

Finite Element Analysis Using MATLAB of Oxidation Properties in H₂O Vapor of Steel-T22 Alloy Coated by Simultaneous Y-Doped Chromizing-Siliconizing Process

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Abstract

The application of a pack cementation of Y-doped chromium and silicon coatings on low alloy steel type-T₂₂ yields a significant improvement in the oxidation resistance. Steel-T22 was coated with Y-doped chromizing-siliconizing. Diffusion coating was carried out at 1050 °C for 6 h under an Ar atmosphere by simultaneous Y-doped chromizing-siliconizing process. Cyclic oxidation tests were conducted on the coated steel-T22 alloy in the temperature range 300-500 °C in H₂O for 100 h at 5 h cycle. The oxidation kinetics for coated system in H₂O was found to be parabolic. Oxide phases that formed on coated system are SiO₂ and Cr₂O₃. Finite element results show that there is a good agreement between FEM and experiments results.

Keywords: SteelT22; Oxidation; Chromizing-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 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 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 Cr₂O₃).
- 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 dispersoid components in bulk alloy, or as surface products produced by coating. They are used predominantly with Cr₂O₃- and Al₂O₃-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 pegs 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 sulfide or by tying up the sulfur by segregation to internal oxide surfaces [5]. Thus, the addition of a small amount of reactive element [Y,Ce, La, Hf, Zr, Th] to an alloy resulted in substantial 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 yttrium-doped chromium and silicon on the surface of steel-T22 alloy using single step pack cementation to enhance the oxidation resistance in steel-T22 was examined. The cyclic oxidation behavior of un-coated and coated steel-T22 alloy will be studied in the temperature range 300-500°C in H_2O

2. Experimental procedure

The substrate alloy used in this study was low alloy steel (Type T22-ASTM). The nominal composition and the spectrochemical analysis of low alloy steel (Type T22-ASTM) are 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 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 chromium-silicon diffusion coating consisting of 16 Wt.%Cr powder (50-60µm in particule size) as an chromium source, 6 Wt.%Si powder (50-60µm in particule size) as a silicon source, 2Wt.% NaF and 2Wt.%NaCl as activator and the balance

was silica-powder (70-120µm in particule size). All pack powders was sized by sieving method and 1Wt.% of the pack silica filler was replaced by yttrium reactive element.. Low alloy steel (type T22-ASTM) 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 79-82µm.

Alloy with yttrium -doped chromium-silicon diffusion sample were accurately weighed and then placed into ceramic coating crucible. Cyclic oxidation tests were carried out in the temperature range 300-500°C in H_2O . 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 H_2O

Acomputer program (Matlab Language) is used to calculate the best fit to the equations ($\Delta W/A=Kt^n$ and $\Delta W/A=Kt^{1/2}$). A plot of the specific weight change vs. time and square root time, for coated systems (Y-doped chromizing-siliconizing) diffusion coatings coated low alloy steel type-T22 cyclic oxidized in H_2O at temperatures 300,400 and500°C conditions for 100 hr at 5 hr cycle, is shown in Figures (1), this figure indicates that the minor elements (Y) additions, seems to play an important role on scale adherence of low alloy steel type-T22.

The improved oxidation resistance of (Y)-doped chromizing-siliconizing diffusion coatings, also attributed to promotion of the selective oxidation of an elements (Cr,Si) which forms a stable oxide diffusivity, (Cr_2O_3 and SiO_2), on substrate as well as reduction of the growth rate for (Cr_2O_3 and SiO_2).

Table (3) show that the K_p values obtained at temperature range (300-500°C) for all coated systems were higher than that for oxidation under air and this result is in good agreement with reference [12]. It was observed that the reaction rates under water vapor cyclic

oxidation are induced because of hydrogen to permeate from water vapor environment.

A considerable amount of (Cr₂O₃ and SiO₂) is also being evident as an oxidation product of all systems coated low alloy steel type-T₂₂ cyclic oxidized in H₂O at temperature 500°C, for 100 hr at 5 hr cycle Figures (2 a-f), show the scale formation on coated low alloy steel type-T₂₂ cyclic oxidized in H₂O at temperatures 300,400 and 500°C.

