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1 T21 Alloy Coated by Simultaneous Germanium-Doped Aluminizing-Siliconzing Process

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ABSTRACT

In this work a pack cementation of germanium-doped aluminum and silicon coatings on low alloy steel type-T21 has been applied. This gives significant improvement in the oxidation. 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-siliconzing process. Cyclic oxidation tests were conducted on the coated steel-T21 alloy in the temperature range oxide 300-900°C in air for 102 h at 3 h cycle. The results showed that the oxidation kinetics for coated system in air can be represented by parabolic curve .Oxide phases that formed on coated system are SiO_2 and Cr_2O_3. A neural network model of oxidation kinetics has been proposed to model the oxidation kinetic. The neural model shows good agreement with the experimental data.

Keywords: Steel-T21; Oxidation; Aluminizing-Siliconizing; Pack cementation; neural Network.

نمذجة حركيات الأكسدة في الهواء للفولاذ نوع T21 المغلّف بطريقة الألمنة-سلكنة الآنية المحورة بالجرمانيوم باستخدام الشبكة العصبية

الخلاصة

يتضمن هذا البحث استخدام طريقة التغليف بالسمنتة للحصول على تغطيات الألمنيوم-سليكون المحورة بالجرمانيوم على الفولاذ المنخفض السبائكية نوع T21 التي تؤدي الى تحسن كبير في الأكسدة.حيث أن الفولاذ قد خضع الى التغطية باستخدام عملية الألمنة-سلكنة المحورة بالجرمانيوم.تم تنفيذ الطلاء الانتشاري عند درجة 1050°C و لمدة ٦ ساعة تحت أجواء الآركون باستخدام طريقة الألمنة –سلكنة الآنية المحورة بالجرمانيوم . اختبارات الأكسدة الدورية أنجزت على الفولاذ في المدى الحراري 300-900°C في الهواء لمدة 102 ساعة (٣ ساعة لكل دورة) أظهرت النتائج أن حركيات

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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 . تم اقتراح نموذج شبكة عصبة لنمذجة حركيات الأكسدة. اظهرت الشبكة العصبية نتائج متوافقة مع التجارب العملية.

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. These materials are 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 provided 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].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 germanium prevents the sulfur segregation to the alloy/scale interface, either by reacting with sulfur to form 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,Ge, 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] and [11], have 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 is studied at temperature rangesfrom 600°C to 800°C under air environment, in addition a neural networkmodel of oxidation kinetics has been proposed.

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 inTable (1and 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 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 μm in particle size) as an aluminum source, 6 Wt.%Si powder (50-60 μm in particle size) as a silicon source, 2Wt.% NaF and 2Wt.%NaCl as activator and the balance was silica-powder (70-120 μm 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 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 attemperature between 300-900ºC in air. Each heating cycle includes heating in the furnace for 3 hours and cooling heating in still air.

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

NEURAL NETWORK MODELING

A neural network is a parameterized non-linear model which can be used to perform regression, in which case, a very flexible, non-linear function is fitted to experimental data. The details of this method have been reviewed in [12] and [13].

Neural networks are basically connectionist system, in which various nodes called neurons are interconnected. A typical neuron receives one or more input signals and provides an output signal depending on the processing function of the neuron. This output is transferred to connected neurons in varying intensities, the signal intensity being decided by the weights. Feed forward networks are commonly used. A feed forward network has a sequence of layers consisting of a number of neurons in each layer. The output of neurons of one layer becomes input to neurons of the succeeding layer. The first layer, called an input layer, receives data from the outside world. The last layer is the output layer, which sends information out to users. Layers that lie between the input and output layers are called hidden layers and have no direct contact with the environment. Their presence is needed in order to provide complexity to network architecture for modeling non-linear functional relationship. After choosing the network architecture, the network is trained by using back propagation algorithm, where back propagation algorithm is the efficient optimization method used for minimizing the error through weight adjustment [13]. The trained neural network has to be tested by supplying testing data.

