

High Temperature Behavior of Yttrium – Doped Siliconized 316L Stainless Steel at CO₂ Environment

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Abstract:

In this study, silicon and yttrium were simultaneously co-deposited by diffusion into austenitic stainless steel (AISI 316L) substrates, by a single-step pack cementation process. Cyclic oxidation tests were conducted on the siliconized coating and on the yttrium doped siliconized coating of stainless steel in CO₂ atmospheric pressure at temperatures 800° C and 900° C for 100h at 10h cyclic. The results show that the initial weight gain is rapid and increased as the temperature increased. The oxidation resistance of the yttrium doped siliconized of stainless steels was significantly improved as compared with the siliconized stainless steels. The scale formed on coated stainless steel after oxidation in CO₂ environment was thick and consisted of Y₂O₃, SiO₂, Fe₂O₃ and chromium oxide. Optical metallography (LOM) and X-ray diffraction (XRD) were used to characterize the resulting coating and cyclic oxidation structures.

Keywords: yttrium; siliconized; pack cementation; cyclic oxidation.

1. Introduction

The oxidation resistance of Fe-Cr-Ni alloys containing greater than 16 wt.% Cr is considered to be due to the formation of tightly adherent chromia (Cr₂O₃) films at the surface [1]. The formation of a continuous Cr₂O₃ scale requires that the alloy contains critical-chromium content, which is dependent upon such variables as the alloys structure and the oxidizing conditions. Most corrosion resistant, Fe-base, high-temperature alloys contain at least 16 wt.% Cr. Commercial chromia forming alloys invariables contain minor amounts of such elements as Mn, Si, Ti, Al and C. These minor additions can greatly influence oxidation behavior, especially under thermal-cycling conditions. The oxides of Si, Ti and Al are more stable thermodynamically than that of Cr and can consequently oxidize internally [2].

The rate-controlling mechanism of oxidation is attributed to the outward diffusion of metal ions. It is also known that relatively minor additions of Al and Si can play a significant role in the oxidation process of Fe-Cr-Ni alloys. Small additions of Si have been reported to have a beneficial effect on oxidation resistance because of the formation of SiO₂ at the metal oxide interface. The role of silicone is typically attributed to the formation of a silicon oxide layer between the oxide and metal interface. The formation of protective chromia scales is promoted by this continuous or noncontinuous silicon oxide layer that is reported to act as a diffusion barrier to Fe and Cr reaching the oxide layer. In some studies, the effect of Si is attributed to the formation of a continuous silica layer between the metal and the external chromia scale [1].

Coating was grown on several Fe-base alloys using the pack cementation process. Ferritic coatings with a surface concentration of approximately Fe-25wt%Cr-3Si were produced on low- alloy and plain- carbon steels. Two phases (ferrite plus austenite) coating containing 25 wt.% Cr-2Si was produced on 304 S.S., and Cr and Si were diffused into the austenitic solid solution of incoloy 800 with no phase change. All of the coated alloys showed greatly improved cyclic oxidation resistance in air compared to uncoated alloys, and the coated low- alloy steel showed extremely slow oxidation kinetics in air at 700C° [3].

The introduction of reactive elements (RE) or reactive- element oxide (REO) has been proposed for many years to avoid cracking and spalling of the protective oxide scales, and therefore to guarantee a good adherence to the metallic substrates. The RE can be introduced as alloying elements, as oxide coatings or they can be implanted onto the alloy surface. The mechanical properties of alloys may be altered by the oxidation of RE or oxide dispersoids. As a consequence, the choice of coating seems to be an attractive solution to introduce RE without altering the mechanical properties of the metallic substrate [4]. Many studies were performed on the influenced of REO coating on the high temperature oxidation behavior of chromia- forming alloys and alumina forming alloys [2, 5, 6, 7]; in most cases, the REO-applied films improved the oxidation resistance by decreasing the oxidation rate and enhancing the chromia- scale adherence [4].

Seal et al. [8] studied the effect of a cerium- oxide coating on the isothermal cyclic oxidation behavior of 316, 321, 304 and 347 austenitic grade steels. The best oxidation resistance was noted for 321, followed by 316, 347 and 304. The internal oxidation of silicon, which acted as apegging action for better scale adherence, was observed.

Yi-Rang He et al. [9] showed that a Ge-doped silicide coating on Cr-Cr₂Nb alloy by pack cementation. The morphology and composition of the coating depended both on the composition of the pack, and also on the composition and microstructure of the substrate. Higher Ge content in the pack favored NbSi₂ formation and suppressed the formation of CrSi₂. Isothermal and cyclic oxidation in air showed that the Ge-doped Cr-silicide coatings decreased the oxidation of Cr-Nb alloys.

The oxidation behavior of an austenitic stainless steel (19Cr- 10N- 1.5Si) containing small amount of Y has been studied by H. Fujikawa et al [10]. Their results showed that Y has found to segregate to oxide grain boundaries and thereby to inhibit outward-cation diffusion and promote the internal oxidation of Si.

The aim of this study, Si and Y has been simultaneously deposited into 316L austenitic stainless steel in a single-step, pack cementation process and to characterize the cyclic-oxidation behavior of coated steel at CO₂ environment. This study represents part of a larger study on the long-term cyclic-oxidation behavior of stainless steel alloys, with focus on characterizing the subsurface microstructural and compositional changes that occur during the oxidation process in order to develop an effective life time-prediction model.

