Universal Behavior of a Cyclic Oxidation Model

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Abstract

A mathematical model has been generated to represent the iterative, discrete growth and spallation processes associated with cyclic oxidation. Parabolic growth kinetics (k_p) over and a constant spall area (F_A) were assumed, with spalling occurring interfacially at the thickest regions of the scale. Although most models require numerical techniques, the regularity and simplicity of this progression permitted an approximation by algebraic expressions. Normalization could now be performed to reflect all parametric effects, and a universal cyclic oxidation response was generated:

$$W_u = ½ \{3J_u^{1/2} + J_u^{3/2}\}$$

where W_u is weight change normalized by the maximum and J_u is the cycle number normalized by the number to reach maximum. Similarly, the total amount of metal consumed was represented by a single normalized curve. The factor $[(S_c\text{-}1)\bullet\text{sqrt}(F_A k_p \Delta t)]$ was identified as a general figure of merit, where S_c is the mass ratio of oxide to oxygen and Δt is the cycle duration. A cyclic oxidation failure map was constructed, in normalized k_p-F_A space, as defined by the locus of points corresponding to a critical amount of metal consumption in a given time. All three constructions describe behavior for every value of growth rate, spall fraction, and cycle duration by means of single curves, but with two branches corresponding to the times before and after steady state is achieved.

1.0 Introduction

Cyclic oxidation is an important mode of environmental durability testing regarding high temperature material applications requiring repeated heating and cooling. The key issue is that, not only does oxide scale growth occur during heating, but scale spallation occurs during cooling from thermal expansion mismatch stresses. The total amount of material consumed is a complex function the growth kinetics and degree of spallation, which usually eludes an analytical solution. There have been a number studies devoted to modeling the iterative growth and spallation processes of cyclic oxidation. These often assume parabolic scale growth kinetics, with various formalisms to define scale spallation.

One early model prescribed a constant area fraction of interfacial spallation, which divided the sample into new segments each cycle and required the same area fraction of spallation, k_s, for each of the new segments [1]. A similar more recent interfacial spallation model was developed from a probabilistic approach [2]. Here a constant probability of spallation, p, was prescribed each cycle, giving spallation every 1/p cycles and the probability of not spalling as (1-p). For j cycles, retained scale and net mass change terms containing $(1-p)^j$ can be envisioned, similar to those and the behavior in [1].

Interfacial spallation is often observed in Ni-Cr-Al high temperature alloys, especially if they are not doped with reactive elements such as yttrium. However, more adherent scales, tightly bound to the metal substrate, are observed to fracture within the scale. Thus another model focused on uniform spallation of an outer layer of the adherent scale, prescribing that the weight (mass) fraction of spalled scale was a linear function of the existing scale weight (i.e., COSP) [3,4]. This model also allowed for a variety of spalling formalisms, including different functions of the thickness and different (bimodal) partitioning of spalling depths, including interfacial spallation. The latter approach entlisted a Monte Carlo technique that allowed one of a predetermined number of equal segments to spall randomly on a given cycle, given that the probability of spallation, summed over all segments, produced a spall fraction as defined above. The general kinetic model is also quite versatile in that it also allows for various growth laws (parabolic, power law, exponential, or logarithmic). More recently it has been made available for current personal computers and compatibility with Windows© [5].

The present study deals with a deterministic interfacial cyclic oxidation spallation model (i.e., DICOSM) [6,7]. This model assumes parabolic growth and interfacial spallation of a constant area fraction of the scale, just as before. However the area that spalls is designated for only the thickest segment of the scale. Growth is assumed to be parabolic. The iterative sequence generates mass change equations containing simple summation series of the square root of an integer that has been effectively approximated by an algebraic solution.

All of the above models produce a number of typical characteristic features. The net weight change curve begins according to the specified growth law, reaches a maximum, begins to decrease, and eventually reaches zero weight gain. This is followed by a linear, steady state rate of weight loss. Retained scale weight increases to a constant value that is reached with steady state. Metal and oxygen reacted follow increasing rates, governed by their stoichiometric ratio, until a steady state rate is reached. All of these outputs show regular trends with all the model inputs. For well behaved systems, the various models have been shown to provide reasonable fits to a number of experimental cyclic oxidation weight change results, including the present DICOSM model [1-9]. Although there are concise summaries of these trends, little has been obtained analytically, except for the polylogarithm or Pi function provided by Poquillon and Monceau and the Good-Smialek approximation to $\Sigma\sqrt{i}$ for the DICOSM model [1-6].

However, the purpose of the present paper is not to demonstrate the degree of fitting to experimental data, but rather to explore mathematically all the implications of one model in the most general terms. The mathematical simplicity of the DICOSM model is used to produce algebraic expressions for the outputs and characteristic features. This directly defines parametric trends with the input parameters. Furthermore, these expressions are explored for the purpose of producing normalized, universal outputs (i.e., oxidation weight change and the amount of metal consumed) for all input parameters. Similarly, a standardized failure locus is constructed on a normalized k_p-F_A cyclic oxidation life map, analogous to the concept first presented by Poquillon and Monceau [2].

