Simplified Paralinear Oxidation Analyses

James Smialek (dr.jsmialek@outlook.com)

Research Article

Keywords:

Posted Date: August 9th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1931147/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License. Read Full License

Additional Declarations: No competing interests reported.

Version of Record: A version of this preprint was published at High Temperature Corrosion of Materials on April 26th, 2023. See the published version at https://doi.org/10.1007/s11085-023-10156-4.
Abstract

Paralinear oxidative behavior, i.e., concurrent parabolic scale growth \( (k_p) \) and linear scale volatility \( (k_l \) or \( k_v \)), was analyzed by an alternative to the Tedmon equation. A convenient \textit{COSP for Windows} cyclic oxidation program analyzed published data for Cr, NiCr, Pb, SiC, Si\textsubscript{3}N\textsubscript{4}, and BN, all exhibiting scale volatility due to CrO\textsubscript{3}, CrO(OH)\textsubscript{2}, PbCl\textsubscript{2}, Si(OH)\textsubscript{4}, and HBO\textsubscript{2}. The ‘cyclic’ model used an iterative constant outer layer loss formalism, whereby a normalized spall constant, \( Q_0 / \Delta t \), defines the scale volatility rate, \( k_l \) (or \( k_v \)). Optimized trial inputs (fitting maximum mass gain \( \Delta W_{max} \), \( t_{max} \)) generated accurate \( k_p \) and \( k_l \) and replicated ideal paralinear form. Initial approximations for \( k_p \) and \( k_l \) can now be obtained directly as \( \sim 4.1 \left( \Delta W_{max}^2 / t_{max} \right) \) and \( \sim 1.2 \left( \Delta W_{max} / t_{max} \right) \), respectively. However, high or low \( k_l \) extremes, (e.g., burner rig tests of SiC and Ti\textsubscript{2}AlC), may elude classic paralinear behavior. Inconsistencies between Tedmon's stated model parameters and actual data are also discussed.

1.0 Introduction

Various systems exhibit paralinear oxidation kinetics, where the scale grows parabolically due to diffusion control, while it simultaneously volatilizes by a surface reaction according to a linear rate. Normally, the Tedmon Eq. (1) is used to model this behavior (Tedmon [1]), where \( x \) is the scale thickness, \( k'_p \) the parabolic growth rate, and \( k'_l \) the linear volatility rate, as given by Opila [2], generally involving numerical methods. No review of mathematical derivations are presented here, but the final results are shown in Eq. 1:

\[
t = \frac{k'_p}{2k'_l^2} \left[ -\frac{2k'_l}{k'_p} x - \ln \left( 1 - \frac{2k'_l}{k'_p} x \right) \right]
\]

1

\[
t = \frac{\alpha^2 k_p}{2k_i^2} \left[ -\frac{2k_l}{\alpha k_p} \Delta w_1 - \ln \left( 1 - \frac{2k_l}{\alpha k_p} \Delta w_1 \right) \right]
\]

2a

\[
\Delta w_2 = -\beta k_l t
\]

2b

This is not especially convenient mathematically and becomes more complicated (Eq. 2a,b) for mass change (more frequently measured rather than scale thickness), where \( k_p, k_l \) (initially referred to as \( k_v \)) are redefined in units of scale mass (from Opila/Hann 1997, Opila/Jacobson 1995) [3, 4]. Here, \( \Delta w_1 \) is the specific weight of \textit{oxygen} reacted (less C or N losses) and \( \Delta w_2 \) is the \textit{scale} lost due to volatilization. The measured sample weight is given by the algebraic sum of \( \Delta w_1 + \Delta w_2 \). Scale stoichiometry and non-
participating volatile substrate components are incorporated in the modified solution: where $\alpha$ is the oxide/(oxygen - C, or N) MW molecular weight ratio and $\beta$ is the compound/oxide MW ratio. Computer algorithms and numerical methods (e.g., COREST, PARALIN) have been used successfully for Ni-40Cr in air, SiC and Si$_3$N$_4$ in O$_2$ - H$_2$O, and BN in O$_2$-H$_2$O, where CrO$_3$, Si(OH)$_4$, and HBO$_2$ are the corresponding volatile species (from Barrett/Presler 1976, Opila/Hann 1997, Fox, et al. 2003, Jacobson et al. 1999).[3, 5–7]. An extended Tedmon mathematical analysis has more recently been applied to paralinear oxidation of Cr in O$_2$-10%H$_2$O which yielded the CrO$_2$(OH)$_2$ volatile species (Pujilaksono, et al. 2008) [8] The final results from these and similar analyses will be presented herein as compared to COSP model fits.

A number of descriptive features arise from such models: there is often a maximum in the mass increase followed by increasing losses as the mass crosses the zero axis. The long-term behavior approaches a linear loss rate, with a steady-state, retained scale thickness, balanced between reacted and removed oxidant gain and loss, respectively. Such features have also been recognized in cyclic oxidation behaviors, where iterative scale spallation produces a downward curvature to the growth curve and eventual linear weight loss (described by Lowell et al. 1991)[9] along with a limiting oxide thickness. Initially this COSP approach successfully described the cubic (growth)-linear (volatility) kinetics of MAX phase Ti$_2$AlC materials in high pressure and high velocity burner rigs (in Smialek 2020).[10]. The purpose of the present study is to determine whether $k_p$ and $k_l$ results extracted via the COSP strategy produce the same values obtained from more classic analyses of published Cr, NiCr, Pb, SiC, Si$_3$N$_4$, and BN paralinear behaviors. By comparison, the COREST program, over 600 lines of FORTRAN code, provided statistically optimized parameters and predictive characteristics from various data input strategies. Except for the pioneering Cr and Pb studies, the published data has been extracted from NASA oxidation studies in the public domain. The present treatment addresses only experimental kinetic rates, not the chemical thermodynamics that predict the actual volatile species and specific gas transport rates.