In this work, three multilayer (feedforward) neural networks have been built under MATLAB® environment to model the relationship between the temperature and time with respect to the weight change. All these networks are consisting of input layer which has two neurons taking the temperature and time as inputs, two hidden layers and one output layer gives the networks output represents the corresponding weight change. The difference between these networks is the number of neurons inside each hidden layer. For the first network, 15 neurons are used in the first hidden layer and 12 neurons for the second hidden layer, whereas for the two other networks the first hidden layers have 4 and 7 neurons, respectively. Finally, the second hidden layers for the last two networks have 6 and 9 neurons, respectively. Figure (1) shows the neural network model of this work. The hyperbolic tangent function ($tanh$) is used as an activation function for all neurons. The back-propagation training algorithm based on Levenberg-Marquardt algorithm is used to train these networks.The Levenberg-Marquardt algorithm appears to be the fastest method for training moderate-sized feedforward neural networks (up to several hundred weights). It also has an efficient implementation in MATLAB® software, because the solution of the matrix equation is a built-in function, so its attributes become even more pronounced in a MATLAB environment [14].The training algorithm parameters used in this work are given in Table (3).

Table (3)Levenberg-Marquardt training algorithm parameters.

Parameter Name	Parameter value
epochs	5000
goal	1.00E-08
max fail	1000
memory reduction	1
minimum gradient	1.00E-08
adaptive value μ	0.001
adaptive value decrement μ_{dec}	0.1
adaptive value increment μ_{inc}	10
maximum of the adaptive value μ_{max}	10000000000
Learning rate	0.0005
learning rate increment	1.005

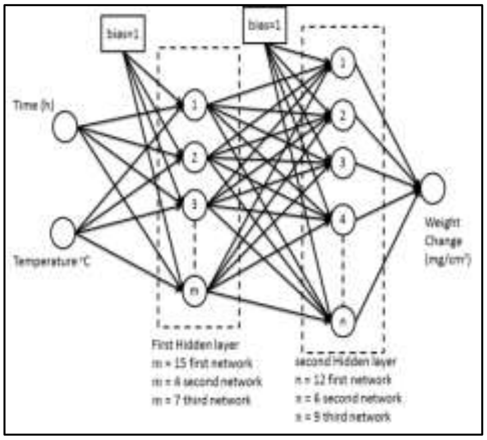

Figure (1) the neural network model.

RESULTS AND DISCUSSION

1-Cyclic oxidation of coated system in air

Coating system germanium-doped aluminizing-siliconizing substrate was subjected to cyclic oxidation. A primary aim was to study the kinetic of oxidation behavior of coated system as a function of the environments. The specific weight change of the samples of coated system during oxidation is plotted as a function of time as shown in Figure (2).

The kinetics behavior of cyclic oxidation of coating system at temperature range between 300-900°C follows the parabolic rate ($\Delta \boldsymbol{W}/\boldsymbol{A} = \boldsymbol{K_P t^{0.5}}$) where ($\Delta \boldsymbol{w}$weight change, $\boldsymbol{A}$ surface area of oxidation, $\boldsymbol{K_p}$ constant of parabolic oxidation rate, $\boldsymbol{t}$ oxidation time and $\boldsymbol{n}$ oxidation exponent)as shown in the curves of Figure (2. In coated systems case, oxidation rate coefficients are obtained and listed in

Table (4. Weight change values are shown in

Table (5).

