

High Temperature Hot Corrosion Resistance of Coated Stainless Steel at NaCl/Na₂SO₄ Mixtures Environments

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ABSTRACT

In this study, Silicon and Aluminum with and without cerium were simultaneously co-deposited by diffusion into austenitic stainless steel (AISI 316L) substrates, by a single-step packcementation process. Cyclic hot corrosion tests were conducted on coated and uncoated austenitic stainless steel alloy with 50wt.% NaCl+50wt.%Na₂SO₄ deposits at 750C° for 120h at 10h cycle. The results show that the hot corrosion resistance of both coated stainless steels, was significantly improved as compared with the uncoated steels. The scale formed on coated stainless steel after oxidation in mixture environment was consisted of NiAl₂O₄, NiFe₂O₄ and NiCr₂O₄. Optical metallography (LOM) and X-ray diffraction(XRD) was used to characterize the resulting coating and cyclic hot corrosion structures.

Key words: Packcementation, Hot corrosion, Oxidation, Coatings stainless steel

1. INTRODUCTION

The performance of different alloys exposed to high temperature depends upon their mechanical resistance as well as their corrosion/oxidation properties. When the mechanical requirements are not critical, austenitic stainless steel may play a role in substituting the more expensive Ni and Co based alloy[1,2]. In general, all grades of austenitic steel receive protection against high temperature degradation due to the formation of a compact Cr₂O₃ heating layer which thickens slowly. The fact that chromia Cr₂O₃ can form volatile suboxides CrO₃ at temperatures above about 900C° [3].

Low-grade fuels with sulfur, sodium and vanadium are used mainly for firing in industrial processes, such as Oil-and coal fired power generation. Sulfur is one of the most corrosive contaminants in high-temperature environments. Sulfidation in oxidizing environments is due to sulfur in the fuel reacting with oxygen to form SO, and SO₂, and is accelerated frequently by fuel impurities, such as sodium, chlorine, and potassium, which may react with themselves and/or with sulfur to form salt vapor, Na₂SO₄ and NaCl, during combustion. The salt vapor may deposit onto cooler component surfaces, resulting in accelerated corrosion known as hot corrosion. Hot corrosion is commonly accompanied by the formation of a porous and non-protective oxide scale which has been attributed mostly to the condensation of Na₂SO₄ that attacks the protective oxide scale. Besides, NaCl has been indicated as a corrodent in high-temperature environments. The presence of NaCl inserted in the intake air together with Na₂SO₄ leads to more severe corrosion of materials[4]. Nagerajan et al.[5]studied the modes of initiation and propagation of corrosion attack on a series of high-temperature alloys [FeCr AlY alloy and types 304 and 347 stainless steels] in synthetic gas mixtures at 900C°. It was found that sulfidation corrosion could be initiated on all the alloys within 0.25 hr, the rate of propagation of the corrosive attack depended on the flux of SO₂ in the environment and on the nickel content of the alloys. The presence of iron in the alloys appeared to slow the initiation of sulfidation, by forming a continuous iron oxide layer.

Rajab mohammed[2] had investigated the behavior of the cyclic oxidation resistance of the uncoated austenitic stainless steel 316L and coated systems(silicon-modified aluminide and cerium-doped silicon modified aluminide diffusion coatings),oxidized with 100wt.% Na_2SO_4 and 100wt.%NaCl deposits at 750°C for 120 h at 10 h cycle.The results show that both coated systems reveal good cyclic oxidation resistance compared with uncoated stainless steel 316L under the same identified conditions and kinetic oxidation follows the parabolic oxidation rate.The temperature capability of superalloys in the gas turbine engine has been progressively increased to improve the fuel efficiency and to use dirtier fuel cost reduction. The surface protection coatings on these hot section components have been gradually changed from the aluminide diffusion coatings to the more complex MCrAlY overlay coatings to protect the substrate from degradation in most severe operating environments[6,7].

In this work ,stainless steel 316L is coated with two different types of coatings, the first one is silicon-modified aluminide coating and the second is the cerium doped silicon modified aluminide coating. Cyclic hot corrosion tests were performed to evaluate the performance of coating stainless steel at high temperatures.