2.0 Results

2.1 Model equations, approximations, and descriptive parameters.

The basic premise of the DICOSM model is that the scale grows according to parabolic kinetics. Spallation occurs over a prescribed area fraction, F_A, each cycle and is interfacial. The region or area segment that spalls is always the thickest portion of the scale. The sample surface can thus be envisioned to be divided into $1/F_A$, or n_o, effective segments, one of which spalls each cycle.

Detailed schematic illustrations of the process are presented in **figures 1 and 2** [6,7]. The appropriate relationships for mass gain (oxygen) and mass loss (metal) for the initial developmental portion of the process (Case A, **figure** 1) are given below, (where, in the following development, all the variables have been defined in the Appendix):

$$\text{oxygen gain}_{\text{A}} = F_A\sqrt{k_p\Delta t}\left\{\sum_{i=1}^{j-1}\sqrt{i}+(n_o-j)\sqrt{j}\right\} \qquad [1a]$$

$$\text{metal lost}_{\text{A}} = -(S_C-1)F_A\sqrt{k_p\Delta t}\left\{\sum_{i=1}^{j}\sqrt{i}\right\} \qquad [1b]$$

The algebraic sum is equal to the specific weight change. This applies until each area segment has just spalled one time. For the steady-state, latter portion of the process (Case B, **figure** 2), the total retained scale achieves a constant amount, even though the amount at each area segment changes each cycle. The amount spalled each cycle is now also a constant, equivalent to n_o $(1/F_A)$ growth increments of Δt. There is the additional loss due to the spallation that occurred up to n_o cycles. The total mass gains and losses for Case B are thus given by the algebraic sum of the relations below:

$$\text{oxygen gain}_{\text{B}} = F_A\sqrt{k_p\Delta t}\left\{\sum_{i=1}^{n_o-1}\sqrt{i}\right\} \qquad [2a]$$

$$\text{metal lost}_{\text{A}} = -(S_c-1)F_A\sqrt{k_p\Delta t}\left\{\sum_{i=1}^{n_o}\sqrt{i}\right\} \qquad [2b]$$

$$\text{metal lost}_{\text{B}} = -(S_c-1)F_A\sqrt{n_ok_p\Delta t}\,(j-n_o) \qquad [2c]$$

In addition to giving the net specific weight change, modifications of these basic equations produce other outputs for the total amounts of oxygen or metal reacted, the amounts of retained or spalled scale, and the fraction of oxide spalled [6].

The summation series of the square root of an integer is seen to be a key mathematical entity of the model, but requires an iterative calculation by numerical methods. A reasonable approximation was therefore obtained (Good-Smialek Approximation) [6,7]:

$$\sum_{1}^{j}{}_{GSA}\sqrt{i} \cong \tfrac{1}{2}\, j^{1/2} + \tfrac{2}{3}\, j^{3/2} \qquad [3]$$

This allows closed-form algebraic representations for the weight change curve and the other outputs:

$$\left(\frac{\Delta W}{A}\right)_{GSA,A} \cong F_A\sqrt{k_p\Delta t}\,\left\{\tfrac{1}{2}(2n_o - S_c)(j)^{1/2} + \tfrac{1}{3}(1 - 2S_c)(j)^{3/2}\right\} \qquad [4a]$$

$$\left(\frac{\Delta W}{A}\right)_{GSA,B} \cong F_A\sqrt{k_p\Delta t}\,\left\{\left((1 - S_c)\,j - \tfrac{1}{2}S_c\right)(n_o)^{1/2} + \tfrac{1}{3}(1 + S_c)(n_o)^{3/2}\right\} \qquad [4b]$$

By setting parts A or B equal to zero and by setting the derivative of [4a] equal to zero, it is found that:

$$\left(\frac{\Delta W}{A}\right)_{GSA,max} \cong \frac{F_A\sqrt{k_p\Delta t}}{3}\left\{\frac{(2n_o - S_c)^{3/2}}{(2\,(2S_c - 1))^{1/2}}\right\} \qquad [5]$$

$$J_{max} \cong \frac{2n_o - S_c}{2\,(2S_c - 1)} \qquad [6]$$

$$J_{o,A} \cong \frac{3\,(2n_o - S_c)}{2\,(2S_c - 1)} \qquad [7a]$$

$$J_{o,B} \cong \frac{2(S_c + 1)n_o - 3S_c}{6\,(S_c - 1)} \qquad [7b]$$

where $(\Delta W/A)_{max}$ and j_{max} are the maximum weight and cycle time to reach maximum, respectively, and j_o is the cycle time to reach cross-over at zero-weight. Numerous families of curves had been created to illustrate graphically how the different input parameters affect the overall weight change behavior. But now the above relations define, in direct mathematical terms, how the characteristic features of every curve vary with the inputs. While the maximum weight is a more complex function of all four inputs, the number of cycles to reach maximum and zero weight vary only with n_o (inversely with F_A) and nearly inversely with S_c. They are invariant with k_p and Δt.