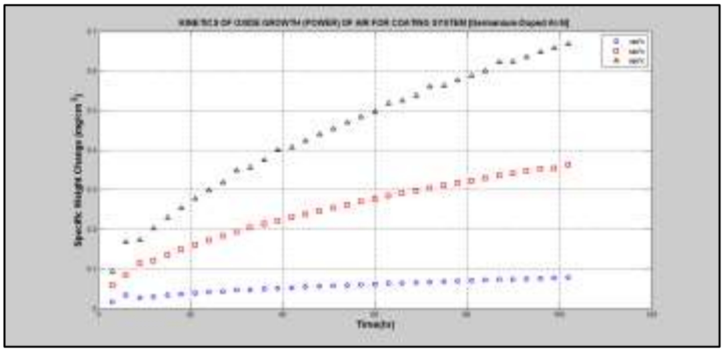

Figure (2) Parabolic fitted results of specific weight change vs. time plot for germanium-doped aluminizing-siliconzing diffusion-coated low alloy steel type-T21 cyclic oxidized in air at temperatures range(300-900oC) at 102 h for 3 h cycle.

Table (4n) values and parabolic oxidation rate constants KP for cyclic oxidation of germanium-Doped Al-Si in air for102 hr at 3 hr cycle.

Temperature ºC	n	K_P (mg^2/cm^4)/sec.
300	0.414	1.361×10^{-7}
600	0.510	5.270×10^{-5}
900	0.543	7.296×10^{-5}

Table (5) Weight change values for cyclic oxidation of germanium-Doped Al-Si in air for102 hr at 3 hr cycle.

Time (hr)	Weight Change (mg/cm2) at 300ºC	Weight Change(mg/cm2) at 600ºC	Weight Change (mg/cm2) at 900ºC
3	0.0162	0.0588	0.0936
6	0.0220	0.0841	0.1378
9	0.0264	0.1037	0.1728
12	0.0300	0.1203	0.2029
15	0.0331	0.1350	0.2298
18	0.0359	0.1484	0.2544
21	0.0385	0.1607	0.2772
24	0.0409	0.1722	0.2987
27	0.0431	0.1830	0.3189
30	0.0451	0.1932	0.3383
33	0.0471	0.2030	0.3567
36	0.0489	0.2124	0.3745

Time (hr)	Weight Change (mg/cm2) at 300ºC	Weight Change(mg/cm2) at 600ºC	Weight Change (mg/cm2) at 900ºC
39	0.0507	0.2213	0.3916
42	0.0524	0.2300	0.4081
45	0.0541	0.2383	0.4241
48	0.0557	0.2464	0.4397
51	0.0572	0.2542	0.4548
54	0.0587	0.2619	0.4696
57	0.0601	0.2693	0.4839
60	0.0615	0.2765	0.4980
63	0.0628	0.2836	0.5117
66	0.0641	0.2905	0.5252
69	0.0654	0.2973	0.5384
72	0.0667	0.3039	0.5513
75	0.0679	0.3103	0.5640
78	0.0691	0.3167	0.5765
81	0.0703	0.3229	0.5888
84	0.0714	0.3291	0.6008
87	0.0726	0.3351	0.6127
90	0.0737	0.3410	0.6244
93	0.0747	0.3469	0.6359
96	0.0758	0.3526	0.6473
99	0.0769	0.3583	0.6585
102	0.0779	0.3638	0.6696

Based on the positive weight change data, the coated system of the low alloy steel substrate appears to be fairly resistance to scale spallation even at temperature range 300-900ºC .Coating system appears good oxidation resistance as a result of the most desirable SiO_2, and Al_2O_3 protective scale layer that formed 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 is 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 Alchanges to inward diffusion of O^{-2}.
- Increase in the scale to alloy adherence.

Figure (2shows 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 300-900ºC), for 102hr at 3hr cycle. Figure (3toFigure (5are showing the cross section view images of LOM of the coated low alloy steel substrate at temperature range between 300-900ºC . 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 cyclic oxidation between (300-900ºC) were continuous protective SiO_2, andAlr_2O_3 layers on the sample surface as anticipated, its amounts increased with exposure duration.

