0,m0
read(1,*)A0,k00,Temper,ER
read(1,*)tA,tB
read(1,*)m1,m2
read(1,*)tau_print,time_end
read(1,*)sig1,sig2,sig3
read(1,*)EA,EB,EC,nyuA,nyuB,nyuC
```

```
read(1,*)mA,mB,H_spes,H_spesD

read(1,*)DA01,DA02,EDA1,EDA2,DB0,EDB,DK

read(1,*)pLA,pLB,pLC

read(1,*)t_imp

read(1,*)rez

read(1,*)jprint

close(1)

PL0=pLB

DA=DA01*exp(-EDA1/RR/TEMPER/DK)+DA02*exp(-EDA2/RR/TEMPER/DK)

DB=DB0*exp(-EDB/RR/TEMPER/DK)

xdif=0.

ddd=0.

write(*,*)'DA,DB=',DA,DB

!specific time of chemical reaction

xxx=ALOG(10.)

tch=exp(AlOG(1./k00)+ER/TEMPER/RR)

write(*,*)'tch=',tch

!stop

do i=1,m

! files for space distributions of concentrations for different time moments

  X_Y(i)='XY'//dn(i)//'.dat'

  end do

write(*,*)(X_Y(i),i=1,m)

write(*,*)(jprint(i),i=1,m)

time=0.

j=0
```

```
j1=1
!molar volumes
mC=mA+mB
omA=mA/pLA
omB=mB/pLB
omC=mC/pLC
znam=(omA+omB+omC)*3.
!concentration expansion coefficients (relative)
alpA=omA/znam
alpB=omB/znam
alpC=omC/znam
write(*,*)'alpA,alpB,alpC=',alpA,alpB,alpC
pL=pL0
!pL,pL0,pLA,pLB,pLC - density, kg/m**3; with indexes - for standart state
! spcific diffusion scales
XDA=sqrt(DA*t_imp*10)
XDB=sqrt(DB*t_imp*10)
write(*,*)'XDA,XDB=',XDA,XDB
!space step
h=H_spesD/n
do i=0,n
  X(i)=h*i
  end do
YA=YA0
YAN=YA0
YANN=YA0
```

```
YC=0.
YCN=0.
YCNN=0.
!diffusion - kinetic problem is solved in cm, g, sec
!when [Pl]=kg/m3 and [m]=kg/mol, then [YB0]=mol/m3. In mol/cm3 we obtain
YB0=(pLB/mB)*1.e-6
YB=YB0
YBN=YB0
YBNN=YB0
YAS=YA0
YBS=YB0
YCS=0.
!only for reaction A+B=C
k0=YB0/tch
kdif=3
!k0=0.
write(*,*)'reaction rate, mol/m3/sec, k0= ',k0
!mol concentrations in diffusion problem are measured in mol/cm**3
RA=tau*DA/h**2
RB=tau*DB/h**2
write(*,*)'tau,h =',tau,h
open(2,file=rez)
!basic cicle
do while((time.lt.time_end).or.(j1.le.m))
write(2,fmt=2)time,YA(0),YB(0),YC(0),YA(50),YB(50),YC(50),xdif
j=j+1
```

```
time=j*tau
YANN=YAN
YAN=YA
YBNN=YBN
YBN=YB
YCNN=YCN
YCN=YC
!moles number in the reaction and during implantation is not conserved
!boundary condition, x=0
!external impulse acts during t_imp
if(time.lt.t_imp)then
Ft=1.
Ftt=0.
else
Ft=0.
Ftt=0.
end if
!substance A
znam=1.+2.*RA+k0*tau*YBN(0)+tA*k0*(2.*YBN(0)-YBNN(0))+tA/tau
alp(1)=2.*RA/znam
kappa=(2.*tau*m0/h)*(Ft+tA*Ftt)+YAN(0)*(1.+k0*tA*YBn(0))+tA*(2.*YAN(0)-YANN(0))/tau
bet(1)=kappa/znam
!double-sweep method; stright marching
do i=1,n-1
  A=RA
  B=RA
```

```
  C=1.+2.*RA+k0*tau*YBN(i)+tA*(2.*YBN(i)-YBNN(i))*k0+tA/tau
  F=tA*(2.*YAN(i)-YANN(i))/tau+YAN(i)*(1.+k0*tA*YBN(i))
  znam=C-alp(i)*A
  alp(i+1)=B/znam
  bet(i+1)=(A*bet(i)+F)/znam
  YKR=bet(i+1)/(1.-alp(i+1))
  kk=i+1
  if((abs(YKR-YAN(i)).le.1.e-20).and.(i.ge.25))then
  YA(kk)=YAN(kk)
  go to 6
  end if
  end do
!boundary condition of second type
kappa=(1.+tA*k0*YBN(n))*YAN(n)+tA*(2.*YAN(n)-YANN(n))/tau
znam=1.+2.*RA+tA/tau+k0*tau*(2.*YBN(n)-YBNN(n))+tau*k0*YBN(n)
kap0=2.*RA/znam
myu0=kappa/znam
YA(n)=(kap0*bet(n)+myu0)/(1.-kap0*alp(n))
6 do i=kk,1,-1
    YA(i-1)=alp(i)*YA(i)+bet(i)
    end do
!end substance A
!substance B
!boundary condition, x=0
znam=1.+2.*RB+k0*tau*YAN(0)+tB*k0*(2.*YAN(0)-YANN(0))+tB/tau
alp(1)=2.*RB/znam
```