1.1 Applying the COSP strategy

For the sake of convenience, paralinear fits of experimental data were attempted using the COSP graphical user interface application, COSP for Windows (described in Smialek/Auping 2002). [11] This is a user-friendly, iterative, cyclic oxidation spalling program with versatile process laws and adjustable variables. Generally, the formalism specifies the portion of the scale removed by a specified amount and morphology, per unit time interval, then repeated. For the paralinear model, a uniform outer layer removal was selected to replicate surface evaporation. In cyclic oxidation, it had been common to postulate that the ‘spall’ fraction, driven by strain energy, increases with scale thickness, Eq. 2. However, to approximate constant volatilization, we employ a fixed removal rate, i.e., independent of scale thickness. The COSP unit ‘spalling’ or scale removal operation therefore sets the spall exponent $\alpha$ to -1 in Eq. 3 below.

One obtains a constant spall (removal) rate:

$$\Delta w_{spall} = Q_0(\Delta w_{retained})^{(\alpha+1)}; \text{ and thus (3)}$$
\[ \Delta w_{\text{spall}} = Q_0 \text{ per cycle, } \Delta t; \] (set to 1 h for rates in convenient mg/cm\(^2\)/h).

The units mask some subtleties. \(\Delta w_{\text{retained}}\) should represent the amount of oxide or scale present. (For \(\alpha = -1\), the units of \(Q_0\) are simply mg/cm\(^2\).) For equivalent scale loss rates per h, the magnitude of \(Q_0\) is normalized to \(\Delta t\). (e.g., COSP models with \(Q_0/\Delta t = 1\) mg/cm\(^2\)/ (1.0 h) are equivalent to \(Q_0/\Delta t = 0.1\) mg/cm\(^2\)/ (0.1 h). Shorter cycle durations did not change the fitted parameters or significantly improve the fit).

For this exercise, the pertinent stoichiometries are fixed by the chemical oxidation reactions given below. They are normalized to one g-atom unit of M (Cr, Pb, Si, B) in the oxidation or chlorination reactions of metals M or compounds \(M_xX_y\):

1. \(\text{Cr} + 3/2 \text{O}_2 = \frac{1}{2} \text{Cr}_2\text{O}_3\)
2. \(\text{Pb} + \text{Cl}_2 = \text{PbCl}_2\)
3. \(\text{Si} + \text{O}_2 = \text{SiO}_2\)
4. \(\text{SiC} + 2\text{O}_2 = \text{SiO}_2 + \text{CO}_2\)
5. \(1/3 \text{Si}_3\text{N}_4 + \text{O}_2 = \text{SiO}_2 + 4/3 \text{N}_2\)
6. \(\text{BN} + 3/4 \text{O}_2 = \frac{1}{2} \text{B}_2\text{O}_3 + \frac{1}{2} \text{N}_2\)

The vapor species formed in high temperature \(\text{O}_2\), \(\text{Cl}_2\), or \(\text{H}_2\text{O}\) have been determined as \(\text{CrO}_3\), \(\text{PbCl}_2\), \(\text{Si(OH)}_4\), and \(\text{HBO}_2\) as described in the original studies. While these are necessary to project the theoretical volatility rates under various conditions, they do not enter in the empirical COSP curve fitting.

### 1.2 Conversions:

1.2.1. **Linear volatility rate**, \(k_l\) (or \(k_v\)). The specific stoichiometry of the 6 reactions listed above are necessary to define the experimental mass gain and loss in terms of retained and removed (volatilized) scale. The rates convert from \(T.S.\), (terminal slope, i.e., linear loss rate of the substance consumed), to \(k_l\) (oxide scale volatility rate):

\[ k_l = \gamma (T.S.) \] (4)

where \(\gamma = MW(\text{oxide})/MW(\text{metal or compound})\), and \(MW\) indicates molecular weight, normalized to one g-atom of the cation in each reaction.

Since \(k_l\) is the constant linear loss rate of oxide, it is equivalent to the normalized ‘spall constant,’ \(Q_0/\Delta t\), previously defined as a ‘constant’ oxide outer layer removal rate.

1.2.2. **Stoichiometric factor**, S. The basic iterative COSP calculation begins with parabolic scale growth during the first unit time ‘cycle’:

\[ \Delta w_{\text{retained}} \text{(as oxide)} = S (k_p\Delta t)^{1/2} \text{ (in oxygen gained),} \] (5)
where $S$ is the stoichiometric constant (MW (oxide)/MW (oxygen) ratio). This conversion arises because $k_p$ is typically determined experimentally as weight gain of oxygen. $S$ converts $O_2$ gained into oxide gained. (e.g., $S$ for $Al_2O_3/(3/2 O_2)$ is $102/48 = 2.125$, $Cr_2O_3/(3/2 O_2)$ is $152/48 = 3.175$, $SiO_2/O_2$ is $60/(32) = 1.875$, etc., Table 1).

