

Improvement of Oxidation Resistance of Austenitic Stainless Steel by Chromizing-Siliconizing

Ali Hobi Halem* Haydar Hassan Jaber* Roaa Hatim Hatif
Babylon University, Materials Engineering Collage-Department of Metallurgy
aliaklihhobi@yahoo.com jaberjd@yahoo.com altaaceroaa8@gmail.com

Abstract

The application of a pack cementation of chromium and silicon coatings on austenitic stainless steel 316L alloy yields a significant improvement in the oxidation and hot corrosion resistance over a wide temperature range (300-900°C). In this work, austenitic stainless steel 316L alloy is coated with chromizing-siliconizing diffusions coatings. Chromium and silicon were simultaneously deposited by diffusion into austenitic stainless steel by the pack-cementation process using a pack mixtures containing (67 wt. % Cr, 8wt. %Si, 2wt. %NH₄Cl and 23wt. %Al₂O₃) when required. It was found that diffusion coating time of six hours at 950°C produces coating thickness of 80-100µm and consist mainly of CrSi₂ and Cr₃Si phase.

Key words: diffusion coating, pack mixture, cementation, hot corrosion, stainless.

الخلاصة

يطبق الطلاء الانتشاري للكروم والسليكون على الفولاذ الاوستنايتي لتحسين مقاومة الأكسدة والتآكل الحار في نطاق واسع من درجات الحرارة (300-900 °م). في هذه الدراسة تم ترسيب الكروم والسليكون أنيا عند سطح الفولاذ الاوستنايتي باستخدام تقنية السمطة باعتماد آلية الطلاء الانتشاري، وباستخدام خليط مكون من: (67% Cr، 8% Si، 2% NH₄Cl، 23% Al₂O₃) جرت عملية الطلاء الانتشاري عند درجة حرارة 950 °م ولمدة 6 ساعة في جو من الأركون. لقد وجد إن سمك طبقة الطلاء (80-100) مايكرومتر وتتكون من الأطوار CrSi₂ و Cr₃Si.

الكلمات المفتاحية: طلاء نشرها، خليط حزمة، التدعيم والتآكل الساخن، غير القابل للصدأ.

1. Introduction

Materials that can be used at the homologous temperature of 0.6 T_m and still remain stable to withstand severe mechanical stresses and strains in oxidizing environments are so-called superalloys (Agarwal, 2012); Super-alloys have been developed for high-temperature applications, but they are not able to meet both the high-temperature strength and the high-temperature corrosion resistance simultaneously, so protective coatings on super-alloys are used to counter the latter (Khang, 2011), usually based on Ni, Fe or Co. On the other hand utilization of super alloys in aerospace and defence industries can't be ignored because of excellent corrosion and oxidation resistance, high strength and long creep life at elevated temperatures (Agarwal, 2012); Iron and its alloys are widely used in many applications, the researches relating to enhancement of corrosion resistance of iron based alloys in various neutral or aggressive environments (Duran, 2013). Austenitic stainless steels have been used in these environments, but their corrosion resistance needs to be improved by surface modifications (Brady, 2000). Among the various surface-modification methods, pack cementation has been applied for many years to enrich chromium or silicon at the alloy surfaces (Park, 1998). However, in siliconizing an austenitic stainless steel substrate, the resulting depletion of chromium from the surface of stainless steel is problematic, especially for materials used in hot-corrosion environments (Duran, 2013).

In addition, chromized alloys have poor oxidation resistance at high temperature; therefore, to alleviate this difficulty, chromizing followed by siliconizing has been used in many cases. Simultaneous deposition of two elements by pack cementation is very effective in protecting substrates from hot corrosion and oxidizing environments at high temperature (Bianco, 1991; Rapp, 1992).

2. The aim of this works

The aim of this work is to deposit chromium and silicon simultaneously on the surface of austenite stainless steel (316L) alloy, using a single step pack cementation process. This single step process is supposed to be a new technique for codeposition of two elements which will reduce the use of materials, labor, time and energy. Furthermore, this study is planned to improve the hot corrosion and oxidation resistance by increasing the amount of chromium and silicon at the surface of 316L alloy. This is related to the formation of an external scale of mainly Cr_2O_3 due to the high volume fraction of Cr present.