```
kappa=YBN(0)*(1.+k0*tB*YAN(0))+tB*(2.*YBN(0)-YBNN(0))/tau
bet(1)=kappa/znam
!double-sweep method; stright marching
do i=1,n-1
  A=RB
  B=RB
  C=1.+2.*RB+k0*tau*YAN(i)+tB*(2.*YAN(i)-YANN(i))*k0+tB/tau
  F=tB*(2.*YBN(i)-YBNN(i))/tau+YBN(i)*(1.+k0*tB*YAN(i))
  znam=C-alp(i)*A
  alp(i+1)=B/znam
  bet(i+1)=(A*bet(i)+F)/znam
  YKR=bet(i+1)/(1.-alp(i+1))
  kk=i+1
  if((abs(YKR-YBN(i)).le.1.e-20).and.(i.ge.25))then
  YB(kk)=YBN(kk)
  go to 7
  end if
  end do
!boundary condition of second type
kappa=(1.+tB*k0*YAN(n))*YBN(n)+tB*(2.*YBN(n)-YBNN(n))/tau
znam=1.+2.*RB+tB/tau+k0*tau*(2.*YAN(n)-YANN(n))+tau*k0*YAN(n)
kap0=2.*RB/znam
myu0=kappa/znam
YB(n)=(kap0*bet(n)+myu0)/(1.-kap0*alp(n))
!bechkward marching
7 do i=kk,1,-1
```

```
   YB(i-1)=alp(i)*YB(i)+bet(i)
   end do
!end substance B
!calculation of product concentration
 do i=0,n
   YC(i)=YCN(i)+k0*YA(i)*YB(i)*tau
   end do
!Properties and mechanical part of the problem
!density  and volume expansion
 do i=0,n
!kg/m**3
   pL(i)=(yA(i)*mA+yB(i)*mB+yC(i)*mC)*1.e6
!mass concentrations
   CA=mA*YA(i)*1.e6/pL(i)
   CB=mB*YB(i)*1.e6/pL(i)
   CC=mC*YC(i)*1.e6/pL(i)
  ! CB0=mB*YB0*1.e6/pL0
   om(i)=3.*(alpA*CA+alpB*(CB-1.0)+alpC*CC)
   Eu(i)=EA*CA+EB*CB+EC*CC
   nyu(i)=nyuA*CA+nyuB*CB+nyuC*CC
   end do
!stresses and strains
!Integrals
 ALP_S=(Eu(0)/(1.-nyu(0))+Eu(n)/(1.-nyu(n)))/2.
 do i=1,n-1
 ALP_S=ALP_S+Eu(i)/(1.-nyu(i))
```

```
 end do
 ALP_S=ALP_S*h+EB*(H_spes-H_spesD)/(1.-nyuB)
BET_S=(X(0)*Eu(0)/(1.-nyu(0))+X(n)*Eu(n)/(1.-nyu(n)))/2.
 do i=1,n-1
 BET_S=BET_S+Eu(i)*X(i)/(1.-nyu(i))
 end do
 BET_S=BET_S*h+EB*(H_spes**2-H_spesD**2)/(1.-nyuB)/2.
 GAM_S=(X(0)**2*Eu(0)/(1.-nyu(0))+X(n)**2*Eu(n)/(1.-nyu(n)))/2.
 do i=1,n-1
 GAM_S=GAM_S+Eu(i)*X(i)**2/(1.-nyu(i))
 end do
 GAM_S=GAM_S*h+EB*(H_spes*H_spes**2-H_spesD*H_spesD**2)/(1.-nyuB)/3.
 N_S=(om(0)*Eu(0)/(1.-nyu(0))+om(n)*Eu(n)/(1.-nyu(n)))/2.
 do i=1,n-1
 N_S=N_S+Eu(i)*om(i)/(1.-nyu(i))
 end do
 N_S=N_S*h/3.
 M_S=(om(0)*X(0)*Eu(0)/(1.-nyu(0))+om(n)*X(n)*Eu(n)/(1.-nyu(n)))/2.
 do i=1,n-1
 M_S=M_S+Eu(i)*om(i)*X(i)/(1.-nyu(i))
 end do
 M_S=M_S*h/3.
 ! integration constants
 znam=bet_S**2-alp_S*gam_S
 F_1=(N_S**bet_S-M_S*alp_S)/znam
 F_2=-(N_S*gam_S-M_S*bet_S)/znam
```

