

High Temperature Cyclic Oxidation of Yttrium Modified Aluminide Diffusion Coatings of Stainless Steel

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Abstract:

In this study, yttrium and aluminum 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 aluminide coating and on the yttrium modified aluminide coating of stainless steel in air under atmospheric pressure at temperatures 700 C° and 800 C° for 100h at 10h cyclic. Optical metallography and X-ray diffraction (XRD) techniques were used to characterize the changes in scale morphology and to identify the phases and oxidation products. The yttrium modified aluminide coating showed very good cyclic oxidation resistance compared to aluminide coating.

Keywords: pack cementation; yttrium; aluminide; cyclic oxidation; stainless steel.

1. Introduction

Materials being used in industrial plants should be resistant to environment attack. They must have appropriate creep strength and high temperature corrosion resistance, especially when used at high temperature. Austenitic steels have been used in these environments.

The current interest is to increase the temperature capabilities of austenitic stainless steel alloys for power generation applications. These alloys have their oxidation and corrosion resistance need to be improved by surface modifications. Among the various surface modifications methods, pack cementation has been applied for many years to enrich Cr or Al at the alloy surfaces. Therefore, simultaneous deposition of two elements by pack cementation is very effective in protecting substrates from hot corrosion and oxidizing environments at high temperature [1].

It has been reported that the addition of small quantity of rare earth elements (such as yttrium) is effective for improving the cyclic oxidation of stainless steel [2]. The effect of yttrium or thorium on the growth of the oxide scale is particularly dominant in the case of chromia scales [3]. The micro structural variations have been studied most widely with yttrium as the prototypical reactive element. For instance, the addition of yttrium to an alumina forming alloy commonly results in an α -Al₂O₃ scale that tends to be very flat with the absence of voids at the interface, whereas the yttrium – free alloys tends to form a convoluted scale with interface voids. Yttrium also tends to promote a columnar grain structure of aluminum oxide scales with a reported finer grain size as compared to the equiaxed grains of the yttrium – free material. Yttrium has also been found to favor O⁻² diffusion through oxide grain boundaries over Al⁺³ diffusion through the oxide grains, such that the new oxide forms preferentially at the interface [4].

The effect of reactive element (RE) on the oxidation behavior of alloys has been confirmed by many studies [3, 4, 5, 6, 7, 8] to be very beneficial in providing more adherent protective aluminum oxide scale under cyclic oxidation conditions. Mechanisms accounting for this beneficial proposed by many investigator [4,6] include oxide pegs to anchor the scale to the substrate, elimination of pore formation, increased scale plasticity, and scavenging sulfur away from scale / metal interface.

In the present work, aluminum with and without yttrium are simultaneously deposited by diffusion into austenitic stainless steel (316L) substrate using one step pack cementation and to evaluate the performance of the aluminide and yttrium – modified aluminide coating under cyclic oxidation conditions.

2. Experimental Procedures

2.1 Pack Cementation Process

The substrate alloy used in this study was austenitic stainless steel (AISI 316L) with normal chemical composition given in **Table (1)**.

Samples were cut into disk shape of 20mm in diameter and 4mm thick. All the specimens were ground through 220, 500, 800 and 1000 grit emery paper of (SiC). These samples were then cleaned with water, degreased with acetone and then ultrasonically cleaned for 15 minutes. The samples dimensions were measured. Also the weight of each sample was measured using Amettler microbalance (Sartorius) with accuracy 0.1mg before coating.

The austenitic stainless steel specimens were placed in an stainless steel crucible in contact with a mixed powder containing element aluminum with and without yttrium powder, chloride-activators (NH_4Cl) and an inert alumina filler powder. The stainless steel crucible was covered with a magnesia lid. The stainless steel 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. The parameters for pack aluminizing and yttrium-modified aluminide coating process are summarized in **Table 2**.