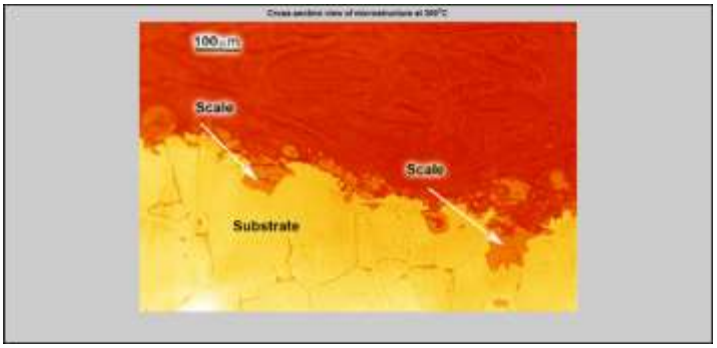

Figure (3) LOM of low alloy steel type-T21 coated with germanium-doped aluminizing-siliconizing after cyclic oxidation under air at 300oC. (cross section view).

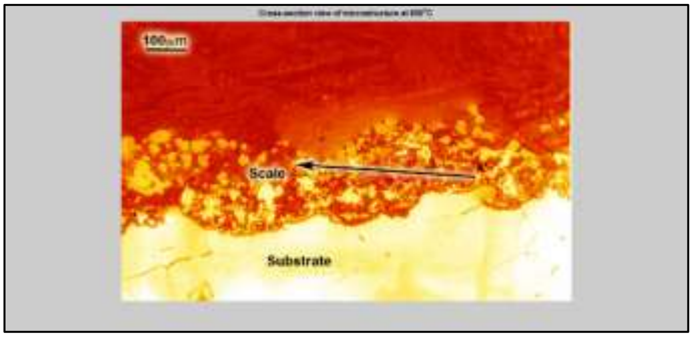

Figure (4) LOM of low alloy steel type-T21 coated with germanium-Doped aluminizing-siliconizing after cyclic oxidation under air at 600oC. (Cross section view).

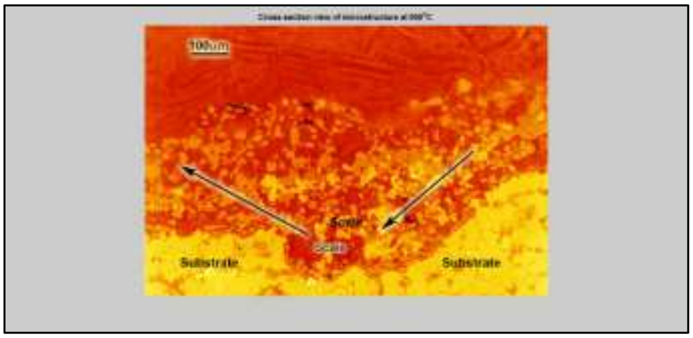

Figure (5) LOM of low alloy steel type-T21 coated with germanium-doped aluminizing-siliconizing after cyclic oxidation under air at 900oC. (cross section view).

2-Neural networks results

The experimental data shown in

Table (5) was rearranged to give 102 sets; the temperature and time are considered as inputs and the weight change as output, to represent the networks inputs and output sets. These sets are divided into two groups the first one is consist of 88 sets representing the training sets. Whereas, the second group is consist of the remaining 14 sets as shown in shaded form in the

Table (**5**), to be used to test the trained networks.Figure (6) to Figure (8showing the best linear regression between the networks responses and the experimental data during the training phase of the proposed networks, in addition to the correlation coefficient (R-Value). It can be seen that the network with m=4 and n=6 has the best fit because of the correlation coefficient is equal to one its means perfect fit. Whereas, the other two networks have acceptable fit (0.99987) for the network of m=15 and n=12 and

(0.99996) for the network of m=7 and n=9. This result is proved by plotting the networks responses with the experimental data of the testing sets as shown in Figure (9) to Figure (11). It is clear from the magnified view of the curved that the output of network with m=15 and n=12 is deviated from the experimental data in two points, the same things happened for the network with m=7 and n=9. In contrary, the output of network with m=4 and n=6 does not give any deviation from the experimental data.