```
do i=0,n
EZY(i)=F_1*X(i)+F_2
EXX(i)=(1.+nyu(i))*om(i)/3./(1.-nyu(i))-2.*nyu(i)*EZY(i)/(1.-nyu(i))
SZY(i)=-EU(i)*om(i)/3./(1.-nyu(i))+Eu(i)*EZY(i)/(1.-nyu(i))
end do
!Diffusion zone thickness
 kdif=1
 do i=n,0,-1
 ddd=(YB(i)-YB(n))/YB(n)
 if(abs(ddd).ge.0.001)then
 xdif=x(i)
 kdif=i
 go to 5
 end if
 end do
!Average composition in the diffusion zone (it is necessary to change the integral calculation)
5 kk=kdif+2
  YAS=(YA(0)+YA(kk))/2.
  YBS=(YB(0)+YB(kk))/2.
  YCS=(YC(0)+YC(kk))/2.
  do i=1,kk
  YAS=YAS+YA(i)
  YBS=YBS+YB(i)
  YCS=YCS+YC(i)
  end do
  YAS=YAS*h/x(kk)
```

```
   YBS=YBS*h/x(kk)

   YCS=YCS*h/x(kk)

!Recording of the results in files with names X_Y(j1)

   !if((j.eq.jprint(j1)).and.(j1.le.m))then

   tt=tau*jprint(j1)

    if((time.eq.tt).and.(j1.le.m))then

        k=j1+2

                        open(k,file=X_Y(j1))

            write(k,fmt=3)(X(i),YA(i),YB(i),YC(i),pL(i),om(i),Eu(i),nyu(i),EXX(i),SZY(i),EZY(i),i
=0,n)

                        close(k)

                        write(*,*)'j1,time,YB(0),YB(n)= ', j1,time,YB(0),YB(n)

                        j1=j1+1

                        end if

            !if(Y(n).ge.1.e-15)then

            !write(*,*)'it is nesessary to evaluate massives!'

            !stop

            !end if

end do

2 format(8(E15.9,2X))

3 format(11(E15.9,2X))

close(2)

stop

end
```

dann file

```
1.e-5 20                       !tau n0
0.0 2.5e-4                     !Y0,m0 2.5 mol/(cm**2 sec)
0.0 2.e16 450.0 1.181e5        !A0,k0  1.e6 1.e2 1.e3 Temper ER
0.0 0.0                        !tA 1.e-4,DA,tB,DB 1.e-3,Sec,
cm**2/sec
5 20                           !m1,m2
1.e-8 1.e-4                    !tau_print, time_end
1.0 1.0 0.0                    !sig1,sig2,sig3
116.0 204.0 200.0 0.32 0.28 0.35   !EA,EB,EC (GPa),nyuA,nyuB,nyuC
48.e-3 59.e-3 0.1 1.e-3        !mA (Ti),mB (Ni), kg/mol  (Ti
                               Ni),H_spes H_spesD (cm) for
                               diffusion
1.09 3.58e-4 251200. 130600. 1.9 279700. 3
!DA01 , DA02, EDA1.EDA2, DB0.EDB, DK
4.54e3 8.902e3 6.44e3    ! pLA(Ti),pLB(Ni),pLC(TiNi), kg/m**3
2.e-                     !t_imp
rez_3.dat                ! <12 symbols
2 10 20 30 40 50 60 70 80 100 120 150 200 250 300 500 750 1000
1250 1500 1750 2000 2250 2500 2750 3000
3500 4000 5000 6000 7000 8000 9000 10000 12000 14000 16000 18000
20000 !jprint
```

Second problem programing

```
program problem_2

implicit none

integer, parameter:: n=1000,m=20

real:: Y1(0:n),Y1N(0:n),Y1NN(0:n),X(0:n),Fx(0:n),alp1(1:n),bet1(1:n)

real:: Y2(0:n),Y2N(0:n),Y2NN(0:n),alp2(1:n),bet2(1:n),S2(0:n),F(0:n)

real:: Y3(0:n),Y3N(0:n),Y3NN(0:n),G1(0:n),H1(0:n),Y1sum,I3,I4

real:: Y4(0:n),Y4N(0:n),Y4NN(0:n),G2(0:n),H2(0:n),S1(0:n)

real:: A1,B1,U1,F1,Y10,m0,t1,D1,time,tau,h,r,time_end,VR1,VR2,DFT

real:: A2,B2,U2,F2,Y20,t2,D2,W1,W2,C1S,C2S,V1,V2,eps,zna1,zna2,Z0

real:: kappa1,kappa2,myu1,myu2,XD1,XD2,XD1R,XD2R,tau_print,tt,k1,k2,k3,k10,k20,k30