2.2 Universal cyclic oxidation curve.

The simplicity of the various descriptive parameters presented in eqn's. [5-7] suggest that a universal function may be developed to describe cyclic oxidation for any set of input parameters. Such a curve should show all the pertinent features of the model curves, but be normalized by characteristic weight and cycle factors. This single curve, in dimensionless parameters, would represent the general behavior produced by any combination of model parameters. From inspection of eqn's. 5-7, the maximum weight gain, $(\Delta W/A)_{max}$, and the cycle time to reach this maximum, j_{max}, were selected as these normalization factors. Substituting normalized weight change and cycle number into equation [4a] gives the following relationship for Case A, $j \leq n_o$:

$$W_u = \frac{1}{2}\left[3 J_u^{1/2} - J_u^{3/2}\right] \qquad [8]$$

where W_u is the normalized weight change and J_u is the normalized cycle number. The results of such a plot are shown as the dashed master curve in **Figure 3**. Thus, for any value of S_c (≥ 2), F_A, k_p, or Δt, the same universal curve is obtained from eqn. [8] for Case A (when $j \leq n_o$).

This concise equation defines the initial branch of a universal cyclic oxidation curve. The characteristic features are simply defined: at the maximum in weight change, $dW_u/dJ_u = 0$, both $J_{u,max} = 1.0$ and $W_{u,max} = 1.0$. Also, at the cross-over point of zero weight change, $W_{u,0} = 0.0$ and $J_{u,0} = 3.0$.

For Case B, starting at the point where $j = n_o$, the secondary branches of the curve require eqn. [4b]. In terms of the universal curve, this transition point is given by $J_u = n_o/j_{max}$. A listing of these critical points and the slopes of the subsequent linear portions of the universal curve are listed in Table 1. It is seen that $J_{u,B}$ is approximately equal to $(2S_c-1)$ for reasonably large values of $n_o \geq 100$ ($F_A \leq 0.01$). For increasing stoichiometric factors, these secondary branches depart from the universal curve at larger values of J_u with increasingly negative slopes and with more sensitivity at low n_o (high F_A). The limiting values, as $n_o \rightarrow \infty$, of these critical points are shown as the diamond symbols in **Figure 3**.

The linear slope of the secondary branches (Case B) is given by normalizing eqn. 3b and differentiating:

$$\left(\frac{dW_u}{dJ_u}\right)_{GSA,B} = \frac{3\,(1-S_c)\,n_o^{1/2}}{[2\,(2n_o - S_c)(2S_c - 1)]^{1/2}} \qquad [9]$$

The slopes are seen to increase with S_c and n_o in a complex fashion and are listed in Table 1. (in the vicinity of $S_c = 2.0$, i.e., $\approx Al_2O_3$, the effect of n_o is minimal). Composite curves are shown in **Figure 3** for the cases where S_c is varied from 1.0 to 5.0, which encompass the vast majority of typical oxides [5]. The secondary branches correspond to the limits approached for reasonably large values of $n_o \geq 100$ ($F_A \leq 0.01$), where the secondary branches converge to on curve for each S_c, Table 1.

For most typical values of S_c (above 2.0), the universal cross-over point at $W_{u,0} = 0$ occurs at $J_{u,0} = 3$, (corresponding to $j = 3j_{max}$). If $S_c < 2$, then j exceeds n_o (Case B) **before** reaching $3j_{max}$, i.e., before J_u reaches 3. Accordingly, the fixed ratio of $j_o/j_{max} = 3$ (defined by eqn's. 6 and 7a) no longer applies; eqn's. 6 and 7b now suggest a variable j_o/j_{max} ratio. For example, the secondary branch of the curve for $S_c = 1.5$ in **Figure** 3 is seen to depart from the universal curve before reaching zero normalized weight, now at $J_u = 3.33$. This abnormality would apply only to oxides of very low cation mass content, such as Li_2O (1.87), BeO (1.56), B_2O_3 (1.45), and SiO_2 (1.88).

Nevertheless, for a given oxide scale (fixed S_c), a single normalized curve may be used to represent the behavior of practically any combination of the input parameters, k_p, Δt, and F_A (n_o). The Good-Smialek approximation of the DICOSM model has allowed for this construction.

