CALCULATION MODEL OF FORMATION OF NONMETALLIC INCLUSIONS OF MULTILAYER MORPHOLOGY IN WELD METAL

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The objective of the work was development of a calculation model for practical prediction of the kinetics of formation of multicomponent endogenous nonmetallic inclusions in the weld metal. The proposed mathematical model is a nonstandard nonlinear boundary problem for a system of diffusion equations with the specific condition on the moving melt-inclusion interphase, and it allows for the kinetics and heterogeneity of the process under the conditions of the real thermal cycle of welding. The calculation program developed as a computer realization of the constructed model allows evaluating in a computer experiment the size and composition of endogenous nonmetallic oxide inclusions, depending on concentration and thermal conditions in the weld pool. 10 Ref., 2 Figures.

Nonmetallic inclusions are a natural component of the structure of any steel, having a significant role in various processes and phenomena, both in its production and in subsequent service [1–3].

Mathematical models for prediction of the composition, size and quantity of nonmetallic inclusions, available in scientific publications, are characterized by that in their attempts to simplify their mathematical and computer realization, the authors have to make certain assumptions that do not completely correspond to the features of physico-chemical and thermo-physical processes in welding [4, 5]. In particular, we are talking about the need to allow for high gradients of temperatures and concentrations, which accompany formation of the weld, as well as an essential nonstationarity and heterogeneity of the respective processes. The above features can be taken into account, using for mathematical model definition the equations of the type of reaction diffusion with addition of a specific condition on the moving surface of the formed nonmetallic inclusion, what exactly was done in this work.

Physico-chemical description of the process. The mathematical model was based on the following physico-chemical description of the process of nonmetallic inclusion formation in the weld metal:

1) range of considered temperatures at cooling of weld pool metal is from 2300 to 1670 K, in keeping with the real thermal cycle of welding (upper limit of the temperature range corresponds to the lowest temperature of formation of Al_2O_3 aluminium oxide, which is the most high-melting compound compared

to other components of nonmetallic inclusions in the specified system);

2) at the initial moment of time the deoxidizer elements (Al, Ti, Si, Mn, etc.) are homogeneously dissolved in the melt;

3) nonmetallic inclusion nuclei have the shape of a sphere (with initial radius equal to critical radius calculated through the free energy of formation) and are uniformly distributed in the melt volume;

4) inclusion formation begins in the liquid metal of the weld pool and goes on in the two-phase zone, inclusion growth occurring in the diffusion cell of a certain size by the reactive diffusion mechanism, namely reagents (oxygen and deoxidizer elements) are transported through diffusion transfer to the inclusion surface, on which the respective chemical reaction of their interaction runs, and reaction products adsorb on the above surface;

5) probability of formation of inclusions of a certain composition depends on their melting temperature and formation energy so that unlike the known models, different sets of chemical reactions are considered within certain temperature subranges, and the composition of the melt metal matrix changes, respectively;

6) diffusion regions of growing inclusions do not overlap;

7) at each moment of time during the entire process a thermodynamically equilibrium state is in place on «inclusion-melt» interface;

8) temperature conditions of the process are assigned as functional dependence of temperature on time variable.

Formulation of the mathematical model. In order to formulate the respective mathematical model by this physico-chemical description, we will introduce the following designations:

N is the total number of reagent elements (oxygen, deoxidizers, etc.) in the system;

i is the number of the considered chemical element;

C_i is the content (concentration) of the i-th element in the melt, mole/cm³;

M_i is the molecular mass of the i-th element;

D_i is the coefficient of diffusion of the i-th element in the melt, mole/(cm²·s);

t is the time variable, s;

r is the geometrical variable in the spherical system of coordinates;

$a(t)$ is the current radius of the inclusion at moment of time t, cm;

