Modeling of Oxidation Kinetics in Air of Steel-T21 Alloy Coated by Simultaneous Germanium-Doped Aluminizing-Silicon zing Process

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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. Steel-T21 was coated with germanium-doped aluminzing-siliconizing. Diffusion coating was carried out at 1050 ^{o}C for 6 h under an Ar atmosphere by simultaneous germanium-dopded aluminizing-siliconizing process. Cyclic oxidation tests were conducted on the coated steel-T21 alloy in the temperature range oxide 600-800 ^{o}C in air for 30 h at 5 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 SiO_2 and Cr_2O_3..Mthamatical model using MATLAB show that there is multiple linear model for oxidation kinetics.

Keywords:

SteelT21;Oxidation;Aluminizing-Siliconizing;Pack cementation

.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 materials and are often used in large quantities in heavy engineering industries. Whilst these materials are not 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_2O_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_2O_3- and Al_2O_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 [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 yttrium-free alloy is typically convoluted or wrinkled and poorly adherent, the yttrium-containing alloy produces a flat and adherent oxide. In recent years yttrium 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 1wt.% 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 chromia (Cr_2O_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 600-800°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) arte shown in Table(1) and Table(2) respectively. The low alloy steel samples were cut into squares shapes with dimensions (20mm× 20×mm×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 emery 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 (50-60□m in particle size) as an aluminum source, 6 Wt.%Si powder (50-60□m in particle size) as a silicon source, 2Wt.% NaF and 2Wt.%NaCl as activator and the balance was silica-powder (70-120□m 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 coating, 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 79-82□m.

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 600-800°C in air. Each heating cycle includes heating in the furnace for 5 hours and cooling heating in still air.

3. Results and Discussion
3.1 cyclic oxidation of coated system in air

Coating system germanium-doped aluminizing-siliconizing substrate were subjected to cyclic oxidation. A primary aim was to study the kinetic of oxidation behavior of coated systems as a function of the environments. The specific weight change of the samples of coated systems during oxidation is plotted as a function of time as shown in Figure (1).

The kinetics behavior of cyclic oxidation of Coatined system at temperature range between 600-800°C follows the parabolic rate ($\Delta W/A = K_p t^{0.5}$) as shown in above figures. In coated systems case, oxidation rate coefficients are obtained and listed in Table (3).

Based on the positive weight change data , the coated systems of the low alloy steel substrate appears to be fairly resistance to scale spallation even at temperature range 600-800°C .Coating system appears good oxidation resistance. First, the most desirable SiO$_2$, and Al$_2$O$_3$ 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 oxidermanium 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_2O_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.

Figures (1) 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 600-800°C), for 30 hr at 5 hr cycle. 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 600-800°C) . From the surface appearance of the samples, the spalled areas are considerably low . It is possible that a small amount of germanium had segregated on grain boundaries in the scale, and little voids are observed near the alloy/scale interface as shown in figures. Since germanium could not be detected with X-ray diffraction at the surface of oxidized samples, the suspected enrichment 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 Cycic oxidation between (600-800°C) were continuous protective SiO_2, andAlr_2O_3 layers on the sample surface as anticipated, its amounts increased with exposure duration.

3.2 Mathematical Model

A model is a representation of something constructed and used for a particular purpose. We use models constantly in all walks of life because they present a simplified view of the world which highlights the parts which interest us [12,13]. In this study we conclude the multiple linear model which interest us in engineering metallurgy.

The multiple linear model can be described as follows: Suppose that y is a linear function of the two or more variables x_1, x_2,…. For example:

$$y = a_o + a_1 x_1 + a_2 x_2 \qquad \boxed{1}$$

To find the coefficient values of a_o, a_1, and a_1 to fit a set of data (y, x_1, $x_2…x_n$) in the least squares sense, we can make use of then fact that the left-division method for solving linear equations uses the least square method when the equation set is overdetermined. To use this method, let n be the number of data points and the linear equation in matrix form as follows:

$$Xa = y \qquad \boxed{2}$$

$$a = \begin{bmatrix} a_o \\ a_1 \\ a_2 \end{bmatrix} \qquad \boxed{3}$$

$$X = \begin{bmatrix} 1 & x_{11} & x_{21} \\ 1 & x_{12} & x_{22} \\ 1 & x_{13} & x_{23} \end{bmatrix} \qquad \boxed{4}$$

$$y = \begin{bmatrix} y_1 \\ y_2 \\ y_3 \end{bmatrix} \qquad \boxed{5}$$

where x_{1i}, x_{2i}, and y_{1i} are the data, i=1……,n. The solusion for the coefficient is given by a=X/Y [5,6].