2.3 Universal metal consumption

The previous construction is useful in generalizing the behavior of cyclic oxidation weight change curves, the most common and readily measured response. However, this does not directly produce the amount of consumed substrate material, it reflects only the net sum of the metal reacted and lost in the spalled scale added to the oxygen retained in the intact scale. The total amount of metal consumed is a more relevant measure of degradation, directly reflecting the loss of load-bearing substrate. The appropriate GSA relations for metal consumed, apparent from **figures** 1-2 and eqn's. 1-3 are [6]:

$$\Sigma W_{met,A}^{GSA} = (S_c - 1)\sqrt{k_p \Delta t}\,\left\{ j^{1/2} + {}^{1}\!/_{3}\, F_A j^{3/2} \right\} \quad for\ j \le 1/F_A \qquad [10a]$$

$$\Sigma W_{met,B}^{GSA} = (S_c - 1)\sqrt{k_p \Delta t}\,\left\{ j\, F_A{}^{1/2} + {}^{1}\!/_{3}\, F_A{}^{-1/2} \right\} \; for\ j \ge 1/F_A \qquad [10b]$$

Eqn. 10a describes the model from the first cycle up to the point where each region of the sample has spalled just once. Likewise, eqn. 10b defines the second portion of the curve corresponding to the linear weight loss rate or steady state portion. The corresponding single term most closely representing an overall attack parameter can be discerned from eqn. 10b as $[(S_c\text{-}1)\bullet(F_A k_p \Delta t)^{1/2}]$. This term reflects the linear metal consumption rates that are obtained for long term exposures. Metal consumption is similarly seen from eqn. 10 to be easily normalized for all values of k_p, Δt, and S_c, but retaining a more complex dependency on F_A [8].

Accordingly, metal consumption kinetic curves for ten values of the spall constant, F_A, spanning 3 decades, are shown in **figure** 4. Metal consumption is seen to increase with the spall fraction. The transitions from the initial portion to the steady state cyclic oxidation behavior (Case A to B) are marked by the solid symbols. There is a corresponding and consistent change in the log-log slope from ½ to 1.0, and these transition points of symmetry are seen to drop to lower cycle numbers as for higher values of F_A.

Since the cycle numbers of the transition points are shifted down in an inverse relationship with F_A, substitution of a modified (normalized) cycle number, $j/(F_A)^{-1}$, is suggested for the universal plot, eqn. 11. The metal consumed at the transition points decreases as the square root of F_A, thus suggesting an appropriately normalized metal consumption term, $\Sigma W_m/(F_A)^{-1/2}$. And considering the effects of the other inputs according to $[(S_c-1)\bullet(k_p\Delta t)^{1/2}]$, the proposed normalized metal consumption term is given as eqn 12 for the universal plot:

$$J_u = j/n_o = jF_A \qquad [11]$$

$$\Sigma W_{met,u} = \frac{\Sigma W_{met}}{\frac{4}{3}(S_c-1)\sqrt{k_p\Delta t/F_A}} \qquad [12]$$

The results are two simple equations in two terms, 13a,b (for Case A and B), with the property that the normalized metal consumption $\Sigma W_{met,u}$ equals 1.0 when the normalized cycle number J_u equals 1.0.

$$\Sigma W_{met,u,A} = \frac{3}{4}\left(J_u^{1/2} + \frac{1}{3}J_u^{3/2}\right) = 1 \ \ at\ J_u = 1 \qquad [13a]$$

$$\Sigma W_{met,u,B} = \frac{3}{4}\left(J_u + \frac{1}{3}\right) = 1 \ \ at\ J_u = 1 \qquad [13b]$$

This universal curve for metal consumption is displayed in **figure 5.** It displays the universal transition point between Case A and B at the coordinates (1,1), with log-log slopes of ½ and 1.0 corresponding to the two branches. This then represents the universal, dimensionless behavior of metal consumption vs cycle number for all values of the model input parameters.

2.4 Universal cyclic oxidation life map

Poquillon and Monceau have presented a new useful construction whereby the cyclic oxidation behavior of alloys is summarized on a p - k_p map, where p is a spalling probability term, not unlike F_A here [2]. Furthermore, iso-attack contours are shown corresponding to different values of the steady-state terminal slope defined by their parameter, $1/\alpha$. Thus as the spalling and growth parameters increase, the map indicates higher attack contours and vice versa.

A similar plot can be constructed for the present model. Here the iso-attack contours are defined, not just by the terminal slope, but by the amount of metal consumed. From eqn's. 10a,b it is expected that two branches will be obtained for the cases before and after steady state is obtained. This differs from the previous construction because it also takes into account exposures that, either because of shorter duration or because of lower growth and spalling parameters, have not reached steady state weight loss.

By rearranging terms in eqns. 10a,b, one obtains the following relations for k_p as a function of F_A:

$$k_p = \frac{\left(\Sigma W^{GSA}_{met,A}\right)^2}{(S_c-1)^2\,\Delta t\left(j^{1/2} + \frac{1}{3} F_A j^{3/2}\right)^2} \qquad [14a]$$

$$k_p = \frac{\left(\Sigma W^{GSA}_{met,B}\right)^2}{(S_c-1)^2\,\Delta t\left(j F_A^{1/2} + \frac{1}{3} F_A^{-1/2}\right)^2} \qquad [14b]$$

Since ΣW_{met} describes the amount of metal consumed, this is the appropriate parameter for defining oxidative life and degradation. For example, if j=100 hr life were to be prescribed, and S_c and Δt were fixed at 2.0 and 1 hr, respectively, the resulting loci defining ΣW_{met} consumption of 1, 10, or 100 mg/cm^2 of metal substrate are shown in **figure 6.** These specific values were selected both for their algebraic simplicity (reducing some of the terms in eqn. 14 to unity) and because a Δt of 1 hr is often used experimentally and S_c =2.0 is close to that of Al_2O_3 scales at 2.1243.