The role of silicon is typically attributed to the formation of silicon oxide (SiO_2) layer between the oxide and metal interface. The formation of protective chromia scales is promoted by this continuous or non-continuous silicon oxide layer that is reported to act as a diffusion barrier to Fe and Cr ions reaching the oxide layer. The cyclic oxidation behavior of 316L alloy with and without chromizing-siliconizing diffusion coating will be studied in the temperature range (700-900°C) in air. The oxidation mechanism will be studied.

3. Experimental procedure

a. Material

The substrate alloy used in this study was austenitic stainless steels. The spectrochemical analysis was carried out at (General Company for examination and rehabilitation engineering) as shown in Table (1).

Table(1):Spectrochemical analysis of austenitic stainless steel 316L alloy in wt. %.

EL%	Fe	C	Mn	Si	Cr	Ni	P	Mo	V	Cu
Wt.%	bal.	0.041	1.42	0.27	19.38	10.24	0.025	0.283	0.080	0.218

The dimensions of specimens are 20mm in diameter and 4mm in thickness with total surface area of $8.8 \times 10^4 \text{ mm}^2$. First all surfaces of these specimens were grinding using 120, 220, 320, 600, 800, and 1200 grit silicon carbide papers. These specimens were then cleaned with water, and then ultrasonically cleaned for 30 minutes using ethanol as a medium. After drying, the specimens were stored in polyethylene zip-lock bags. The dimensions of all specimens were measured. The specimen dimensions were measured in two places along the length to a precision $\pm 0.01 \text{ mm}$ using a calibrated micrometre. The measured dimensions were averaged to provide the specimen diameter, height in order to be used in surface area calculation. The balance was calibrated frequently using standard weights. Prior to weighing, all specimens were held overnight in glass desiccator in order to eliminate any effect of humidity on the specimen weight determination. The initial microstructure of austenitic stainless steel 316L was characterized using light optical microscopy (LOM). As shown in figure (1), the grain structure of the uncoated austenitic stainless steel 316L is homogenous over the specimen surface. The microstructure of austenitic stainless steel 316L alloy surface was observed after being etched for approximately 20s in an etchant containing 80 ml distilled water, 10 ml hydrochloric acid (specific gravity 1.19 and 36 % conc.) and 10 g Cr_2O_3 .

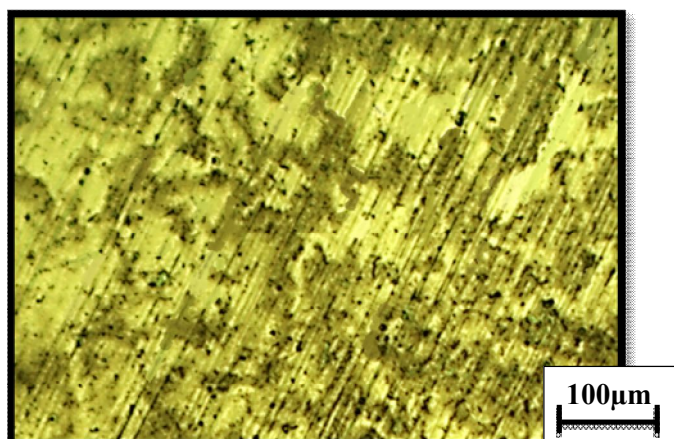


Figure (1): The microstructure of austenitic stainless steel 316L alloy surface was observed after being etched for approximately 20s in an etchant containing 80 ml distilled water, 10 ml hydrochloric acid (specific gravity 1.19 and 36 % conc.) and 10 g Cr_2O_3 .

b. Processing

Austenitic stainless steel specimen was placed in a sealed carbon steel cylindrical retort of 50mm in diameter and 80mm in height in contact with the pack mixture. The retort was then put in another stainless steel cylindrical retort of 80 mm in a diameter and 140mm in height. The outer retort has a side tube through which argon gas passes and second in the top cover for argon gas outlet. This combined system is put in an electrical holding furnace under an argon atmosphere with a flow rate of 1.5 L/min. to avoid the oxidation of the underlying materials during the process. Schematic diagram of pack cementation apparatus was observed in figure (2).