2. EXPERIMENTAL WORK.

2.1 Materials.

The austenitic stainless steel alloy(316L) used in this study was received in bar form.The nominal composition is given in **Table(1)**.The samples were cut into disc shape 20mm in diameter and 3mm thick from a bar. Small hole 2mm diameter was drilled in each sample for holding .All the specimens were ground through 220,320,500,600,800,1000 and 1200 grit silicon carbide papers. Samples were polished up to 1- μm diamond paste and cleaned in alcohol in an ultrasonic bath prior to the coating process or corrosion tests. The dimensions and weight of each sample were measured using a mettler microbalance (sartorius,Germany),with an accuracy of ± 0.01 mg ,before and after coating and corrosion tests.

2.2 Coating Process.

In this study ,two types of coated austenitic stainless steel were performed to investigate the feasibility of simultaneous deposition of aluminum and silicon , and simultaneous deposition of aluminum, silicon and cerium on austenitic stainless steel (316L) by packcementation process to increase its high temperature durability in corrosive environment.The parameters for coating process are summarized in **Table(2)**.

The substrate samples were placed in stainless steel crucible in contact with the pack mixture. The crucible was covered by 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 coatings, 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 also made. Each sample was 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) were used to characterize the resulting coating structures.

2.3 Hot Corrosion.

The stainless steel (316L) samples with and without coatings were used for hot corrosion experiments. Samples were deposited with mixed NaCl/Na₂SO₄ [50/50wt.% concentration] until a total coating weight of 2mg/cm² was reached. The samples were measured and weighed first, then placed on a hot plate heated to 110C°. An air gun sprayed one of two saturated aqueous-salt solutions in an air mist, and a coat of fine salt particles formed on the samples surface after the mist settled and the water evaporated. The process was repeated until the dry particles were deposited up to 2mg/cm² according to Wang et al.[4] procedure. Hot corrosion test was performed in static air at 750C° for 120h at 10h cycle in carbolite programmable furnace. Each heating cycle included heating in the furnace for 10h at the test temperature and cooling to room temperature at the same atmosphere.

After testing, the samples were cleaned in ultrasonic bath, first in distilled water and then in ethanol. Then they were weighed on a digital balance to determine the change in weight. The surface of the specimen was observed by a light optical microscopy (LOM). Also, all the specimens after cyclic hot corrosion test were sectioned for metallographic examination. The phases formed after cyclic hot corrosion tests were identified by X-ray diffraction (XRD).

3. RESULTS AND DISCUSSION.

In this study, aluminum and silicon with and without cerium were simultaneously deposited by diffusion into austenitic stainless steel (316L) substrates using one step pack cementation process. **Fig.(1)** shows the cross section coating thickness. The coating thickness of approximately 220µm and composed of two zones (an outer layer of iron aluminide and inner diffusion zone). The phases formed in the surface layer of as coated specimens for 3h periods of coating time were identified by X-ray diffraction analysis (XRD) as in **Fig.(2)**. These phases are FeAl and (Cr₄Si₄Al₁₃)_{84F}.

Both oxidation kinetics of diffusion coated (silicon-modified aluminide and cerium-doped silicon modified aluminide) and uncoated stainless steel 316L substrate was subjected to cyclic oxidation at 50wt.%NaCl+50wt.%Na₂SO₄ deposits at 750C° for 120h at 10h cycle and specific weight change vs. time are plotted as shown in **Figs.(3)** and **(4)** respectively. A primary aim was to study the kinetic of oxidation behavior of the coated system as a function of the environments. The weight measurements were 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.

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 $\Delta w/A = kt^n$ [8], 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 plots of specific weight gain vs time. The calculated value of the power index n for each test is shown in **Table (3)**. It seems that the oxidation kinetics of both coated and uncoated systems follows parabolic rate law, when the value of n is greater or lower than 0.5, then oxidation kinetic does not fall in the simple parabolic behavior and this implies slower oxidation rate. For the parabolic kinetics, the rate equation takes the form $\Delta w/A = k_p t^{0.5}$. The parabolic oxidation rate constant (k_p) for series of experiments were calculated from **Figs.(7)** and **(8)** and listed in **Table(3)**. The results show that both coated systems reveal good cyclic oxidation resistance compared with uncoated stainless steel 316L under the same identified condition. Also, it was evident that cerium improved the hot corrosion resistance of the silicon modified aluminide coated 316L substrates. Also, the present results show that (50wt.%Na₂SO₄+50wt.%NaCl) environments are more corrosive than that of 100wt%Na₂SO₄ environment[2]. This behavior is due to acidic and basic characteristics exhibited by the salt mixture at elevated temperatures. This aspect

was studied by Rapp et al.[9],by measuring the solubilities of various oxides in sodium sulfate. They showed that the solubility of oxides(Al_2O_3 , Cr_2O_3 ,etc) is high in acidic and basic media and low in neutral media. For $\text{Na}_2\text{SO}_4/\text{NaCl}$ salt mixture, it is indicated that the addition of NaCl to Na_2SO_4 results in changing the environment from acidic to basic. Similarly in the presence of Na_2SO_4 , the accelerated corrosion may also come about by the mechanical damage of the oxide scale caused by thermal cycling or cracking in the presence of NaCl vapour [10].