Note that the sloped region [B] reflects an inverse relation between k_p and F_A and corresponds to the steady state spallation regime, eqn 14b, applying at lower k_p and higher F_A. The maximum possible value for F_A is defined as 1.0 (complete area spallation each cycle), as shown in this figure. Conversely, the vertical portion [A] approaches a limiting value of k_p as F_A approaches zero. This corresponds to the initial portion of the cyclic oxidation curve, eqn. 14a, where the primary consumption of material remains in the retained scale as opposed to that lost in spalled oxide. Finally, the transition point, where eqn's. 14a and 14b are equivalent, occurs when $j = 1/F_A$, as indicated by the large circles.

Pairs of k_p and F_A values above and to the right of this curve indicate failure according to the prescribed criteria. Conversely, values below and to the left of the curve have useful life remaining. It is also shown in this figure that as the consumption criteria is increased by factors of 10, the corresponding k_p and F_A values of the life contour are also increased, basically by shifting the entire curve to the right by a factor of 100.

Similarly, failure maps are shown in **figure 7** for prescribed 1-hr cycle lifetimes of j=100, 1000 and 10,000 hr, now for a critical metal consumption of 10 mg/cm^2 (i.e., ≈ Al mass in a conversion aluminide (NiAl) coating). These exhibit the same characteristic forms as in **figure 6**, shifting to progressively lower values of k_p and F_A as the lifetime criteria is raised. As the failure time is increased by factors of 10, the entire failure loci curve can be seen to shift down a line with a slope equal to 1.0, reducing k_p by factors of 10 for part A portions and F_A by factors of 100 for part B portions of the model. These inverse relations can be surmised from inspection of eqn's. 14a and b for the limiting cases where F_A approaches 0 and 1.0, respectively.

It is thus clear that variable failure loci on the k_p-F_A map define various selected failure criteria, i.e., the critical amount of metal consumed and the number of cycles to achieve same. Furthermore the specifics of the material and cycle duration (S_c and Δt) add additional levels of variation and complexity.

To assess the universal aspect of all these dependencies, the failure locus can be defined in general terms by means of normalized values of k_p and F_A. Characteristic values of k_p vary according to $(\Sigma W^*_{met})^2$, the critical level of metal consumed (**figures 6, 7** and eqn's. 14a and b).

Furthermore, eqn. 14 can be rewritten to show the desired functional dependencies between normalized k_p and F_A parameters:

$$\frac{j^* k_p \Delta t\,(S_c - 1)^2}{\left(\Sigma W^{*GSA}_{met,A}\right)^2} = \frac{1}{\left[1 + 1/3\left(j^* F_A\right)\right]^2} \qquad [15a]$$

$$\frac{j^* k_p \Delta t\,(S_c - 1)^2}{\left(\Sigma W^{*GSA}_{met,B}\right)^2} = \frac{1}{\left[\left(j^* F_A\right)^{1/2} + 1/3\left(j^* F_A\right)^{-1/2}\right]^2} \qquad [15b]$$

From eqn. 15 it can be seen that the normalized k_p term is a simple function of the product j^*F_A, where j^* is the critical number of cycles prescribed for failure at the corresponding critical amount of metal consumed, ΣW^*_{met}. When plotted thus in **figure 8**, it is seen that all possibilities for failure loci, defined by various values of metal consumed, number of cycles, cycle duration, and oxide type, collapse onto a single curve.

The universal failure locus exhibits distinguishing characteristic features and values: when F_A approaches zero in branch A, the normalized k_p factor approaches unity in eqn. 15a and is essentially independent of the spalling constant. The transition from branch A to branch B is defined by $j^*=1/F_A$ (or n_o), where the number of spalling events has just achieved complete spallation of all n_o segments. At this juncture with $j^*F_A = 1.0$, both eqn's. 15a and b converge to yield the normalized k_p value of 1.0 (transition point marked by the large symbol). Finally, as $j^*F_A >> 1.0$, the normalized k_p term varies according to eqn. 15b as $1/(j^*F_A)$, giving the sloped upper portion of the curve.

In more descriptive terms, the portion described by eqn. 15a relates to the initial portion of oxidation curves. Here sample weight gain is most common, with some effects of spallation and the trend toward a weight loss becoming more prominent as the transition point is approached. The metal consumed is controlled primarily by the factor $\sqrt{k_p}$. The portion described by eqn. 15b relates to the linear, steady-state rate of weight loss in cyclic oxidation. It generally occurs in the regime of negative net sample weight change, and the metal consumed is primarily controlled by the factor $\surd(k_pF_A)$.

