

# Ceramic matrix composite corrosion models

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## Abstract

This paper discusses physical and empirical models for the description of corrosion processes. Physical strict models are advantageous for simple ceramics and simple composites. In additive-containing ceramics and composites with such matrices, the transport properties will vary with time; in these cases simple physical models alone are not adequate. The use of an empirical equation of the form  $x = k_1 t + k'_p \sqrt{t} + k_{\log} \log(t)$ , fitted by simple multiple linear regression, is capable to describe many versions of corrosion processes, if  $k_1$  is allowed to become negative or positive ( $x$ : scale thickness or specific mass change,  $t$ : time). The equation is recommended for complex cases, but the variability of the corrosion function makes it often necessary to have more than one parameter of evaluation of the material to deduce the most important engineering parameter, penetration depths.

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## 1. Introduction

Ceramic matrix composites are by definition multiphase materials. Every material has a specific reaction to the environment it is exposed to and therefore the behavior is bound to be more complex, unless a component may be treated as inert.

In this paper, we review a number of models for the description of corrosion processes in view of their usefulness for composite evaluation.

## 2. Models for simple mass gain or loss

We begin the discussion with models for simple one-phase materials. For oxidation as a special case of the corrosion of non-oxides, the modeling is often done by assuming a simple parabolic law. A simple parabolic law is the result of assuming steady-state conditions with a constant oxygen partial pressure in the atmosphere and at the gas–scale interface approaching zero at the scale–substrate interface. The last assumption seems justified in view of the very low equilibrium

partial pressures of oxygen calculated for the coexistence of substrate and scale material at high temperatures. An example is the  $P_{O_2}$  of approximately  $10^{-28}$  bar at  $1000^\circ\text{C}$  for an equilibrium between Si and  $\text{SiO}_2$ , calculated by a thermochemical program<sup>3</sup> or straight from the tabulated values<sup>4</sup> of the reaction:



This situation is a classic diffusion problem for oxygen through a growing layer of silica. Relating the flux of the oxidant through the scale  $J$  to reflect the growth in scale thickness  $x$  with time  $t$ , we derive the basic parabolic relation already from Fick's first law ( $D$ : effective diffusion coefficient,  $c_0$ : oxygen concentration at the scale top = solubility):

$$J = \frac{dx}{dt} = D \frac{c_0 - 0}{x} \Rightarrow \int x dx = \int (Dc_0) dt \\ \Rightarrow x^2 = 2k_p t \quad (2)$$

Incorporating the factor 2 into  $k_p$  we have  $x^2 = k_p t$ , the simplest form of the parabolic law, which is often used in the analysis of oxidation and corrosion data.

Deal and Grove<sup>5</sup> showed that this analysis does not take into account the effects of gas phase transport and chemical

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reaction rate, which must be acting and which have to be controlling parameters at least in the beginning of an oxidation process. Their detailed analysis yielded the equation

$$x^2 + Ax = B(t + \tau) \quad (3)$$

in which the factors  $A$  and  $B$  incorporate the physical transport parameter and  $\tau$  represents the shift in the time coordinate, which allows for the presence of a pre-existing oxide scale of thickness  $x_i$ . Numerically it was found that at long times the behavior approached simple parabolic relations, while at short times we have almost linear kinetics.

For practical use we can transform Eq. (3) by the definition of parabolic and linear rate constant  $k_p = B$  and  $k_l = B/A$  to derive

$$\frac{x^2}{k_p} + \frac{x}{k_l} - \tau = t \quad (4)$$

This is a useful analytical form of the Deal and Grove relationship, because now  $\tau$ ,  $1/k_p$  and  $1/k_l$  may be obtained from a simple multiple linear regression. The action of the parameters is illustrated in Fig. 1, where an arbitrarily chosen value of  $0.5 \mu\text{m}^2/\text{cm}$  is linked to widely varying values of  $k_l$ . It is obvious from Fig. 1 that  $k_l$  values smaller than  $k_p$  do cause growth retardation and significant linearization of the curve, while high  $k_l$  values induce an almost perfect parabolic behavior. The higher  $k_l$  is the more it is insignificant. Physically this makes sense because the chemical reaction rate has to be high to allow the scale-substrate interface to get towards equilibrium with very little oxygen.