The major phases formed in the surface layer after hot corrosion tests and identified by X-ray diffraction (XRD) analysis are NiAl_2O_4 , NiFe_2O_4 and NiCr_2O_4 as indicated in **Figs. (9)** and **(10)**.

Figs. (11) and **(12)** show the oxidized surface features of coated stainless steel alloy being examined by light optical microscope(LOM) at 750°C for 120h at 10h cycle. The scale appears with numerous nodules and with scale spallation.

The results are in agreement with those given by Gurrappa[11],EPMA results clearly reveal that sulfur is the only element diffusing into the substrate along the grain boundaries. Other alloying elements are present either at the affected zone or in the oxide layer. Sodium and chlorine are present only in the oxide layer and do not diffuse into the substrate. These observations reveal that small amount of NaCl in Na_2SO_4 results in cracking and spallation of the protective oxide layer formed on the alloy. As a result, the corrosion rate was very high. This was confirmed by observing no cracking or spallation in pure Na_2SO_4 [2].

Figs.(13) and **(14)** show cross section images of LOM of coated 316L substrate after cyclic hot corrosion respectively, under the same oxidation conditions indicated before.

4. CONCLUSIONS.

- 1-The oxidation kinetics of both coated and uncoated systems follows parabolic rate law.
- 2-Both coated systems revealed good cyclic oxidation resistance compared with uncoated stainless steel 316L under the same identified condition.
- 3-The addition of 0.5wt.% cerium to silicon modified aluminide diffusion coating ,improved the hot corrosion resistance of coated stainless steel substrates.
- 4-The $\text{Na}_2\text{SO}_4/\text{NaCl}$ salt mixture are more corrosive than that of 100wt. % Na_2SO_4 environment.

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

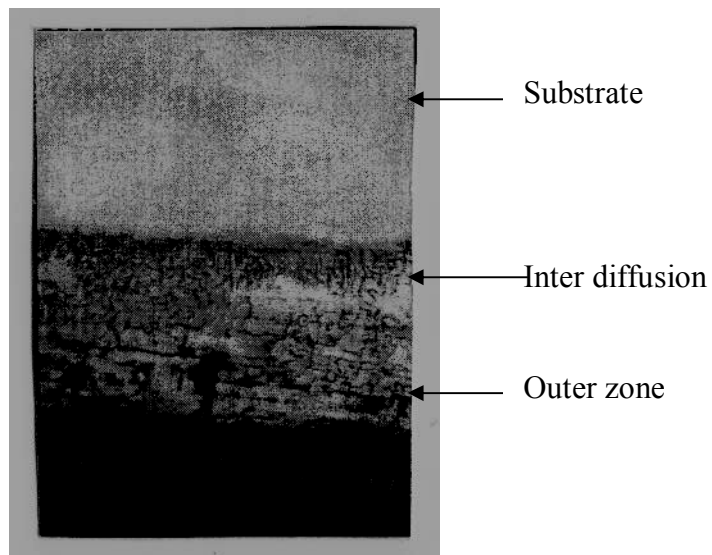
Element	C	Cr	Ni	Mn	Si	P	S	Mo	Fe
Wt. %	< 0.03	16-18	10-14	2.0	1.0	-	-	2-3	Remainder

Table(2): The pack mixture composition and heating cyclic used for pack cementation process [2].

pack mixture composition wt. %							
Pack cementation process	Al	Si	Ce	NH ₄ CL	AL ₂ O ₃	Holding Temp.	Coating Time (h)
Silicon modified aluminide diffusion coating process	18	7	-	2	73	970C°	3h
Cerium doped silicon modified aluminide diffusion coating process	18	7	0.5	2	72.5	970C°	3h

Table(3) : n values and parabolic oxidation rate constants K_p for cyclic hot corrosion of coated and uncoated system in NaCl/Na₂So₄ mixture for 120h at 10h cycle.

