FINITE ELEMENT ANALYSIS USING MATLAB OF
OXIDATION KINETICS IN AIR OF STEEL-T21 ALLOY
COATED BY SIMULTANEOUS GERMANIUM-DOPED
ALUMINIZING-SILICONIZING PROCESS

ABBAS KHAMMAS HUSSEIN, LAITH KAIS ABBAS
AND EMAD SAADI AL-HASSANI
University of Technology,
Department of Materials Engineering, Baghdad

Abstract
This work includes the application of a pack cementation of germanium-doped aluminum and silicon coatings on low alloy steel type-T21 yields a significant improvement in the oxidation resistance. Steel-T21 was coated with germanium-doped aluminizing-siliconizing. Diffusion coating was carried out at 1050 °C for 6 h under an Ar atmosphere by simultaneous germanium-doped aluminizing-siliconizing process. Cyclic oxidation tests were conducted on the coated steel-T21 alloy in the temperature range 300-900 °C in air for 60 h at 3 h cycle. The results showed that the oxidation kinetics for coated system in air was found to be parabolic. Oxide phases that formed on coated system are SiO₂ and Al₂O₃. Statistical analysis show that there is a good agreement between experiments results and Finite element results. In addition there is a good agreement between experiments results and theory results.

Keywords: Steel-T21, oxidation, aluminizing-siliconizing, pack cementation.
1. INTRODUCTION

Low alloy steels are generally considered to comprise plain carbon steels and steels with a total alloying content of up to 12%. As such, they are much cheaper than more highly alloyed alloyed materials and are often used in large quantities in heavy engineering industries. Whilst these materials are not yttrium generally selected for resistance to high temperature corrosion (the material choice is largely dictated by cost, ease of fabrication and mechanical properties) they are often required to operate in high temperature aggressive environments. For instance, the power generation, refuse incineration and chemical process industries use many miles of low alloy steel heat exchanger tubes. Hence, the high temperature oxidation properties of low alloy steels are often important in determining component life [1].

The development of a surface oxide scale limits the degradation of a pure metal or alloy in a hot oxidizing environment. The addition of reactive elements which have a high affinity for oxygen (such as Ge, Y, Ce, Hf) may further improve the oxidation resistance through various effects [2]:

- Promotion of the selective oxidation of an element which forms a stable oxide of low diffusivity (such as Al$_2$O$_3$).
- Reduction of the growth rate of oxide scale.
- Inhibition of scale failure (i.e. through thickness cracking and scale/substrate interfacial decohesion) [2].

Reactive-Element (RE) additions may be provide either as metallic or oxide dispersoide components in bulk alloy, or as surface produced by coating. They are used predominantly with Cr$_2$O$_3$- and Al$_2$O$_3$-forming alloys to resist aggressive environment [3]. V.Provenzano and coworkers [4] proposed a model of mechanical keying due to the formation of oxide pegs rich in active elements, the role of these peg being to anchor the oxide scale to the coating alloy. It was found that the addition of yttrium prevents the sulfur segregation to the alloy/scale interface, either by reacting with sulfur to form a stable sulfides or by tying up the sulfur by segregation to internal oxides surfaces [5]. Thus, the addition of small amount of reactive element [Ge, Y, Ce, La, Hf, Zr, Th] to an alloy resulted in substational improvements in the adherence of their oxide scales during thermal cycling [6]. Previous work [7,8,9,10,11], has shown that such reactive element additions are effective in improving the high temperature corrosion of iron-base alloys by improving the resistance of
protective scales to spallation. It was found that the scale formed on germanium-free alloy is typically convoluted or wrinkled and poorly adherent, the germanium-containing alloy produces a flat and adherent oxide. In recent years, germanium has become the most commonly used of these reactive elements. The amount of the reactive element needed to produce the beneficial effect is small, (typically 1 wt.% or less). Heat-resisting alloys depend on the formation of a protective oxide on the metal surface to limit section loss by oxidation. Generally, this protective oxide is alumina (Al$_2$O$_3$), or silica (SiO$_2$). In practice, the most common way that a protective oxide fails is by exfoliation or spalling from the metal surface. This spallation may be induced by stresses arising from the oxide growth process itself, strains resulting mechanical flexing of the component in the service, or from stresses arising from thermal cycling because of the difference in the coefficients of thermal expansion of the oxide and the metal. Spallation of oxide may involve fracture in the oxide adjacent to the metal surface, fracture in the metal immediately below the interface, or by separation at the interface itself. In the last case, failure involves not only the magnitude of the stresses, but also a consideration of the interfacial adhesion.