The negative counterpart of this relation, the loss of material to the atmosphere in a composite, has been investigated with the aid of Eq. (4) by Eckel et al.<sup>6</sup> The modeled composite was a reactive carbon fiber within an inert matrix of alumina. In this case  $\tau$  becomes 0 and the parabolic rate constant is predictable from known gas kinetics. The diameter of the oxidized carbon fiber is decisive for this situation: small fibers at relatively low temperatures had a  $k_l$  small enough to have a significant effect with process retardation and kinetics becoming linear.

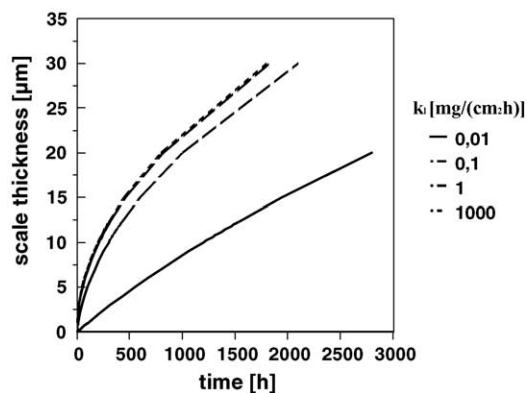


Fig. 1. Influence of varying  $k_l$  for a fixed value of  $k_p = 0.5 \mu\text{m}^2/\text{cm}$ .

Particulate composites, in which the reinforcing particles are oxidized within an oxide matrix, were addressed by Mogilevsky and Zangvil.<sup>1,7</sup> Their analysis introduced an effective grain size of the particles  $R$  and the value  $x$  is now the propagation of the oxidation front  $z$  divided by  $R$ . The parameters  $A$  and  $B$  in their equation contain permeabilities, oxygen partial pressures and particle fraction and are thus not identical to  $A$  and  $B$  of Deal and Grove,<sup>5</sup> but the form is very similar to Eq. (3):

$$x + Ax^{(1+b_n)} = \frac{Bt}{R^2} \quad (5)$$

Eq. (5) contains the parameter  $b_n$ , which adjusts for non-molecular diffusion through the oxide matrix.

For the purpose of this paper, it is only necessary to observe the change of the function of corrosion front with time in differing situations. This is done in Fig. 2, where the likely values for  $b_n$  act on a set of fixed arbitrarily chosen  $A = 0.1$  and  $B = 0.5$  parameters with  $R = 1$ . A value of  $b_n = 1$  yields a quadratic relation similar to Deal and Grove's Eq. (3); changing  $b_n$  to lower plausible values steepens the function.

It should be noted that the deviation from parabolic kinetics with decreasing  $b_n$  is towards linear behavior and increasing absolute  $x$  and  $z$  values, i.e. acceleration of the corrosion process. This is very different from the processes described in Fig. 1, where a linearization meant process retardation.

The corrosion of ceramics and glasses by liquids is often modeled empirically.<sup>8</sup> The problem encountered is that two processes, the leaching of components of a glass phase and the complete dissolution of a glass phase, occur simultaneously at a given time. Dissolution in a steady-state situation is usually limited by the dissolution (=reaction) rate, which should induce a linear process with time. Leaching produces a residue and diffusion through this growing residue can become rate controlling. When both rates operate at comparable velocities, the dissolution is reducing the residue thickness. Hence, a deviation from parabolic kinetics occurs. The equa-

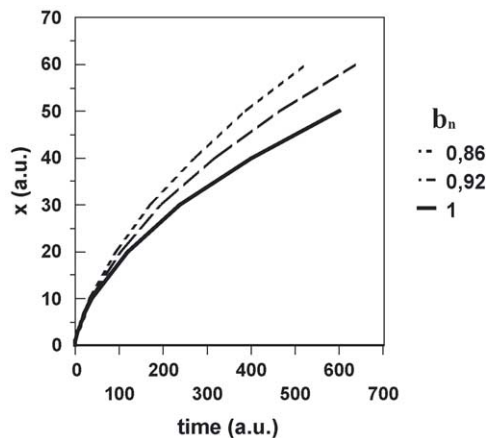


Fig. 2. Influence of varying  $b_n$  in Eq. (5) for fixed values of  $A$  and  $B$  from the model of Ref. 1.