Since the first three reactions do not entail other elemental losses, there is no adjustment to stoichiometry needed. The last three reactions entail compounds that release elements (C, N) during oxidation. These are not part of the scale but do contribute to lower observed mass gains. The mass gain formalism above must account for those losses via a modified stoichiometric factor, $S_{\text{eff}}$.

$$\Delta w_{\text{retained}} = S_{\text{eff}} (k_p \Delta t)^{1/2} \quad (6)$$

where $S_{\text{eff}} = \frac{\text{MW(scale)}}{\text{MW(oxygen consumed - X element released)}}$

and the $k_p$ so indicated refers only to the measured weight parameter and needs a correction factor to yield a true scaling constant for just the oxygen reacted in the retained scale. The iterative process accounts for the volatilized scale removed each cycle and calculates an effective time, $t_{\text{eff}}$, corresponding to the remaining scale thickness. The next growth cycle obtains an increment in parabolic scale growth based on $S_{\text{eff}} (k_p (t_{\text{eff}} + \Delta t))^{1/2}$, then ‘volatilized’ (spalled) according to Eq. 3, all described in (Lowell et al.) [9]. The process is repeated for any number of cycles. Oxygen and metal reacted, oxide removed, and weight change are all bookkept. COSP for Windows simply provides a convenient tool for instant model results with adjustable growth, spalling, and stoichiometric parameters.

The $\gamma$, $S$, and $S_{\text{eff}}$ parameters used in this paralinear analysis are listed in Table 1 for the six materials. Since the measurements and the paralinear parameters are all directly based on mass, density conversions from thickness measurements (Eq. 1) are not needed.

### 2.0 Results. Cosp Fits To Experimental Paralinear Oxidation Data

#### 2.1 Case 1. $Cr_2O_3$

Figure 1 presents the experimental and fitted weight change results for the case of $Cr_2O_3$ formed on Ni-40Cr at 1200°C shown in (Barrett/Presler 1976).[5] The experimental data (Fig. 1a) exhibits a clear maximum, crosses the zero axis at ~ 1000 h, with a weight loss rate approaching a constant linear value. For $Cr_2O_3$, the stoichiometric factor for oxide gained/oxygen reacted, $S = 3.167$. The best COSP fit (1b) was obtained by iterative trial and error, with parabolic rates matching the initial portion of the curve and linear loss rates targeting $\Delta W_{\text{max}}$ and $t_0$ as discriminating features. The final data point at the end of the test could be used if $t_0$ had not been reached. (These targeted data points were also suggested in Barrett/Presler, but requiring the COREST program to extract the rate constants.) Subsequent attempts
focus in with successively smaller changes to \( k_p \) and \( Q_0 \). The experimental curve was matched graphically, yielding:

\[
k_p = 0.173 \text{ mg}^2/\text{cm}^4/\text{h}, \quad Q_0/\Delta t = 0.0149 \text{ mg/cm}^2/\text{h}, \quad \text{final slope} = -0.0100 \text{ mg/cm}^2/\text{h}.
\]

Close agreement is observed compared to the data and validated analytical COREST model fit from (Barrett/Presler)[5]:

\[
k_p = 0.171 \text{ mg}^2/\text{cm}^4/\text{h}, \quad k_l = -0.0150 \text{ mg/cm}^2/\text{h}, \quad 1000 \text{ h slope} = -0.0065 \text{ mg/cm}^2/\text{h}.
\]

At steady state, oxygen-reacted equals oxygen-lost, with no net effect on the retained scale mass. At that stage, the only mass change consists of Cr losses, equal to \( (Q_0/\Delta t)/\gamma \) (where \( \gamma \) is the ratio of Cr\(_2\)O\(_3\) oxide lost to Cr substrate lost) or \( 0.149/1.462 = -0.010 \text{ mg/cm}^2/\text{h} \). There is agreement for both model predictions \( (k_l/\gamma, \text{Eq. 3}) \), but the experimental slope at 1000 h is less severe, \( -0.0065 \text{ mg/cm}^2/\text{h} \). This implies that the final linear loss rate had not been reached, consistent with the slight downward curvature of the gravimetric curve.

These results and those of the remaining systems are summarized in Table 2 for easy reference. Paralinear parameters from the original studies are listed and compared directly to the corresponding results from COSP fits. (Decimal format rather than scientific notation was used to be consistent with COSP for Windows parametric input). The COSP models can also be extended to longer times, as needed, for convenient projection of the time to reach zero weight change and for the long term, steady state, linear weight loss slope.

Also, descriptive characteristics for paralinear behavior can be predicted from analytical solutions presented in Wajszel 1963 [12] and Barrett/Presler [5] for \( \Delta W_{\text{max}} \) at \( t_m \) (as addressed in Appendix A). These and the final slopes predicted from \( k_l/\gamma \) are summarized in Table 3. The predicted values agree when obtained by the either the paralinear analysis or the COSP treatment. They also correspond well (5%) with those obtained graphically, Table 2, especially considering large scatter in the experimental data. The comparisons for Cr-0.2%Y oxidation in Tedmon [1] requires a more involved analysis, Appendix B. There was general, but less precise, correspondence between the data and paralinear fits based on a single set of \( k_p \) and \( k_l \) kinetic parameters. Parameters for improved fit are offered as well as rationales for the discrepancies.