2. Experimental Procedure

The austenitic stainless steel alloy used in this investigation was received in bar form. The nominal composition is given in **Table (1)**. Cylinder coupons of 20mm diameter and 3mm thickness were cut from a bar. All the specimens were ground through 220, 500, 600 and 800 grit emery (Sic) paper. Samples were polished up to 1- μm diamond paste and cleaned in alcohol in an ultrasonic bath prior to the coating process or the oxidation tests. The samples dimensions were measured, also, the weight of each sample was measured using amettler microbalance (sartorius) before and after of coating.

In this study, two types of coated austenitic stainless steel were performed. Silicon with and without yttrium have been simultaneously deposited into 316L austenitic stainless steel in a single-step, pack cementation process. The parameters for pack siliconizing and yttrium doped siliconized coating process are summarized in **Table 2**.

The substrate samples were placed in an stainless steel crucible in contact with a mixed powder containing element silicon with and without yttrium powder, chloride-activators (NH₄Cl) and an inert alumina (Al₂O₃) filler powder. The crucible was covered by an alumina lid using alumina-base cement. The crucible was then put in another stainless steel cylindrical retort. The outer retort has a side tube through which argon gas passed and second hole in the top cover for argon gas out let. Type-K thermocouple was inserted through the

cover of outer retort for recording real temperature near inner retort. This combined system was then put in an electrical holding furnace under an argon atmosphere with a flow rate of 1.5 L/min.

After diffusion, the packs were cooled to room temperature in the same atmosphere. The samples were removed from the pack and ultrasonically cleaned to remove any loosely embedded pack material; thickness and weight measurements were made. Each sample were cut using a low-speed diamond saw, mounted in epoxy, and polished for metallographic examination. The samples were then examined in cross section by the optical microscopy. X-ray diffraction (XRD) and energy dispersive spectrometry (EDX) were used to characterize the resulting coating structures and compositions.

The oxidation experiments were performed at 800C° and 900 C° in CO₂ atmospheric, for 100h at 10h cyclic. Each heating cyclic included heating in the furnace for 10h at the test temperature and cooling to room temperature at the same atmosphere. The samples are ultrasonically cleaned and weights changing before and after each oxidation cyclic were measured.

The surface of the specimen was observed by a light optical microscopy (LOM); also, all the specimens after cyclic oxidation test were sectioned for metallographic examination. The phases formed after cyclic oxidation tests are identified by X-ray diffraction (XRD).

3. Results and Discussion

In this study, silicon with and without yttrium are simultaneously deposited by diffusion into austenitic stainless steel (316L) substrates using one step pack cementation. The samples were analyzed by XRD to determine the phases present after siliconizing. The surface phases are FeSi₂, Fe₅Si₃ and Cr-Fe-Ni as in **Fig. (1)**. The depth of penetration for XRD is about 7 μm; therefore, XRD characterized the near surface region rather than the surface top atomic layers [11]. As shown in **Fig. (2)**, the coated stainless steel has a coating thickness of approximately 170 μm microns and consists of two zones, an outer layer and inter diffusion zone.

Both siliconized coating and yttrium doped siliconized austenitic stainless steel (316L) substrates was subjected to cyclic oxidation at CO₂ atmosphere. A primary aim was to study the kinetic of oxidation behavior of the coated system as a function of the environments. The weight measurements are taken at various exposure times during cyclic oxidation testing, which represent the overall weight gain loss due to both oxide scale growth and oxide scale spallation. Weights changes were recorded for kinetics identification in CO₂ at temperatures 800C° and 900 C° for up to 100h at 10h cycle the specific weight change data of coated stainless steel 316L for each temperature tests is plotted in **Figs. (3 and 4)** as a function of time. These results show that, the initial kinetic is rapid, but the rate of specific weight change gradually decreases at longer times, and the weight gain increased as the temperature increased. This result is consistent with those given by Chao-Yi Lin et al. [12]. This indicates that the decomposition of CO gas to form carbon was mainly responsible for the weight gain observed. Though oxygen partial pressure was quite low, the contribution to the weight increases due to oxidation could not be ruled out. The kinetics can be described by examining the growth rate time constant or n-values, which is found as the exponent in the following rate equation $\frac{\Delta w}{A} = Kt^n$, where Δw is the weight changes, A is the sample surface area, K is the oxidation rate constant, n is the growth-rate time constant.

Figs. (5 and 6) show double log plots of specific weight gain vs. time. The calculated values of the power index n for each test are shown in **Table (3)**. It is found that the relationship is parabolic, when the value of n is greater or lower than 0.5, then oxidation kinetics does not fall in the simple parabolic behavior and this implies a faster or slower

oxidation rate. For the parabolic kinetics, the rate equation takes the form: $\frac{\Delta W}{A} = k_p t^{0.5}$. The parabolic oxidation rate constant (K_p) for four series of experiments are calculated from **Figs. (7 and 8)** and listed in **Table (3)**. The results, shows that, the oxidation rates are increased at temperature increased. The oxidation resistance of the yttrium doped siliconized of stainless steels was significantly improved as compared with siliconized stainless steels.

Figs. (9 and 10) show the oxidized surface features of coated stainless steel alloy being examined by light optical microscope (L.O.M) at 800 c° for 100h at 10h cycle. The scale appears with numerous nodules and with scale spallation.