2.2 Cyclic Oxidation

In order to evaluate the oxidation resistance of the coated sample, cyclic oxidation tests for coated stainless steel were carried out in the temperatures range of 700°C and 800°C in air at atmospheric pressure, for 100h at 10h cyclic. Each heating cyclic included heating in the furnace for 10h at the test temperature and cooling in still air. Samples weights changing before and after each oxidation cycle 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, aluminum with and without yttrium are simultaneously deposited by diffusion into austenitic stainless steel (316L) substrates using one step pack cementation. **Fig. (1)** Shows the cross section coating thickness of simply aluminized (316L) stainless steel. The coating thickness 220 μm and composed of two zones: an outer layer of iron aluminide and an inter diffusion zone. The phases formed in the surface layer of as coated specimens were confirmed from X-ray diffraction analysis (XRD) as in **Fig. (2)**. The outer layer consists of FeAl intermetallic phase, FeAl_2 , Al_3Fe and Al_5Cr_3 .

Both aluminide coating and yttrium modified aluminide coated austenitic stainless steel (316L) substrates was subjected to cyclic oxidation. 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 dry air at temperatures

700°C and 800°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. This results shows that, the initial kinetic is rapid, but the rate of specific weight change gradually decreases at longer times. The kinetics can be described by examining the growth rate time constant or n-value, which is found as the exponent in the following rate equation $\frac{\Delta w}{A} = Kt^n$ [9], where Δw is the weight change, 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 tests 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 kinetic 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 forms: $\frac{\Delta W}{A} = k_p t^{0.5}$ [9].

The parabolic oxidation rate constants (k_p) for four series of experiments are calculated from **Figs.(7 and 8)** and listed in **Table (3)**. The results show that the oxidation rates are increased as the temperature is increased.

The major phases formed in the surface layer after oxidation for both test temperatures were identified by X-ray diffraction (XRD) analysis as in **Figs.(9&10)**, it is found that the scale formed on aluminized steel consisted of δ - Al_2O_3 , and FeAl, while the scale formed on the yttrium modified aluminide of steel consisted mainly of Al_2O_3 , Y_2O_3 , $Al_2Y_4O_9$ and AlFe.

The results are in agreement with those given by Heo et al. [10] when an alloy containing Cr or Al is exposed to a high-temperature oxidation environment, Al_2O_3 and Cr_2O_3 scales are formed on the surface of the alloy. These scales prevent the rapid oxidation of iron in the alloy, there by eliminating the dissolution and inward diffusion of oxygen.

The FeAl intermetallic phase of the outer layer, which was not completely consumed after oxidation, act as an aluminum source for forming a protective Al_2O_3 scale at the coating surface, and the same time for the interdiffusion zone.

Figs. (12 and 13) shows cross section images of LOM of aluminized and yttrium modified aluminide diffusion coated 316L substrates after cyclic oxidation in at 700 C° respectively, under the same oxidation conditions indicated before.

The improvement in oxidation resistance of the aluminized 316L stainless steel, due to a protective Al_2O_3 formed on the surface; also, excellent oxidation resistance was obtained after codeposition yttrium and aluminum, therefore, due to a protective Al_2O_3 scale and $Al_2Y_4O_9$ formed. This morphology is in good agreement with the one observed by Hwan and Kyoo [11]. During the oxidation test, the coated yttrium initially reacts with oxygen to form Y_2O_3 , and some Y_2O_3 reacts with Al_2O_3 to form a (Y, Al) O-type oxide or a mixture of Y_2O_3 and Al_2O_3 . The presence of Y-containing oxide in a lattice or grain boundaries of Al_2O_3 reduces the diffusion rate of Al and oxygen and reduces the grain size of the oxide as well.

4. Conclusions

The code position of yttrium and aluminum on 316L stainless steel was successfully realized by the pack cementation process. The major phases formed in the surfaced layer of as coated specimens for 4h of coating time are FeAl and Al_3Fe . The cyclic oxidation resistance of aluminide with and without yttrium was evaluated by cyclic oxidation test. From the test, it was evident that yttrium remarkably improved the oxidation resistance of aluminide coating on 316L stainless steel. Alumina oxide scale is not the only phase present on the surface of yttrium modified aluminide coated stainless steel, other phases are obtained such as Y_2O_3 and $Al_2Y_4O_9$.

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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.