The parabolic oxidation rate constant (y) as a function of the oxidation time $x_1,x_2,….x_7$ gives the linear model obtaining from the data shown in Table(4) using MATLAB language. The script file is shown in Figure(3).These models at temperature range (600-800°C) are respectively as follows:

- $Y = 0 + 1.1416 \times 10^6 X1 + 2.283 \times 10^6 X2 + 3.4247 \times 10^6 X3 + 4.5662 \times 10^6 X4 + 5.7078 \times 10^6 X5 + 6.8493 \times 10^6 X6$

- $Y = 0 + 0.4425 \times 10^6 X1 + 0.8850 \times 10^6 X2 + 1.3274 \times 10^6 X3 + 1.7699 \times 10^6 X4 + 2.2124 \times 10^6 X5 + 2.6549 \times 10^6 X6$

- $Y = 0 + 1.3928 \times 10^6 X1 + 2.7855 \times 10^6 X2 + 4.1783 \times 10^6 X3 + 5.5710 \times 10^6 X4 + 6.9638 \times 10^6 X5 + 8.3565 \times 10^6 X6$

In the same way the oxidation exponent (n)-oxidation time relationships are as follows:

- $Y = 0 + 10.5175 X1 + 21.0349 X2 + 31.5524 X3 + 42.0698 X4 + 52.5873 X5 + 63.1048 X6$

- $Y=0+10.4690X1+20.9380X2+31.4070X3+41.8760X4+52.3451X5+62.8141X6$

- $Y=0+10.2124X1+20.4248X2+30.6373X3+40.8497X4+51.0621X5+61.2745$

Also the dependent of oxidation exponent on temperature can be expresses as follows:
$Y=0+0.4312X1+0.0001X2$
and the maximum error is 0.6840%. The script file is shown in Figure(4).

4. Conclusions

From the cyclic oxidation tests of coated low alloy steel type-T22 in air temperatures range between 600-800 ^{o}C for 30 hr at 5 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 and hot corrosion are SiO_2 and Al_2O_3.

3. A multiple linear model was shown between the parabolic oxidation rate constant and oxidation time.

4. A multiple linear model was shown between the oxidation exponent and oxidation time.

5. A multiple linear model was shown between the oxidation exponent and oxidation temperature.

5. Refeences

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Table(1) Nominal composition of low alloy steel (Type T21-ASTM)								
Element	Fe	C	Mn	P_{max}	S_{max}	Si	Cr	Mo
Wt.%	Rem.	0.05-0.15	0.3-0.6	0.025	0.025	0.5max	2.65-3.35	0.87-1.13

Table(2) Spectrochemical analysis of low alloy steel T21									
Element	Fe	C	Mn	P	S_m	Si	Cr	Mo	V	Ti
Wt.%	Rem.	0.04	0.34	0.014	0.012	0.35	2.96	0.10	0.002	0.01

Table (3) n values and parabolic oxidation rate constants K_P for cyclic oxidation of germanium-Doped Al-Si in air for 30 hr at 5 hr cycle.

Temperature ^{o}C	n	K_P (mg^2/cm^4)/sec.
600	0.4754	4.38×10^{-6}
700	0.4776	1.13×10^{-5}
800	0.4896	3.59×10^{-5}