The major phases formed in the surface layer after oxidation for both test temperature's was identified by X-ray diffraction (XRD) analysis as in **Figs. (11 and 12)**, it is found that the scale formed on siliconized steel consisted of SiO₂, Fe₂SiO₄, Fe₂O₃ and chromium (III) oxide (cubic), while the scale formed on the yttrium doped siliconized of steel consisted mainly of Y₂O₃, SiO₂, Fe₂O₃ and chromium (III) oxide (cubic).

The results are in agreement with those given by Fuikawa et al. [10] added 0.03 wt.% Y to an austenitic stainless steel containing a small amount of Si, the oxidation resistance was improved, and the spallation resistance was also remarkably improved during the cyclic oxidation. As a result, it was found that the segregation of Y at the oxide grain boundaries occurred, and inhibited the out ward diffusion of cations, and promoted the internal oxide of Si. They presupposed that the formation of the scale. In the present study, as shown by cross-sectional observations, **Figs. (13 and 14)**.

Figs. (13 and 14) show cross section images of LOM of silicized and yttrium doped siliconized diffusion coated 316L substrates after cyclic oxidation in CO₂ at 800°C respectively, under the same oxidation conditions indicated before.

4. Conclusions

For the coatings developed from the present experimental work on austenitic stainless steel 316L, the following conclusions can be concluded:

- 1- The code position of yttrium and silicon on 316L stainless steel was successfully realized by a single-step pack.
- 2- The results of cyclic oxidation at CO₂ environment showed that the initial weight gain is rapid and increased as the temperature increased.
- 3- The oxidation resistance of the yttrium doped siliconized of stainless steels was significantly improved as compared with the siliconized stainless steels.
- 4- The major phases that exist in the outer layer are: Y₂O₃, SiO₂, Fe₂O₃ and chromium oxide.

5. References:

- [1] J.S. Dunning, D.E. Alman, and J.C. Rawers, "Influence of Silicon and Aluminum Additoion on the Oxidation Resistance of a Lean-chromium Stainless steel", *Oxidation of Metals*, vol.57, nos.5/6, pp. 409-425, June (2002).
- [2] B. Li and B. Gleeson, "Effect of Minor Elements on the Cyclic-Oxidation Behavior of Commercial Fe-base 800-Series Alloys", *Oxidation of Metals*, vol.62, no.112, pp.45-71, August (2004).
- [3] Mark A. Harper and Robert A. Rapp, "Codeposited Chromium and Silicon Diffusion Coatings for Fe-Base Alloys Via Pack Cementation", *Oxidation of Metals*, vol.42, no.3/4, pp. 303-333, (1994).
- [4] S. Chevalier, C. Nivot, and J.P. Larpin, "Influence of Reactive Element Oxide Coatings on the High Temperature Oxidation Behavior Of Alumina-Forming Alloys", *Oxidation of Metals*, vol.61, no.3/4, pp. 195-217, April (2004).

- [5] Stela Maria de Carvalho Fernandes, Lalgudi Venkataraman Ramanathan, “Rare Earth Oxide Coatings to Decrease High Temperature Degradation of Chromia Forming Alloy”, *Materials Research*, vol.7, no.1, pp. 1-6, Jan/Mar (2004)
- [6] L.Xhu, X. Peng, J. Yan, and F. Wang, “Oxidation of a Novel Chromium Coating with CeO₂ Dispersions”, *Oxidation of Metals*, vol.62, nos.5/6, pp. 411-426, December (2004).
- [7] B.A. Pint and L.W. Hobbs, “The Oxidation behavior of Y₂O₃-Dispersed B-NiAl”, *Oxidation of Metals*, vol.61, no.314, pp. 273-290, April (2004).
- [8] S.Seal, S.K. Roy,S.K.Bose, and S.C.Kuiry, “Ceria-Based High-Temperature Coatings For Oxidation Prevention”, *Jom-e*,52(1), pp.163-177, January (2000).
- [9] Yi-Rong He, Robert A.Rapp, P.F. Tortorelli, “Oxidation-Resistant Ge-doped Silicide Coating on Cr-Cr₂ Nb Alloy: by pack Cementation”, *Materials Science and Engineering. A222*, pp. 109-117, (1997).
- [10] H. Fujikawa, T. Morimoto, Y. Nishiyama, and S.B. Newcomb, “The Effect of Small Additions of Yttrium on the High-Temperature Oxidation Resistance of a Si- Containing Austenitic stainless Steel”, *Oxidation of Metals*, vol.60, nos.1/2, pp. 23-39, August (2003).
- [11] A.L. Cabrera and J.F. Kirner, “Formation of Silicon Diffusion Coatings on Ferrous Alloys from Their Reaction with Silicone”, *surface and Coatings Technology*, vol.39/40, pp. 43-51, (1989).
- [12] Chao-Yi Lin, Chia-Hao Chang, and Wen-Ta Tsai, “Morphological and Microstructural Aspects of Metal Dusting on 304L Stainless Steel with Different Surface Treatments”, *Oxidation of Metals*, vol.62, nos.3/4, pp. 153-174, October (2004).

Table (1) Chemical composition of austenitic stainless steel (AISI 316L) in wt %

Fe	Cr	Ni	C	Mn	Si	P	S	Mo	N	Cu
Bla.	16-18	10-14	<0.03	2.0	1.0	-	-	2-3	-	-

Table (2) the pack mixture composition and heating cyclic used for pack cementation process.