Pack cementation process	Powder pack composition wt%				Holding temperature °C	Coating Time (h)
	Al	Y	NH ₄ Cl	Al ₂ O ₃		
Aluminizing	15	-	2	83	950	4
Yttrium-modified Aluminide	15	0.5	2	82.5	950	4

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

Temperature C°	Aluminide 316L		Yttrium modified Aluminide 316L	
	n	k_p (g ² /cm ⁴ /s)	n	k_p (g ² /cm ⁴ /s)
700	0.49	3.29×10^{-10}	0.508	2.264×10^{-10}
800	0.47	3.33×10^{-10}	0.553	2.28×10^{-10}

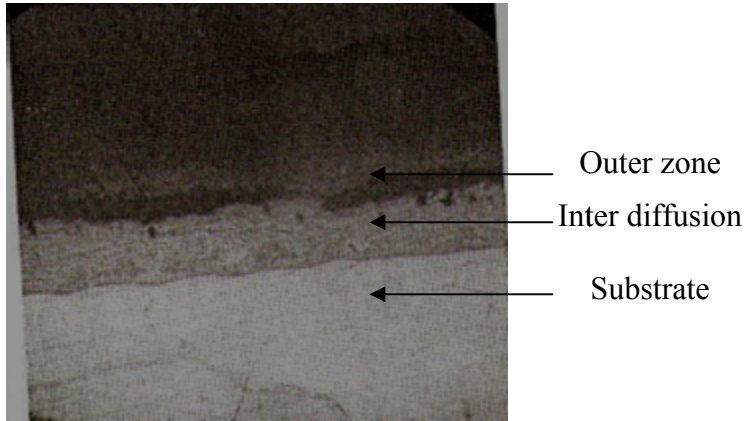


Figure (1): LOM images of cross section of coated stainless steel (316L) at 950°C for coating times 4h (250X)

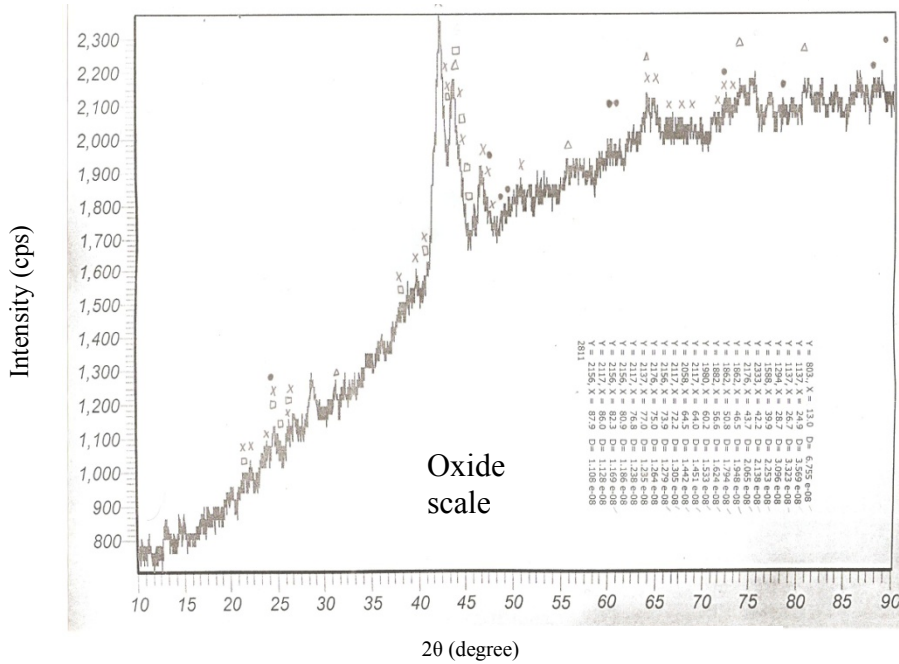


Figure (2): X-ray diffraction pattern of aluminide coated stainless steel 316L

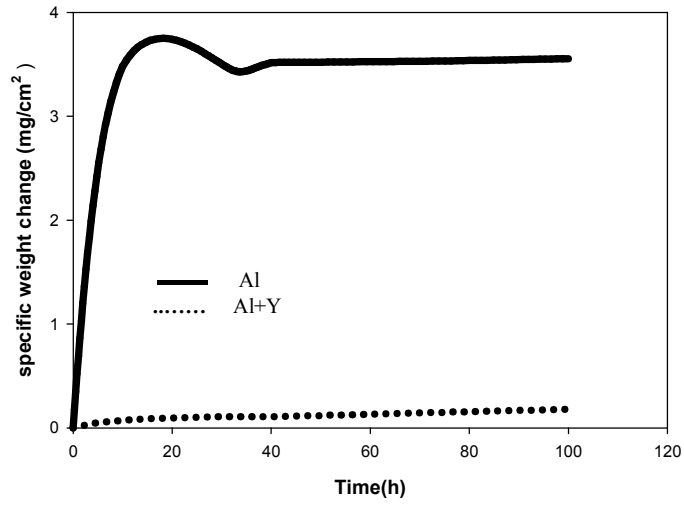


Figure (3): Specific weight change vs-time plotted for coated stainless steel 316L cyclic oxidized in air at temperature 700°C for 100h at 10h cycle