It is apparently, that the three coated systems (Y-doped chromizing-siliconizing) diffusion coatings coated low alloy steel type-T₂₂ cyclic oxidized in H₂O at temperatures 300,400 and 500°C, do not show severe scale spalling, and appeared uniform and smooth after thermal cycling as shown in above figures. A detailed examination of the alloy/scale interface on the coated system reveals that the scale remain in contact with the metal during oxidation over almost the whole surface.

3.2 Finite Element Analysis

3.2.1 Method of weighted residual

Methods of weighted residual is useful to obtain approximate solution to different gravity equation . in order to explain the methods , we consider the following sample

$$\frac{d^2u}{dx^2} - u = -x \quad \text{problem :}$$

$$0 < x < 1 \quad u(0)=0 ; u(1)=1$$

at first step , we assumed a trial function as :

$$\tilde{u} = ax(1-x) \quad \text{which satisfy}$$

boundary condition. The residual (R) become :

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

We next step is to determine the unknown constant (a) such that the chosen test function best approximates the exact solution . a weighted function (w) is selected and the weighted average of the residual over the problem domain is set to zero . That is :

$$I = \int_0^1 w R dx = \int_0^1 w \left(\frac{d^2\tilde{u}}{dx^2} - \tilde{u} + x \right) dx = 0$$

$$I = \int_0^1 w (-2a - ax(1-x) + x) dx = 0$$

In this work ; the weak formulation is used to solve the differential equation :

$$\frac{dx}{dt} = \frac{k}{x}$$

Where

x: Specific weight change (cm²/sec).

t : Oxidation time (hr).

k: oxidation rate constants (mg/cm⁴)/hr.

There are two method to describe the model of solving the weak formula in this method as :

First method :

$$\frac{dx}{dt} = \frac{k}{x} \quad 0 < x < L \quad \text{with B.C}$$

$$[x(0)=0]$$

The weak formulation of the equation is :

$$\int_0^L \left(\frac{x}{k} w \frac{dx}{dt} \right) dx = \int_0^L w \times 1 \times dx$$

The second weak formulation [13]

$$\int_0^L \left(\frac{k}{x} w \frac{dt}{dx} \right) dx = \int_0^L w \times 1 \times dx$$

3.2.1 Galerkins finite element formulation

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(3) the element has two nodes , one at each end. The corresponding coordinate value (Xi or Xi+1) and the nodal variable (Ui or Ui+1) are assignment .

The proposed unknown trial function to be (to solving eq.(1)).

$$u = c_1 x + c_2 \quad \text{We want to express eq.(7)}$$

interms of nodal variables .In other words , (C1 and C2) need to be replaced by Ui and Ui+1 . To this end , we evaluate (u) at X=Xi and X=Xi+1

$$u(x_i) = c_1 x_i + c_2 = u_i \quad \text{then :}$$

$$u(x_{i+1}) = c_1 x_{i+1} + c_2 = u_{i+1} \quad \text{Solve eq(8)}$$

$$C_2 = \frac{U_i X_{i+1} - U_{i+1} X_i}{X_{i+1} - X_i}$$

and eq(9) for
obtain (C1)
and

(C2) :

$$U = H_1(x)U_i + H_2(x)U_{i+1}$$

Sub eq(10 and 11) into eq.(6) :

$$H_1(x) = \frac{X_{i+1} - X}{h_i}$$

Where:

$$H_2(x) = \frac{X - X_i}{h_i}$$

$$h_i = X_{i+1} - X_i \quad \text{: element length}$$

H1, H2 : linear shape functions (Figure 4)
Or in another form [14].

Figure (5) illustrates the comparison between theory, finite element, and experimental results, it is clear that there is a good agreement between theory, finite element, and experimental results.

4. Conclusions

From the cyclic oxidation tests of uncoated and coated low alloy steel type-T₂₂ in water-vapour temperatures range between 300-500 °C for 100 hr at 5 cycle the following results can be concluded:

1. Coated system (Y-doped chromizing-siliconizing diffusion coating) revealed good cyclic oxidation resistance for low alloy steel type-T₂₂, 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 SiO₂ and Cr₂O₃.
3. There is a good agreement between theory, finite element, and experimental results.