real:: SZY(0:n),EXX(0:n),EZY(0:n),Eu(0:n),nyu(0:n),alpB,alpA,alpC,alpD
```

```
real:: E1,E2,E3,E4,nyu0,nyu1,nyu2,nyu3,nyu4,pL(0:n),pL0,pL1,pL2,pL3,pL4
real:: om(0:n),om1,om2,om3,om4,H_spes,H_spesD,kap0,myu0,t_imp
real:: ALP_S,BET_S,GAM_S,N_S,M_S,F_1,F_2,CA(0:n),CB(0:n),CC(0:n),CD(0:n),m1,m2,m3,m4
real:: k0,A0,Ax,Ft,FtN,A,B,C,T,znam,znam1,znam2,znam4,znam6
real:: RR,TEMPER,D10,ED1,D20,ED2,DK
real:: E1A,E2A,E3A
integer:: i,j,jprint(1:m),j1,k,n0,n1,n2,n3,n4,iend
character*9 X_Y(m)
character*2 dn(m)
character*12 rez
data dn/'01','02','03','04','05','06','07','08','09','10',&
'11','12','13','14','15','16','17','18','19','20'/
!molar concentrations Y1 - [Al]; Y2 - [Ni]; Y3 - [NiAl]; Y4 - [Ni3Al]
!mass concentrations  CA,CB,CC,CD
!Al enters into Ni
open(1,file='dann.dat')
!time step, point number <n
read(1,*)tau,n0
write(*,*)'tau,n0=',tau,n0
!mass flux density,source parameters
read(1,*)m0,A0,Ax
write(*,*)'m0,A0,Ax=',m0,A0,Ax
!temperature
read(1,*)TEMPER
write(*,*)'TEMPER=',TEMPER
!relaxation times
```

```
read(1,*)t1,t2
write(*,*)'t1,t2=',t1,t2
!parameters for calculation of diffusion coefficients
read(1,*)D10,ED1,D20,ED2,DK
write(*,*)'D10,ED1,D20,ED2=',D10,ED1,D20,ED2
!pre-exponential factors for reactions
!Z0 serves for normalization of reaction rates
read(1,*)k10,k20,k30,Z0
write(*,*)'k10,k20,k30,Z0=',k10,k20,k30,Z0
!activation energies for reactions
read(1,*)E1A,E2A,E3A
write(*,*)'E1A,E2A,E3A=',E1A,E2A,E3A
! Time for calculation (observation time)
read(1,*)time_end
write(*,*)'time_end=',time_end
!elastic modules
read(1,*)E1,E2,E3,E4
write(*,*)'E1,E2,E3,E4=',E1,E2,E3,E4
!molar masses
read(1,*)m1,m2
m3=m1+m2    !NiAl
m4=3*m2+m1  !Ni3Al
write(*,*)'m1,m2,m3,m4=',m1,m2,m3,m4
!specimen size (thickness)
read(1,*)H_spes,H_spesD
write(*,*)'H_spes,H_spesD=',H_spes,H_spesD
```

```
!Poisson coefficients
read(1,*)nyu1,nyu2,nyu3,nyu4
write(*,*)'nyu1,nyu2,nyu3,nyu4=',nyu1,nyu2,nyu3,nyu4
!densities
read(1,*)pL1,pL2,pL3,pL4
write(*,*)'pL1,pL2,pL3,pL4=',pL1,pL2,pL3,pL4
!impulce duration
read(1,*)t_imp
write(*,*)'t_imp=',t_imp
read(1,*)rez
read(1,*)jprint
close(1)
!Universal gas constatnt
RR=8.3144621
!initial molar concentrations
!mol/cm**3
Y10=0.
Y20=pl2/m2
PL0=PL2
write(*,*)'y20= ',y20
! Diffusion coeffecients D1 and D2
D1=D10*exp(-ED1/RR/TEMPER/DK)
D2=D20*exp(-ED2/RR/TEMPER/DK)
write(*,*)'D1,D2, cm**2/sec= ',D1,D2
!files for space distribution of consentration for different time moments
do i=1,m
```

```
X_Y(i)='XY'//dn(i)//'.dat'
  end do
write(*,*)(X_Y(i),i=1,m)
write(*,*)(jprint(i),i=1,m)
time=0
j=0
j1=1
! molar volumes
om1=m1/pL1
om2=m2/pL2
om3=m3/pL3
om4=m4/pL4
znam=(om1+om2+om3+om4)*3.
! concentration expansion coefficients
alpA=om1/znam
alpB=om2/znam
alpC=om3/znam
alpD=om4/znam
write(*,*)'alpA,alpB,alpC,alpD=',alpA,alpB,alpC,alpD
! basic material density
pL=pL2
! Specific diffusion scales
XD1=sqrt(D1*t_imp*10.)
XD1R=sqrt(D1*t1)
XD2=sqrt(D2*t_imp*10)
XD2R=sqrt(D2*t2)
```