T is the temperature as a function of time, $T = T(t)$, K;

r_m is the size of the diffusion cell related to volume fraction V_f and average volume of inclusions V_m, cm

$$r_m = \frac{1}{2}\sqrt[3]{\frac{V_m}{V_f}}.$$

We will describe the volume mass transfer (beyond the inclusion) by Fick's diffusion equation, which has the following form in the spherical system of coordinates:

$$\frac{\partial C_i(r,t)}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(D_i(T)r^2\frac{\partial C_i(r,t)}{\partial r}\right), \tag{1}$$

$$a(t) < r < r_m;$$

on the interface the reagent concentration is calculated as equilibrium value $C_{i,\text{eq}} = f\left(C_j\Big|_{r=a(t)}, T(t)\right)$, in keeping with assumption 4):

$$C_i(r,t)\Big|_{r=a(t)} = C_{i,\text{eq}}; \tag{2}$$

on the diffusion cell boundary the substance flow is absent that corresponds to the following equation:

$$\frac{\partial C_i(r,t)}{\partial r}\Big|_{r=r_m} = 0; \tag{3}$$

during the inclusion growth its radius becomes greater due to simultaneous precipitation of products of the respective chemical reaction on the inclusion surface:

$$\frac{1}{3}\frac{d}{dt}\left(\rho a^3(t)\right) = a^2(t)k\left(C_{j,\text{eq}}, T\right)\times$$
$$\times\sum_{i=1}^{N} X_i(T)M_iD_i(T)\frac{\partial C_i(r,t)}{\partial r}\Big|_{r=a(t)}, \tag{4}$$

where $X_i(T)$ is the characteristic function, which actually determines the set of oxides, which can be present in the nonmetallic inclusions in each temperature range:

$$X_i(T) = \begin{cases} 0, & T > T_i, \\ 1, & T \le T_i, \end{cases}$$

where T_i denotes the melting temperature of i-th oxide. Thus, assuming that $T_1 > T_2 > T_3 > T_4 > ...$, we obtain that at temperature below T_2 the nonmetallic inclusion contains just the first oxide; at further lowering of temperature to T_3 the nonmetallic inclusion will form from both the first and second oxides; in the next temperature range it will form already from three oxides, and so on (note that such a pattern corresponds to the one described in monograph [1]); coefficient $k(C_{j,\text{eq}}, T)$ depends on the current concentration state at the inclusion surface, and it can be determined at any moment of time, on condition of an equilibrium redistribution of the substance transported to the surface of the inclusion between the metal and slag phases.

The initial condition consists in that the reagent concentration fields are spatially homogeneous (in the area between the inclusion surface and boundary of the diffusion cell):

$$C_i(r,t)\Big|_{t=0} = C_{i,0}, \quad a(0) < r < r_m, \tag{5}$$

● here, the initial conditions are calculated by a separate algorithm, which allows for the actual welding conditions;

● initial radius of the inclusion, according to assumption 3), is equal to the nucleus critical radius:

$$a(0) = r_{\text{crit}}\left(C_{i,0}, T(0)\right). \tag{6}$$

Thus, the mathematical model of nonmetallic inclusion formation is formulated as a nonlinear boundary problem (1)–(6) for a system of equations of diffusion type in a region with moving boundary, being a reactive diffusion problem in its sense.

A distinctive feature of this model is allowing for the nonstationarity of the process under the conditions of multicomponent nature of the system, in which inclusions form. Moreover, owing to nonstandard condition (4) on a moving surface of the growing inclusion, it is possible to avoid the technically difficult determination of constants of the mentioned reaction rates, the values of which are also strongly dependent on temperature.

On the other hand, boundary condition (4) on the interface makes it necessary to calculate the equilibrium state of the multicomponent system, which can be presented as that made of two solutions, namely metal and slag one.

An important stage of numerical modelling of the process of formation of endogenous nonmetallic inclusions is calculation of the initial content of alloying elements in the weld pool. Algorithm of this calculation is presented in detail in [6]. The above-mentioned algorithm is based on the model of alloying elements transition into the weld pool and the weld for submerged-arc welding and allows a numerical

evaluation of weight fractions of alloying elements in the weld pool and weld metal, based on information on the chemical composition of the used welding consumables.

Algorithm of calculation of the concentrations on the moving interface. Applying the approach outlined in [7], we will believe that on the interface of the nonmetallic inclusion and liquid steel the reaction runs by the following equation:

$$xM + yQ = M_xQ_y, \qquad (7)$$

where M is the metal (alloying) element (Al, Mn, Ti, Si, etc.), Q is the nonmetal element (O, N, S, etc.).

For such a reaction the equilibrium constant is given by the following equation:

$$k_{eq} = \frac{a_{M_xQ_y}}{a_M^x a_Q^y} = \frac{1}{\left[f_M c_M^i \right]^x \left[f_Q c_Q^i \right]^y} = \exp\left(-\frac{\Delta G^0}{RT} \right), \qquad (8)$$

where $a_{M_xQ_y}$, a_M, a_Q are the activities of substances M_xQ_y, M, Q; c_Q^i are the concentrations on M and Q interphase, respectively, wt.%; f_M, f_Q are the coefficients of activity of M and Q, respectively; ΔG^0 is the standard free energy of exchange for reaction (7).