Temperature	3L6L coated with Al+Si		3L6L coated with Al+Si+Ce		3L6L uncoated	
	n	K _p (mg ² /cm ⁴ /s)	n	K _p (mg ² /cm ⁴ /s)	n	K _p (mg ² /cm ⁴ /s)
750C°	0.45	5.4×10 ⁻¹⁰	0.4	3.48×10 ⁻¹⁰	0.445	-3.7×10 ⁻¹⁰



Figure(1): LOM images of cross-section of coated stainless steel(316L) at 970C° for coating time 3h(250X).

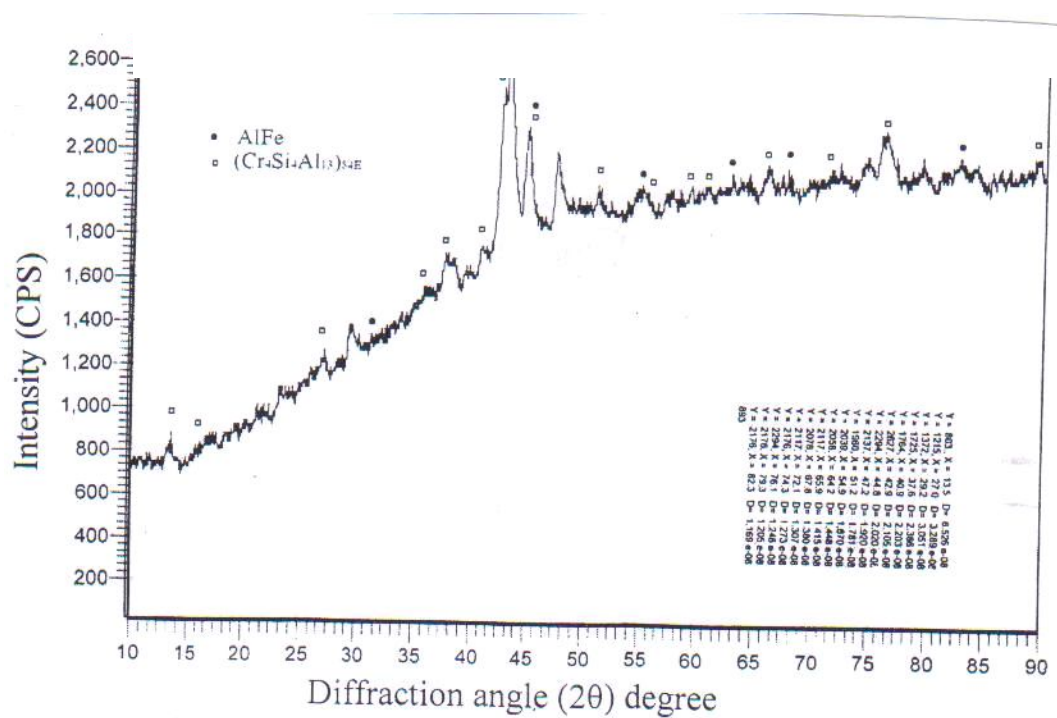


Figure (2):X-ray diffraction pattern of coated stainless steel (316L).

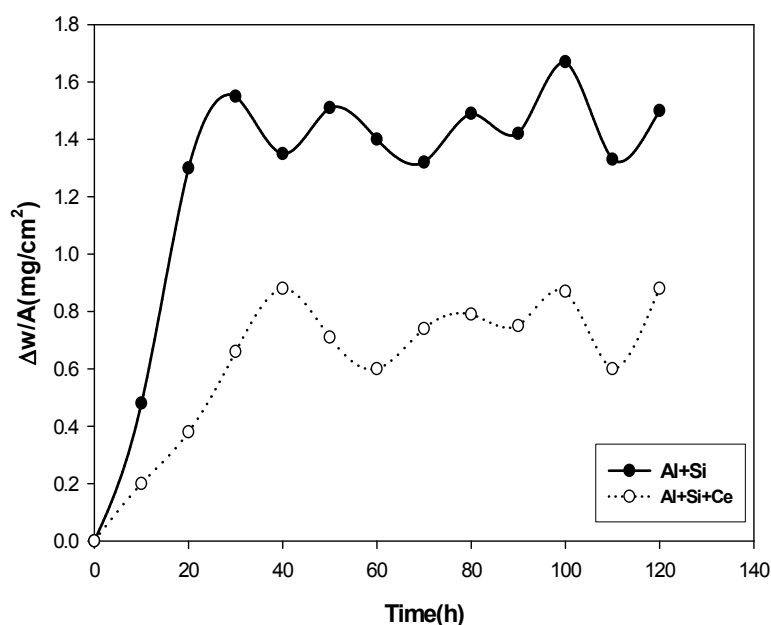


Figure (3): Specific weight change VS-time plotted for coated stainless steel 316L cyclic oxidized in Na₂SO₄/NaCl mixture at temperature 750C° for 120h at 10h cycle.