Table(4a) Values of independent variables

i	1	2	3	4	5	6	7	
Xi	0	5	10	15	20	25	30	

Table(4b) Values of dependent variables

i	1	2	3
Temperatue	600	700	800
Y1i	4.38×10^{-6}	1.13×10^{-5}	3.59×10^{-5}
Y2i	0.4754	0.4776	0.4896
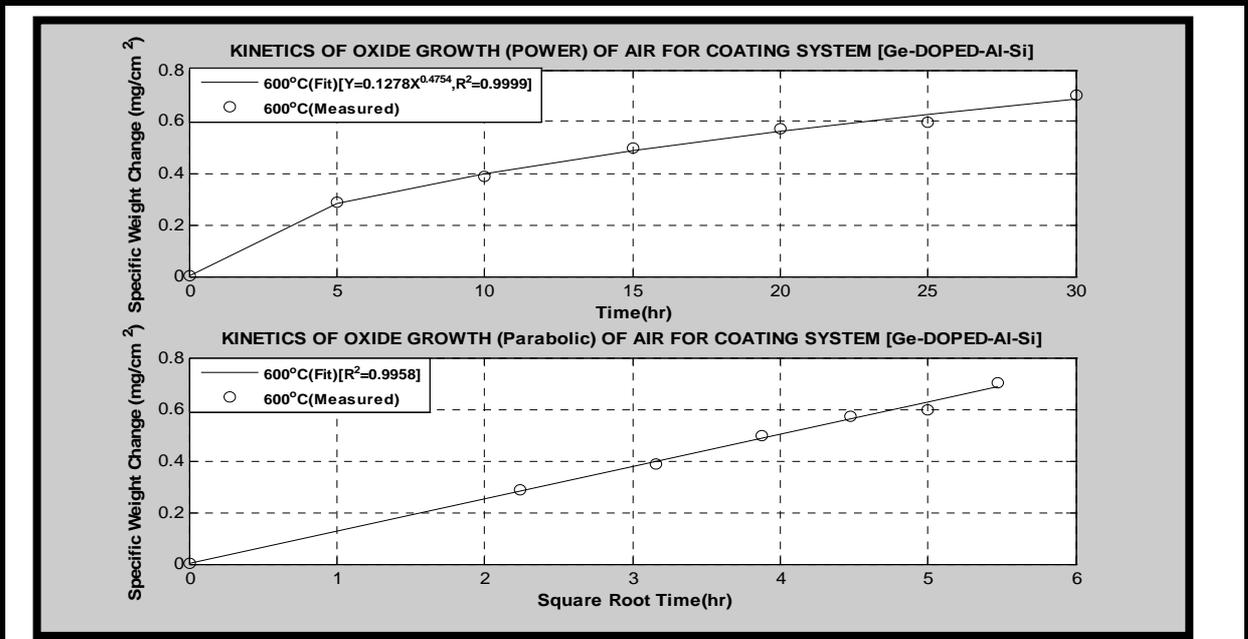