Any values of the normalized factors below and to the left of the failure locus (region I) describe cases which have not achieved the critical amount of metal consumption according to the prescribed criteria. Whereas those above (region II) and to the right (regions III and IV) have failed. Furthermore, specific quadrants can be detailed according to their primary failure modes as controlled by the associated k_p and F_A values.

This construction is thus a concise technique for representing a generalized failure locus as a single curve. However, it should be recognized that experimental data points plotted for comparison must first be adjusted according to pre-selected failure criteria, ΣW^*_{met}, j^*, as well as be normalized by the appropriate S_c and Δt factors.

In an initial attempt to give a broad perspective to actual material performance on such a life map, data for a variety of scales formed on $MoSi_2$, NiAl, Ni, and Cu alloys was selected. Their cyclic oxidation behavior was fitted by the DICOSM model, even though some alloys did not necessarily exhibit much spallation, if any. The pertinent test and fit parameters are summarized in Table 2. The failure criteria for $MoSi_2$ and NiAl was set at 10 mg/cm^2 of material consumption at 1000 total oxidation hours, whereas that for Cu and Ni was set less stringently for only 100 hr. The test temperatures were 1200-1250°C for all alloys except Cu which was 500°C. Thus a strict one-to-one comparison should be made only for those cases with identical test conditions and failure criteria. However it is illustrative to present such widely dissimilar materials to examine overall trends without severe adjustment of the axis scaling.

Three $MoSi_2$ studies [10-12] were characterized, each with very low growth and spallation factors, as is the norm for this highly oxidation resistant heater element compound. All three $MoSi_2$ alloys fall well within the survival Region I with low normalized values (≤ 1.0) of both F_A and k_p. Only one alloy (Hebsur [10]) appears within the scale of the particular universal life plot of Fig. 7, as now plotted in Fig. 8. None of these studies presented data showing a negative weight change or turn around in the weight gain trend. Because of such minimal spallation, F_A

parameters were approximated as the upper limit below which no divergence from the weight change data or change in the DICOM fit was observed. It is thus likely that even lower F_A values may be appropriate, but with no noticeable effect on a weight change model curve. While MoO_3 volatility may be an issue in producing errors in the DICOSM fit because of Tedmon-like behavior, the accepted convention is that $MoSi_2$ oxidizes to form primarily SiO_2 and Mo_5Si_3 above 800°C.

Zr-doped NiAl is a very oxidation resistant Al_2O_3-foming alloy. It is generally accepted that reactive element doping prevents sulfur segregation, void formation, and interfacial weakening, giving rise to very adherent scales. Its cyclic oxidation behavior is generally excellent up to 1200°C, but does exhibit the turnaround in weight change behavior and eventual weight losses over the 1000-3000 hr time span. Thus NiAl(Zr) tends toward higher spalling and growth characteristics than $MoSi_2$, and lies nearer the failure boundary, Fig. 8.

For undoped NiAl, considerable interfacial spallation occurs, and the failure criterion is exceeded, Region II. Also, repeated spallation results in sufficient aluminum depletion to trigger oxidation mechanism changes and a considerable amount of $NiAl_2O_4$ spinel formation, especially at corners and edges. This scale stoichiometry thus provided a better fit to the long term, high weight loss data for undoped NiAl, although initially α-Al_2O_3 was the primary scale formed.

Copper alloys are not known for especially high temperature oxidation resistance and so provide a dramatic contrast on such a plot. At 500°C both the spallation and growth are relatively high [14] and produce cyclic oxidation behavior in the two-parameter failure quadrant (Region III), even at this low temperature and for only a 100 hr life criterion.

Finally, pure Ni alloys exhibit minimal spallation because of the good thermal expansion match between scale and base metal and the relative ductility of these phases compared to other scales and base metals. However the growth rate of NiO is relatively high. Thus Ni 270 (99.99% pure) exhibits Region IV behavior in which failure is primarily by excessive scale growth, not spallation. Again, the lenient life criteria of only 100 hr was used, but Ni 270 still compared very unfavorably with NiAl alloys lifed at 1000 hr. It should be noted that, if only the terminal slope (Case B) rate of weight loss failure criteria were applied to Ni 270, it would pass, despite the fact that an excessive amount of material consumed resides in the intact oxide.

3.0 Discussion

3.1 Comparison to other models and experimental data

While the details of data fitting and critical comparisons to other models are beyond the scope of this work, there are a few points worth making. Some initial attempts had been made to fit universal DICOSM curves to 1100°C cyclic oxidation data for alloy PWA1480 having various sulfur contents, since interfacial spallation had been documented as a primary degradation mode [7]. This data had been closely fitted by a power law expression (for a quartic $kt^{1/4}$ growth law) using the COSP models to account for strong initial transient oxidation effects [5]. While reasonable fits could still be obtained here (parabolic), it became clear on the universal oxidation curve that deviations increased with time for less adherent cases. One factor appeared to be the trend toward increasing S_c as the material became less able to sustain Al_2O_3 growth (2.1243) and tended toward more NiO growth (4.669).