The COSP fit for the extended Tedmon analysis of Cr in \( \text{O}_2-10\%\text{H}_2\text{O} \) [8] yielded \( k_p = 2.3 \cdot 10^{-4} \), and \( 2.3 \cdot 10^{-4} \text{ mg}^2/\text{cm}^4/\text{h} \) at 600° and 700°C, respectively. Also, \( k_l = 3.35 \cdot 10^{-3} \) and \( 4.35 \cdot 10^{-3} \text{ mg/cm}^2/\text{h} \) were obtained for 600° and 700°C, respectively. This approach targeted only the maxima in weight gain \( (\Delta W_{\text{max}} = 0.0192, 0.0185 \text{ mg/cm}^2) \) and the corresponding times to reach maximum \( (t_{\text{max}} = 6.5, 3.3 \text{ h}) \) for 600° and 700°C, respectively.

### 2.2 Case 2. PbCl\(_2\)
For the case of PbCl₂ formed on 99.98% pure Pb at 300°C in Cl₂ gas (Wajszel),[12] the experimental data shown in Fig. 2 exhibits a clear maximum, but does not yet cross the zero axis or exhibit a weight loss rate approaching a terminal linear value (up to 200 h). The best COSP fit (S = PbCl₂/Cl₂ = 3.922) was obtained by iterative trial and error, matching ΔW_{max} and endpoint values, giving:

\[ k_p = 0.0355 \text{ mg}^2/\text{cm}^4/\text{h}, \quad Q_0/\Delta t = 0.0135 \text{ mg/cm}^2/\text{h}, \quad \text{final slope} = -0.0100 \text{ mg/cm}^2/\text{h}. \]

The actual data from the PbCl₂ paper indicates paralinear constants, as shown below:[12]

A = 4.2E-11 g²/cm⁴/s or 0.1512 mg²/cm⁴/h.

and B = 2.8 x 10⁻⁴ g/cm²/s or 0.0101 mg/cm²/h,

According to the Wajszel/Tedmon formalism defined in Barrett/Presler (p.3),[5] \( k_p = 2A/a^2 \), where \( a = \text{Pb/Cl}_2 = 2.922 \), Appendix A. This produces \( k_p = 0.0356 \text{ mg}^2/\text{cm}^4/\text{h}, \) in excellent agreement with the COSP fit. B is equivalent to the metal loss rate (−0.0101 mg/cm²/h) and is in good agreement with the COSP final slope (metal consumption) rate (−0.0100 mg/cm²/h). The Tedmon \( k_l = (b/a) B \) gives the oxide loss rate, with \( b = a + 1 = 3.922 \), i.e., the chloride/chlorine stoichiometric constant, S. This produces \( k_l = 0.0135 \text{ mg/cm}^2/\text{h}, \) identical to \( Q_0/\Delta t \) obtained from the COSP fit.

The final COSP slope predicted from \( -Q_0/\Delta t/\gamma \), is \( -0.0135/1.342 = -0.010 \text{ mg/cm}^2/\text{h}, \) corresponding to Pb losses. The predicted slopes from \( (k_l/\gamma) \) are identical for both models, but the measured slope at the end of 200 h testing is −0.0043 mg/cm²/h, i.e., the steady state linear loss had not been reached, nor had \( t_0 \) (i.e., at zero mass change) been achieved.

2.3. Case 3. Si

For elemental Si, the pertinent stoichiometric factor, \( S = \text{SiO}_2/\text{O}_2 = 60/32 = 1.875 \). However, there is no experimental data available for paralinear oxidation of Si in water vapor. Instead, the appropriate \( k_p \) and \( k_l \) were applied from the Opila/Hann study of SiC in water vapor [3] (see next case). That \( k_l (-0.0053 \text{ mg/cm}^2) \) is consistent with a final slope of -0.0028 mg/cm²/h. Figure 3 shows what should occur for 100 h and 1000 h exposures, with the pertinent parameters listed in Table 2. The values predicted for Si are not too different than those predicted for SiC, considered next, that includes losses of one g-atom C per reaction for each 1 mole of \( \text{O}_2 \) reacted. Note that the same exposure determined \( k_l =-0.0022 \text{ mg/cm}^2/\text{h} \) for bulk \( \text{SiO}_2 \) compared to −0.0025 mg/cm²/h projected for Si.

2.4. Case 4. SiC

The next 3 cases are characterized by a secondary substrate species released by the oxidation reaction and decomposition of the compound. That is, losses of carbon or nitrogen occur for SiC, Si₃N₄, and BN, elements not contained in the scale. For COSP fits to SiC, for example, Fig. 4, the measured gain for CVD
SiC must account for the loss of 1 mole of carbon per mole of SiO₂ formed, per mole O₂ in the scale, and per mole SiC consumed. Thus, \((k_{p,\text{meas}} \Delta t)^{1/2}\) (measured as O₂ gain, less C) is actually \(((O₂ - C)/O₂) \{k_{p,t} \text{(true oxide)} \Delta t\}^{1/2}\), Eq. 6.

Accordingly, the basic COSP algorithm for SiC, \(\Delta w_{\text{retained}} = S(k_{p,t} \Delta t)^{1/2}\) is now adjusted as \((k_{p,\text{meas}} \Delta t)^{1/2}\) (O₂/(O₂-C)). \(S_{\text{eff}} = \text{SiO}_2/(O₂-C) = 60/(32 - 12) = 3.0\) (vs 1.875 for Si).