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Table(2) Spectrochemical analysis of low alloy steel (Type T₂₂-ASTM)

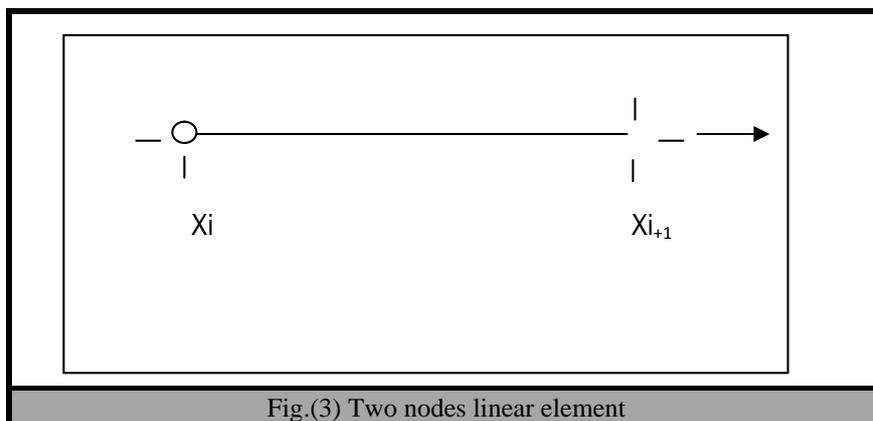
Element	Fe	C	Mn	P	S _m	Si	Cr	Mo	V	Ti
Wt.%	Rem	0.06	0.35	0.012	0.011	0.46	1.96	0.91	0.002	0.001

Table(1) Nominal composition of low alloy steel (Type T₂₂-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	1.9-2.6	0.87-1.13

Table (3) n values and parabolic oxidation rate constants K_P for cyclic oxidation of coated system in H₂O for 100 hr at 5 hr cycle.

Temperature °C	Y-doped Cr-Si	
	n	K _P (mg/cm ⁴)/hr
300	0.4705	7.29×10 ⁻⁶
400	0.5064	5.336×10 ⁻⁴
500	0.6038	5.490×10 ⁻³