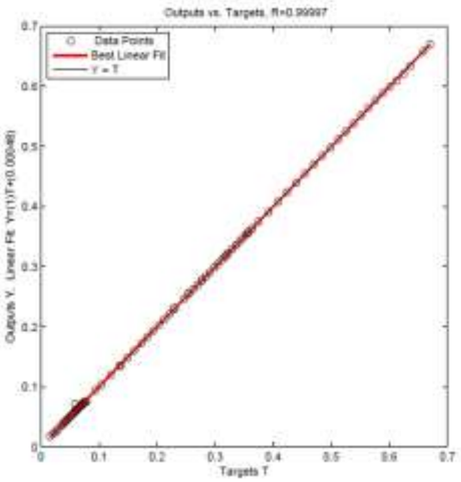

Figure (6) the linear regression and correlation coefficient (R-value) between the network response (15 and 12 neurons at first and second hidden layer, respectivly) and the experimental data for training sets.

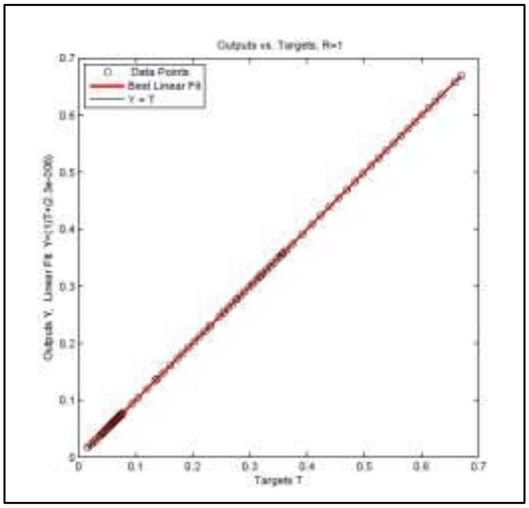

Figure (7) the linear regression and correlation coefficient (R-value) between the network response (4 and 6 neurons at first and second hidden layer, respectivly) and the experimental data for training sets.

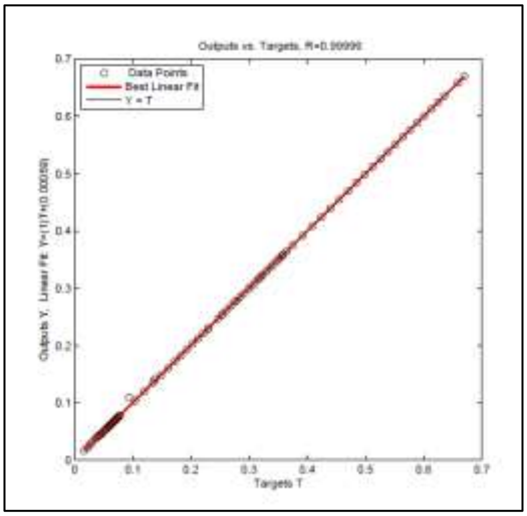

Figure (8) the linear regression and correlation coefficient (R-value) between the network response (7 and 9 neurons at first and second hidden layer, respectivly) and the experimental data for training sets.