The best COSP fit to superimpose on \(\Delta w_{\text{max}}\) and \(t_0\), obtained by iterative trial and error, yielded:

\[
k_{p,\text{meas}} = 0.0027 \text{ mg}^2/\text{cm}^4/\text{h}, \quad Q_0/\Delta t = 0.0052 \text{ mg/cm}^2/\text{h}, \text{ slope at 100 h} = -0.0034 \text{ mg/cm}^2/\text{h}.
\]

Compared to the data obtained and modeled by Opila/Hann [3]:

\[
k_{p,\text{meas}} = 0.0027 \text{ mg}^2/\text{cm}^4/\text{h}, \quad k_l = -0.0053 \text{ mg/cm}^2/\text{h}, \text{ slope at 100 h} = -0.0018 \text{ mg/cm}^2/\text{h}.
\]

The final slope predicted by COSP and \((Q_0/\Delta t)/\gamma\) is 0.0052/1.5 = -0.0035 mg/cm²/h. The slopes predicted by both models are identical, but the experimental slope at the end of 100 h testing is ~ -0.0018 mg/cm²/h. Again, steady state linear loss and zero mass change had not been reached. Initially, the mass change is slightly lower than that predicted for Si, Table 2, then produces a slightly steeper loss rate, but not dramatically different.

### 2.5. Case 5. Si₃N₄

Similarly, for CVD Si₃N₄, Fig. 5, SiO₂ is formed as the scale. The measured mass change includes the O₂ gain and the loss of 4/3 mole nitrogen per mole SiO₂ and O₂, and per 1/3 mole Si₃N₄. \((k_{p,\text{meas}} \Delta t)^{1/2}\), (measured as O₂ gain, less N loss), is given by \((k_{p,\text{true}})^{1/2}(O₂ - 4/3 \text{ N})/O₂\). The basic COSP algorithm, Eq. 4, \(\Delta w_{\text{retained}} = S_{\text{eff}} (k_{p,\text{meas}} \Delta t)^{1/2}\), uses \(S_{\text{eff}} = (60/(32-(4/3*14))) = 4.5\).

The best COSP fit was obtained for:

\[
k_{p,\text{meas}} = 0.00097 \text{ mg}^2/\text{cm}^4/\text{h}, \quad Q_0 = 0.00493 \text{ mg/cm}^2/\text{h}, \text{ slope at 100 h} = -0.0029 \text{ mg/cm}^2/\text{h}.
\]

These are essentially the same as those parameters determined by Fox, et al. [6]

\[
k_{p,\text{meas}} = 0.00094 \text{ mg}^2/\text{cm}^4/\text{h}, \quad k_l = -0.0052 \text{ mg/cm}^2/\text{h}, \text{ slope at 100 h} = -0.0028 \text{ mg/cm}^2/\text{h}.
\]

The final slope projected by COSP, \((Q_0/\Delta t)/\gamma\), is -0.0038 mg/cm²/h for Si plus N lost, essentially the same as that projected from the paralinear model, \(k_l/\gamma\), but ~35% more severe than the experimental 100 h values. Similar parameters were obtained for sintered Si₃N₄, doped with Lu₂O₃ (SN282) or (La,Y)₂O₃ (AS800). Fox, et al. [6]

### 2.6. Case 6. BN

---

Page 8/21
Finally, for CVD BN, Fig. 6, nitrogen is lost in the oxidation process. Measured gain includes the loss of 2 moles of nitrogen per mole of $B_2O_3$ formed, per 3/2 mole $O_2$ and per 2 mole BN reacted. Thus $S_{\text{eff}} = (3/2 O_2 - 2N)/O_2 = (2*10.8 + 3*16)/((3*16)-(2*14)) = 3.48$ in the basic COSP algorithm, Eq. 4. The best COSP fit, Table 2, thus identified:

$$k_{p,\text{meas}} = 0.00042 \text{ mg}^2/\text{cm}^4/\text{h},\ Q_0/\Delta t = 0.0057 \text{ mg/cm}^2/\text{h},\ \text{slope at 50 h} = -0.0035 \text{ mg/cm}^2/\text{h}.$$  

These are essentially the same as those parameters determined by Jacobson et al., with a paralinear fit to the data [7]:

$$k_{p,\text{meas}} = 0.00042 \text{ mg}^2/\text{cm}^4/\text{h},\ k_i = -0.006 \text{ mg/cm}^2/\text{h},\ \text{slope at 50 h} = -0.0033 \text{ mg/cm}^2/\text{h}$$

The projected COSP $(Q_0/\Delta t)/\gamma$ and paralinear $k_i/\gamma$ final slope is $-0.0041 \text{ mg/cm}^2/\text{h}$, again indicating the experimental plot has not achieved a final linear rate.