In this study, the applicability to deposit germanium-doped aluminum and silicon on the surface of steel-T21 alloy using single step pack cementation to enhance the oxidation resistance in steel-T21 was examined. The cyclic oxidation behavior of coated steel-T21 alloy will be studied in the temperature range 300-900°C in air in addition to the modeling of oxidation kinetics.

2. EXPERIMENTAL PROCEDURE

The substrate alloy used in this study was low alloy steel (Type T21-ASTM A200-94). The nominal composition and the spectrochemical analysis of low alloy steel (Type T21-ASTM) are shown in Table(1) and Table(2) respectively. The low alloy steel samples were cut into squares shapes with dimensions (20mm×20mm×5mm) with small hole of 2mm diameter was drilled in each sample for holding. All surfaces, including the edges were wet ground using 120, 220, 320, 600, 800, and 1200 grit silicon carbide papers. These samples were then cleaned with water, degreased with acetone, and then ultrasonically cleaned for 30 minutes using ethanol as a medium. After drying, the samples were stored in polyethylene zip-lock bags. The dimensions of all samples were measured. The pack mixture used for aluminum-silicon diffusion coating consisting of 16 Wt.% Al powder (50-60µm in particle size) as an
aluminum source, 6 Wt.% Si powder (50-60µm in particle size) as a silicon source, 2Wt.% NaF and 2Wt.% NaCl as activator and the balance was silica-powder (70-120µm in particle size). All pack powders was sized by sieving method and 1Wt.% of the pack silica filler was replaced by germanium. Low alloy steel was placed in a sealed stainless steel cylindrical retort of 50mm in a diameter and of 80mm in a height in contact with the pack mixture. The retort was then put in another stainless steel cylindrical retort of 80mm in a diameter and 140mm in a height. The outer retort has a side tube through which argon gas passes and second in the top cover for argon gas outlet. Type-k calibrated thermocouple was inserted through the cover of the outer retort for recording real temperature near inner retort. Pack cementation process was carried out at 1050 °C for 6 h under an Ar atmosphere. After pack cementation process, the samples were ultrasonically cleaned, and weighed. It was found that the diffusion coating time of 6 h at 1050°C give a coating thickness of 66-65µm.

Alloy with germanium-doped aluminum-silicon diffusion samples were accurately weighed and then placed into ceramic coating crucible. Cyclic oxidation tests were carried out in the temperature 300-900°C in air. Each heating cycle includes heating in the furnace for 3 hours and cooling heating in still air.

3. RESULTS AND DISCUSSION

3.1 Cyclic oxidation of Ge-doped aluminizing-siliconizing coated system in air

Coating system germanium-doped aluminizing-siliconizing substrate were subjected to cyclic oxidation. The specific weight change of the coated and uncoated samples during oxidation is plotted as a function of time as shown in Figure 1. The kinetics behavior of cyclic oxidation at temperature range between 300-900°C follows the parabolic rate (ΔW/A=Kpt0.5) as shown in Figure 1. Weight change values are shown in Table 3. Oxidation rate coefficients are obtained and listed in Table 4. Figures 1 also show the important in oxidation resistance of the improvement in oxidation resistance of coated system (germanium-doped aluminizing-siliconizing coated low alloy steel substrate at temperature range between 300-900°C), for 60 hr at 3 hr cycle compared to uncoated samples. Based on the weight change data, the coated systems of the low alloy steel substrate appears to be fairly resistance to scale spallation even at temperature range 300-900°C. Coating system appears good oxidation resistance. First, the most desirable SiO₂, and Al₂O₃ protective scale layer forms on the sample surface during oxidation, and these
scales layer has sufficient adherent with the substrate to withstand the imposed cyclic heating and cooling environments. This evident from the continuous weight gain noted during oxidation. Second, the (Al+Si) phase of the coating remaining untransformed totally over the entire exposure period indicates that the Al, Si loss from the coating during oxidation is very slow because of the formation of a spall-resistant silica, alumina layer especially at higher temperatures. The presence of the reactive elements such as germanium oxidizer affects the high temperature oxidation in three main ways [11]:

- Increase in the selective oxidation of the elements forming the scale (Al, Si) at the beginning of the oxidation process. A lower content of this element is needed to produce a continuous protective SiO$_2$, and Al$_2$O$_3$ layers.
- Reduction in the scale growth rate at higher temperature by means of altering the transport mechanism in the oxide. The outward diffusion of Al change to inward diffusion of O$^2$.
- Increase in the scale to alloy adherence.

