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Numerical Simulation of Oxygen Diffusion Problems with Moving Oxidation Fronts by Network Method

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Abstract – *In present paper, it is studied a moving oxidation front on unbounded domains. Only planar diffusion of oxygen through the Metal Matrix Composites, SiC/Ti-15-3, will be considered. Numerical solution is carried out by using the network method whose application follows two steps: To design a network model from the finite-difference differential equations derived by spatial discretization of the governing equations (times remains as a continuous variable) and to simulate it in a suitable code such as Pspice. By this moving-boundary problem each volume element requires the implementation of electrical switches to confine the phenomena involve in the oxidation front.*

Keywords*: Moving Oxidation Front, Titanium, Network Method, Pspice Code*

Nomenclature

A	Frequency factor
c	Oxygen concentration
$\hat{c}$	Prescribed oxygen concentration
C	Capacitor
D	Diffusivity
Ea	Activation energy
$\widehat{m^n}$	Normal components of oxygen mass fluxes
$\mathbf{n}$	Outward unit normal vectors
R	Resistor
S	Switch.
t	Time
V_e	Electric voltage
V	Battery
X	Position of interface
Δc	Jump of the oxygen concentration in the interface
Ω	Subdomain
τ	Interface curve

Subscripts:

1	Metal matrix composites
2	Oxide
cr	Critical value

I. Introduction

Metal Matrix Composites (MMC) are used for elevated temperature advanced applications due to their high strength and ability to retain their mechanical integrity.Most of the systems that have been investigated are different SiC/Ti metal matrix composites [1], [2].

Environmental effects, such as oxidation, have been shown experimentally to contribute significantly to damage development in these systems at elevated temperatures.

Oxidation degrades the composite due to a brittle oxide layer on the titanium matrix at elevated temperatures.

Three primary reasons – safety, economy and conservation –justify the study of oxidation, whose high relative cost is mainlydue to failures, the capital invested, the operations involved andmaintenance [3]-[5].

Following the rules of the network simulation method [6], the aim of this work is to design a reliable and efficient numerical model, applicable to the problem of oxidation.

The model, which can be simulated in a commercial circuit analysis software such as Pspice [7], [8] to provide the solution, is based on the formal equivalence between finite-difference differential equations of the model and those of the physical process – to this end the PDEs that form the governing equations are spatially discretized to establish the finite difference equations, which are the start point of the network design, while time remains as a continuous variable in the model. The network analogy goes beyond the scope of classical electrical analogy of many books [9], [11], which mainly deal with linear problems and treat the subject of academic order.

The network method is a numerical tool whose efficiency has been demonstrated in many science and engineering problems, such as heat transfer, electrochemistry, fluid flow and solute transport, inverse problems, etc [12]-[15]. Once the equivalence between electric and mechanical variables has been chosen, linear terms of the PDE are easily implemented by linear electrical devices such as resistors, capacitors and coils, while non-linear and coupled terms are implemented using auxiliary circuits or controlled sources of either voltage or current. The latter are a special kind of source, whose output can be specified (by software) as a function of the dependent or independent variables defined in any

node or any component of the model. In addition, boundary and initial conditions (linear or not) are immediately implemented by suitable electric components.

Once the network model has been designed, it can be run with no need for other mathematical manipulations since the simulation code does this work. The well tried, optimized and powerful software for the solution of Pspice circuits, which implements the most recent numerical algorithms to simulate the complex non-linear networks, requires relatively short computing times because is continually and rapidly adjusted the internal time step required for the convergence. In addition, the solution simultaneously provides all the variables of interest, either tabulated or graphically, in the output ambient of the code.

II. The Governing Equation

In this problem, one of the species that diffuses into the metal is oxygen. This reacts with metal and gives rise to a new phase, rust, with different diffusivity. Therefore, a new interface is generated. This interface moves inside the metal as it is converted into oxide. The position of this interface can be represented by a function $X(t)$.