Pack cementation proce	Powder pack composition wt%				Holding temperature c°	Coating Time (h)
	Si	Y	NH ₄ Cl	Al ₂ O ₃		
Siliconizing	10	-	2	88	920	3
Yttrium-doped Siliconizing	10	0.5	2	87.5	920	3

Table (3): n values and parabolic oxidation rate constants Kp for cyclic oxidation of coated system in Co₂ for 100h at 10h cycle.

Temperature C°	Siliconized 316L			Yttrium doped siliconized 316L	
	n	Kp (g ² /cm ⁴ /S)	K _L (g/cm ² /s)	n	Kp (g ² /cm ⁴ /S)
800	0.3684	-0.7×10 ⁻¹²	-	0.474	0.4×10 ⁻¹²
900	0.757	-	-2.09×10 ⁻⁸	0.43	0.43×10 ⁻¹¹

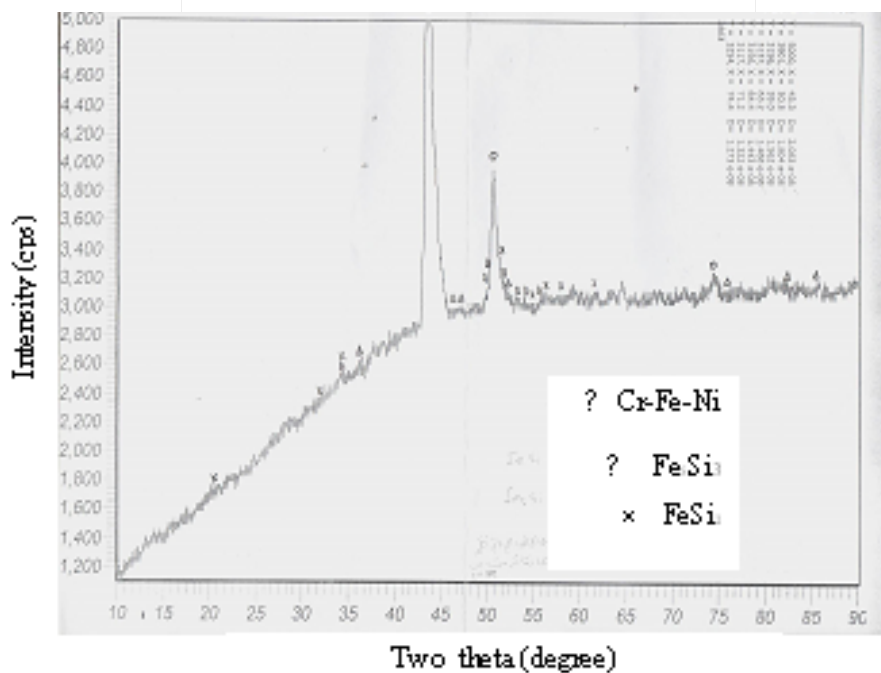


Figure (1): X-ray diffraction pattern of Siliconized coated stainless steel 316L

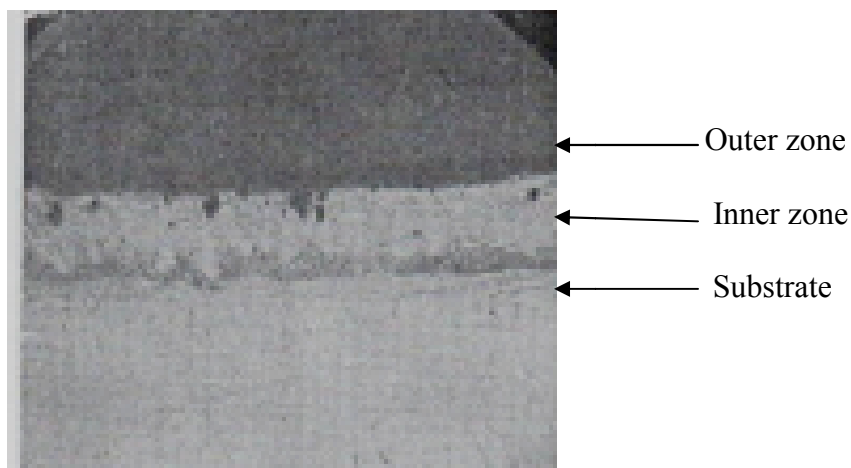


Figure (2): LOM images of cross section of coated stainless steel (316L) at 920°C for coating times 3h (250X)