### 3.0 Discussion

In all six cases the shapes of the curves are isomorphous, with $t_m/t_0$ hovering very close to the theoretical ratio of 0.25. Experimental scatter may induce some deviation. In other possible conditions, a very low $k_i$ may result in no maximum or negative slope in the mass change curve, while a very high $k_i$ could compress the curve and obscure or prevent the maximum at the very beginning of rapid mass loss. The former occurs for less volatile TiO$_2$ and Al$_2$O$_3$ scales, Smialek 2020 [10], the latter for SiO$_2$ exposed to aggressive burner rig tests, Robinson/Smialek 1999 [13], Yuri/Hisamatsu, etc. 2003 [14]

Opila has described regions of primarily parabolic, mixed paralinear, or primarily linear consumption based on multiples of a characteristic time constant, $t_c$, proportional to $k_p/2(k_i)^2$.[2] This parameter refers to the time to reach a limiting oxide thickness (Opila) [2], reported as orders of magnitude greater for SiC in furnace tests as compared to burner rig tests. The characteristic time constants for all the examples in the present study are listed in Table 3 for reference. There is general agreement between those obtained from published parameters and those obtained by the COSP analysis. Furthermore, the overall trend in the paralinear $t_{\text{max}}$ with $t_c$ can be seen in Fig. 7, ranging from a few hours for BN to hundreds of hours for Ni-40Cr. In general, $\sim 1.6 t_{\text{max}} = t_c$ over this broad time range. The COSP models (square symbols) adhere well to this correlation. The experimental $t_{\text{max}}$ data (up triangles) show some deviation, presumably due to lost precision at shorter $t_{\text{max}}$ for BN and Si$_3$N$_4$. The precise model relationship can be shown from $t_c$ and eqns. A2-A6, solved for $t_{\text{max}}$. The results predict $t_c \approx 1.55-1.70$ $t_{\text{max}}$ for the scales shown in this analysis, varying slightly with the stoichiometric factor, as specified in eqns. A2-A6. This correlation compares favorably to the 1.52–1.66 factor measured by COSP and is near the average $t_{\text{max}}/t_c = 1/1.60$ relation. The overall agreement is another indicator that the COSP strategy is equivalent to prior techniques. (The outlier experimental Cr*data point is from the published Tedmon parameters that do not match the experimental data as closely, see Appendix B. The red circles apply to COSP fits for Cr TGA in
yielding \( k_p = 2.3 \cdot 10^{-4} \) and \( 4.3 \cdot 10^{-4} \text{ mg}^2/\text{cm}^4\text{h} \) at 600° and 700°C, respectively. Also, \( k_l = 3.35 \cdot 10^{-3} \) and \( 6.45 \cdot 10^{-3} \text{ mg/cm}^2\text{h} \) were obtained for 600° and 700°C, respectively. This approach targeted only the maxima in weight gain (\( \Delta W_{max} = 0.0192, 0.0185 \text{ mg/cm}^2 \)) and the corresponding times to reach maximum (\( t_{max} = 6.5, 3.3 \text{ h} \)) for 600° and 700°C, respectively.

Experimental \( \Delta W_{max} \) can also be compared to values predicted from the paralinear rate ratio, \( k_p/k_l \) and stoichiometry, eqns. A1-A6, as shown in Fig. 8. The \( \Delta W_{max} \) correlation factor varied from only 0.27–0.28 times the rate ratio for the six materials (i.e., \( 3.6 \Delta W_{max} = k_p/k_l \text{ on average} \)), over the entire \( \Delta W_{max} \) range of 0.02–3.2 mg/cm². Conversely, shorthand approximations for \( k_p \) and \( k_l \) can be obtained as 4.06 \( (\Delta W_{max}^2/t_{max}) \) and 1.16 \( (\Delta W_{max}/t_{max}) \), respectively. A more direct and thorough approach is presented in Appendix A, eqn's. A8-A9, with results summarized for various oxides in Table A1.

In general, the maximum in weight gain can be defined for experiment durations longer than \( t_c \). But the length of test needs to be multiple time constants to yield the full picture of paralinear behavior, \( t_0 \), and accurate kinetic parameters. Accordingly, the next examples present cases where \( k_p \) and \( k_l \) are ‘unbalanced’, showing either mostly growth (only mass gain, with \( t << t_c \)) or mostly volatility (with only mass loss, \( t > > t_c \)). The latter occurred for SiC and Si₃N₄ materials subjected to high pressure combustion gas with ~10% H₂O. An example is shown in Fig. 9 for CVD SiC exposed in a high pressure (6 atm) burner rig (HP-BRT) using Jet A1 fuel (Robinson/Smialek 1999).[13] Linear mass loss was obtained over the 1250° − 1450°C temperature range, with the first data point generally taken at ~ 6 hr. The slope corresponds to the steady state loss rate of SiC. While the volatile species in water vapor was still likely Si(OH)₄, the same as that in the TGA furnace test, the rate loss is much more severe. This has a tendency to constrict \( t_{max} \) to times shorter than the first data point, or eliminate it altogether in an ‘active’ oxidation regime (Opila). [2]

The other extreme can be demonstrated by similar high-pressure HP-BRT and high velocity HV-BRT burner rig tests of a MAX phase material, sintered Ti₂AlC (MAXthal 211™). Here an initial rapid transient scale of TiO₂ is formed, followed by a slow-growing, healing layer of Al₂O₃. The kinetics in furnace tests can be described by cubic growth (‘corrected’ for the rapid initial growth of a transient TiO₂ scale), as shown in Smialek 2015 [15]. Kinetics in the burner rig tests, @ ~10% H₂O, also require modification to allow for some volatility of TiO₂ and Al₂O₃ scales via TiO(OH)₂ and Al(OH)₃ gaseous species, respectively (Nguyen et al. 2017 [16], Opila/Myers 2004 [17]). Burner rig results for 1300°C tests at 25 m/s, 6 atm., (HP-BRT), and 100 m/s, 1 atm., (HV-BRT), are shown in Fig. 10, (from Smialek [10]). They show the measured burner data to be considerably lower than furnace (quiet air) data. They were well-fit with a ‘corrected’ cubic-linear model. Here grain growth in Al₂O₃ scales is known to decrease their growth rate. Thus, a cubic (growth) – ‘linear’ (volatility) ‘Chen-Tedmon’ model was employed (Chen et al. 2008).[18] The volatility rate also decreased over time as the initial TiO₂ scales were removed. Accordingly, the COSP model fit
employed a decreasing $k_l (\alpha = -3$ in COSP, Eq. 3), to account for TiO$_2$ removal, eventually leaving an Al$_2$O$_3$ surface with lower volatility.