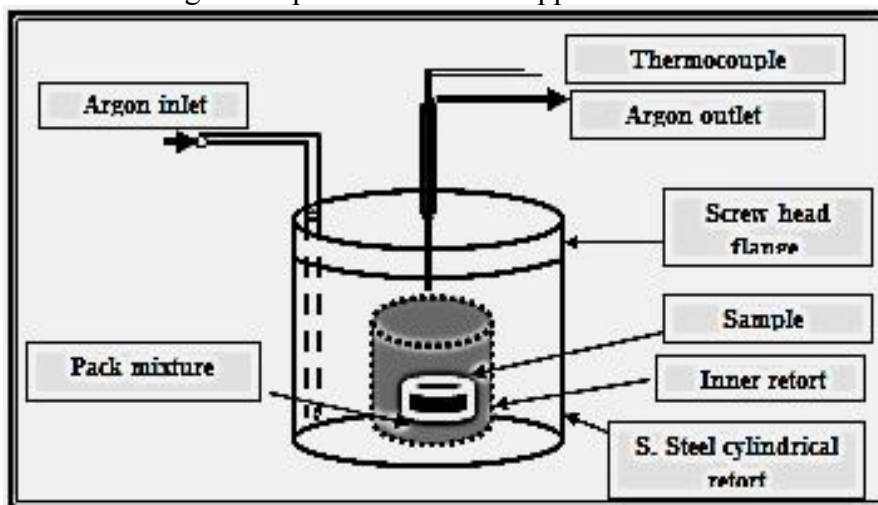


Figure (2): Schematic diagram of pack cementation apparatus.

The simultaneous chromizing and siliconizing treatments were conducted at 950°C for a constant time of 6hrs as shown in figure (3), after coating, the packs were cooled to room temperature in the same furnace, and the specimens were ultrasonically cleaned to remove only loosely entrapped pack material on the surface.

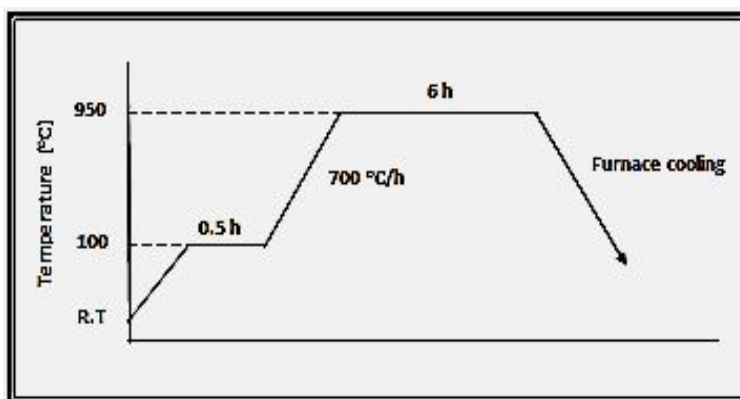


Figure (3): Heating cycle for one step pack cementation process.

c. Characterization

After coating, X-ray diffraction (XRD) was used to determine the phase structures at the surface layer. The cross sections of each specimen were cut using low speed saw and polished for examination using optical microscopy, scanning electron microscopy (SEM) as shown in figure (4).

To investigate oxidation characteristics, the specimens were subjected to 13 cycles of oxidation in air for 4hrs at 700, 800 and 900°C for a total oxidation time of 52hrs after every heating cycle; the specimens were cooled to room temperature, and then weighed measured using a balance with three digits type-kern, manufactured in Japan, with an accuracy of ± 0.1 mg.

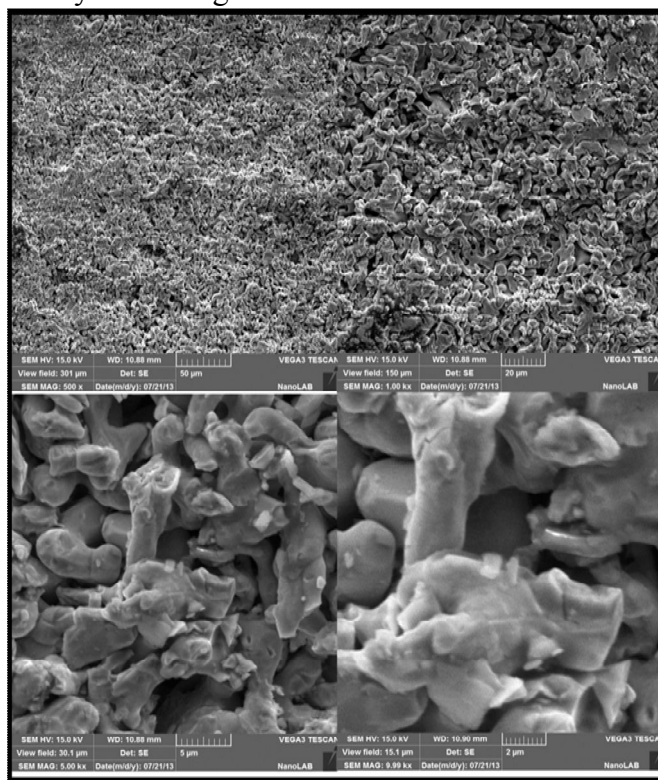


Figure (4): SEM image of austenitic stainless steel 316L in the as coated.