```
write(*,*)'XD1,XD1R =',XD1,XD1R

write(*,*)'XD2,XD2R =',XD2,XD2R

! Space step

h=H_spesD/n

write(*,*)'tau,h =',tau,h

eps=0.00001

!spatial points and space source distribution

do i=0,n

  X(i)=h*i

  Fx(i)=exp(-Ax*X(i)**2)

  end do

write(*,*)'X(i)='

write(*,*)(X(i),i=0,n,100)

write(*,*)'Fx(i)='

write(*,*)(Fx(i),i=0,n,100)

!initial concentrations

do i=0,n

Y1(i)=Y10

Y2(i)=Y20

Y3(i)=0.

Y4(i)=0.

Y1N(i)=Y10

Y2N(i)=Y20

Y3N(i)=0.

Y4N(i)=0.

end do
```

```
!mol concentrations in diffusion problem are measured in mol/cm**3

!diffusion - kinetic problem is solved in sm, g, sec

I3=0.

I4=0.

if((t1.gt.1.e-10).and.(t2.gt.1.e-10))then

  VR1=sqrt(D1/t1)

  VR2=sqrt(D2/t2)

  write(*,*)'VR1,VR2= ',VR1,VR2

  end if

 !reactin rates

k1=Z0*k10*exp(-E1A/RR/TEMPER)

k2=Z0*k20*exp(-E2A/RR/TEMPER)

k3=Z0*k30*exp(-E3A/RR/TEMPER)

write(*,*)'k1,k2,k3 =',k1,k2,k3

r=tau/h**2

kappa1=t1/tau

kappa2=t2/tau

write(*,*)'kappa1,kappa2= ',kappa1,kappa2

open(2,file=rez)

Y1sum=0.

!moles number in the reaction and during implantation is not conserved

!boundary condition, x=0

!external impulse acts during t_imp

do while(time.lt.time_end)

if(j1.gt.m)then

stop
```

```
end if
!write(*,*)'1'
write(2,fmt=2)time,Y1(0),Y2(0),Y3(0),Y4(0),Y1(n0),Y2(n0),Y3(n0),Y4(n0),Y1sum,I3,I4
!write(*,*)'2'
j=j+1
time=j*tau
Y1NN=Y1N
Y1N=Y1
Y2NN=Y2N
Y2N=Y2
Y3NN=Y3N
Y3N=Y3
Y4NN=Y4N
Y4N=Y4
FtN=Ft
if(time.lt.t_imp)then
!Ft=(-A0*time)
Ft=1.
DFT=0.
else
Ft=0.
DFT=0.
!write(*,*)'Ft= ',Ft
end if
!equations coefficients for intermediate calculation
do i=0,n0
```

```
  H1(i)=k1*t1*Y1NN(i)+3.*k2*t1*Y1NN(i)*Y2NN(i)**2
G1(i)=k1*t1*Y2NN(i)+k2*t1*Y2NN(i)*Y2NN(i)**2+4.*k3*t1*Y1NN(i)*Y4NN(i)+1.

S1(i)=k1*Y2NN(i)+k2*Y2NN(i)*Y2NN(i)**2+2.*k3*Y4NN(i)*Y1NN(i)+2.*k3*k2*t1*Y1NN
(i)**2*Y2NN(i)*Y2NN(i)**2
  H2(i)=k1*t2*Y1NN(i)+9.*k2*t2*Y1NN(i)*Y2NN(i)**2+1.
  G2(i)=k1*t2*Y2NN(i)+3.*k2*t2*Y2NN(i)*Y2NN(i)**2
  S2(i)=k1*Y1NN(i)+3.*k2*Y1NN(i)*Y2NN(i)**2
  F(i)=FX(i)*Ft
  end do
!first concentration
!boundary condition on external surface x=0
znam1=G1(0)+2.*D1*r+kappa1+tau*S1(0)
alp1(1)=2.*D1*r/znam1
bet1(1)=kappa1*(2.*Y1N(0)-
Y1NN(0))+tau*(m0*(F(0)+t1*FX(0)*DFT)+2.*k3**2*t1*Y4NN(0)*Y1NN(0)**2*Y1NN(0)**
2)
bet1(1)=(bet1(1)+G1(0)*Y1N(0)-H1(0)*(Y2N(0)-Y2NN(0)))/znam1
!write(*,*) '1', alp1(1),bet1(1)
 ! Double sweep method, Stright marching
 do i=1,n-1
  A1=D1*r
  B1=D1*r
  U1=kappa1+G1(i)+2.*A1+tau*S1(i)
  F1=2*tau*k3**2*t1*Y4NN(i)*Y1NN(i)**2*Y1NN(i)**2+G1(i)*Y1N(i)-H1(i)*(Y2N(i)-
Y2NN(i))+ &
  m0*tau*(t1*DFT+F(i))-kappa1*(Y1NN(i)-2.*Y1N(i))
  znam=U1-alp1(i)*A1
```