An analogous universal construction was produced by running a number of COSP models for the case of uniform outer layer spallation and a spall fraction that increased linearly with retained oxide thickness (α =1.0) [7]. Again, single curves were obtained for all values of k_p and Δt, but different S_c again produced different branches of the steady state portion. Furthermore, the universal curves exhibited different j_o/j_{max} ratios for different S_c, whereas universal DICOSM curves always produced a ratio of 3.0.

Some success was met with fitting 1100 and 1200°C data for NiAl+Zr with adherent Al_2O_3 scales to the COSP uniform layer model [5]. A universal construction superimposed these two curves nicely, but it was noted that the normalized data was extremely sensitive to the assignment of j_{max}, a value that is not always graphically precise given low growth rates and some variability in the experimental data [7].

The utility of the cyclic oxidation life mapping had been demonstrated by Poquillon and Monceau for similar PWA 1480, PWA 1484, Ni-xAl, and Ni(Pt)Al alloys, including aluminide coatings [2]. Sulfur, platinum, aluminum, and temperature effects all were demonstrated by their mapping technique. Their approach was modified here by using total metal consumption, rather than final slope, as the measure of degradation. This comes in to play, for example, when an alloy property/test condition combination is plotted that does not achieve a steady state weight loss. Alternately stated, their iso-attack contours represent material consumption only for cases where steady state weight loss has been achieved.

Thus, while there is a general insight gained by the universal constructions developed in this model, it is recognized that for many cases the specifics of DICOSM may simply not apply to the case at hand. In these instances, the main utility may be to identify where deviation from the model occur. Also, there is a shortfall to any model when a mechanism change occurs experimentally, since these are rarely pre-determined. Nevertheless, it is intriguing to suggest that universal or semi-universal behavior may occur for any cyclic oxidation model, accounting for well-behaved response over a wide range of material and experimental parameters.

4.0 Summary

An interfacial cyclic oxidation model was developed, stipulating parabolic growth on heating followed by spalling of a constant area fraction on cooling. The iterative process led to series summation equations for all the outputs, namely, net weight change, amount of retained and spalled scale, and the amount of metal consumed. An algebraic approximation to these series allowed for a closed form solution for all outputs. The weight change curve and its characteristic features could then be expressed as simple functions of the input parameters.

This simplicity allowed for normalization of the outputs and construction of universal relationships for: 1) the cyclic oxidation weight change curve, 2) the amount of material consumed, and 3) a failure map based on the growth and spalling constants. By normalizing the weight change to the weight change at maximum and the cycle number to the cycle number at maximum, a simple universal relation for the developmental portion of the curve was obtained: $W_u = ½(3J_u^{1/2} - J_u^{3/2})$. The latter steady state portion of the curve varied with oxide type (stoichiometry), but achieved a final slope equal to
$-(S_c-1)\bullet(F_A k_p \Delta t)^{1/2}$.

Metal consumption was governed by all the input parameters and varied primarily with $j^{1/2}$ for the initial portion (up to the maximum), then as $j^{1.0}$ for the steady state portion. Material consumed was also used as the basis for a cyclic oxidation life map, constructed with k_p-F_A model parameter coordinates. Depending on the chosen criteria for the critical amount of consumption in a given time, families of failure loci could be represented on this construction. The basic form was an inverse k_p-F_A relationship (i.e., k_pF_A = constant) for steady state behavior and little or no dependence on F_A for initial growth. The universality of this dependency was illustrated on a normalized k_p-F_A life map, where a single dimensionless curve represented the combined effects of all input parameters and all possible values.

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Appendix: Glossary of Terms

i = oxide segment counting index

j = number of oxidation cycles

j_{max} = cycle number to reach maximum weight gain

j_o = cycle number to reach zero weight change

$(\Delta W/A)$ = specific weight change, (mg/cm^2)

$(\Delta W/A)_{max}$ = maximum in cyclic oxidation weight change curve, (mg/cm^2)

n_o = number of effective oxide segments

F_a = spall area fraction constant = $1/n_o$

k_p = parabolic growth rate, (mg^2/cm^4h)

Δt = heating cycle duration, (h)

S_c = stoichiometric constant, weight fraction of oxide/oxygen

W_r = weight of oxide retained after cooldown, (mg/cm^2)

W_r' = weight of oxide retained before cooldown, (mg/cm^2)

ΣW_{met} = cumulative amount of metal consumed, (mg/cm^2)

ΣW_{oxy} = cumulative amount of oxygen consumed, (mg/cm^2)

ΣW_{spall} = cumulative amount of oxide spalled, (mg/cm^2)

F_s = weight fraction of oxide spalled

TS = terminal slope of weight change curve

$_{GSA}$ = notation when Good-Smialek Approximation for $\Sigma^j \sqrt{i}$ is used,

i.e. $\Sigma^j \sqrt{i}_{GSA} \cong \frac{1}{2} j^{1/2} + 2/3\, j^{3/2}$

Figure Captions

1. Schematic cross-section for DICOSM initial sequential development ($j<n_o$, Case A) of ten (n_o) cyclic oxidation scale segments (intact, green above the line and spalled, blue below the line). Unit height refers to one growth cycle interval, Δt; constant area fraction (F_A) spalled each cooling cycle.