4. Results and discussion

During pack cementation chromium and silicon diffuses into the substrate and results in a phase transformation. The coating surface is finally composed mainly of CrSi_2 phase. In cyclic oxidation, 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.

Studies of oxidation kinetics provide valuable information about the oxidation mechanism and the rate-limiting step of the total reaction. Oxidation rate measurements also commonly serve as a basis for a quantitative numerical description of the oxidation behavior. Weight changes were recorded for kinetics identification in dry air in the temperature range (700-900°C) for 52 hrs at 4 hrs cycle. The specific weight change data of the uncoated austenitic stainless steel alloy for each temperature test is plotted in figure (5) as a function of time. 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 (Rohr, 2005):

$$\Delta W/A = k t^n \quad (1)$$

Where ΔW is the weight change, A is the specimen surface area, k is the rate constant, n is the growth-rate time constant, and t is the time of oxidation. From figure (5), n -value for each temperature is calculated from a computer program according to the best fit to equation (1). 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 example, for $n > 0.5$ it is an over-parabolic, while for $n < 0.5$ the rate is under parabolic (sub-parabolic). The results show that sub-parabolic may be found because of grain boundary (short circuits) mechanisms. Deviation from theoretical value of $n = 0.5$ can be explained by an oxide layer cracking, leading to a sudden increase of the surface area in contact with oxygen and then accelerating the oxidation kinetics. The weight gain during the transient stage corresponds to the complete consumption of the chromium in the uncoated austenitic stainless steel 316L alloy can be calculated. Indeed, if most of the Cr content in the uncoated austenitic stainless steel 316L alloy is transformed into Cr_2O_3 and the weight gain of the NiO phase is neglected. In addition to the above interpretation, experimental condition and the many variables like area and weight measurement, and others may play an important role in this case (Htab, 2004).

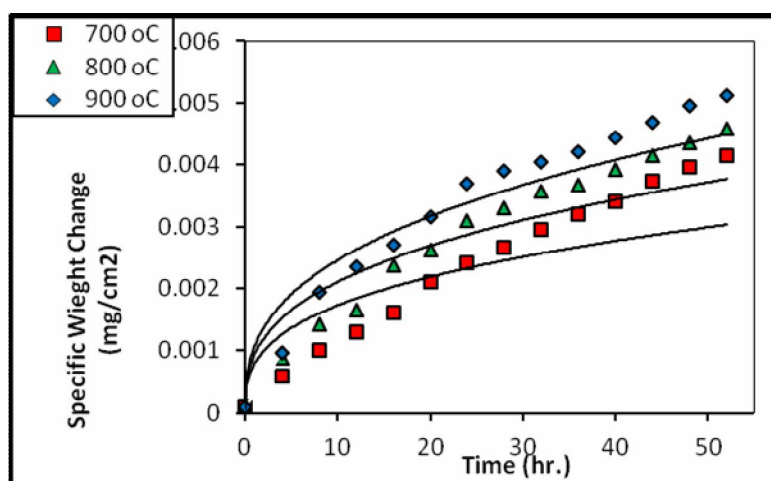


Figure (5): parabolic fitted results of weight change vs. - time plotted for uncoated austenitic stainless steel 316L cyclic oxidized in air at temperatures between 700 and 900°C for 52hrs at 4hrs cycle.

These results show that the parabolic kinetics at this temperature range can be quantified on the modified parabolic rate law with the assumption that oxidation is controlled by diffusion mechanism and the grain boundaries are the only effective short circuit diffusion paths. The grain boundary diffusion mechanism provides an initially high oxidation rate. As time passes, oxide grain growth occurs, which decreases the number of easy diffusion paths and slows the oxidation rate. Therefore, the easy pathways cut off, and the oxidation rate is decreased beyond that for parabolic kinetics (Bieraggi, 2005).