For the HP-BRT data, Fig. 10a, $k_c = 0.212$ mg$^3$/cm$^6$ h was used, as determined by furnace TGA. $Q_0 = 0.220$ was then determined. But the HP-BRT linear loss rate of a pre-oxidized Ti$_2$AlC sample (300 h at 1300°C) was determined as only $-0.017$ mg/cm$^2$h, presumably from Al$_2$O$_3$ at this point. The latter accounted for about 75% of the TGA furnace - HPBR burner rig differential, but was insufficient to produce negative weight change over realistic (just 50–100 h) test durations.

A similar analysis of Mach 0.3 HV-BRT data of the same material, Fig. 10b, yielded $k_c = 0.050$ mg$^3$/cm$^6$ h and $Q_0 = 0.038$. (The lower $k_c$ is due to temperature gradients in the HV-BRT test bar, having a direct impingement maximum temperature of 1300°C). Here, the HV-BRT COSP model loss rate, presumably from Al$_2$O$_3$, was only $-0.001$ mg/cm$^2$h after 500 h. Thus, overall, high pressure or high velocity burner tests of Ti$_2$AlC exhibit volatility in the form of lower weight gains, but not rapid enough to achieve a maximum or cross zero. This is in clear contrast to linear losses for SiC and Si$_3$N$_4$ high temperature materials in the same tests.

4.0 Summary And Concluding Remarks

The COSP cyclic oxidation spalling program, COSP for Windows, has been used successfully to fit paralinear, oxidative growth and volatility mass change behavior of various materials. Examples were shown for Cr, Ni-40Cr, Pb, SiC, Si$_3$N$_4$, and BN oxidized in air, O$_2$, H$_2$O/O$_2$ or Cl$_2$. The stoichiometric molecular weights of the reactants and scale product were required inputs. (The stoichiometric species was not necessary for the present data fitting). Descriptive parameters of the COSP mass change curves matched those already described by analytical paralinear model fits. These include: the maximum in mass gain, the times to maximum and zero mass change, and the terminal slope. The parabolic rate, $k_p$, used in the COSP model, represents the same growth factor contained in the paralinear relations. A normalized spall factor, $Q_0 / \Delta t$, was shown to faithfully represent the linear volatility rate, $k_l$ (or $k_v$) of the scale. A cycle duration, $\Delta t$, of 1 h was sufficiently small to approximate a continuous, differential process for various cases spanning 50-1000 h durations. Small $\Delta t$, of 0.1 h, are useful for precisely defining $\Delta W_{\text{max}}$ and short $t_{\text{max}} < 50$ h. Both COSP and paralinear treatments predict the same invariant $t_{\text{max}} / t_0$ ratio of 0.25 and the same final slope based on the volatility rate.

In order to provide the correct mass gain per interval, the required stoichiometric oxide/oxidant gm-atom ratio must be adjusted for losses not contained in the scale (i.e., C in SiC, N in Si$_3$N$_4$ or BN). These reduce the measured scale weight, but not the scale quantity. Published analytical treatments predict that $t_{\text{max}}$ and $\Delta W_{\text{max}}$ are functions of this effective stoichiometric constant, $S_{\text{eff}}$ (see $a$ and $b$ in Appendix A) and the paralinear rate constant ratios, $k_p / k_l^2$ and $k_p / k_l$, respectively. Accordingly predicted $t_{\text{max}}$ and $\Delta W_{\text{max}}$ values agreed entirely with those determined from COSP model curves. Conversely, very useful initial
approximations for $k_p$ and $k_l$ (or $k_v$) are obtained as $\sim 4.1 (\Delta W_{max}^2 / t_{max})$ and $\sim 1.2 (\Delta W_{max} / t_{max})$, respectively (for most stoichiometries studied). This is believed to be the first time that both paralinear constants have been defined from just one set of coordinates. The paralinear constants possess profound implications in that they can reconstruct an entire paralinear curve, with long term projections of scale thickness, volatilized oxide, and substrate material wastage.

However, an experimental linear weight loss slope requires long oxidation test times or high $k_l$ to actually be observed. And full model parameters cannot be determined as accurately when the form of the curve is incomplete. This may occur where volatility is too rapid to define an initial maximum (SiC burner data), too slow for the mass gain to achieve a maximum (Ti$_2$AlC burner data), or the test too short to exhibit a steady-state, linear volatility rate (NiCr $\leq 1000$ h). Here, the Opila characteristic time constant ($t_c = k_p/2k_l^2$) is a useful benchmark for manifesting all paralinear features. That is, test times $\geq 1.6 t_c$ are needed to exhibit $t_{max}$ or $\geq 6.4 t_c$ to exhibit $t_0$. Modeling precision is better for larger experimental weight gains and longer test times. Sensitivity limits of the microbalance and scatter in the output may also obscure $\Delta W_{max}$.