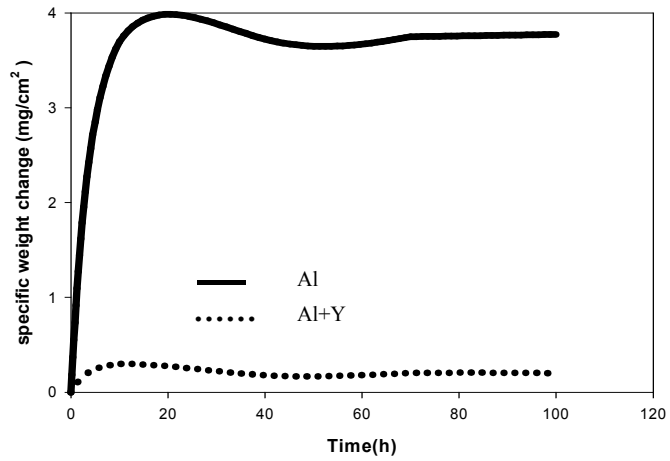


Figure (4): Specific weight change vs-time plotted for coated stainless steel 316L cyclic oxidized in air at temperature 800°C for 100h at 10h cycle

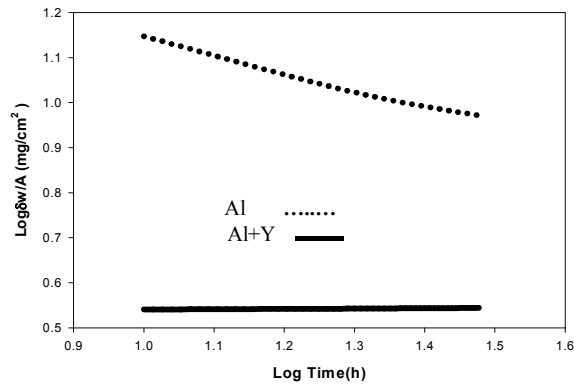


Figure (5): Log-Log of specific weight change vs-time plotted for coated stainless steel 316L cyclic oxidized in air at temperature 700°C for 100h at 10h cycle

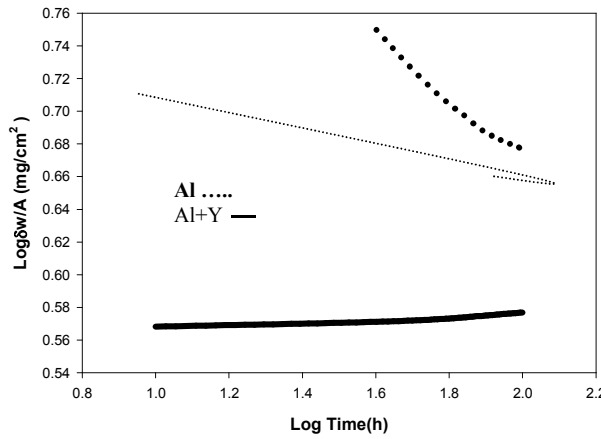
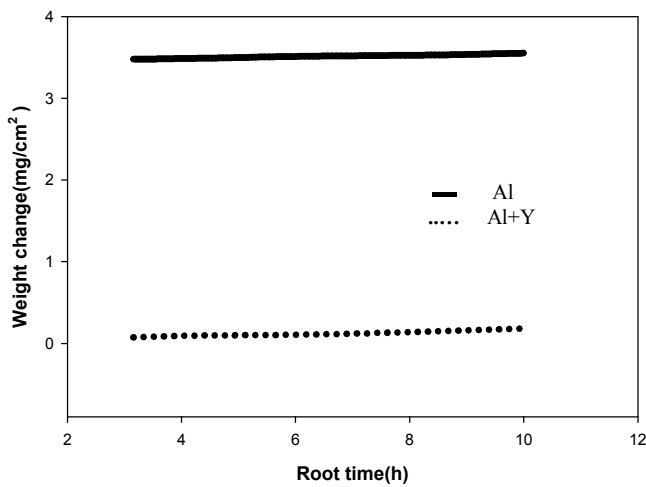