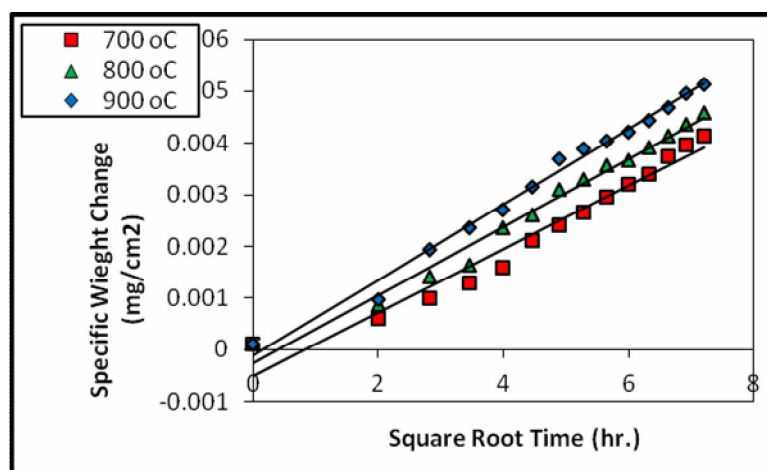


Figure (6): Linear fitted results of weight change vs. square root of time plotted for uncoated austenitic stainless steel 316L cyclic oxidized in air at temperature between 700C° and 900C° for 52hrs at 4hrs cycle.

For the parabolic kinetics, the rate equation takes the form:

$$\Delta W/A = k t^{0.5} \quad (2)$$

Where k now refers to the parabolic rate constant. A plot of specific weight change vs. square root of time gives a line as in figure (6); the slope is the parabolic rate constant in units of $(\text{mg}/\text{cm}^2)/\text{h}^{1/2}$. The k_p value is then squared to give k_p in units of $(\text{mg}^2/\text{cm}^4)/\text{h}$, as in the following expression:

$$(\Delta W/A)^2 = k_p t \quad (3)$$

The parabolic oxidation rate constants for three series of experiments are calculated and the linear lines represent the least squares curve fits to the data in figure (7), the parabolic oxidation rate constants (k_p) for the set of experiments are listed in table (2).

Over the temperatures range from 700 to 900°C, the parabolic oxidation rate coefficients and thus the oxidation rates of uncoated austenitic stainless steel 316L alloy in air, vary in magnitude from a low value of $1.77 \times 10^{-10} (\text{mg}^2/\text{cm}^4)/\text{s}$. at 700°C to a high value of $3.36 \times 10^{-10} (\text{mg}^2/\text{cm}^4)/\text{s}$. at 900°C. The point to be noted is that the weight gain calculated by application of the parabolic oxidation rate coefficient in table 2 with equation 3 results in the weight of oxygen gained by the specimen under cyclic oxidation.

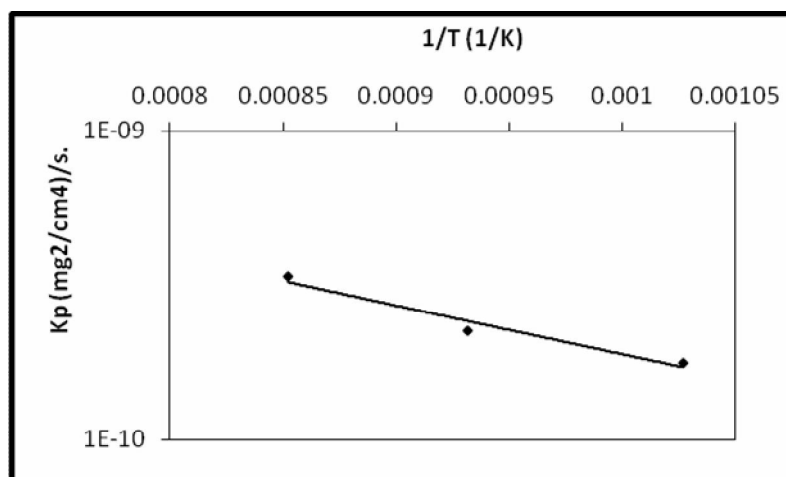


Figure (7): Plot of k_p vs. $1/T$ for uncoated austenitic stainless steel 316L alloy cyclic oxidized in air for 52hrs at 4hrs cycle.