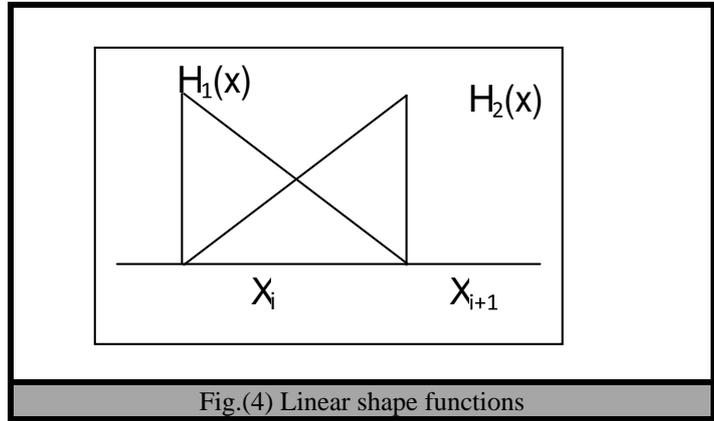
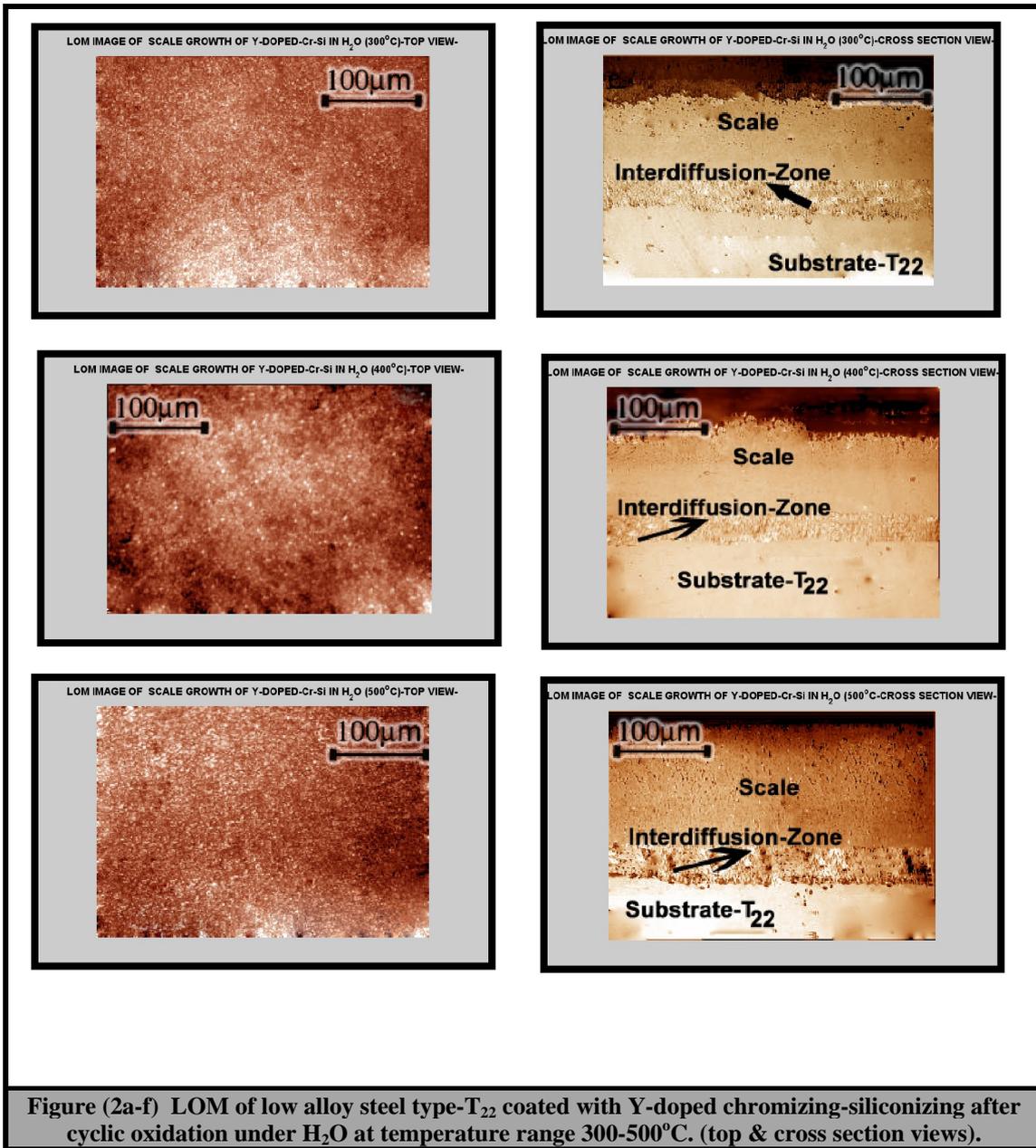


Fig.(4) Linear shape functions



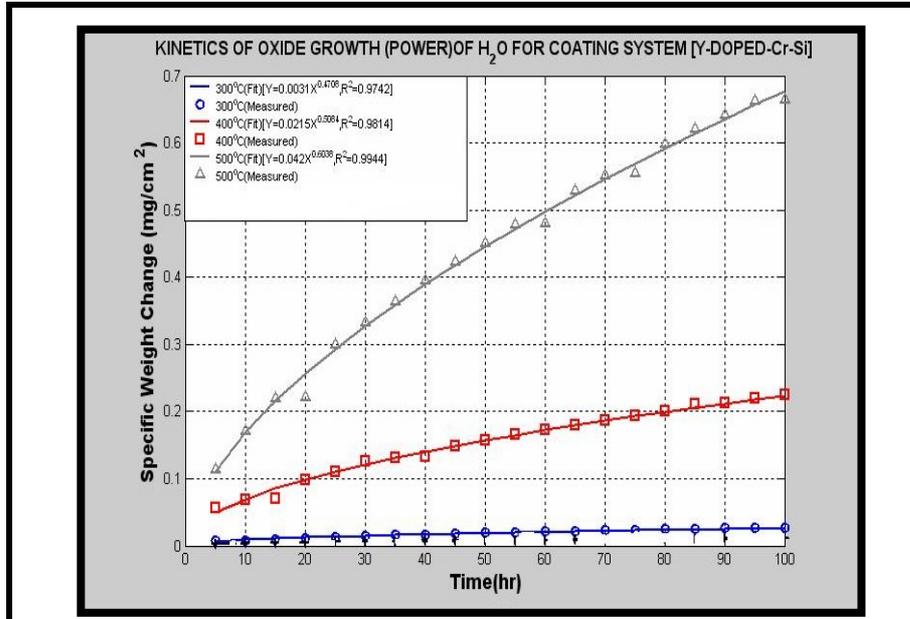


Figure (1a) Parabolic fitted results of specific weight change vs. time plot for Y-doped chromizing-siliconizing diffusion-coated low alloy steel type-T₂₂ cyclic oxidized in H₂O at temperatures 300,400 and 500°C .