Figure (1a)Parabolic fitted results of specific weight change vs. time plot for germanium-doped aluminizing-siliconzing diffusion-coated low alloy steel type-T21 cyclic oxidized in air at temperatures 600°C at 30 h for 5 h cycle.
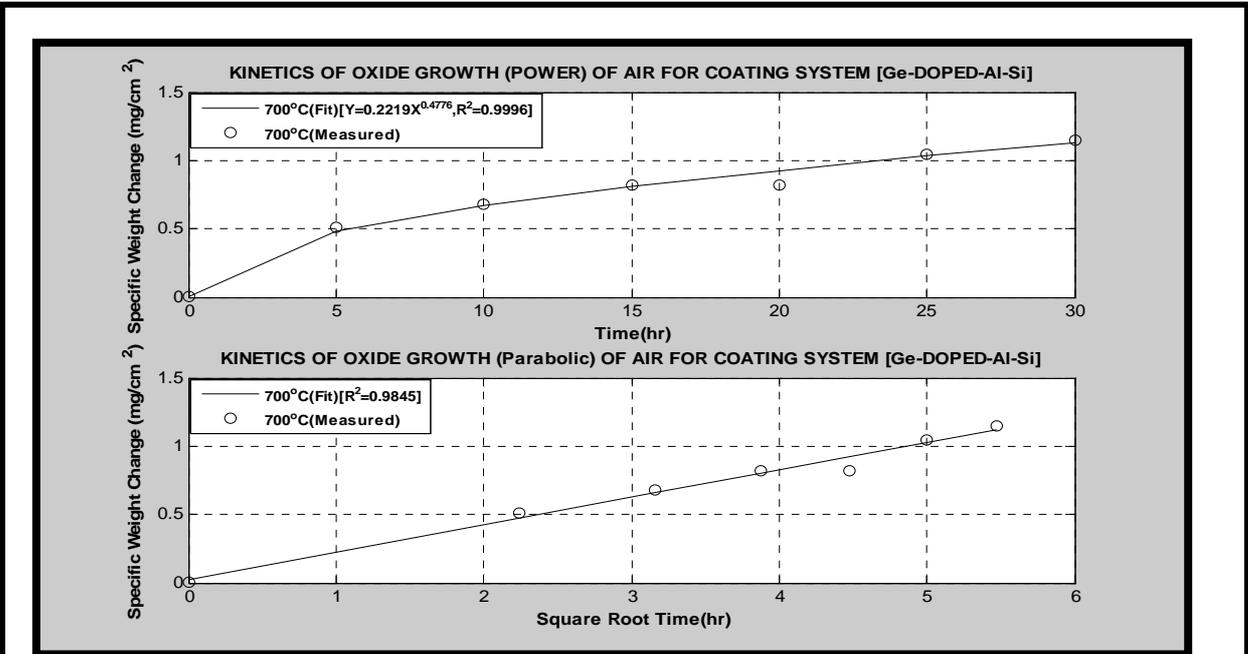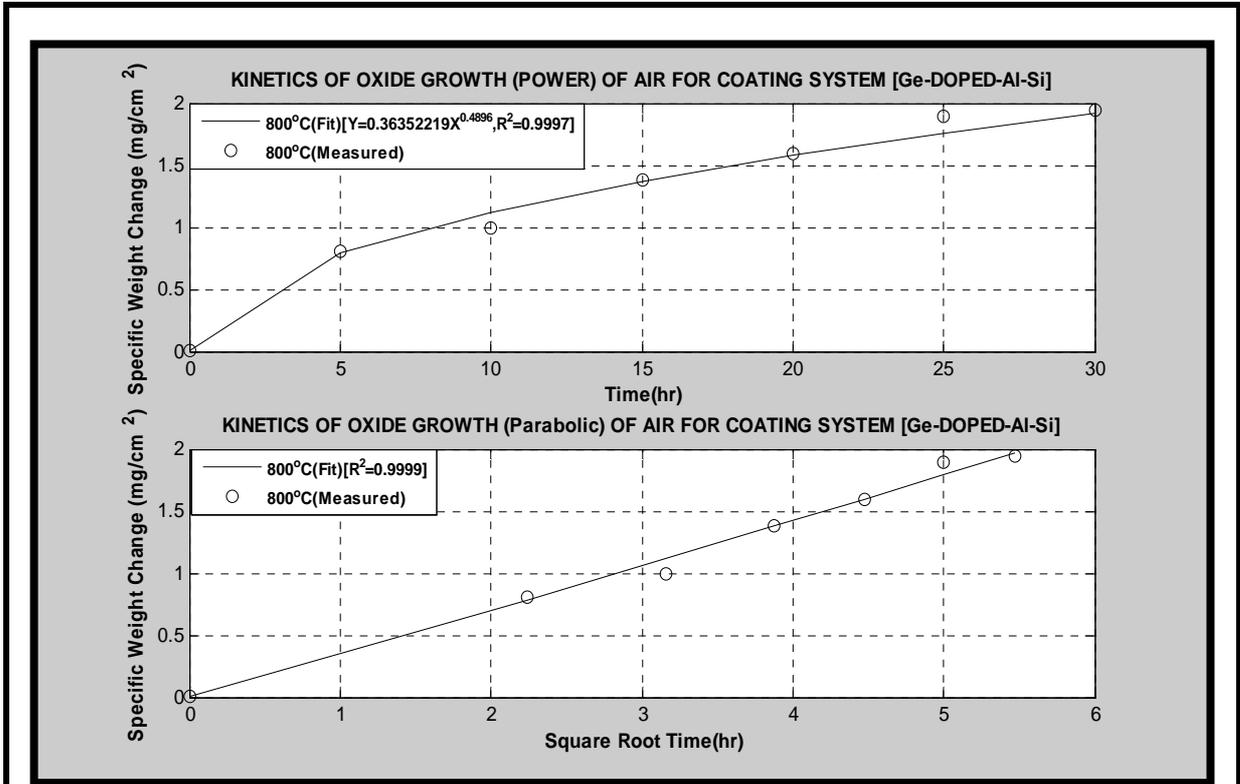