Figure 2 showed the cross section view images of LOM of the coated system used in this study coated low alloy steel substrate at temperature range between 300-900°C. From the surface appearance of the samples, the spalled areas are considerably low. According to [12]. It is possible that a small amount of germanium had segregated to grain boundaries in the scale, and little voids are observed near the alloy/scale interface as shown in Figure 2. Since germanium could not be detected with X-ray diffraction at the surface of oxidized samples as shown in Figure 3, the suspected levels for germanium segregation must be very low. The addition of germanium had no visible effect on the external scale morphology developed during the cyclic oxidation of germanium-doped aluminizing-siliconizing. The phase constitution of the coatings was determined using XRD analysis. The major phases as a result of cyclic oxidation between (300-900°C) were continuous protective SiO$_2$, and Al$_2$O$_3$ layers on the sample surface as anticipated, its amounts increased with exposure duration.

4. FINITE ELEMENT METHOD

Methods of weighted residual is useful to obtain approximate solution of differential equation [13]. We consider the following differential equation:

$$\frac{d^2u}{dx^2} - u = -x$$  \hspace{1cm} (1)
Hence the approximate solution of function \((u)\) according to boundary conditions (B.C) in the range of variable \(x\) (\(0 < x < 1\)) will be:

\[
0 = u(0), \quad 1 = u(1).
\]

At first step it is assumed the following function:

\[
\tilde{u} = ax(1 - x)
\]  
(2)

Where:

\(\tilde{u}\) = Assumed function which satisfy boundary condition .

\(a\) = Unknown constant.

Then, the residual \((R)\) can be determined by sub. eq(2) in eq(1):

\[
R = \frac{d^2\tilde{u}}{dx^2} - \tilde{u} + x = -2a - ax(1 - x) + x
\]  
(3)

The next step is to determine the unknown constant \((a)\) such that the chosen test function \(\tilde{u}\) give a best approximates as comparing with the exact solution . Then a weighted function \((w)\) is selected and the weighted average of the residual \((I)\) over the problem domain is set to zero . That is:

\[
I = \int_{0}^{1} wRdx = \int_{0}^{1} w\left(\frac{d^2\tilde{u}}{dx^2} - \tilde{u} + x\right)dx = 0
\]  
(4)

\[
I = \int_{0}^{1} wRdx = \int_{0}^{1} w(-2a - ax(1 - x) + x)dx = 0
\]  
(5)

In this work, the weak formulation is used to solve the differential equation of cyclic oxidation kinetics [1]:

\[
\frac{dx}{dt} = k
\]  
(6)

Where:

\(x(t)\) = specific weight change \((\text{cm}^2)\)

\(t\) = oxidation time \((\text{hr})\)

\(k\) = oxidation rate constant \((\text{cm}^2/hr)\)
According to [14] the weak formula can be solving as follows:

\[ \frac{dx}{dt} = \frac{k}{x} \]

Where initial boundary conditions:

\[ x(0) = 0 \] at \( t = 0 \) and \( x(T) = l \)

\( l \) = the maximum value of specific weight change.

Thus, the solution will be:

\[ \int_0^1 \left( \frac{x}{k} \frac{dx}{dt} \right) dx = \int_0^1 w \times l \times dx \] \hspace{1cm} (7)

### 4.1 Galerkins Finite Element Method

This section shows how to compute weighted residual in a symmetric manner using finite element and piece wise continuous functions. Consider a sub-domain or finite element shown in Figure(4) the element has two nodes, one at each end. The corresponding coordinate value \((x_i, x_{i+1})\) and the nodal variable \((u_i, u_{i+1})\) are assignment.

The proposed unknown trial function required to solve eq.(1) is as follow:

\[ u(x) = c_1 x + c_2 = u_i \] \hspace{1cm} (8)

Which represent a linear function, where \(c_1\) and \(c_2\) are constants.

\[ u(x_{i+1}) = c_1 x_{i+1} + c_2 = u_{i+1} \] \hspace{1cm} (9)

Solve eq.(8) and eq.(9) for obtain \((c_1)\) and \((c_2)\):

\[ c_1 = \frac{u_{i+1} - u_i}{x_{i+1} - x_i} \] \hspace{1cm} (10)

\[ c_2 = \frac{u_i x_{i+1} - u_{i+1} x_i}{x_{i+1} - x_i} \] \hspace{1cm} (11)

Sub. eq.(10 and 11) into eq.(7):

\[ u = H_2(x) u_i + H_2(x) u_{i+2} \]

Where:

\[ H_2(x) = \frac{x_{i+1} - x}{h_i} \] \hspace{1cm} (12)
Where:

\[ h_i = \frac{x_{i+1} - x_i}{l} \]

\[ H_1(x) = \frac{x - x_i}{h_i} \]

\[ H_2(x) = \frac{1}{2} \left( 1 + \frac{x - x_i}{h_i} \right) \]

These functions are shown in Figure 5 [14]. Figure (6) illustrates the comparison between theory, finite element, and experimental results.