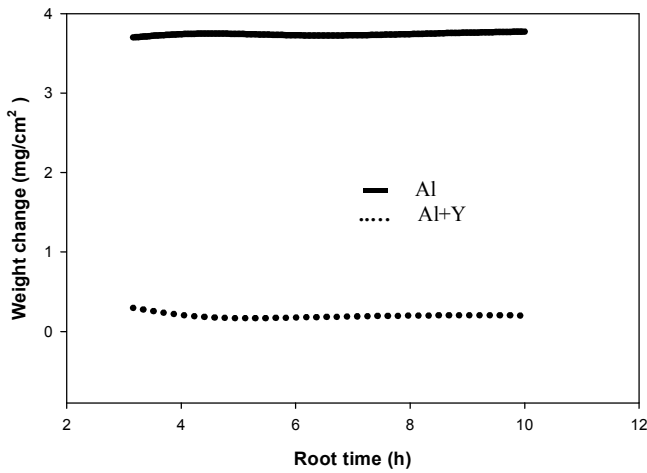
Figure (6): Log-Log of specific weight change vs-time plotted for coated stainless steel 316L cyclic oxidized in air at temperature 800°C for 100h at 10h cycle



$$k_p = 3.29 * 10^{-10} (g^2 / cm^4 / s) \text{ Al}$$

$$k_p = 2.264 * 10^{-10} (g^2 / cm^4 / s) \text{ Al+Y}$$

Figure (7): Parabolic fitted results of specific weight change vs-time plotted for coated stainless steel 316L alloy cyclic oxidized in air at temperature 700°C for 100h at 10h cycle



$$k_p = 3.33 * 10^{-10} (g^2 / cm^4 / s) Al$$

$$k_p = 2.28 * 10^{-10} (g^2 / cm^4 / s) Al+Y$$

Figure (8): Parabolic fitted results of specific weight change vs-time plotted for coated stainless steel 316L alloy cyclic oxidized in air at temperature 800°C for 100h at 10h cycle