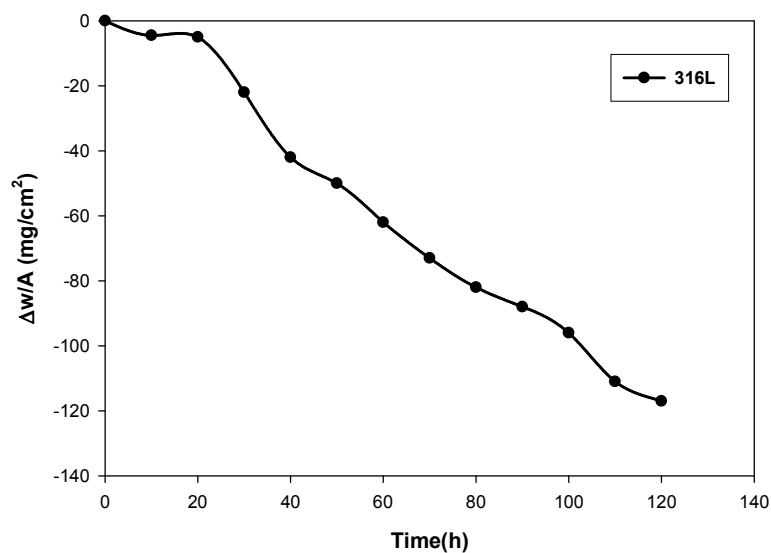
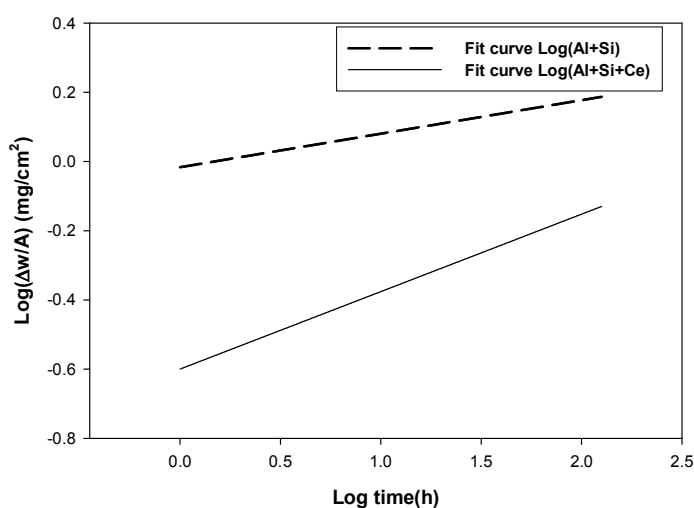


Figure (4): Specific weight change VS-time plotted for uncoated stainless steel 316L cyclic oxidized in Na₂SO₄/NaCl mixture at temperature 750C° for 120h at 10h cycle.



Figure(5): Log-Log of specific weight change VS-time plotted for coated stainless steel 316L cyclic oxidized in $\text{Na}_2\text{SO}_4/\text{NaCl}$ mixture at temperature 750°C for 120h at 10h cycle.