5. STATISTICAL ANALYSIS

The root mean square error (RMSE) was used to estimate the variation, expressed in the same unit as the data between simulated and measured values. This parameter is defined by [15]:

\[ RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (S_i - M_i)^2} \]

Where \( M_i \) and \( S_i \) are the measured and simulated values respectively, for \( i \)th data point of \( n \) observations. The RMSE of modeling analysis is presented in Table (5) for the test cases. As shown from this table that all values of RMSE are less than one i.e. there is approximately good agreement between the experimental and predicted values (Theory & finite element results).

Another statistical tool used to evaluate the quality of a curve fit is the coefficient of determination, also known as the R-squared value. The closer the \( R^2 \) is to 1, the better the fit. The largest \( R^2 \) can be is 1. It is defined as[15]:

\[ R^2 = 1 - \frac{\sum_{i=1}^{m} (f(x_i) - y_i)^2}{\sum_{i=1}^{m} (y_i - \bar{y})^2} \]

Where:
- \( m \) = No. of data.
- \( f(x_i) \) = function of data values.
- \( y_i \) = data values.
- \( \bar{y} \) = mean of y data.

According to \( R^2 \) shown in Table(5) there is approximately good agreement between experimental and theory results, and between experimental and FEM results.
6. STATISTICAL ANALYSIS
The root mean square error (RMSE) was used to estimate the variation, expressed in the same unit as the data between simulated and measured values. This parameter is defined by [15]:

\[ RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (M_i - S_i)^2} \]

Where \( M_i \) and \( S_i \) are the measured and simulated values respectively, for \( i \)th data point of \( n \) observations. The RMSE of modeling analysis is presented in Table (5) for the test cases. As shown form this table that all values of RMSE are less than one i.e. there is approximately good agreement between the experimental and predicted values (Theory & finite element results).

Another statistical tool used to evaluate the quality of a curve fit is the coefficient of determination, also known as the R-squared value. The closer the \( R^2 \) is to 1, the better the fit. The largest \( R^2 \) can be is 1. It is defined as[15]:

\[ R^2 = 1 - \frac{\sum_{i=1}^{n} (y_{pred,i} - y_{act,i})^2}{\sum_{i=1}^{n} (y_{act,i} - \bar{y})^2} \]

Where:

= No. of data.
= function of data values.
= data values.
= mean of y data.

According to \( R^2 \) shown in Table(5) there is approximately good agreement between experimental and theory results, and between experimental and FEM results.

CONCLUSIONS
From the cyclic oxidation tests of coated low alloy steel type-T22 in air temperatures range between 300-900 °C for 60 hr at 3 cycle the following results can be concluded:

1. Coated system (Germanium-doped Aluminizing-siliconizing diffusion coating) revealed good cyclic oxidation resistance, and oxidation kinetics was following the parabolic oxidation rates.
2. Phases present on the surface of all coated systems subjected cyclic oxidation are \( \text{SiO}_2 \) and \( \text{Al}_2\text{O}_3 \).
3. There is a good agreement between theory, finite element, and experimental results.
Table (1) Nominal composition of low alloy steel (Type T21 ASTM)

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe (%)</th>
<th>C (%)</th>
<th>Mn (%)</th>
<th>P (%)</th>
<th>S (%)</th>
<th>Si (%)</th>
<th>Cr (%)</th>
<th>Mo (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt. %</td>
<td>rem.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.05-0.15</td>
<td>0.3-0.6</td>
<td>0.025</td>
<td>0.025</td>
<td>0.5max</td>
<td>2.65-3.35</td>
<td>0.87-1.13</td>
<td></td>
</tr>
</tbody>
</table>

Table (2) Spectrochemical analysis of low alloy steel T21

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe (%)</th>
<th>C (%)</th>
<th>Mn (%)</th>
<th>P (%)</th>
<th>S (%)</th>
<th>Si (%)</th>
<th>Cr (%)</th>
<th>Mn (%)</th>
<th>V (%)</th>
<th>Ti (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt. %</td>
<td>rem.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>0.34</td>
<td>0.014</td>
<td>0.012</td>
<td>0.35</td>
<td>2.96</td>
<td>0.10</td>
<td>0.002</td>
<td>0.01</td>
<td></td>
</tr>
</tbody>
</table>