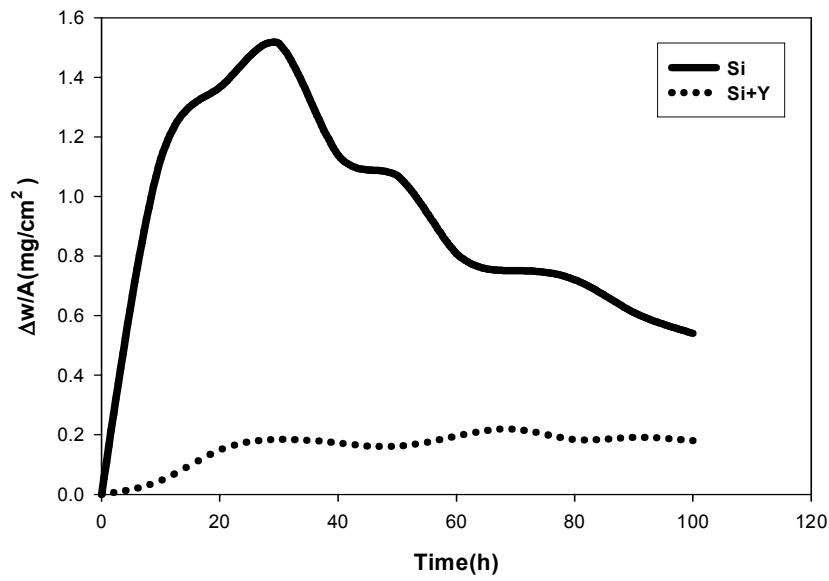


Figure (3): Specific weight change VS-time plotted for coated stainless steel 316L cyclic oxidized in CO₂ at temperature 800°C for 100h at 10h cycle

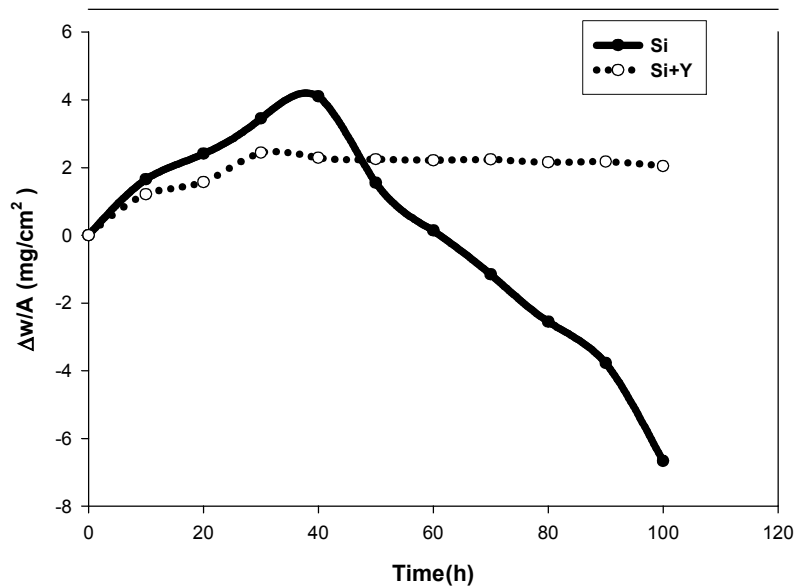


Figure (4): Specific weight change VS-time plotted for coated stainless steel 316L cyclic oxidized in CO₂ at temperature 900°C for 100h at 10h cycle

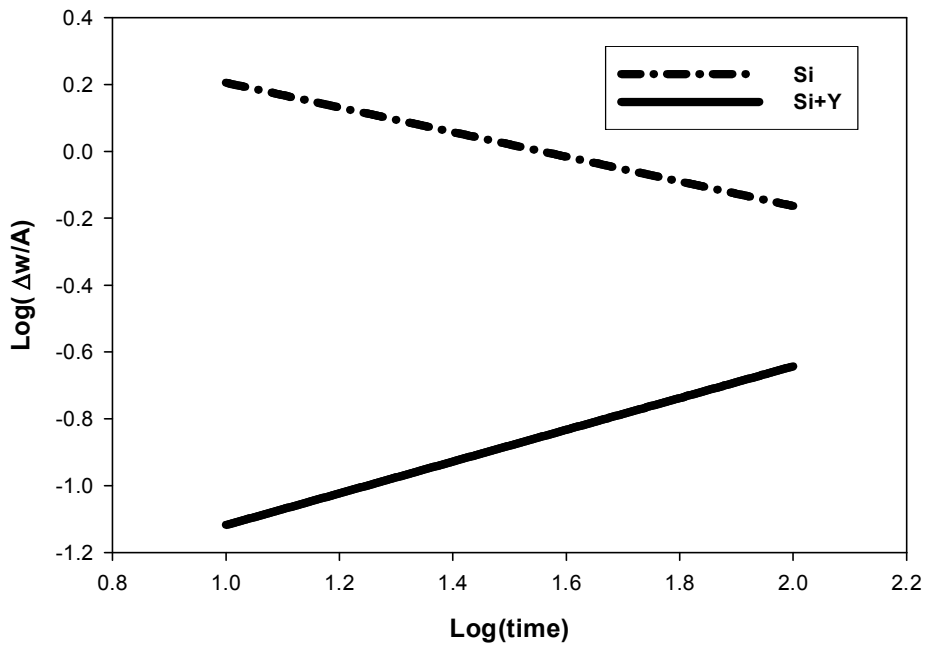


Figure (5): Log-Log of specific weight change VS-time plotted for coated stainless steel 316L cyclic oxidized in CO₂ at temperature 800°C for 100h at 10h cycle