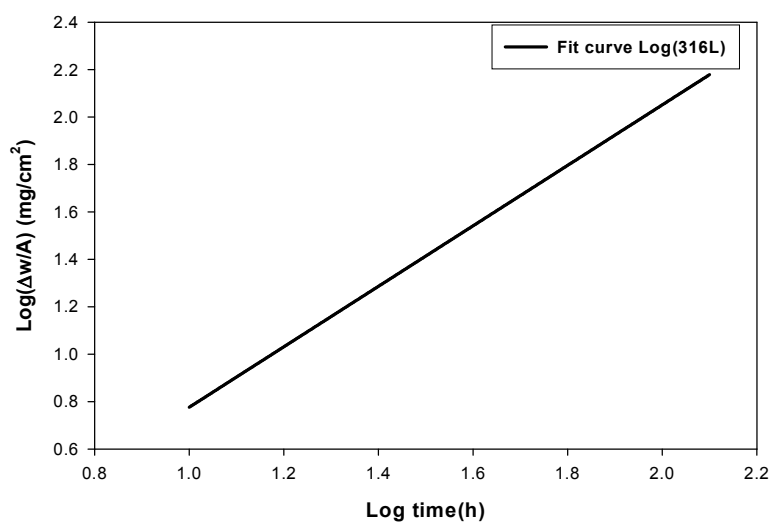


Figure (6): Log-Log of specific weight change VS-time plotted for uncoated stainless steel 316L cyclic oxidized in $\text{Na}_2\text{SO}_4/\text{NaCl}$ mixture at temperature 750°C for 120h at 10h cycle.

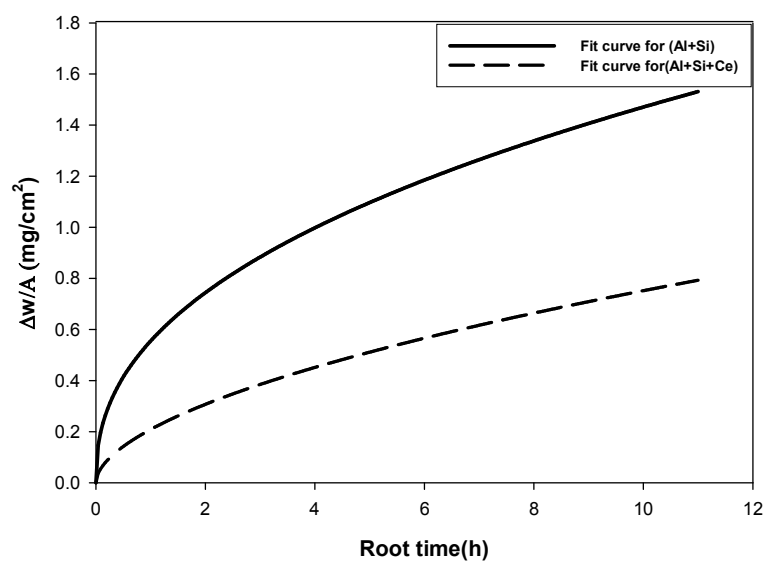


Figure (7): Specific weight change VS-Root time plotted for coated stainless steel 316L cyclic oxidized in Na₂SO₄/NaCl mixture at temperature 750C° for 120h at 10h cycle.

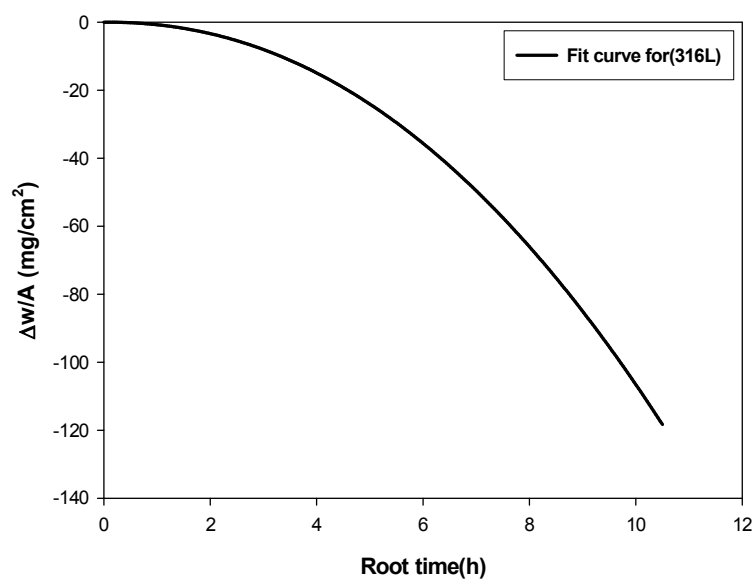


Figure (8): Specific weight change VS-Root time plotted for uncoated stainless steel 316L cyclic oxidized in Na₂SO₄/NaCl mixture at temperature 750C° for 120h at 10h cycle.