Considering the ratio of M and Q flows on the interface of the growing inclusion, the following equation can be derived:

$$c_M^i = c_M^b - \frac{xm}{ym_Q} \sqrt{D_M} \left(c_Q^b - c_Q^i \right) \qquad (9)$$

where c_M^b, c_Q^b are the concentrations of M and Q (wt.%) in the metal depth; m_M, m_Q are the atomic masses of M and Q; D_M, D_Q are the atomic masses of M and Q in the liquid steel.

Then, the interphase concentrations of M and Q, i.e. c_M^i, c_Q^i can be found by solving equations (8) and (9).

Considering the special structure of equations of this system, we obtained the following equation for the sought value of oxygen concentration c_Q^i on the interface

$$c_Q^i = \left(c_Q^i \right)^{-y/x} \frac{1}{P \sqrt[x]{k_{eq}} f_M f_Q^{y/x}} - \frac{c_M^b}{P} + c_Q^b, \qquad (10)$$

where for brevity we denote:

$$P = (x/y)\left(m_M / m_Q \right)\sqrt{D_Q / D_M}.$$

We will solve equation (10) approximately by bitwise division method with the number of digits 10, providing the number of decimal places, corresponding to the order of the specified accuracy of the solution.

Finding c_Q^i for the i-th element, we numerically determine the value of concentration of the alloying element on the interface by equation (9).

Algorithm for evaluation of average density of nonmetallic inclusion. In condition (4) the current value of nonmetallic inclusion density, depending on the process time, appears on the moving interphase. Used as the estimate of the above density, was average density of the nonmetallic inclusion, determined from those considerations that the ratio between the quantity of oxides in the nonmetallic inclusion at each moment of time is numerically the same, as that in the equilibrium state of the oxide phase for the given temperature. It is rational to calculate the quantitative composition of the oxide phase by the slag theory, as that of a system with a collective electron phase, which in practically important cases is supported by the required set of numerical parameters [8].

In what follows, we shall number the values relating to elements and respective oxides by i index, for brevity.

Having denoted as $C_i (i = 1, n)$, C_0 the concentrations of i-th element-deoxidizer and oxygen, respectively; their coefficients of activity as $f_i (i = 1, n)$, f_0; coefficients of activity of oxides in molten slag relative to standard state of pure oxides as γ_i, we determine equilibrium constants K_i of reactions (6) of i-th oxide formation by the following formula:

$$K_i = \frac{x_i \gamma_i}{C_i^m C_0^n f_i^m f_0^n}, \qquad (11)$$

where x_i are the mole fractions of the oxide phase components.

Set of relations (11) is a system of equations with respect to the molar fractions of the oxide phase components. Solving this system, taking into account the calculated coefficients of activities, we obtain the refined content of oxygen in steel and the respective composition of the slag phase, formed at certain equilibrium conditions.

Calculated composition of the oxide phase is equal to, (wt.%):

$$X_i(\%) = \frac{x_i M_i}{\sum\limits_{i=1}^{n} x_i M_i},$$

where index i denotes the following oxides of elements in slag: FeO, MnO, SiO_2, Al_2O_3, TiO, etc.; M_i is the molecular mass of the respective oxide.

Algorithm of numerical realization of problem (1)–(6) and calculated model. The main difficulty when solving problem (1)–(6) is the need to allow for boundary condition (4) on the moving interface. Used for this purpose was the grid method from the numerical solution of this type of problems in the so-called variant of «catching» the unknown melt-inclusion interphase in the discrete grid node, earlier used in [4] for a problem with one diffusion equation.

As in mathematical model (1)–(6) the diffusion equations in the system are connected only through the condition on the moving interphase (4), the mentioned condition can be used for iterative refining of the step in time, that allows considering diffusion equations (1) in each time step as independent ones.