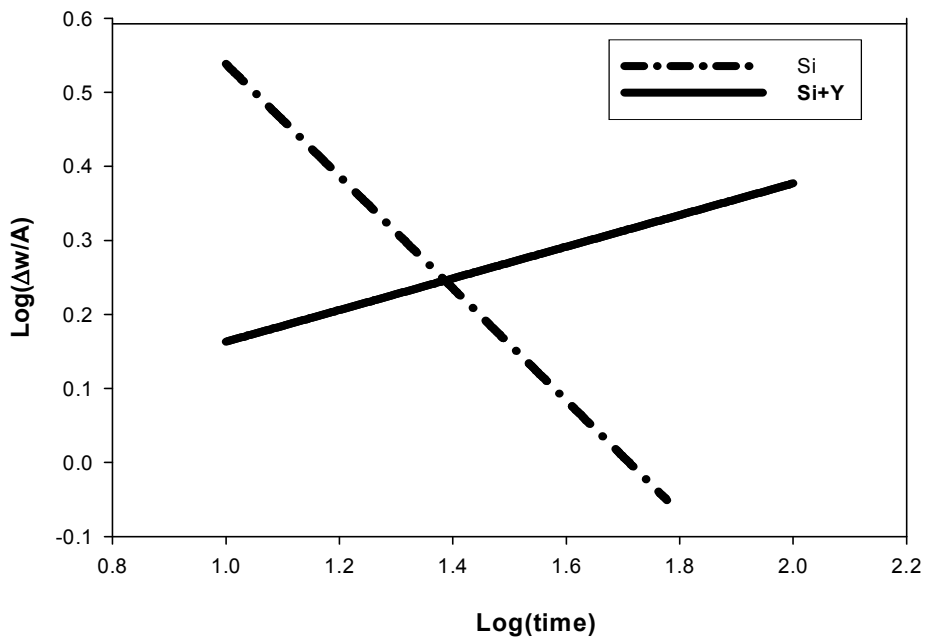


Figure (6): Log-Log of specific weight change VS-time plotted for coated stainless steel 316L cyclic oxidized in CO₂ at temperature 900°C for 100h at 10h cycle

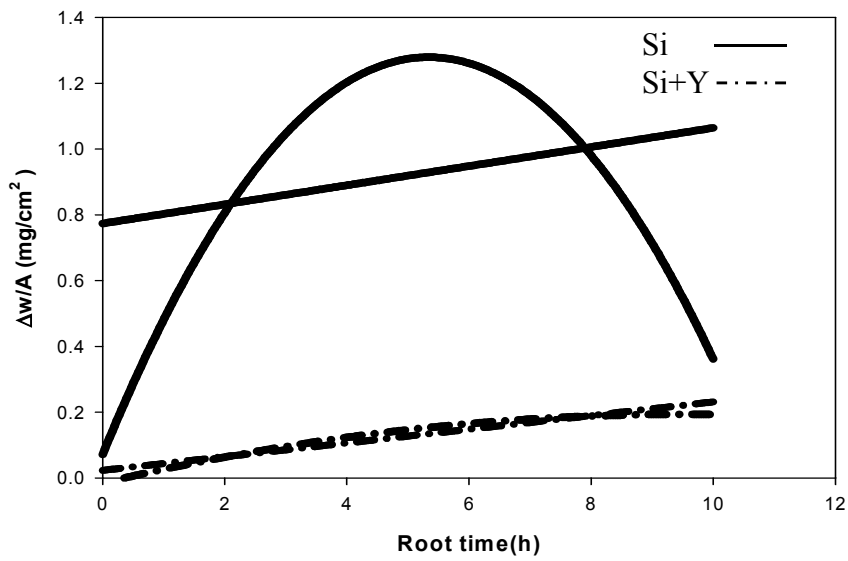


Figure (7): Specific weight change VS-Root time plotted for coated stainless steel 316L alloy cyclic oxidized in air at temperature 800°C for 100h at 10h cycle

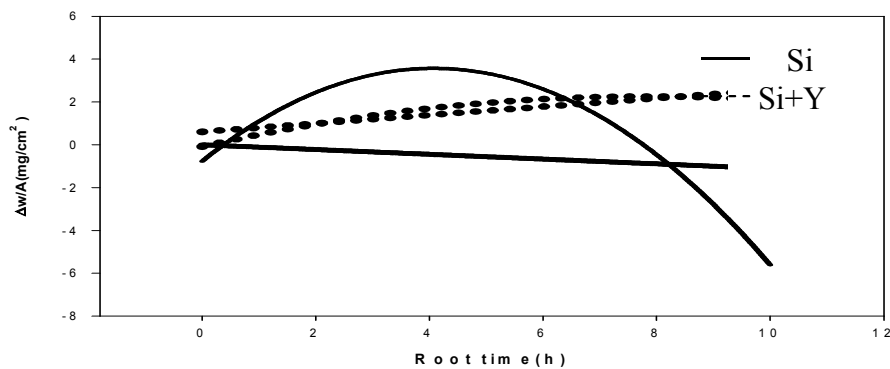


Figure (8): Specific weight change VS-Root time plotted for coated stainless steel 316L alloy cyclic oxidized in air at temperature 900°C for 100h at 10h cycle



Figure (9): Top view images of LOM of siliconized stainless steel 316L substrates after cyclic oxidation in CO₂ at 800°C for 100 h at 10 h cycle (250X).