Assuming the speed of the chemical reaction is much greater than that of the diffusion, it can be considering snapshot. Therefore, as soon as the oxygen concentration reaches a critical value, c_{cr}, at one point, oxidation interface will move to that point. The phenomenon described is a moving boundary problem.

The main governing equations of the problem are:

$$D_1 \nabla^2 c_1(x,t) = \frac{\partial c_1(x,t)}{\partial t} \; ; x \in \Omega_1(t) \tag{1}$$

$$D_2 \nabla^2 c_2(x,t) = \frac{\partial c_2(x,t)}{\partial t} \; ; x \in \Omega_2(t) \tag{2}$$

The initial conditions are:

$$c_1(x,0) = f_1(x);\; c_2(x,0) = f_2(x);\; r(s,0) = r_0(s) \tag{3}$$

while the boundary conditions on $\partial\Omega$ are:

$$c_1(x,0) = \hat{c}_1(x,t) \; or - D_1 \nabla c_1 \cdot \boldsymbol{n_1} = \widehat{m_1^n}(x,t) \;\; on \; (\partial\Omega_1 - \tau) \tag{4}$$

$$c_2(x,0) = \hat{c}_2(x,t) \; or - D_2 \nabla c_2 \cdot \boldsymbol{n_2} = \widehat{m_2^n}(x,t) \;\; on \; (\partial\Omega_2 - \tau) \tag{5}$$

$$-D_1 \frac{\partial c_1}{\partial x}(X(t),t) = -D_2 \frac{\partial c_2}{\partial x}(X(t),t) + \Delta c \frac{dX}{dt}(t) \tag{6}$$

where Ω c R^2 is a fixed material domain with $\partial\Omega$ being its boundary. Ω is partitioned by the interface curve $\tau(t)$ with parameterization r(s,t), $s_1(t) \leq s \leq s_2(t)$ into two subdomains Ω_1 and Ω_2,respectively, such that $\Omega = \Omega_1 U \Omega_2$, $\tau(t) = \Omega_1 \cap \Omega_2$ and $\partial\Omega = \partial\Omega_1 U \partial\Omega_2$.

$c_1(x,t)$ and $c_2(x,t)$ are the mass concentrations of oxygen in Ω_1 and Ω_2,respectively. D_1 and $D_2$are the diffusivities of the two phases that occupy Ω_1 and Ω_2.

$\hat{c}_1(x,t)$, $\hat{c}_2(x,t)$, $\widehat{m_1^n}(x,t)$, and $\widehat{m_2^n}(x,t)$ are prescribed oxygen concentrations and normal components of oxygen mass fluxes through the external boundaries of Ω_1 and Ω_2 for t > 0, with outward unit normal vectors $\mathbf{n_1}$and $\mathbf{n_2}$, respectively.

The interface $\tau(t)$ that partitions Ω into two regions is a phase boundary that separates the oxidized part from the metallic part, where oxidation has not taken place, where Δc is the jump of the oxygen concentration in the interface and dX/dt is the speed of the interface.

The dependence of these diffusivities with temperature is defined by the Arrhenius equation:

$$D_j = A \cdot e^{\frac{-E_{aj}}{R \cdot T}} \tag{7}$$

where A is frequency factor and Ea is the activation energy of the diffusion process

III. The Network Model

The detailed rules for designing the model can be found in González-Fernández and Alhama [6]. Nevertheless, for a better understanding of this paper we will describe the steps followed for the design.

Firstly, the equivalence between chemical and electric variables must be established. For the problem under consideration, among different options, the following equivalence is established for each dependent variable in the basic network: oxygen concentration, c $\equiv V_e$ (electric voltage). Then, spatial variable x, which covers all metal, are split into n segments or volume elements.