```
  alp1(i+1)=B1/znam
  bet1(i+1)=(A1*bet1(i)+F1)/znam
  iend=i
  C1S=bet1(i+1)/(1.-alp1(i+1))
  if((abs(C1S-Y1N(i)).le.Y1N(i)*eps).and.(i.ge.25))then
  go to 4
  end if
end do
  iend=n
  zna1=2.*D1*r+kappa1+G1(n)+tau*S1(n)
   V1=2.*D1*r/zna1
   V2=kappa1*(2.*Y1N(n)-Y1NN(n))+G1(n)*Y1N(n)-H1(n)*(Y2N(n)-Y2NN(n))+&
        tau*(m0*F(n)+t1*m0*Fx(n)*DFT+2.*k3**2*t1*Y4NN(n)*Y1NN(n)**2*Y1NN(n)**2)
        V2=V2/zna1
  Y1(iend)=(V1*bet1(iend)+V2)/(1.-V1*alp1(iend))
  go to 5
 4 Y1(iend)=C1S
5 do i=iend-1,0,-1
!write(*,*)'3'
   Y1(i)=alp1(i+1)*Y1(i+1)+bet1(i+1)
        if(Y1(i).le.0)then
        Y1(i)=0.
        end if
         end do
!write(*,*)'2', Y1(1),Y1(N)
!stop
```

```
Y1sum=(Y1(0)+Y1(n))/2.
do i=1,n-1
Y1sum=Y1sum+Y1(i)
end do
Y1sum=Y1sum*h
!Second concentration
znam4=2.*D2*r+kappa2+H2(0)+tau*S2(0)
alp2(1)=2.*D2*r/znam4
bet2(1)=(kappa2*(2.*Y2N(0)-Y2NN(0))+H2(0)*Y2N(0)-G2(0)*(Y1N(0)-Y1NN(0)))/znam4
do i=1,n-1
  A2=D2*r
  B2=D2*r
  U2=kappa2+H2(i)+2.*A2+tau*S2(i)
  F2=kappa2*(2.*Y2N(i)-Y2NN(i))+H2(i)*Y2N(i)-G2(i)*(Y1N(i)-Y1NN(i))
  znam=U2-alp2(i)*A2
  alp2(i+1)=B2/znam
  bet2(i+1)=(A2*bet2(i)+F2)/znam
  iend=i
  C2S=bet2(i+1)/(1.-alp2(i+1))
  if((abs(C2S-Y2N(i)).le.Y2N(i)*eps).and.(i.ge.50))then
  go to 6
  end if
  end do
  iend=n
  zna2=2.*D2*r+kappa2+H2(n)+tau*S2(n)
   W1=2.*D2*r/zna2
```

```
    W2=(kappa2*(2.*Y2N(n)-Y2NN(n))+H2(n)*Y2N(n)-G2(n)*(Y1N(n)-Y1NN(n)))/zna2
    Y2(iend)=(W1*bet2(iend)+W2)/(1.-W1*alp2(iend))
   go to 7
6 Y2(iend)=C2S
7 do i=iend-1,0,-1
Y2(i)=alp2(i+1)*Y2(i+1)+bet2(i+1)
if(Y2(i).le.0)then
            Y2(i)=0.
            end if
   end do
!kinetic equation
!It is necessary to use more rigorous methods for stiff problem!!!
do i=0,n
   Y3(i)=Y3N(i)+tau*(k1*Y1N(i)*Y2N(i)+3.*k3*Y4N(i)*Y1N(i)**2)
   if(Y3(i).le.0.)then
            Y3(i)=0.
            end if
   Y4(i)=Y4N(i)+tau*(k2*Y1N(i)*Y2N(i)*Y2N(i)**2-k3*Y4N(i)*Y1N(i)**2)
   if(Y4(i).le.0.)then
            Y4(i)=0.
            end if
    end do

!Properties and mechanical part of the problem
do i=0,n
   !Density and mass concentrations g/cm**3
```