In order to solve the defined problem by the difference method, we will form grid ω, uniform along radial coordinate r, with constant step h, which at each moment of time $t = t_k$ consists of a plurality of points.

$$\omega^{(k)} = \left\{ r_i^{(k)} = a(t_k) + ih, i = \overline{0, M} \right\}.$$

Let moment of time τ_k be such that during time from t_k to $t_{k+1} = t_k + \tau_k$ inclusion radius changes by the value of grid step h, so that $a(t_{k+1}) - a(t_k) = h$. Then plurality of grid nodes at moment of time $t = t_{k+1}$ will be described by the following equation

$$\omega^{(k+1)} = \left\{ r_i^{(k+1)} = r_{i+1}^{(k)}, i = \overline{0, M-1} \right\}.$$

Denoting the content of an arbitrary melt component by $C_n = C_n(r, t)$ and using standard designations, we will write a discrete equation, approximating the respective differential equation in system (1) on grid $\omega^{(k+1)}$, in the following form

$$\frac{C_{n,i}^{(k+1)} - C_{n,i+1}^{(k)}}{\tau_k} = \frac{1}{\left(r_i^{(k+1)} \right)^2 h} \times$$

$$\times \left[d_{n,i+1/2}^{(k+1)} \left(r_i^{(k+1)} + \frac{h}{2} \right)^2 \frac{C_{n,i+1}^{(k+1)} - C_{n,i}^{(k+1)}}{h} - \right. \tag{12}$$

$$\left. - d_{n,i-1/2}^{(k+1)} \left(r_i^{(k+1)} - \frac{h}{2} \right)^2 \frac{C_{n,i+1}^{(k+1)} - C_{n,i}^{(k+1)}}{h} \right], i = \overline{1, M-2},$$

where

$$C_{n,i}^{(k+1)} = C_n \left(r_i^{(k+1)}, t_{k+1} \right),$$

$$C_{n,i}^{(k)} = C_n \left(r_i^{(k)}, t_k \right), d_{n,i\pm1/2}^{(k+1)} = D_n \left(T \left(t_k \pm \frac{\tau_k}{2} \right) \right).$$

Difference analogs of boundary conditions (2) and (5) have the following form

$$C_{n,0}^{(k+1)} = C_{n,0}^{(k)}; \tag{13}$$

$$C_{n,M-1}^{(k+1)} = C_{n,M-2}^{(k)}. \tag{14}$$

Value of time step τ_k, during which inclusion boundary moves per one node of the grid is obtained as the limit of time iterations $\tau_k^{(0)}, \tau_k^{(1)}, \tau_k^{(2)}, ..., \tau_k^{(s)}$. The above iteration process for refining the time step for transition from the k-th to $(k+1)$-th time layer was realized as follows:

1) the value of time step in the previous layer, i.e. $\tau_k^{(0)} = \tau_{k-1}$ was used as the initial approximation for τ_k;

2) having $\tau_k^{(s)}$ values, we solve by the method of sweeping N systems of linear difference equations

of (12)–(14) form with $\tau_k = \tau_k^{(s)}$ for $n = \overline{1, N}$ and thus determine $C_{n,i}^{(k+1)}$ values. Note that here the following quantity $\dot{X}_n$ of n-th component of the melt will be transported to inclusion surface during time $\tau_k^{(s)}$:

$$X_n = 4\pi a^2 \left(t_{k+1} \right) M_n d_{n,1/2}^{(k+1)} \frac{C_{n,1}^{(k+1)} - C_{n,0}^{(k+1)}}{h} \tau_k^{(s)};$$

3) we solve problem (9)–(10) for calculation of equilibrium concentrations of metal elements on boundary $a(t_{k+1})$;

4) proceeding from the found equilibrium composition, we calculate the average inclusion density $\rho_{k+1}^{(s)}$ and mass $m^{(s)}$ of the substance which precipitated into a layer of thickness $h^{(s)}$;

5) if the condition of completion of iteration process is true

$$\left| 1 - \tau_k^{(s)} / \tau_k^{(s-1)} \right| < \varepsilon,$$

for sufficiently small values ε (for instance, ε = 10⁻⁴), then we assume time step value $\tau_k = \tau_k^{(s)}$ and go over to the next time layer; if this condition is not fulfilled, we find the next approximation $\tau_k^{(s+1)}$ for the time layer from the following relationship

$$4\pi \rho_{k+1}^{(s)} \left[a^3 \left(t_{k+1} \right) - a^3 \left(t_k \right) \right] / 3\tau_k^{(s+1)} = m^{(s)} / \tau_k^{(s)},$$

which is the difference analog of condition (6);

6) in equality (11) we establish $C_{n,0}^{(k+1)} = C_{n,eq}^{(s)}$ and go back to item 2).