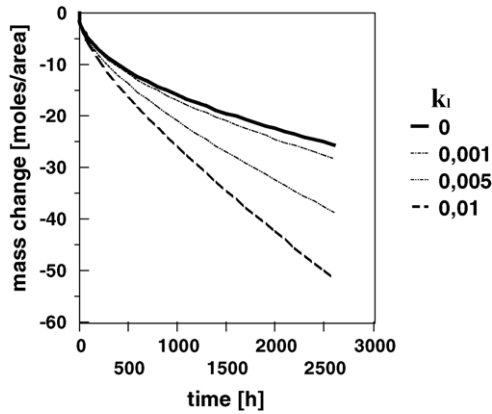


Fig. 3. Effect of increasing  $k_1^*$  values on an arbitrary chosen value of  $k_p^*$  in Eq. (6).

tion, which is often successful in describing this behavior, is

$$x = k_1^* t + k_p^* \sqrt{t} \quad (6)$$

Eq. (6) looks very similar to Eq. (4), but this is deceptive. In Eq. (6) the dependent variable of fitting is  $x$ , while in Eq. (4) it is  $t$ . In Eq. (6) any increase in  $k_1^*$  will automatically increase the total of  $x$ , i.e. it accelerates the process (Fig. 3), while the opposite is observed in Eq. (4) (Fig. 1). The deviation from simple parabolic kinetics is here more akin to the case of Eq. (5).

### 3. Models for combined mass gain and loss

In composites we often have the problem of simultaneous processes acting in differing directions. An example is the evaporation of a scale material, which is formed on oxidation of a substrate. Thus, growth and recession are the opposing factors in terms of a scale thickness and mass gain and loss in terms of the total mass function.

It has been shown that the so called Tedmon equation is capable of modeling this behavior.<sup>9–11</sup> The two forms of the Tedmon equation for scale thickness and mass change are

$$t = \frac{k_p'}{2(k_1')^2} \left[ -\frac{2k_1'x}{k_p'} - \ln \left( 1 - \frac{2k_1'x}{k_p'} \right) \right] \quad (7)$$

and

$$t = \left[ \frac{\alpha^2 k_p}{2k_1^2} \left[ -\frac{2k_1 \Delta w_1}{\alpha k_p} - \ln \left( 1 - \frac{2k_1 \Delta w_1}{\alpha k_p} \right) \right] \right] - \frac{\Delta w_2}{\beta k_1} \quad (8)$$

In those equations  $\alpha$  and  $\beta$  are stoichiometric factors, which account for the mass balance of the appropriate reactions. The form of the functions with varying  $k_1$  is illustrated in Fig. 4.

In Fig. 4 it can be seen that now an increase in  $k_1$  implies a different behavior: for scale thickness it means a retardation of process velocity, but this time approaching an asymptotic behavior. Mass change with small  $k_1$  is also seen as a process

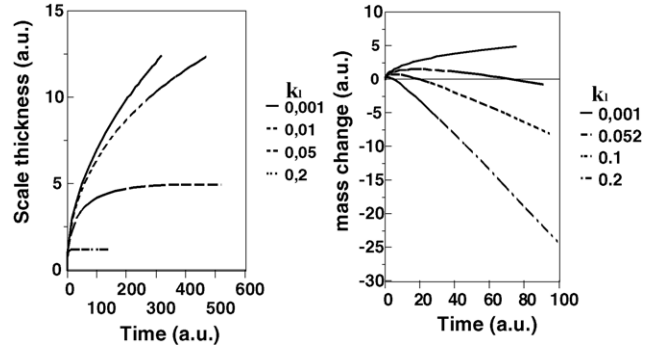


Fig. 4. Effect of increasing  $k_1$  values on an arbitrary chosen value of  $k_p^*$  in Eqs. (7) (left) and (8) (right).

retardation, but at long times or higher  $k_1$  it turns into near linear mass loss. This behavior was termed “para-linear”<sup>10</sup> and is physically well constrained.

As examples for fiber-reinforced ceramics we have in SiC/C and SiC/BN systems the recession of fibers in combination with SiC oxidation. The formation of annular holes around fibers from the active oxidation of their interface materials is retarded and eventually stopped by silica growth, which seals the pathway for oxygen. Models for these cases have been presented by.<sup>12,13</sup> The latter calculates the sealing time by an application of Eq. (3), the former via numerical integration of differential equations.

We have presented a modeling scheme, which is an extension of the empirical model of Eq. (6):<sup>14</sup>

$$x = k_1' t + k_p' \sqrt{t} + k_{\log} \log(t) \quad (9)$$

In this equation, there is a third term ( $k_{\log}$ ). The physical basis behind this term is the behavior of materials with asymptotic passivation. If a corrosion product is completely blocking its substrate from further attack, we have a simple reduction in effective exposed area approaching 100%. Mathematically this is a retardation function with a constant scaled by the logarithm of time.