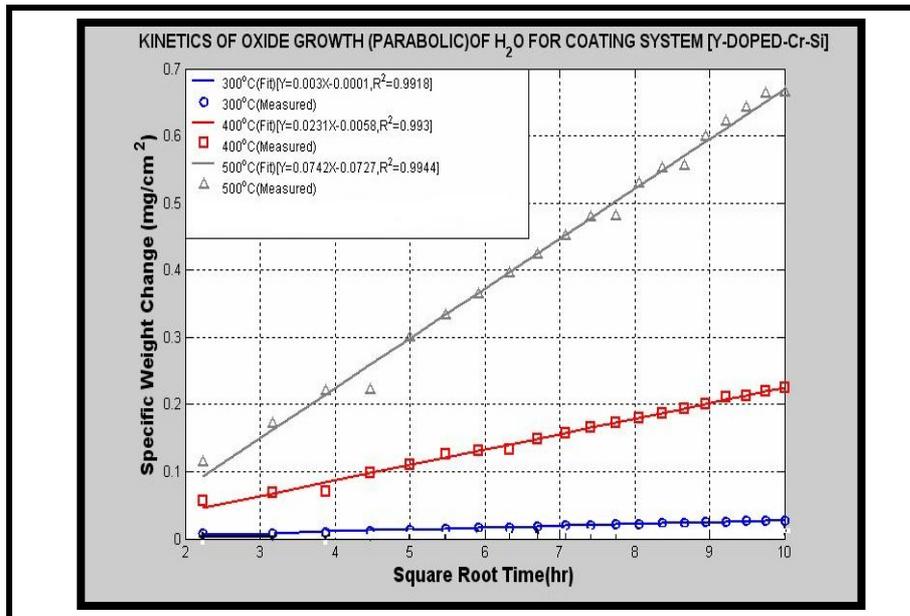


Figure (1b) Linear fitted results of specific weight change vs. t^{1/2} plot for Y-doped chromizing-siliconizing diffusion-coated low alloy steel type-T₂₂ cyclic oxidized in H₂O at temperatures 300,400 and 500°C