Secondly, if using the nomenclature of Figure 1, equations (1) and (2) provide the following differential equations of finite differences:

$$\frac{\partial c_1(x,t)}{\partial t} = \frac{c_{1,x+\frac{\Delta x}{2}} - c_{1,x}}{\frac{\Delta x^2}{2D_1}} - \frac{c_{1,x} - c_{1,x-\frac{\Delta x}{2}}}{\frac{\Delta x^2}{2D_1}} \quad 0 < x < X(t) \tag{8}$$

$$\frac{\partial c_2(x,t)}{\partial t} = \frac{c_{2,x+\frac{\Delta x}{2}} - c_{2,x}}{\frac{\Delta x^2}{2D_1}} - \frac{c_{2,x} - c_{2,x-\frac{\Delta x}{2}}}{\frac{\Delta x^2}{2D_1}} \quad X(t) < x < \infty \tag{9}$$

The last two terms linear equations (8) and (9), $I_{j,in}$ e $I_{j,out}$, are implemented as simple resistances, $R_{j,in}$y $R_{j,out}$, respectively, as the constitutive equation of the electrical component is $i_R = V_R/R$. The value of the resistor $R_{j,in} = R_{j,out} = (\Delta x)^2/2\, D_j$. As mentioned, there is a change of state in the volume element, and the resistors used should have two different values. Since you cannot change these settings with this software has been chosen to introduce

each adding two resistors. An open switch enabled only resistance that represents the metallic state, when closing enables two resistors in parallel whose combined effect represents the oxidized state.

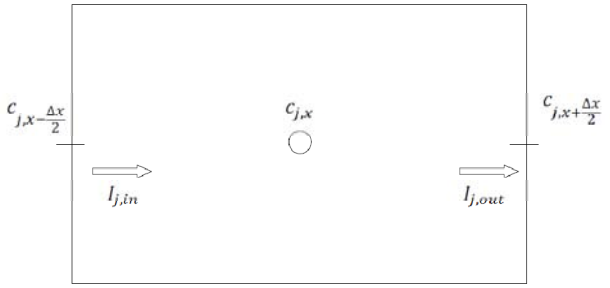

Fig. 1. Nomenclature of the segments or volume elements

Thirdly, the terms on the right of the equations (8) and (9), dcj/dtare the currents that cross each capacitor, Cj. The voltage across each capacitor, $V_{C,j} = C_{jz}^{-1} \cdot \int (d\theta_j/dt)dt$ or $V_{C,y} = C_y^{-1} \cdot \int (dy/dt)dt$, is simply the variable cj when Cj =1F.

Fourthly, the equation (6) gives the following differential equation finite difference:

$$-D_1 \frac{c_{1,x+\frac{\Delta x}{2}} - c_{1,x-\frac{\Delta x}{2}}}{\Delta x} + \\ +D_2 \frac{c_{2,x+\Delta x/2} - c_{2,x-\Delta x/2}}{\Delta x} - \Delta c \cdot \frac{dX}{dt} = 0 \quad (10)$$

The first two addends are represented by a voltage source controlled by voltage. The third addend is represented by the potential difference generated by the current flowing through resistor with unit value.

Finally, it is proceed to the design of network model. Figure 2 represents a volume element inside the domain. In this circuit, each term of the equations (8) and (9) are equal to an electric current. These currents are balanced with the current of other term at a common node.

The model is run in a Turion(tm) 64X2 CPU processor from AMD, using the code Pspice [7], [8]. There are two ways of introducing the network model in Pspice: as a text file or directly as a symbolic interface using the schematic option of the code. In both cases, since the number of different electrical components is small, very few rules are required for the design of the model.

IV. Simulation and Results

The parameters of the problem are the same as those used by Lagoudas et al [1], [2] so that the results can be compared. The coefficients to calculate the diffusivity are defined in Table I.

The boundary condition, the oxygen concentration at the surface, c_0 remains constant and is used as reference for all concentrations. This normalized concentration is unit. The jump of the oxygen concentration in the interface, Δc, is 0.5 in standard format. The critical value c_{cr}, is 0.65 in standard format. The second boundary condition, zero concentration, applied by Lagoudas at infinity, is applied sufficiently far from the surface of the metal.