One or two constants in Eq. (9) can become zero for a given data set. In these cases Eq. (9) reduces to simpler forms of corrosion equations.

In view of the reality of corrosion processes with combined mass gain and loss, Eq. (9) may be used including negative values for  $k_1$ . With this change to the original proposal<sup>14</sup> the function is very variable in fitting corrosion processes. Typical variations are shown in Fig. 5.

By varying the parameters it is possible to describe acceleration or retardation of the process by Eq. (9), including parabolic characteristics.

### 4. Discussion

The physical models reviewed above work well for the simple systems for which they have been developed and are certainly of great value to find the physical border param-

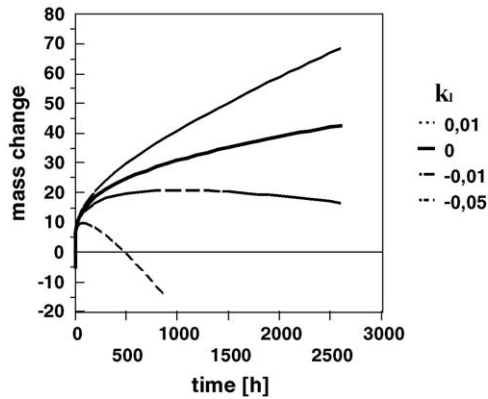


Fig. 5. Effect of increasing  $k'_i$  values on an arbitrary chosen set of values of  $k'_p$  and  $k_{log}$  in Eq. (9).

eter for the best use of these materials under those conditions. However, if we deal with ceramic matrix composites of higher complexity they are not likely to give reliable answers.

Most ceramics based on  $\text{Si}_3\text{N}_4$  and an increasing number of liquid phase sintered SiC ceramics contain additives, which change the oxidation behavior drastically. There is a great wealth of literature data, which is collected in textbooks on the simple base ceramics and illustrates the decisive influence.<sup>15–18</sup>

However, from those textbook data it is also clear that for many cases the behavior is distinctly non-parabolic. The physical reason behind this is not just found in the deduction of Eq. (3) by Ref. 5. The main reason is the change of properties of scales with time. In additive-containing systems we have a continuous change of chemistry and crystallization state with time and we may additionally find self-destruction of the protective character of a scale with time. None of the physical models described above is capable of handling these processes.

In earlier papers<sup>19,20</sup> we have attempted to model some features on a physical basis. These studies showed how the changes introduced by crystallization and scale chemistry change influence the function of mass change or scale growth with time. The complex mathematical solution gave curves, which showed both the possibility of deviation from parabolicity towards a linear acceleration as well as towards asymptotic retardation, because the effective diffusion coefficient is changing with time.

Eq. (9) is capable of reproducing these features. Fig. 6 shows that long-time experiments on silicon nitride ceramics<sup>2</sup> do deviate from a simple parabolic behavior and that it is much better described by Eq. (9) than by Eq. (4). This not surprising, because the model according to Eq. (4) allows only for a time shift to reflect an initial first scale. Eq. (9) correctly describes the early relative fast period and the deceleration process.

A recent example for the application of Eq. (9) to composites is shown in Fig. 7. The example comes from a paper on

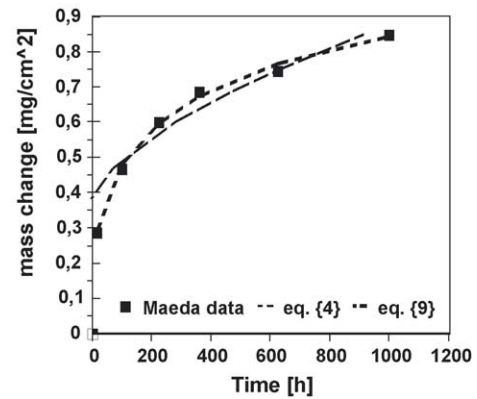


Fig. 6. Long-time experimental data of a  $\text{Si}_3\text{N}_4$  ceramic ( $M$  of Ref. 2 and fits by Eqs. (4) and (9)).

AlN–SiC–ZrB<sub>2</sub> composites at high temperature (this volume) and shows the strong deviation from parabolic behavior.