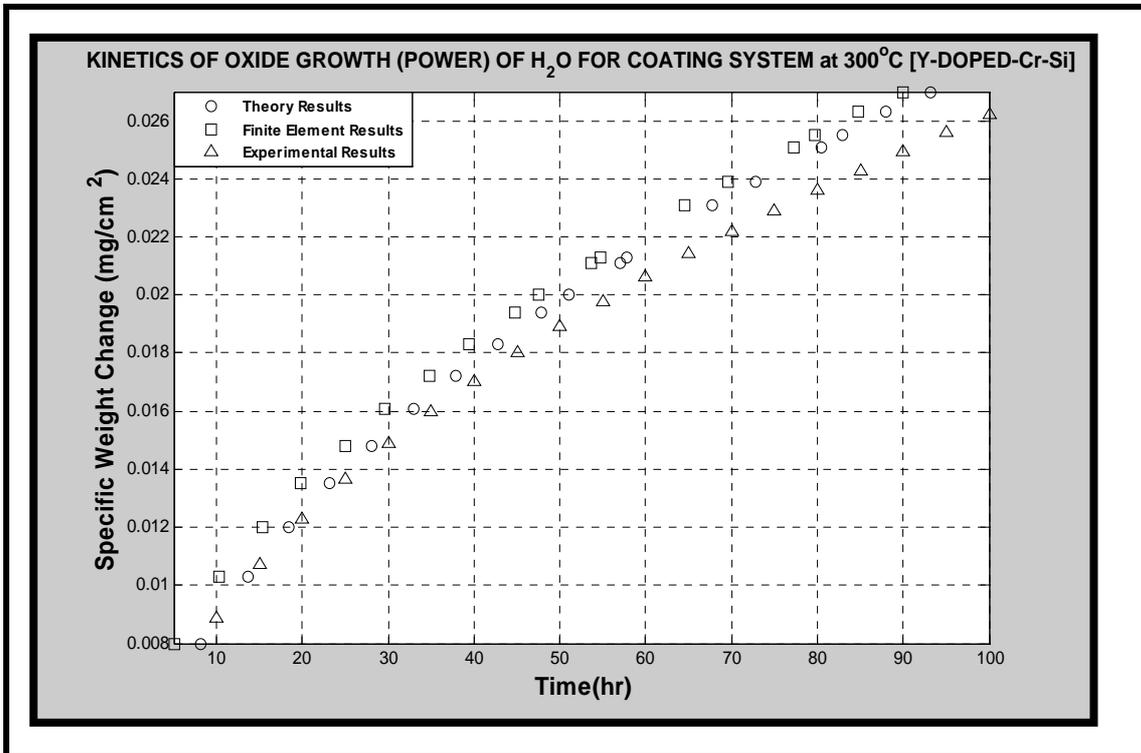


Figure (5a) comparison between theory, finite element, and experimental results at 300°C.

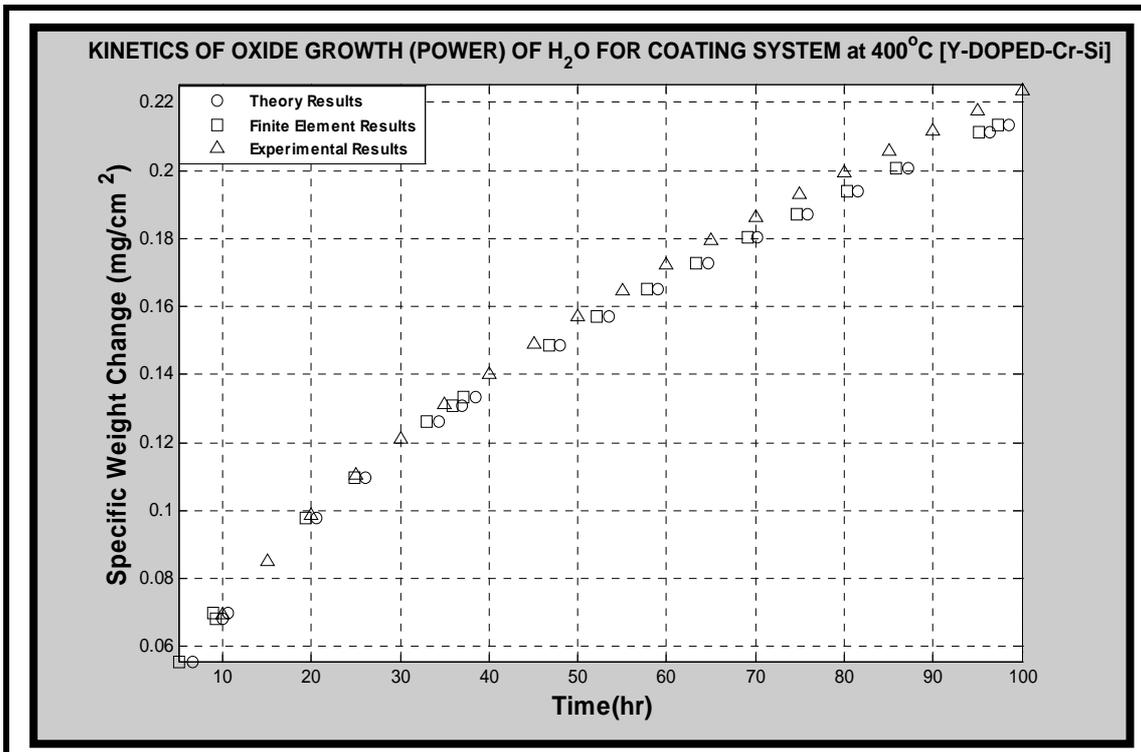
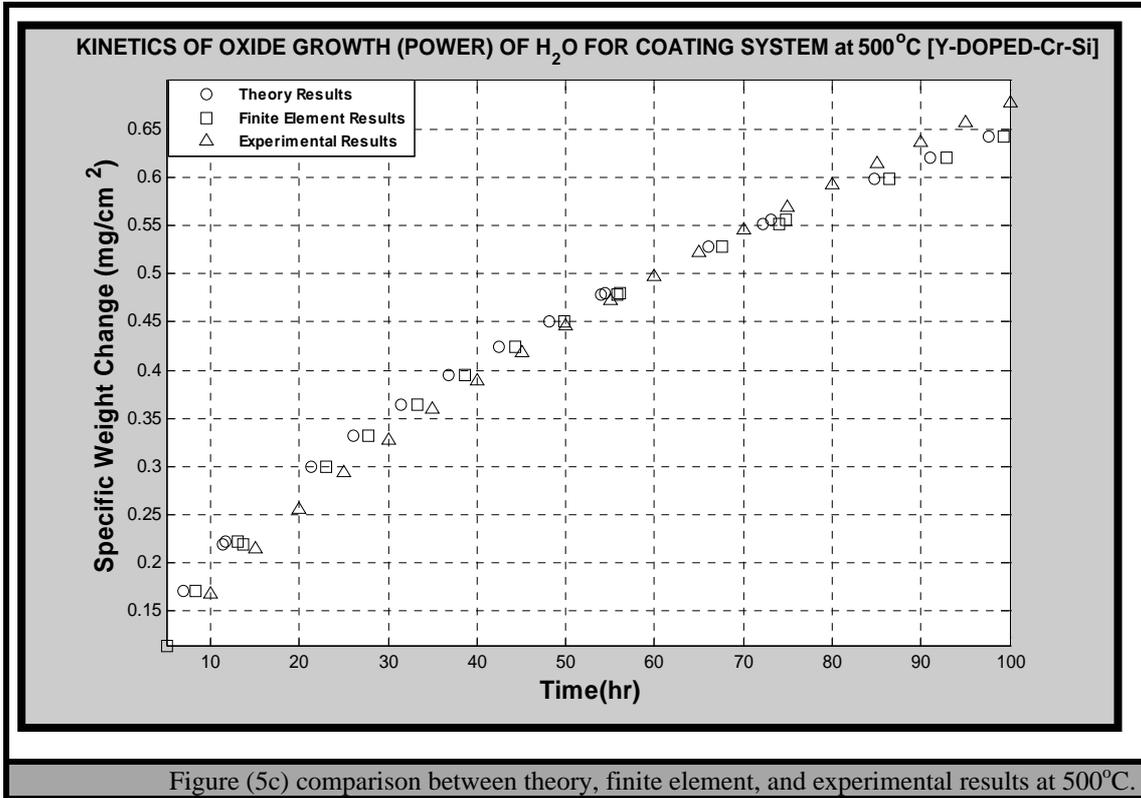