Example of computation results. Computer realization of the developed calculation model was performed using Visual C⁺⁺ programming system.

Figures 1, 2 give graphic illustrations of the respective computations by the developed computer program for one of the 20 studied variants of the metal of welds deposited by arc welding process using experimental fluxes, in keeping with the requirements of DSTU ISO 6847 standard [10].

Complete description of the conditions of performance of comparative analysis, as well as computation and experimental results requires separate consideration in the next publication.

The following values were used as input parameters during numerical estimation of initial content of alloying elements in the weld pool:
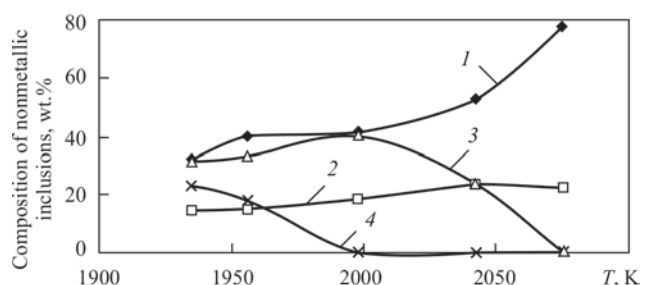
Figure 1. Change of the composition of nonmetallic inclusions at cooling of the weld pool: $1 - Al_2O_3$; $2 - TiO_2$; $3 - MnO$; $4 - SiO_2$
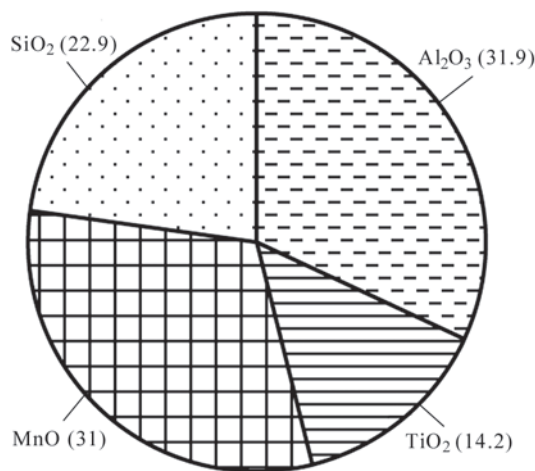
Figure 2. Results of calculation of final composition of nonmetallic inclusions in the deposited metal, wt.%

● flux composition, represented in the oxide layer; it was assumed that the initial composition of the slag system coincides with that of flux and contains the following (all or some of those listed below) components: $SiO_2 = 40$ %, $Al_2O_3 = 40$ %, $CaF_2 = 20$ %, $MgO = 0$ %, $MnO = 0$ %, $TiO_2 = 0$ %, $CaO = 0$ %, the sum of percentages of which should be equal to 100 %;

● alloying element content in steel, wt.%: 0.88 Si, 0.001 Ti, 0.64 Mn; 0.02 Al;

● alloying element content in welding wire, wt.%: 0.065 Si, 0.01 Ti, 0.98 Mn, 0.002 Al;

● oxygen content, wt.%: 0.02 in steel and 0 in the wire;

● relative fraction (0.33) of base metal in weld pool metal;

● temperature characteristics of the modeled process were calculated by the procedure of N.N. Rykalin.

Conclusions

A mathematical model of the considered process was developed on the basis of physico-chemical description of formation of endogenous nonmetallic multicomponent inclusions in the weld metal. The mathematical model allows for the kinetics and heterogeneity of the process, in particular, the nonstationary diffusion transfer of reagents (specifically, deoxidizer-elements) to the inclusion surface and reaction on melt-inclusion interface, as well as pres-

ence of a two-phase zone during weld solidification. The mathematical model is a nonstandard nonlinear boundary problem for a system of diffusion equations with the specific condition on a moving interface.

The mathematical model was the basis for development of a calculation model, which envisages thermodynamic calculation of the local equilibrium state on the moving interface and numerical solution of the boundary problem for a system of differential equations of parabolic type based on discretization, using the grid method in the variant of catching the moving boundary into the grid node.

Developed respective computer program can be used for numerical prediction in a computational experiment of the size and composition of oxide (after some modification also oxysulphide) nonmetallic inclusions, depending on the concentration and thermal conditions in the weld pool.

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