The original paralinear Tedmon parameters are seen not to match the Cr data very closely. Some improvement can be made using $k_p$ and $k_l$ values lower than those originally reported, but not so as to match the entire curve. No fully satisfactory explanation is apparent, but mechanism changes may be indicated.

**Glossary of COSP Model Terms**

- $k_p$ parabolic growth rate, gas (oxidant) reacted (mg$^2$/cm$^4$h)
- $k_l$ (or $k_v$) linear volatility rate of scale (oxide) removed (mg/cm$^2$h)
- $\alpha$ spall exponent, set to -1 in COSP algorithm: $\Delta W_{spall} = Q_0(\Delta W_{retained})^{(\alpha+1)}$
- $Q_0$ ‘spall constant,’ set here for constant differential scale removal (mg/cm$^2$)
- $\Delta t$ ‘cycle’ duration, defined here as a differential time increment (h)
- $S$, $S_{eff}$ stoichiometric constant, MW ratio of scale to gas (e.g., oxide/(oxygen - C or N))
- $\gamma$ stoichiometric constant, MW ratio of scale to compound (e.g., oxide/carbide)
- $\Delta W$, $\Delta W_{max}$ specific net weight change of substrate, or weight at maximum (mg/cm$^2$)
- $t_{max}$, $t_0$ time to reach maximum or zero weight change, (h)
- T.S. terminal slope (final, steady state; mg/cm$^2$h)

**Declarations**
Acknowledgements

The author appreciates many helpful discussions with N.S. Jacobson. J. Auping is gratefully acknowledged for creating the versatile COSP for Windows program that enabled this study. The scale volatility fundamentals covered herein had received sustained support from the Fundamental Aeronautics Program at the NASA Glenn Research Center.

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Data availability statement: The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

References


Figures
Figure 1

Paralinear weight change curves for Ni-40Cr in air at 1200°C, 1000 h. a) experimental data with analytical COREST fit from [Barrett, Presler, 1976];[5] b) COSP fit.

Figure 2

Pb (PbCl₂) Paralinear Behavior and COSP Fit
Paralinear weight change curve for Pb in Cl₂ (100 ml/min) at 300°C, 165 h. Experimental data points with analytical fit from [Wasczel, 1963][12] and superimposed exact COSP fit.

Figure 3

Projected COSP paralinear curve for Si in 50% H₂O/O₂ (1200°C, 4.4 cm/s). Parameters taken from SiC, next figure, i.e., [Opila, Hann, 1997][3]: a) 100 h detail; b) 1000 h long term projection.

Figure 4

Paralinear weight change curves for SiC in 50% H₂O/O₂ (1200°C, 4.4 cm/s, 100 h): a) experimental data with analytical Paralin fit from [Opila, Hann, 1997][3]; b) COSP fit.
Figure 5

Paralinear weight change curves for Si$_3$N$_4$ in 50% H$_2$O/O$_2$ (1200°C, 4.4 cm/s, 100 h):

a) experimental data with analytical Paralin fit from [Fox, et al., 2003][6]; b) COSP fit.

(https://ntrs.nasa.gov/api/citations/20020072851/downloads/20020072851.pdf)

Figure 6

Paralinear weight change curves for BN in O$_2$ -trace H$_2$O (900°C, 4.4 cm/s, 50 h):

a) experimental data with analytical Paralin fit from [Jacobson, et al., 1999][7]; b) COSP fit.
Figure 7

Correlation of $t_{\text{max}}$ with time constant $t_c$ for paralinear oxidation of Cr, BN, Si$_3$N$_4$, SiC, Pb, and NiCr. Published measurements (filled teal triangles) and COSP model fits (open diamonds, filled red circles). (Cr* applies to original published Cr-0.2%Y Tedmon $k_p$, $k_i$ parameters that do not fit data well). Tests at 1200°C, unless indicated otherwise.
Correlation of $\Delta W_{\text{max}}$ with paralinear oxidation rate ratio for Cr, BN, Si$_3$N$_4$, SiC, Pb, and NiCr. Published measurements (filled teal triangles) and COSP model fits (open diamonds, filled red circles). (Cr* applies to original published Cr-0.2%Y Tedmon $k_p$, $k_i$ parameters that do not fit data well). Tests correspond to Figure 7.
Figure 9

Rapid linear weight loss for CVD SiC exposed in high pressure burner rig (1250-1450°C, 6 atm., 20 m/s, 10% H₂O/air) from [Robinson, Smialek, 1999]. [13]
Figure 10

Steadily increasing, cubic-linear, 1300°C weight change behavior of Ti₂AlC MAX phase in burner tests: a) high pressure burner rig (6 atm., 25 m/s, 10% H₂O/air); and b) high velocity burner rig (1 atm., 100 m/s, 10% H₂O/air) from [Smialek, 2020][10] Cubic-linear COSP model fit (dashed) to data (symbols), and compared to parabolic furnace TGA (solid).

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- Table1.pptx
- Table2.pptx
- Table3.pptx
- TableA1.pptx
- TableB1.pptx
- auxiliarydata.xlsx
- Appendices.docx
- Supplementaryfigure.pptx