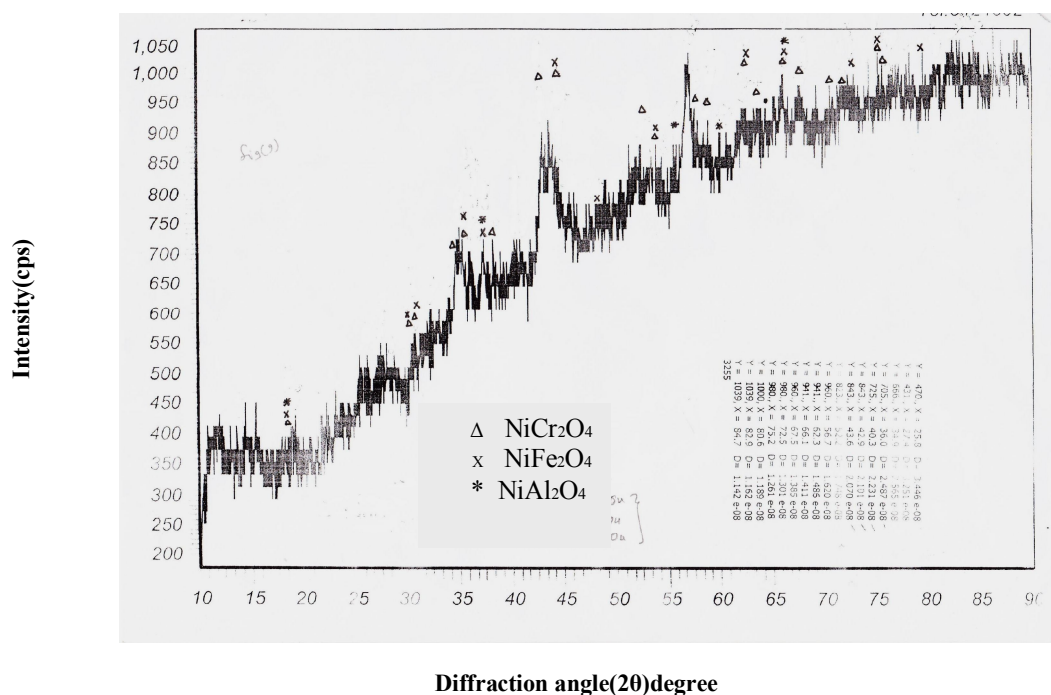


Figure (9): Diffractograms from the surface of silicon modified aluminide coated stainless steel 316L cyclic oxidized in Na₂SO₄/NaCl mixture at temperature 750C° for 120h at 10h cycle.

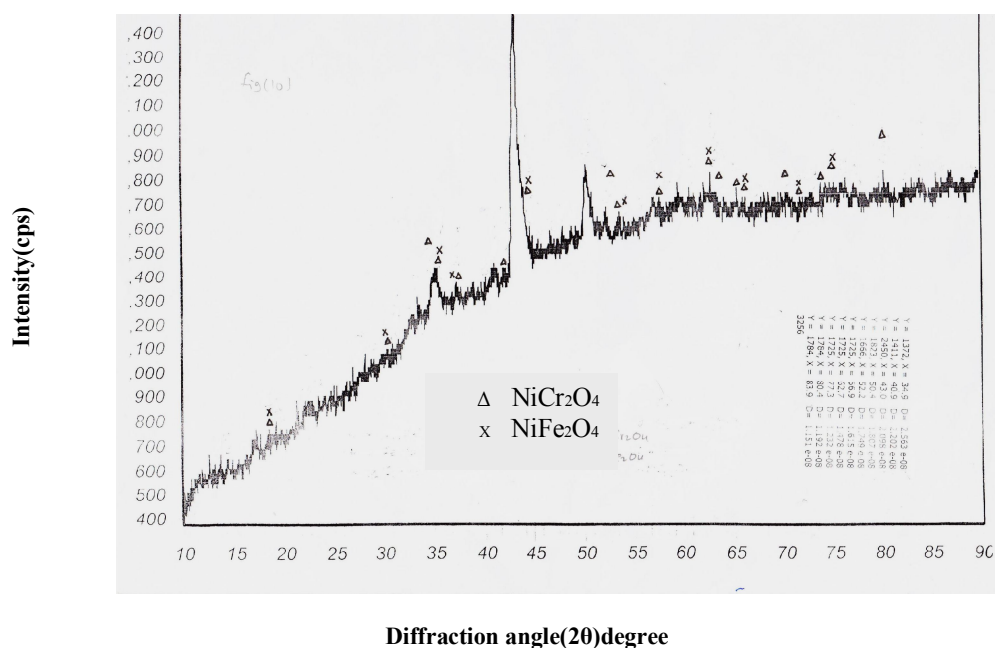
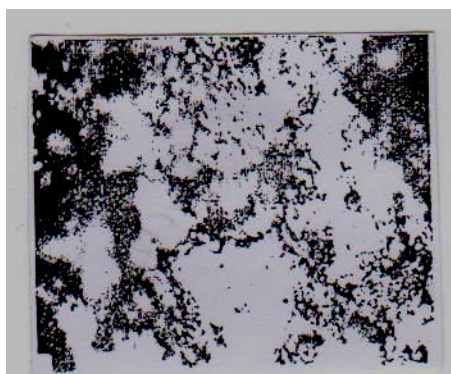