Table (2): n values and parabolic oxidation rate constants k_p for cyclic oxidation of uncoated austenitic stainless steel 316L in air for 52hrs at 4hrs cycle.

Temperature (°C)	n values	k_p (mg^2/cm^4)/s.
700	0.34	1.77×10^{-10}
800	0.35	2.25×10^{-10}
900	0.36	3.36×10^{-10}

The point to be noted, also is that the other values of n and k_p in this study are calculated with the same procedure explained above. From the experimental work, data revealed that a parabolic oxidation rate (k_p) obeys an Arrhenius- type equation of the form:

$$k_p = k_0 \exp (-Q/RT) \quad (4)$$

Where k_p is the parabolic oxidation rate, k_0 is the pre-exponential factor, Q is the activation energy, T is the temperature, and R is the universal gas constant ($8.33 \text{ J/K}^{\cdot} \cdot \text{mol}^{\cdot}$) (Balcut, 2012). Plot of $\log(k_p)$ vs. $(1/T)$, the effective energy is calculated from the least square fitting ($R^2 = 0.96$) of the observed data in the temperature range from 700 to 900°C is to be 30.104 KJ/mol. as shown in figure 5.

The results of uncoated austenitic stainless steel 316L cyclic oxidized in air at temperature between 700°C and 900°C for 52hrs at 4hrs cycle (figure 5 and table 2), show that, the oxidation rates are increased as temperature increased. This results from external Cr_2O_3 layer which protects them from rapid oxidation. Indeed, the progress of oxidation is then controlled by outwards Cr cation which diffuses inwards oxygen anion diffuses through this existing chromic scale. Cr_2O_3 is astoechimetric oxide; therefore this diffusion is particularly low. However, at temperature close to 950 °C, the chromia scale usually grown to protect the alloy may be further oxidized into CrO_3 , which is a volatile oxide and thus, the naked material may undergo a catastrophic oxidation.

Effects of oxidation behaviors as well as the microstructural stability of high temperature oxidation and protective coating is determined by combining the results of kinetics studies with extensive analytical investigations using light optical microscopy (L.O.M) and X – ray diffraction (XRD) analysis.

Figures (8a ,8b and 8c) shows the oxidized surface features of uncoated stainless steel 316L alloy being examined by L.O.M at 700 °C, 800°C and 900°C respectively for 52h at 4h cycles.