```
  pL(i)=Y1(i)*m1+Y2(i)*m2+Y3(i)*m3+Y4(i)*m4
  !Mass consentrations
  CA(i)=m1*Y1(i)/pL(i)
  CB(i)=m2*Y2(i)/pL(i)
  CC(i)=m3*Y3(i)/pL(i)
  CD(i)=m4*Y4(i)/pL(i)
  !Mechanical properties
  !volume expansion
  om(i)=3.*(alpA*CA(i)+alpB*CB(i)+alpC*CC(i)+alpD*CD(i))
  !elastic stresses
  Eu(i)=E1*CA(i)+E2*CB(i)+E3*CC(i)+E4*CD(i)
  !Poisson coefficicent
  nyu(i)=nyu1*CA(i)+nyu2*CB(i)+nyu3*CC(i)+nyu4*CD(i)
  end do
!Total mass consentration CC(i) i.e integral from 0 to L CC(x) dx
I3=(CC(0)+CC(n))/2
do i=1,n-1
I3=I3+CC(i)
end do
I3=I3*h/H_spesD
!Total mass consentration CD(i) i.e integral from 0 to L CD(x) dx
I4=(CD(0)+CD(n0))/2
do i=1,n-1
I4=I4+CD(i)
end do
I4=I4*h/H_spesD
```

```
!Stresses and strains

!Integrals

ALP_S=(Eu(0)/(1.-nyu(0))+Eu(n)/(1.-nyu(n)))/2

do i=1,n-1

        ALP_S=ALP_S+Eu(i)/(1.-nyu(i))

        end do

        ALP_S=ALP_S*h+E2*(H_spes-H_spesD)/(1.-nyu2)

BET_S=(X(0)*Eu(0)/(1-nyu(0))+x(n)*Eu(n)/(1.-nyu(n)))/2.

do i=1,n-1

        BET_S=BET_S+Eu(i)*X(i)/(1.-nyu(i))

        end do

        BET_S=BET_S*h+E2*(H_spes**2-H_spesD**2)/(1.-nyu2)/2.

GAM_S=(X(0)**2*Eu(0)/(1-nyu(0))+x(n)**2*Eu(n)/(1.-nyu(n)))/2.

do i=1,n-1

GAM_S=GAM_S+Eu(i)*X(i)**2/(1.-nyu(i))

end do

GAM_S=GAM_S*h+E2*(H_spes*H_spes**2-H_spesD*H_spesD**2)/(1.-nyu2)/3.

N_S=(om(0)*Eu(0)/(1.-nyu(0))+om(n)*Eu(n)/(1.-nyu(n)))/2.

do i=1,n-1

N_S=N_S+Eu(i)*om(i)/(1.-nyu(i))

end do

N_S=N_S*h/3.

M_S=(om(0)*X(0)*Eu(0)/(1.-nyu(0))+om(n)*x(n)*Eu(n)/(1.-nyu(n)))/2.

do i=1,n-1

M_S=M_S+EU(i)*X(i)*om(i)/(1.-nyu(i))

end do
```

```
M_S=M_S*h/3.
!Integration constants
znam6=bet_S**2-alp_S*gam_S
F_1=(N_S*bet_S-M_S*alp_S)/znam6
F_2=-(N_S*gam_S-M_S*bet_S)/znam6
do i= 0,n
  EZY(i)=F_1*X(i)+F_2
  EXX(i)=(1.+nyu(i))*om(i)/(1.-nyu(i))/3.-2.*nyu(i)*EZY(i)/(1.-nyu(i))
  SZY(i)=-Eu(i)*om(i)/(1.-nyu(i))/3.+Eu(i)*EZY(i)/(1.-nyu(i))
  end do
!According to the results in files with names X_Y(j1)
!If ((j1.eq,jprint(j1)) and (j1,le.m) then
tt=tau*jprint(j1)
 if((time.eq.tt).and.(j1.le.m))then
 k=j1+2
 open(k,file=X_Y(j1))
write(k,fmt=3)(X(i),Y1(i),Y2(i),Y3(i),Y4(i),pL(i),CA(i),CB(i),CC(i),CD(i),om(i),&
Eu(i),nyu(i),EXX(i),SZY(i),EZY(i),i=0,n)
  close(k)
  write(*,*)'j1,time,Y1(0),Y1sum=',j1,time,Y1(0),Y1sum
 j1=j1+1
 end if
 end do
 2 format(12(E15.9,2X))
3 format(16(E15.9,2X))
close(2)
```