Figure (5b) comparison between theory, finite element, and experimental results at 400°C.



تحليل العناصر المحددة باستخدام الماتلاب لخواص الأكسدة في بخار الماء للفولاذ T22 المطلي بالكرمنة-السلكنة الأنيّة المحورة باليتيريوم

ان تطبيق طريقة التغليف بالسمنتنة لتغطيات الكروم-السليكون المحورة باليتيريوم على الفولاذ المنخفض السبائكية نوع T22 يؤدي الى تحسين كبير في مقاومة الأكسدة. حيث أن الفولاذ T22 قد خضع الى طلاء كروم-سليكون المحورّ باليتيريوم . و تم تنفيذ الطلاء الانتشاري عند (1050°C) و لمدة ٦ ساعة تحت أجواء الأركون باستخدام الطلاء الأني للسليكون المحور باليتيريوم. و تم اجراء اختبارات الأكسدة الدورية على الفولاذ المطلي في المدى الحراري (300-500) في بخار الماء و لمدة ١٠٠ ساعة عند دورة مقدارها ٥ ساعة. و لوحظ أن آليات الأكسدة تسلك سلوك القطع المكافئ . اما أطوار الأكسدة فانها تتضمن تكون SiO₂ و Cr₂O₃. نتائج تحليل العناصر المحددة تشير الى التطابق مع النتائج التجريبية.

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