Figure (1b)Parabolic fitted results of specific weight change vs. time plot for germanium-doped aluminizing-siliconzing diffusion-coated low alloy steel type-T21 cyclic oxidized in air at temperatures 700°C at 30 h for 5 h cycle.

Figure (1c)Parabolic fitted results of specific weight change vs. time plot for germanium-doped aluminizing-siliconzing diffusion-coated low alloy steel type-T21 cyclic oxidized in air at temperatures 800°C at 30 h for 5 h cycle.
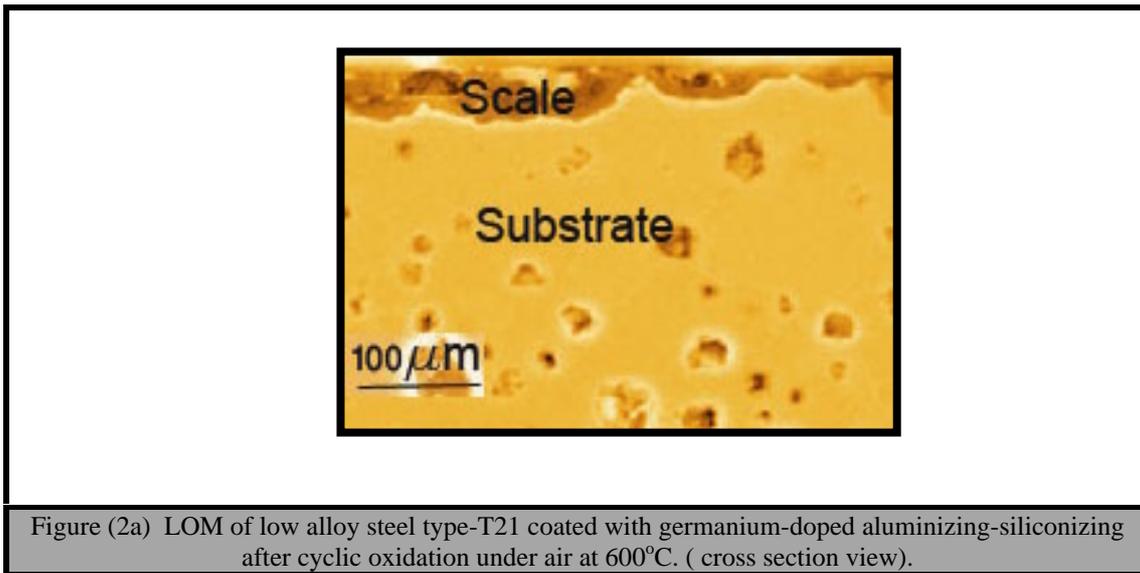
Figure (2a) LOM of low alloy steel type-T21 coated with germanium-doped aluminizing-siliconizing after cyclic oxidation under air at 600°C. (cross section view).
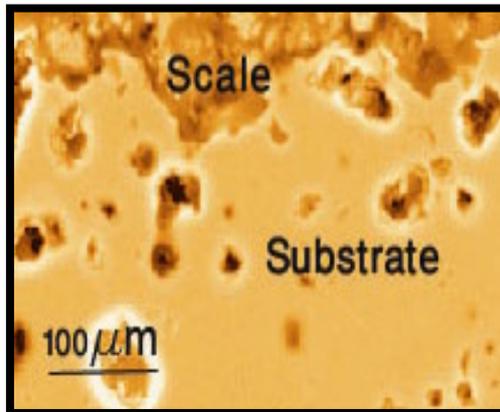
Figure (2b) LOM of low alloy steel type-T21 coated with germanium-doped aluminizing-siliconizing after cyclic oxidation under air at 700°C. (cross section view).
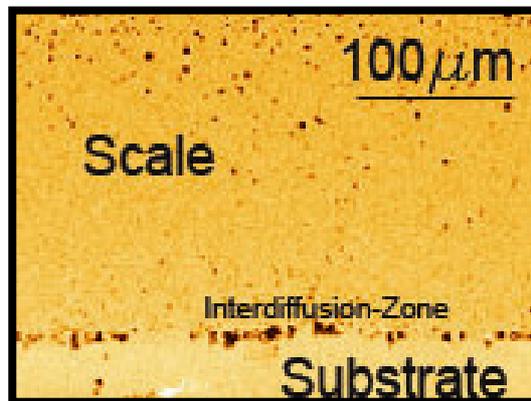

Figure (2c) LOM of low alloy steel type-T21 coated with germanium-doped aluminizing-siliconizing after cyclic oxidation under air at 800°C. (cross section view).