There have been other attempts to model non-parabolic behavior. In particular, Nygren and coworkers<sup>21,22</sup> have developed models which include an arctan-function of time. This was successful for a number of SiAlON ceramics and allowed them to model retardation problems. However, with more data available, more parameters were added to their equation, because in those ceramics linearization can also occur. A later version was then<sup>23</sup>

$$x = a \arctan \sqrt{b(t+q)} + c \sqrt{t+q} + k_1 t \quad (10)$$

Eq. (10) has similarities to Eq. (9) by consisting of terms for linear and parabolic terms plus a retardation term. Eq. (10) has more constants ( $a$ ,  $b$ ,  $c$ ,  $q$  and  $k_1$ ) to be fitted, which makes the fitting procedure more cumbersome. Ogbuji<sup>24</sup> investigated the problem of non-parabolic oxidation of SiC and found that an increasing number of fit parameters did not help to get a better agreement with the data and that Eq. (9) was the most consistently useful approach.

In particulate composites with a matrix containing sintering additives, such as  $\text{Si}_3\text{N}_4$ –TiN composites, the situation does not become simpler. On top of all the complications

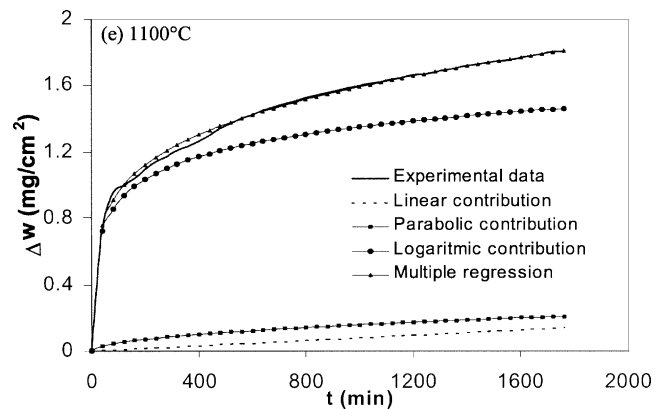


Fig. 7. Application of Eq. (9) to AlN–SiC–ZrB<sub>2</sub> composites (Brach et al., this volume).

discussed above for the matrix ceramic there is an additional oxidation of the reinforcing phase, in this case to yield  $\text{TiO}_2$ , and an initial amount of this oxide present in the starting material. It is highly unlikely that  $\text{TiO}_2$  is not interacting with the oxides of the matrix system and the newly formed oxides from the matrix oxidation, because there is a solubility for it.  $\text{TiO}_2$  is also a known opacifier, i.e. an agent to induce crystallization of silicate glasses. Therefore, it cannot be expected that the assumption of constant diffusion coefficients, which is the base for all the physical models, holds for such composites.

Even stronger effects are expected for composites with second phases, which become volatile upon oxidation. Examples are the boride reinforcement systems. Certainly the parabolic behavior of oxide formation and evaporation can be handled by physically strict models such as Eqs. (7) and (8). But in a reactive matrix with silicate glass and/or borate formation the diffusion coefficients must change with time and temperature. Examples for strongly non-parabolic corrosion – both in oxidation as well as in liquid corrosion – can be found in this volume.

As long as such complex changes cannot be treated adequately in a strict physical model, their use is no real advantage over empirical models in those systems. It is thus concluded that Eq. (9) is a simple and robust empirical approach to model the corrosion behavior and should be useful for many ceramics and composites thereof.

The freedom of shapes of corrosion curves implied by the empirical model necessitates in practice that we need more independent information about the process to be able to evaluate it correctly. The translation of mass data into scale thickness, penetration depths, and component size or vice versa is not straightforward for the complex cases. Each system has to be calibrated by detailed investigations using a multiplicity of investigation techniques, aiming for the most important engineering parameter, penetration depth.<sup>25</sup>

## 5. Conclusions

Physically strict models for oxidation and corrosion can be successful for simple ceramics and composites. In the appropriate systems they should be used and will allow the best extrapolation outside of the experimental range.

Complex systems, in particular those involving additive-containing matrices, will have transport properties, which change with time. It is a challenge to handle this in physical models. First results indicate that this is possible with complex models and a good deal of detailed information on the systems.

For the purpose of describing, comparing, ranking and developing materials it is often sufficient – and far less expensive in terms of time, effort and money – to use empirical models. A relatively simple and robust form of such an empirical model is given in Eq. (9).

Allowing the linear term in Eq. (9) to become negative it handles a great variety of differing mechanisms and processes and is the preferred tool also for composite corrosion.

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