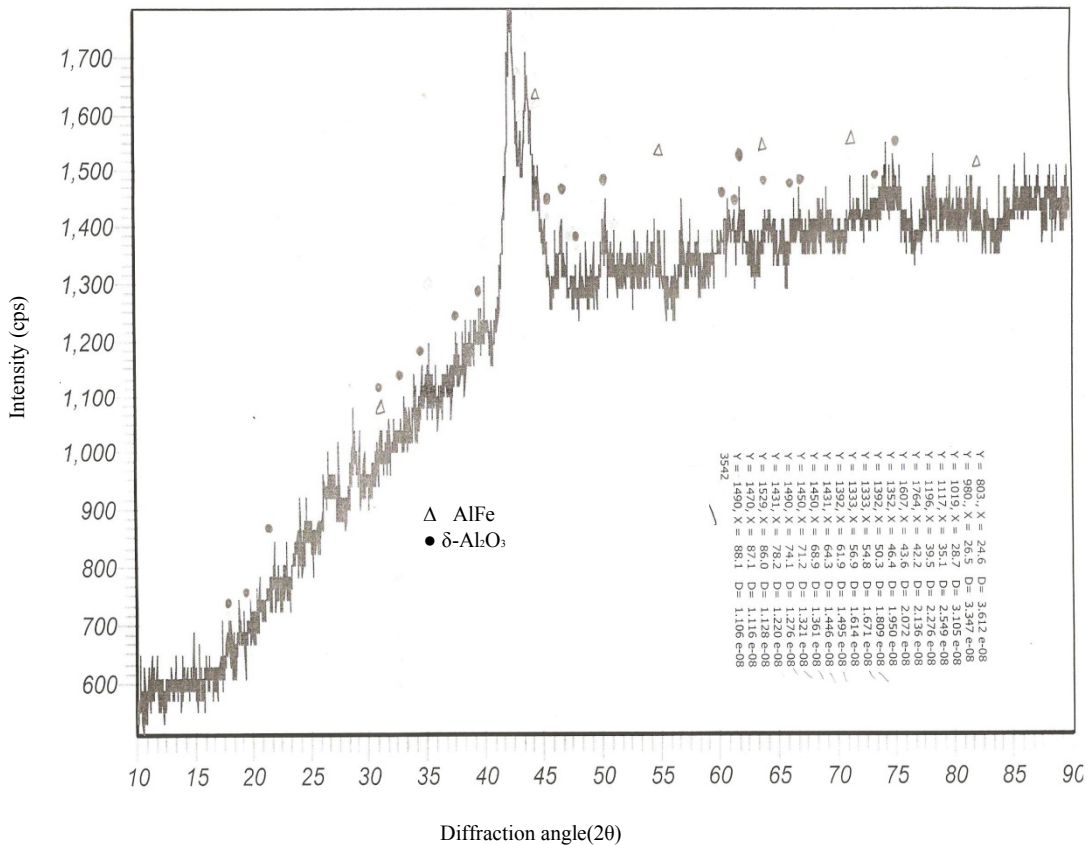


Figure (9): Diffractograms from the surface of aluminide coated stainless steel 316L after cyclic oxidation in air at 700°C for 100h at 10h cycle.

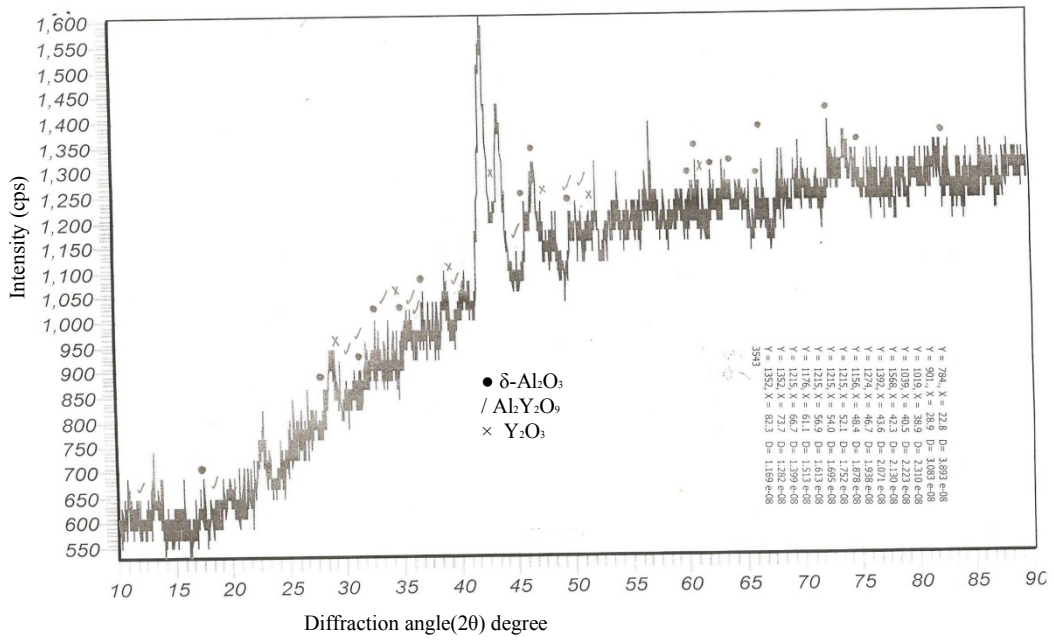


Figure (10): Diffractograms from the surface of coated stainless steel 316L with yttrium-modified aluminide coated sample after cyclic oxidation in air at 700°C for 100h at 10h cycle.