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%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%MODELING OF OXIDATION KINETICS IN AIR OF STEEL-T21
%ALLOY COATED BY SIMULTANEOUS GE-DOPEDALUMINIZING-
%SILICONIZING PACK CEMENTATION PROCESS
%LINEAR MODEL OF OXIDATION TIME [30HR AND 5CYCLE]AND
%PARABOLIC OXIDATION RATE CONSTANT Kp AT TEMPERATURE
%RANGE (600-800oC).
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%FOR TEMPERATURE EQUAL TO 600oC
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
x1=[0 5 10 15 20 25 30];
y=[ 0.4754];


a=y\x1
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%FOR TEMPERATURE EQUAL TO 700oC
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
x1=[0 5 10 15 20 25 30];
y=[ 0.4776];
a=y\x1
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
```

Figure (3a) Script file for K_P and oxidation time

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%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%MODELING OF OXIDATION KINETICS IN AIR OF STEEL-T21

%ALLOY COATED BY SIMULTANEOUS GE-DOPEDALUMINIZING-

%SILICONIZING PACK CEMENTATION PROCESS

%LINEAR MODEL OF OXIDATION TIME [30HR AND 5CYCLE]AND

%PARABOLIC OXIDATION EXPONENT (n) AT TEMPERATURE

%RANGE (600-800oC).

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%FOR TEMPERATURE EQUAL TO 600oC

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

x1=[0 5 10 15 20 25 30];

y=[ 0.4754];


a=y\x1

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%FOR TEMPERATURE EQUAL TO 700oC

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

x1=[0 5 10 15 20 25 30];

y=[ 0.4776];
```

Figure (3b) Script file for n and oxidation time

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%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%MODELING OF OXIDATION KINETICS IN AIR OF STEEL-T21

%ALLOY COATED BY SIMULTANEOUS GE-DOPEDALUMINIZING-

%SILICONIZING PACK CEMENTATION PROCESS

%LINEAR MODEL OF OXIDATION TEMPERATURE AND

%PARABOLIC OXIDATION EXPONENT (n) AT TEMPERATURE

%RANGE (600-800oC).

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%FOR TEMPERATURE EQUAL TO 600-800 oC

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

x1=[600 700 800]';

y=[0.4754 0.4776 0.4896 ]';


X=[ones(size(x1)) x1 ];

a=X\y

yp=X*a;

Max_Percent_Error=100*max(abs((yp-y)./y))


%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%RESULTS
```

Figure (3c) Script file for n and oxidation temperature

نمذجة حركيات الأكسدة في الهواء للفولاذ نوع T21 المغلّف باستخدام طريقة الألمنةـسلكنة الآنية المحورة بالجرمانيوم

د. عباس خماس حسين

الخلاصة

يتضمن هذا البحث استخدام طريقة التغليف بالسمنتة للحصول على تغطيات الألمنيومـسليكون المحورة بالجرمانيوم على الفولاذ المنخفض السبائكية نوع T21 التي تؤدي الى تحسن كبير في الأكسدة.حيث أن الفولاذ قد خضع الى التغطية باستخدام عملية الألمنةـ سلكنة المحورة بالجرمانيوم.تم تنفيذ الطلاء الانتشاري عند درجة ١٠٥٠C° و لمدة ٦ ساعة تحت أجواء الآركون باستخدام طريقة الألمنة ـسلكنة الآنية المحورة بالجرمانيوم . اختبارات الأكسدة الدورية قد أنجزت على الفولاذ في المدى الحراري ٦٠٠ـ٨٠٠C° في الهواء لمدة ٥ ساعة. أظهرت النتائج أن حركيات الأكسدة لنظام الطلاء في الهواء كانت من نوع القطع المكافئ . أما أطوار الأكسدة التي تكونت على أنظمة الطلاء فانها كانت SiO_2 ، Cr_2O_3 . أما النموذج الرياضي لحركيات الأكسدة باستخدام الماتلاب فانه كان من النوع الخطي المتعدد المتغيرات