Table (3) Weight change values for cyclic oxidation of germanium-Doped Al-Si in air for 60 hr at 3 hr cycle.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Time (hr)</th>
<th>Weight Change (mg/cm²) at 300 °C</th>
<th>Weight Change (mg/cm²) at 600 °C</th>
<th>Weight Change (mg/cm²) at 900 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>0.0162</td>
<td>0.0588</td>
<td>0.0936</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>0.0220</td>
<td>0.0841</td>
<td>0.1378</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>0.0264</td>
<td>0.1037</td>
<td>0.1728</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>0.0300</td>
<td>0.1203</td>
<td>0.2029</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
<td>0.0311</td>
<td>0.1350</td>
<td>0.2298</td>
</tr>
<tr>
<td>6</td>
<td>18</td>
<td>0.0359</td>
<td>0.1484</td>
<td>0.2544</td>
</tr>
<tr>
<td>7</td>
<td>21</td>
<td>0.0385</td>
<td>0.1607</td>
<td>0.2772</td>
</tr>
<tr>
<td>8</td>
<td>24</td>
<td>0.0409</td>
<td>0.1722</td>
<td>0.2987</td>
</tr>
<tr>
<td>9</td>
<td>27</td>
<td>0.0431</td>
<td>0.1830</td>
<td>0.3189</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>0.0451</td>
<td>0.1932</td>
<td>0.3383</td>
</tr>
<tr>
<td>11</td>
<td>33</td>
<td>0.0471</td>
<td>0.2030</td>
<td>0.3567</td>
</tr>
<tr>
<td>12</td>
<td>36</td>
<td>0.0489</td>
<td>0.2124</td>
<td>0.3745</td>
</tr>
<tr>
<td>13</td>
<td>39</td>
<td>0.0507</td>
<td>0.2213</td>
<td>0.3916</td>
</tr>
<tr>
<td>14</td>
<td>42</td>
<td>0.0524</td>
<td>0.2300</td>
<td>0.4081</td>
</tr>
<tr>
<td>15</td>
<td>45</td>
<td>0.0541</td>
<td>0.2383</td>
<td>0.4241</td>
</tr>
<tr>
<td>16</td>
<td>48</td>
<td>0.0557</td>
<td>0.2464</td>
<td>0.4397</td>
</tr>
<tr>
<td>17</td>
<td>51</td>
<td>0.0572</td>
<td>0.2542</td>
<td>0.4548</td>
</tr>
<tr>
<td>18</td>
<td>54</td>
<td>0.0587</td>
<td>0.2619</td>
<td>0.4696</td>
</tr>
<tr>
<td>19</td>
<td>57</td>
<td>0.0601</td>
<td>0.2693</td>
<td>0.4839</td>
</tr>
<tr>
<td>20</td>
<td>60</td>
<td>0.0615</td>
<td>0.2765</td>
<td>0.4980</td>
</tr>
</tbody>
</table>

Table (4) n values and parabolic oxidation rate constants Kp for cyclic oxidation of germanium-Doped Al-Si in air for 60 hr at 3 hr cycle.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>n</th>
<th>Kp (mg/cm²)sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.446</td>
<td>1.061×10⁷</td>
</tr>
<tr>
<td>600</td>
<td>0.517</td>
<td>4.210×10⁵</td>
</tr>
<tr>
<td>900</td>
<td>0.558</td>
<td>6.211×10⁵</td>
</tr>
</tbody>
</table>

Table (5) Statistical analysis of results

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Experimental &amp; theory results</th>
<th>Experimental &amp; FRM results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RMSB</td>
<td>R²</td>
</tr>
<tr>
<td>300°C</td>
<td>0.006</td>
<td>0.9131</td>
</tr>
<tr>
<td>600°C</td>
<td>0.005</td>
<td>0.951</td>
</tr>
<tr>
<td>900°C</td>
<td>0.611</td>
<td>0.812</td>
</tr>
</tbody>
</table>
Figure 1: Cyclic oxidation kinetics for coated and uncoated samples.

Figure 2: LOM of low alloy steel type T21 coated with germanium-doped aluminiun-oxide coating after cyclic oxidation for 60 hr under air at 300°C, 600°C, and 900°C (cross section view).
Figure 3 XRD of low alloy steel type-T21 coated with germanium-doped aluminizing-siliconizing after cyclic oxidation for 60 hr under air at 300, 600, and 900°C.

Figure 4 Two nodes linear element

Figure 5 Linear shape functions
Figure 6 Comparison between experimental, theory (exact solution), and FEM (numerical solution) results.
REFERENCES