2. Schematic after $j>n_o$ cycles; each area has spalled once (Case B), achieving a steady state equivalent to 10 (n_o) growth intervals (shown as red spall blocks).

3. Single, universal, normalized curve represents any and all combinations of model parameters for the developmental portion, Case A, shown as the black solid and dashed line. Steady state portion (Case B) develops at different points with different slopes.

4. Metal consumption curves for various spall constants, F_A, showing downward shifting transitions in the log-log slope (from ½ to 1.0).

5. Universal, normalized curve for metal consumption; universal transition point between Case A and B at the coordinates (1,1), partitioning branches with log-log slopes of ½ and 1.0.

6. Cyclic oxidation F_A-k_p life map; effect of metal consumption for designated 1000 cycle life.

7. Cyclic oxidation F_A-k_p life map; effect of cycle life for designated metal consumption of 10 mg/cm^2.

8. Normalized F_A-k_p, universal cyclic oxidation life map; quadrants represent combinations of scale growth-spalling characteristics.

9. Normalized behavior of four classes of materials on a universal cyclic oxidation life map showing survival of $MoSi_2$ and Zr-doped NiAl in Region I, failure of pure NiAl, Cu, and Ni in Regions II, III, IV by varying modes. 10 mg/cm^2 metal consumption life criterion in 1000 hr for $MoSi_2$ and NiAl, in 100 hr for Cu and Ni.

S_c	$2S_c$-1	$J_{u,B}$*	$J_{u,B}$*	$J_{u,B}$*		$dW_u/dJ_u)_B$	$dW_u/dJ_u)_B$	$dW_u/dJ_u)_B$	$dW_u/dJ_u)_B$
	limit as $n_o \to \infty$ ∞	n_o = 1000	= 100	n_o = 10		limit as $n_o \to \infty$ ∞	n_o = 1000	n_o = 100	n_o = 10
1	1.00	1.00	1.01	1.05		0.00	0.00	0.00	0.00
2	3.00	3.00	3.03	3.33		-0.87	-0.87	-0.87	-0.91
3	5.00	5.01	5.08	5.88		-1.34	-1.34	-1.35	-1.46
4	7.00	7.01	7.14	8.75		-1.70	-1.70	-1.72	-1.90
5	9.00	9.02	9.23	12.00		-2.00	-2.00	-2.03	-2.31
6	11.00	11.03	11.34	15.71		-2.26	-2.26	-2.30	-2.70
7	13.00	13.05	13.47	20.00		-2.50	-2.50	-2.54	-3.10
8	15.00	15.06	15.63	25.00		-2.71	-2.72	-2.77	-3.50
9	17.00	17.08	17.80	30.91		-2.91	-2.92	-2.98	-3.92
10	19.00	19.10	20.00	38.00		-3.10	-3.10	-3.18	-4.38

Table 1. Critical values of the normalized cycle number, $J_{u,B}$*, marking the commencement of the linear slope branch, and corresponding $dW_u/dJ_{u,B}$ values for the universal cyclic oxidation curve. Effect of stoichiometric constant S_c and n_o.

alloy	T,	Δt,	oxide	Sc	j*	ΣW*$_m$,	k_p,	F_A	norm. k_p	norm. F_A	ref.
	°C	hr			cycles	mg/cm^2	mg^2/cm^{4}hr				
$MoSi_2$ (Hebsur)	1250	1	SiO_2	1.8777	1000	10	0.0031	0.000015	0.04246	0.015	10
$MoSi_2$ (Cook)	1200	0.92	SiO_2	1.8777	1091	10	0.000176	0.0001	0.00241	0.109	11
$MoSi_2$ (Meschter)	1200	20	SiO_2	1.8777	50	10	0.000105	0.0001	0.00144	0.005	12
NiAl (Zr)	1200	1	Al_2O_3	2.1243	1000	10	0.0175	0.00049	0.393	0.49	13
undoped NiAl	1200	1	$NiAl_20_4$	2.7603	1000	10	0.0175	0.02	0.964	20	13
Kanthal	1200	1	Al_2O_3	2.1243	1000	10	0.024	0.0005	0.539	0.5	13
OFHC Cu	500	0.5	Cu_2O	8.9435	200	10	0.075	0.23	8.41	46	14
Narloy Z	500	0.5	Cu_2O	8.9435	200	10	0.05	0.18	5.61	36	14
Ni270	1200	1	NiO	4.6685	100	10	3.1	0.000025	74.17	0.0025	13

Table 2. Cyclic oxidation test conditions, DICOSM parameter fits, and normalized F_A, k_p of diverse materials representative of regions I, II, II, and IV on a universal failure map.