```
end
```

dann file

```
0.00001 1000                  !tau 2.0 n0<n
1.5e5 0.0 1.e9      !m0 2.5 (e3) mol/(cm**2 sec), A0, Ax1.5e5
1000.0              !TEMPER
1.e-3 1.5e-3        !t1 1.e-4,t2,1.e-3,Sec,
4.36 2.69509e5 1.9 2.797e5 2.0
!D10,ED1 (Al),D20,ED2 (Ni) cm**2/sec, J/mol !Ni c Al???
8.994e16 1.517e21 0.853e14 1.e-8
!k10,k20,k30,Z0 - transition to measurement unit 1.e-12 1.e-4
86128.0 169149.0 48715.0      !E1A, E2A,E3A
1.e7                          !time_end
200 70 270 670                !E1, E2,E3,E4 GPa
26.98 58.69                   !m1(Al),m2 (Ni)Molar masses, g/mol
0.1 1.e-3                     !H_spes cm H_spes H_spesD (cm)
0.31 0.35 0.27 0.28      !nyu1,nyu2,nyu3,nyu4 Poisson Coefficient
2.7 8.9 11.6 29.4        !pL1(Al),pL2(Ni),pL3,pL4 Density g/cm**3
2.e-3                    !t_imp 2.0
rez.dat                  ! <12 symbols
4 10 30 50 60 80 100 120 140 160 200 220 240 260 280 300 320 340
360 400 15000 20000 25000 30000 35000 40000 45000 50000
20 50 100 200 300 400 500 600 700 800 1000 1100 1200 1300 1400
1500 1600 1700 2500 3000 5000 7500           !jprint tau=0.1
8 20 40 80 120 160 200 240 280 320 400 440 480 520 560 600 640
680 720 800 1000 1250 1500 1750 2000 2250 2500 2750 3000 3500
4000 5000 6000 7000 8000 9000 10000 12000 14000 16000 18000
20000   !jprint tau=0.25
4 10 20 40 60 80 100 120 140 160 200 220 240 260 280 300 320 340
360 400 600 1000 1250 1500 1750 2000 2250 2500 2750 3000 3500
4000 5000 6000 7000 8000 9000 10000 12000 14000 16000 18000
20000   !jprint tau=0.5
2 5 10 20 30 40 50 60 70 80 100 110 120 130 140 150 160 170 180
300 500 750 1000 1250 1500 1750 2000 2250 2500 2750 3000 3500
4000 5000 6000 7000 8000 9000 10000 12000 14000 16000 18000
20000   !jprint tau=1
When t1=t2=0, this problem is interested only for slow
processes, when reaction rates are limited by slow diffusion.
2 50 75 150 300 500 750 1000 1250 1500 1750 2000 2250 2500 2750
3000 3500 4000 5000 6000 7000 8000 9000 10000 12000 14000 16000
18000 20000   !jprint
0.1 400             !tau 2.0 n0<n
0.35 0.0 50.0       !m0 2.5 (e3) mol/(mkm**2 sec), A0, Ax1.5e5
```

```
1000.0              !TEMPER
0.0 0.0             !t1 1.e-4,t2,1.e-3,Sec,
1.09 2.512e5 3.58e-4 1.306e5 1.9 2.797e5
!D101 ,ED11,D102,ED12,D20,ED2 cm**2/sec, J/mol
8.994e16 1.517e21 0.853e14 1.e-12
!k10, k20, k30, Z0 - transition to measurement unit 1.e-12 1.e-4
86128.0 169149.0 48715.0      !E1A ,E2A,E3A
1.e7                          !time_end
200 70 270 670                !E1 ,E2,E3,E4 GPa
26.98 58.69                   !m1,m2 Molar masses
1.0                           !H_spes mkm
0.31 0.35 0.27 0.28  !nyu1, nyu2, nyu3, nyu4 Poisson Coefficient
2.7 8.9 11.6 29.4       !pL1, pL2, pL3, pL4 Density g/cm**3
4.e2                    !t_imp 2.0
0.0 1.8        !Y10,Y20 - initial molar concentration, mol/mkm**3
rez.dat                 ! <12 symbols
20 50 200 400 800 1600 2400 3200 4000 4800 5600 7200 8000 9000
10000 12000 15000 20000 25000 30000 35000 40000 45000 50000
20 50 100 200 300 400 500 600 700 800 1000 1100 1200 1300 1400
1500 1600 1700 2500 3000 5000 7500           !jprint tau=0.1
8 20 40 80 120 160 200 240 280 320 400 440 480 520 560 600 640
680 720 800 1000 1250 1500 1750 2000 2250 2500 2750 3000 3500
4000 5000 6000 7000 8000 9000 10000 12000 14000 16000 18000
20000   !jprint tau=0.25
4 10 20 40 60 80 100 120 140 160 200 220 240 260 280 300 320 340
360 400 600 1000 1250 1500 1750 2000 2250 2500 2750 3000 3500
4000 5000 6000 7000 8000 9000 10000 12000 14000 16000 18000
20000   !jprint tau=0.5
2 5 10 20 30 40 50 60 70 80 100 110 120 130 140 150 160 170 180
300 500 750 1000 1250 1500 1750 2000 2250 2500 2750 3000 3500
4000 5000 6000 7000 8000 9000 10000 12000 14000 16000 18000
20000   !jprint tau=1
When t1=t2=0, this problem is interested only for slow
processes, when reaction rates are limited by slow diffusion.
2 50 75 150 300 500 750 1000 1250 1500 1750 2000 2250 2500 2750
3000 3500 4000 5000 6000 7000 8000 9000 10000 12000 14000 16000
18000 20000   !jprint
```

*****