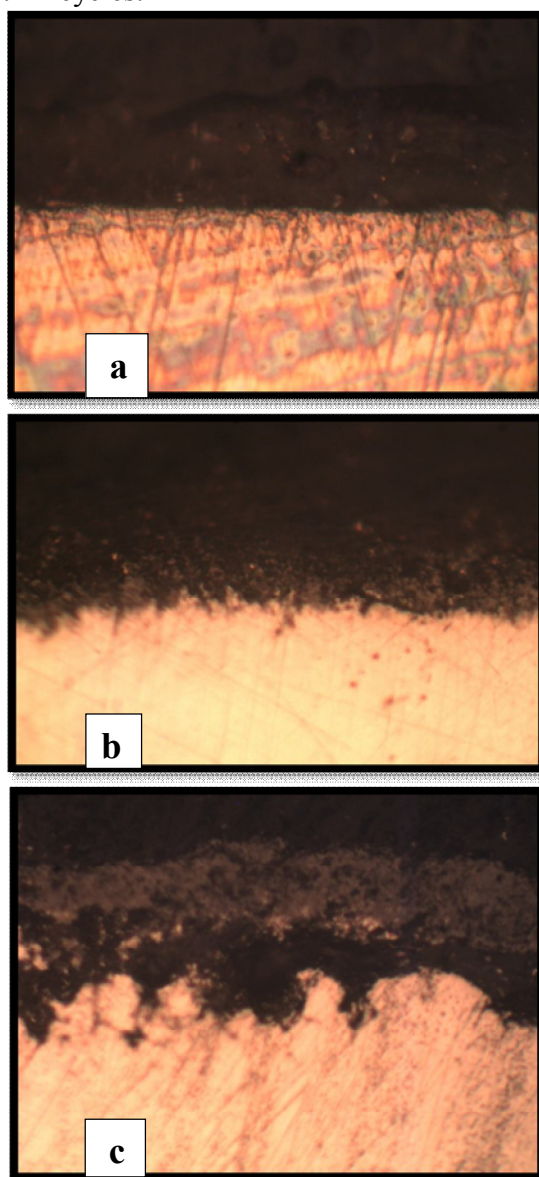
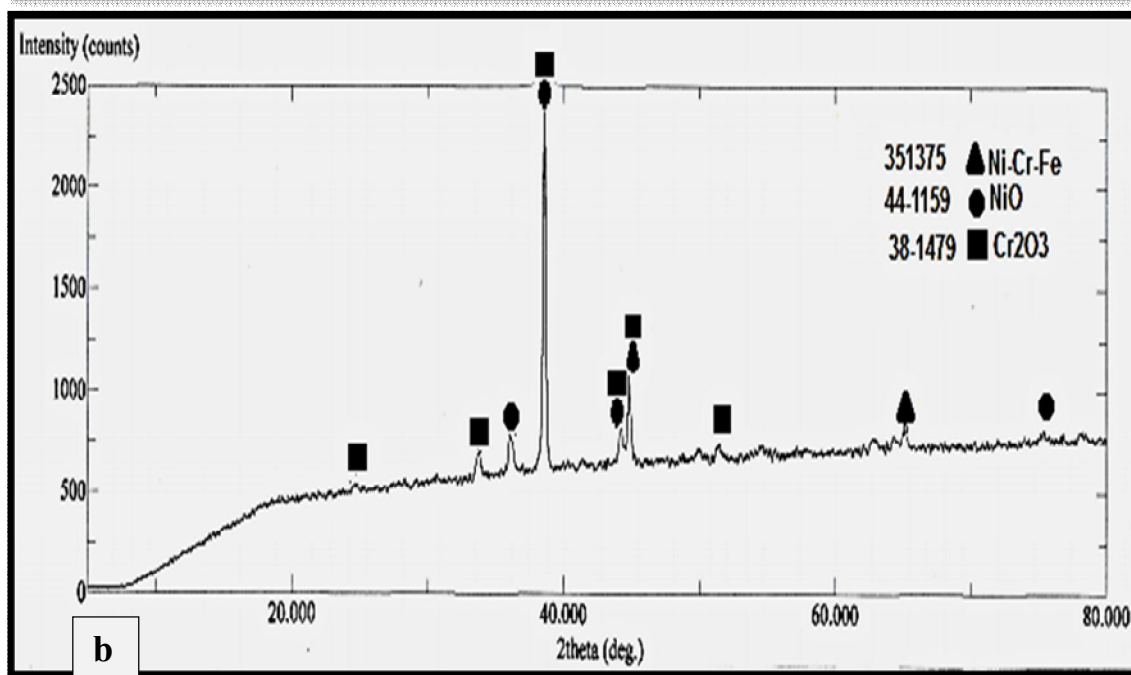
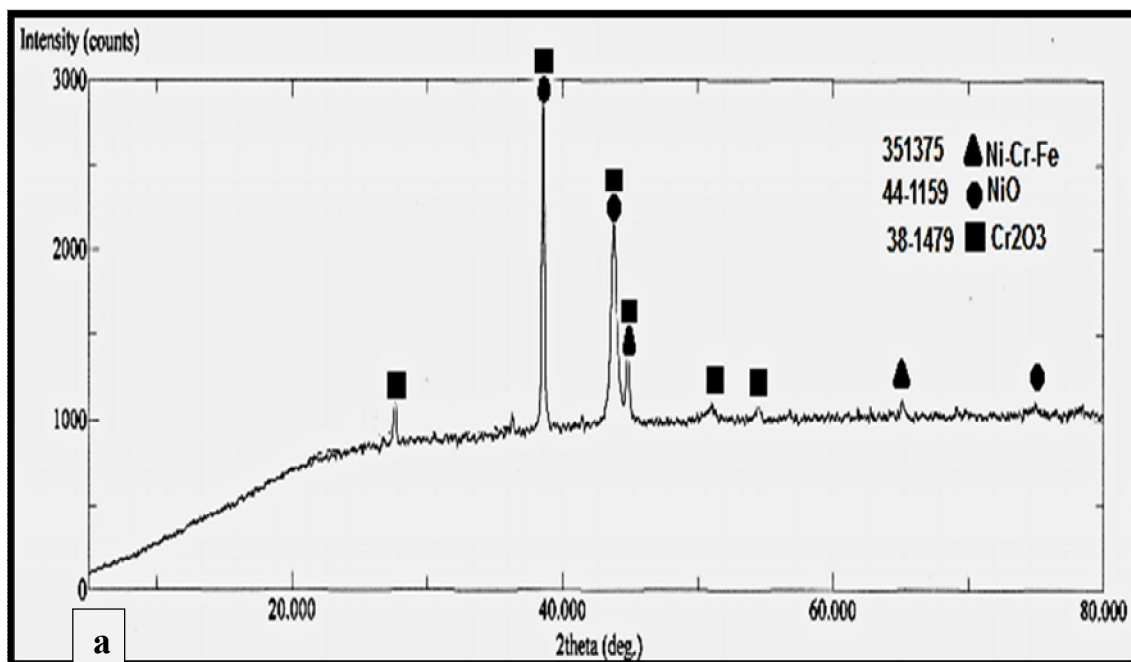