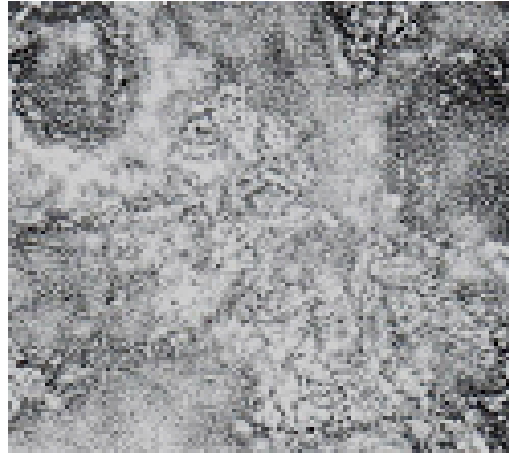
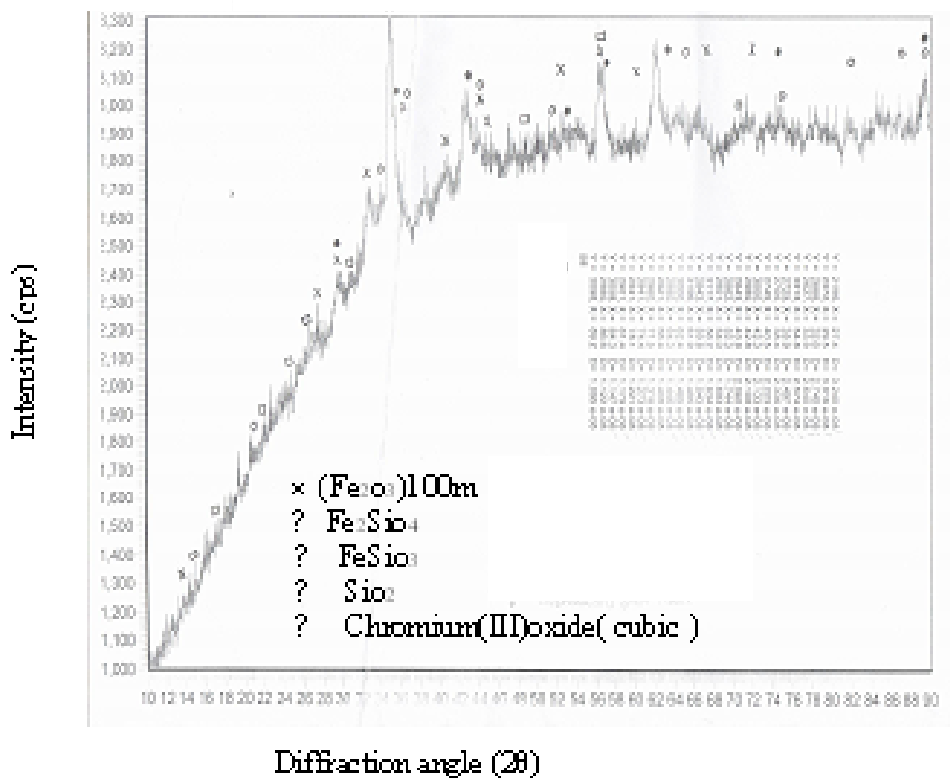
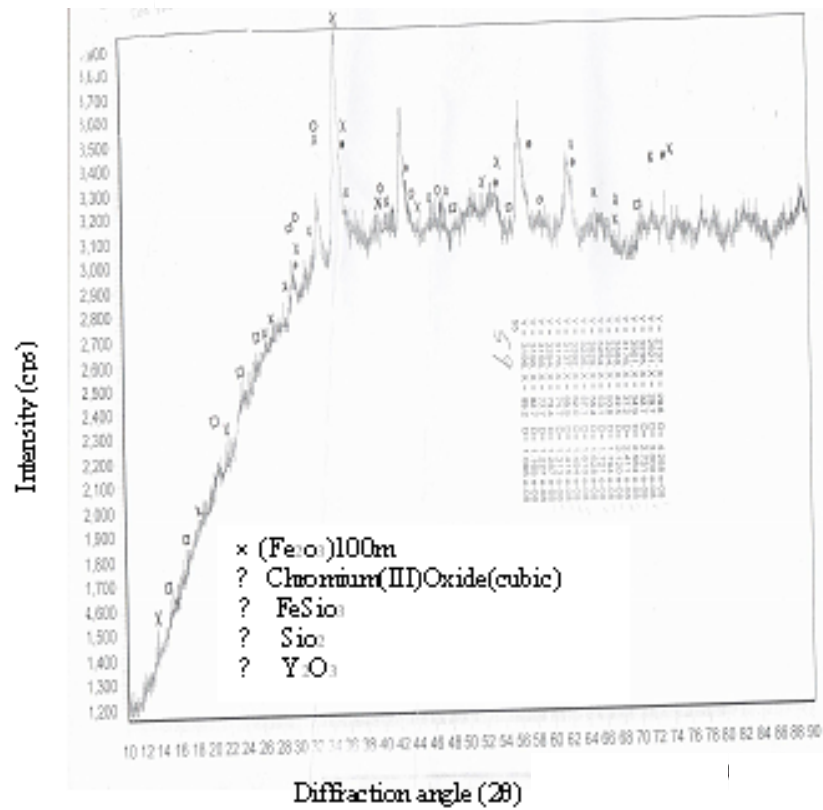


Figure (10): Top view images of LOM of Yttrium-modified siliconized diffusion coated stainless steel 316L substrates after cyclic oxidation in CO₂ at 800°C for 100 h at 10 h cycle (250X).



Fig(11): Diffractograms from the surface of siliconized coated stainless steel 316L after cyclic oxidation in CO₂ at 800°C for 100h at 10h cycle.