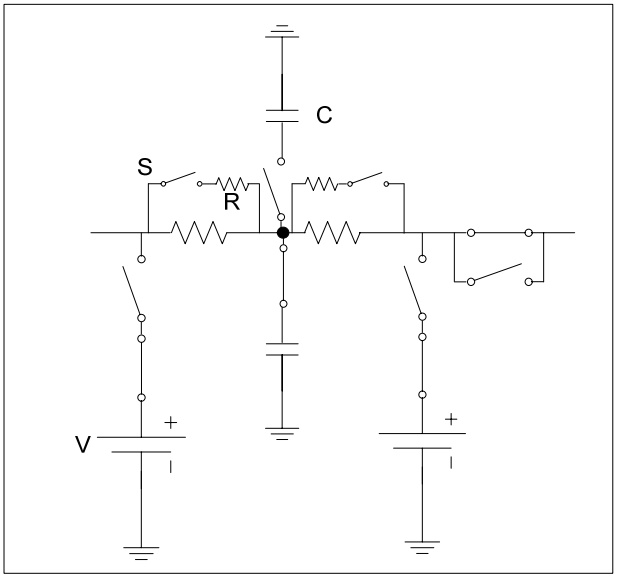

Fig. 2. Equivalent electrical scheme of diffusion process in oxide-metal system

TABLE I
COEFFICIENTS TO CALCULATE THE DIFFUSIVITY

Species	A μm²/s	E_a cal/mol
Metal	$7.37 \cdot 10^6$	39960
Oxide	317.3	22756.2

The results for these conditions for different time intervals are shown in Figure 3. As immediate conclusion we can observe the progressive slowing down of the progress of oxidation. These results are not as appreciable in figure published by Lagoudas. The explanation for this discrepancy lies in the different application of the second boundary condition, and the use by Lagoudas of a function to approximate the solution. In our model, the problem is solved numerically.

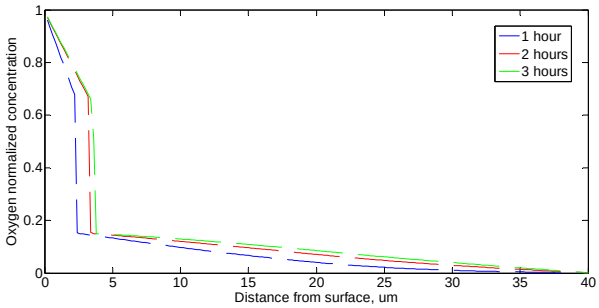

Fig. 3. Distribution of oxygen concentration of the planar oxidation for 1 hour, 2 hours and 3 hours at 700ºC

Figure 4 best shows the slowing of the rate of advance of oxidation at different temperatures. As expected with increasing temperature is an increase of the oxidation rate.To validate the model are included experimental results in Figure 4.

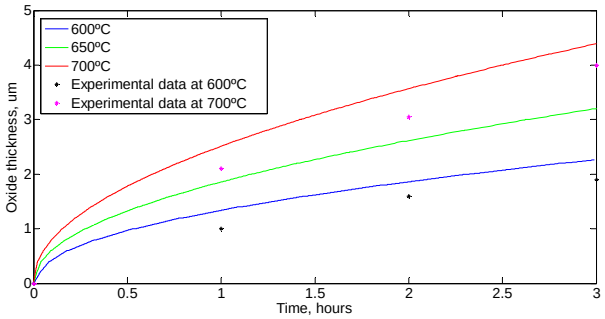

Fig. 4. Evolution of interface at different temperatures

V. Conclusion

A numerical model based on network method has been designed and used to successfully simulate – with negligible computing times in a suitable circuits simulation code.

The influence of the main parameters of the problem is studied for a practical range of these parameters. The present results are quite similar to those obtained experimentally. In contrast with other software, the proposed method has no limitations.

Figure 3 shows the results for these conditions at the end of several time intervals. As immediate conclusion we can observe the progressive slowing down of the progress of corrosion. In our model, the interface $\tau(t)$ is solved numerically.

Figure 4 best shows the slowing progress of corrosion at different temperatures. As expected the oxidation rate increases with the temperature.

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