Figure (10): Diffraction patterns from the surface of cerium doped silicon modified aluminide coated stainless steel 316L cyclic oxidized in Na₂SO₄/NaCl mixture at temperature 750C° for 120h at 10h cycle.



Figure (11): Tope view images of LOM of silicon modified aluminide coated stainless steel 316L after cyclic oxidized in $\text{Na}_2\text{SO}_4/\text{NaCl}$ mixture at temperature 750°C for 120h at 10h cycle.



Figure(12): Tope view images of LOM of cerium doped silicon modified aluminide coated stainless steel 316L after cyclic oxidized in $\text{Na}_2\text{SO}_4/\text{NaCl}$ mixture at temperature 750°C for 120h at 10h cycle.

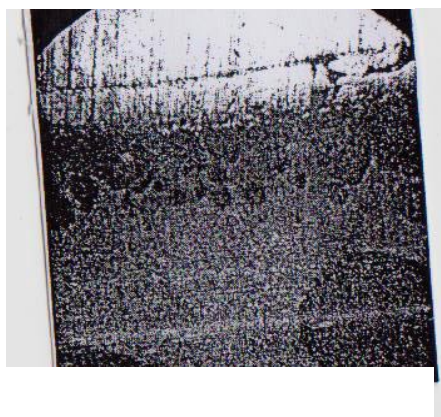


Figure (13): LOM images of cross-section of silicon modified aluminide coated stainless steel 316L after cyclic oxidized in $\text{Na}_2\text{SO}_4/\text{NaCl}$ mixture at temperature 750°C for 120h at 10h cycle.



Figure(14): LOM images of cross-section of cerium doped silicon modified aluminide coated stainless steel 316L after cyclic oxidized in $\text{Na}_2\text{SO}_4/\text{NaCl}$ mixture at temperature 750C° for 120h at 10h cycle.

مقاومة التآكل الحار للصلب المقاوم للصدأ المطلي عند الدرجات الحرارية العالية في وسط خليط

مكون من $\text{NaCl}/\text{Na}_2\text{SO}_4$

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الخلاصة.

في هذه الدراسة، تم طلاء الصلب الاوستنايتي المقاوم للصدأ (AISI316L) بنوعين من الطلاء الانتشاري وهما الطلاء بالسليكون المدعم بالالمنيوم وكذلك الطلاء بالسليكون المدعم بالالمنيوم والسيريوم، باستخدام تقنية الطلاء الانتشاري بالسمنتنة (packcementation). جرى اختبار التآكل الحار بشكل دوري للعينات المطلية والغير مطلية في وسط من خليط مكون من $50\text{wt.}\% \text{NaCl} + 50\text{wt.}\% \text{Na}_2\text{SO}_4$ عند درجة حرارة 750°C ولمدة 120 ساعة وبمعدل 10 ساعة للدورة الواحدة. وقد بينت النتائج بأن مقاومة التآكل الحار لكلا نوعي الطلاء قد تحسنت مقارنة بمقاومة التآكل الحار للصلب الغير مطلي. وأن طبقة الاوكسيد (Scale) المتكون بعد الاكسدة في وسط $\text{NaCl}/\text{Na}_2\text{SO}_4$ متكون من NiCr_2O_4 , NiFe_2O_4 , NiAl_2O_4 . وقد استخدم في هذا البحث المجهر الضوئي (LOM) وجهاز حيود الاشعة السينية X-Ray (XRD) لدراسة (structures) بعد الطلاء والاكسدة الحارة.

الكلمات الرئيسية: الطلاء الانتشاري، التآكل الحار، الأكسدة، طلاء الصلب.