Fig(12): Diffactograms from the surface of coated stainless steel 316L with yttrium-modified siliconized coated sample after cyclic oxidation in CO₂ at 900°C for 100h at 10h cycle.

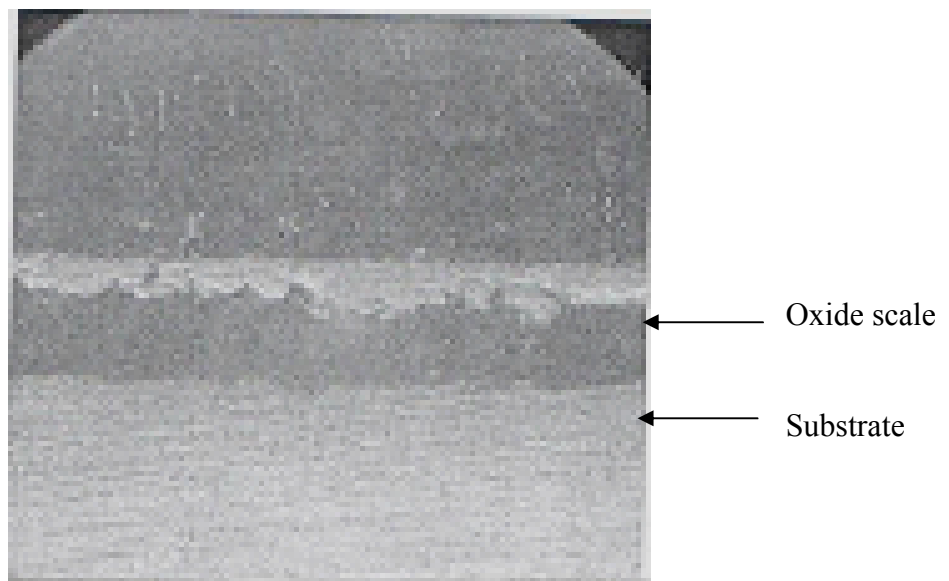


Figure (13): LOM images of cross section of siliconized diffusion coated stainless steel (316L) substrates after cyclic oxidation in CO₂ at 800°C for 100 h at 10 h cycle (250X).

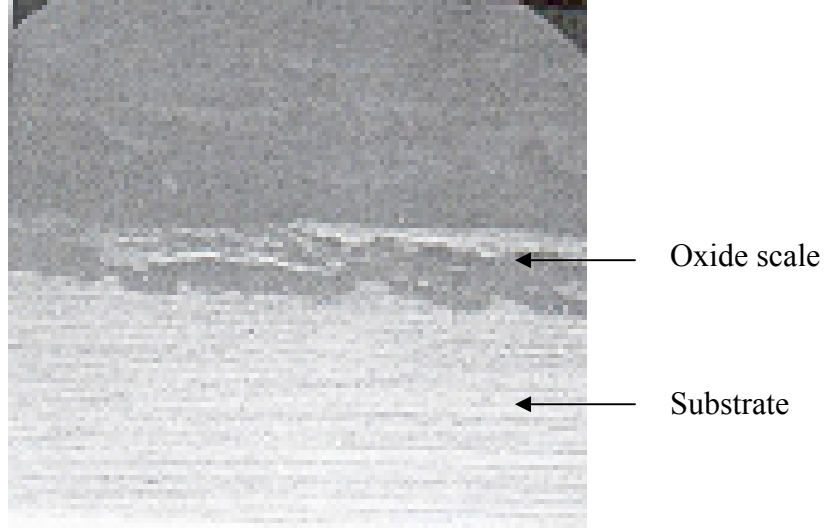


Figure (14): LOM images of cross section of Yttrium-modified siliconized diffusion coated stainless steel (316L) substrates after cyclic oxidation in CO₂ at 800°C for 100 h at 10 h cycle (250X).

سلوك الصلب المقاوم للصدأ (316L) المطلي بالسليكون المدعم باليتريوم عند الدرجات الحرارية العالية في وسط CO₂

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الخلاصة:

في هذه الدراسة، تم طلاء الصلب الاوستنايتي المقاوم للصدأ (AISI 316L) بنوعين من الطلاء الانتشاري وهما الطلاء بالسليكون والطلاء بالسليكون المدعم باليتريوم باستخدام تقنية الطلاء الانتشاري بالسمنتة.

جرت اختبارات التاكسد بشكل دوري للعينات المطلية في وسط ثاني اوكسيد الكربون CO₂ وعند درجات الحرارة 800 م و 900 م ° لمدة 100 ساعة وبمعدل 10 ساعة للدورة الواحدة.

وقد بينت النتائج بأن الزيادة في الوزن Weight gain كانت في البداية كبيرة وقد زادت بزيادة درجة الحرارة. وان مقاومة الاكسدة للصلب الاوستنايتي المطلي بالسليكون المدعم باليتريوم قد تحسنت مقارنة بطلاء السليكون لوحده. وان طبقة الاوكسيد (scale) المتكونة بعد الاكسدة في وسط CO₂ للصلب المطلي كانت سميكة ومتكونة من الاطوار التالية SiO₂, Y₂O₃, FeO₃ واوكسيد الكروم.

وقد استخدم في هذا البحث المجهر الضوئي (LOM) وجهاز حيود الاشعة السينية (XRD) لتحديد (structures) بعد الطلاء والاكسدة الدورية.