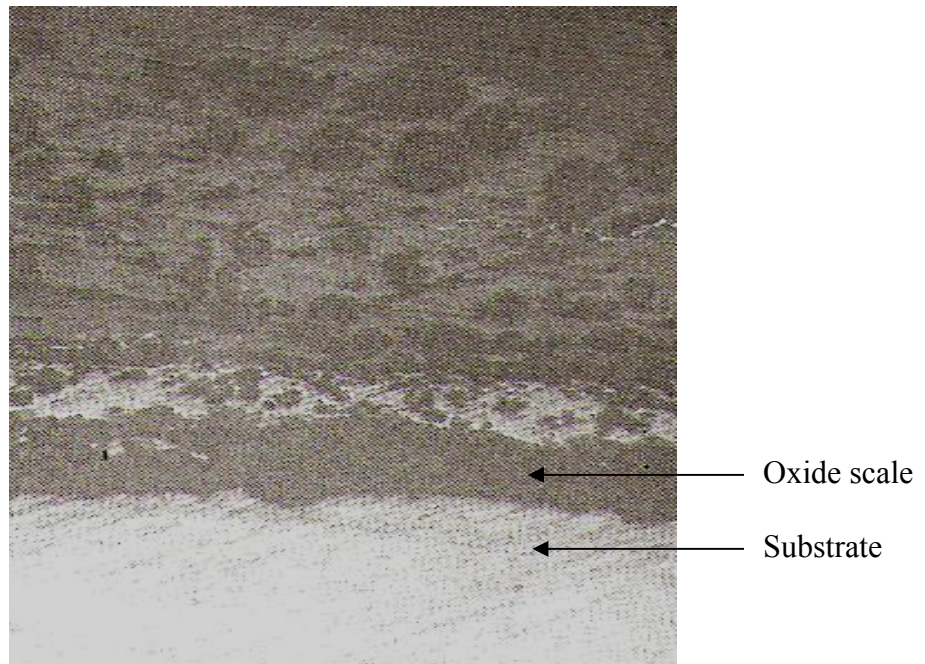


Figure (11): LOM images of cross section of Aluminized diffusion coated st. steel 316L substrate after cyclic oxidation in air at 700°C for 100h at 10h cycle (250X)

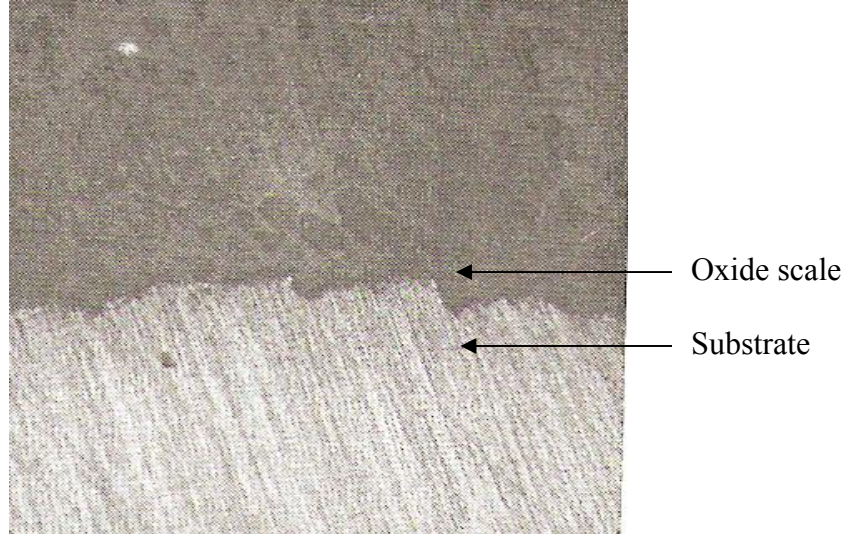


Figure (12): LOM images of cross section of Yttrium-modified aluminide diffusion coated st. steel 316L substrate after cyclic oxidation in air at 700°C for 100h at 10h cycle (250X).

الاكسدة الدورية عند الدرجات الحرارية العالية للصلب المقاوم للصدأ المطلي بالالمنيوم المدعم باليتريوم

د. رجب محمد حسين
قسم الهندسة الميكانيكية
جامعة الانبار

المستخلص :-

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

جرت اختبارات التاكسد بشكل دوري للعينات المطلية في وسط الهواء عند الضغط الجوي وعند درجات الحرارة 700 م° و 800 م° لمدة 100 ساعة وبمعدل 10 ساعة للدورة الواحدة.

تم استخدام المجهر الضوئي وجهاز حيود الاشعة السينية (XRD)، لدراسة سطح العينات وتحديد الاطوار بعد الطلاء والاكسدة الدورية.

وقد اثبتت النتائج بان طلاء الالمنيوم المدعم باليتريوم للصلب الاوستنايتي له مقاومة عالية للاكسدة الدورية مقارنة بطلاء الالمنيوم لوحده.