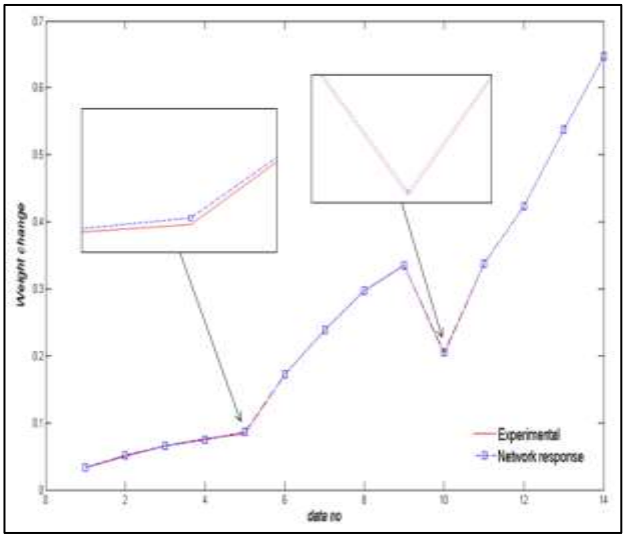

Figure (9) the network response with respect to experimental testing sets for m=15 and n=12 netwoeks.

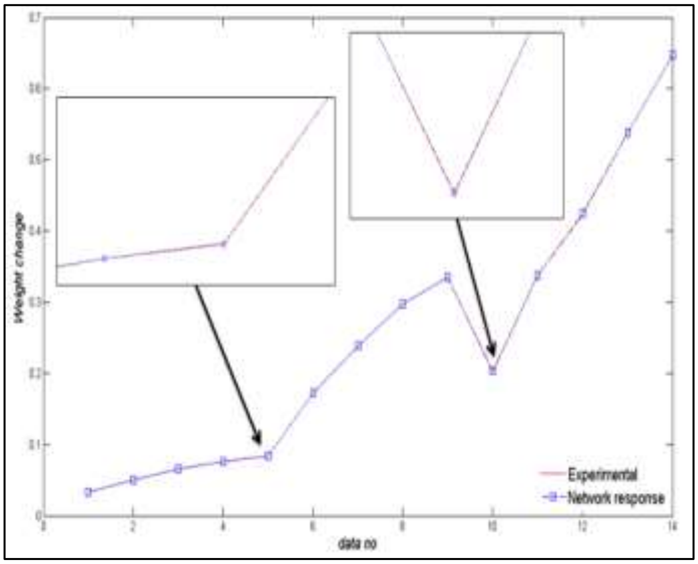

Figure (10) the network response with respect to experimental testing sets for m=4 and n=6 netwoeks.

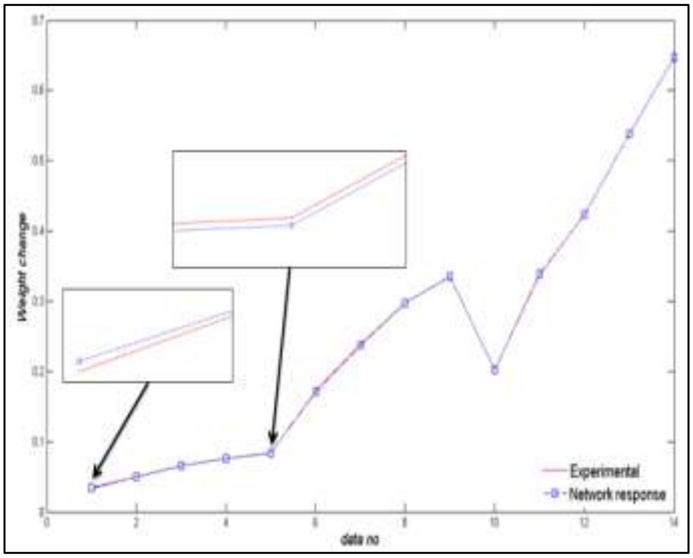

Figure (11)the network response with respect to experimental testing sets for m=7 and n=9netwoeks

CONCLUSIONS

From the cyclic oxidation tests of coated low alloy steel type-T22 in air temperatures range between 300-900 ºC for 102hr at 3 cycle, and the neural network modeling 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. The neural network showed good results to fit the data of the coating system and it can be considered reliable to predict the weight change for the corresponding temperature and time as shown in Figure (6 to Figure (11.
3. The network with 4 neurons in the first hidden layer and 6 neurons in the second hidden layers has the best results and give perfect fit with experimental data.

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