Figure (8): Cross section view images of LOM of surface scale growth uncoated stainless steel 316L alloy after cyclic oxidation in air at (a) 700°C (b), 800°C (c) and 900°C for 52h at 4h cycle.

The phases of scale formed on uncoated austenitic stainless steel 316L in air after 52h at 4h cycle at temperatures range (700-900°C) was examined in x-ray diffraction analysis (XRD). Figures (9a-9c) illustrate the major phases expected on uncoated stainless steel 316L alloy surfaces at oxidizing temperatures (700-900°C) in air for 52h at 4h cycle and the major phases that exist on uncoated stainless steel 316L surfaces after cyclic oxidation in air at (700-900°C) for 52hrs at 4hrs cycle are (Cr_2O_3), Ni-Cr-Fe, NiO.



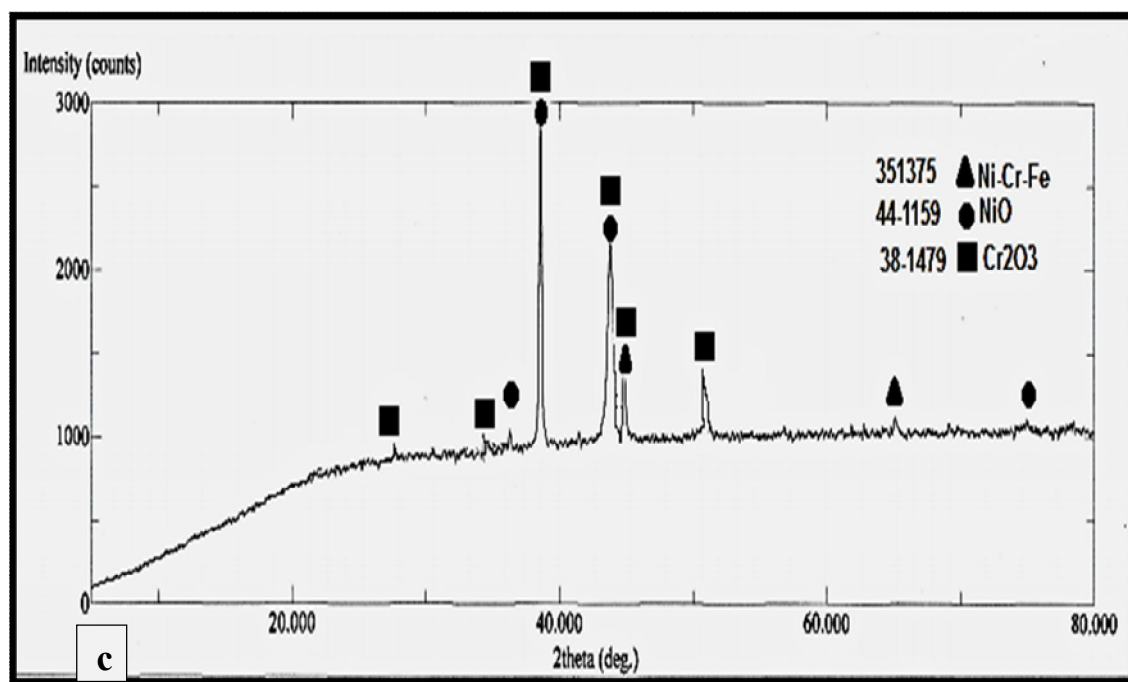


Figure (9) Diffractograms from the surface of uncoated 316L alloy after cyclic oxidation in air at (a) 700°C, (b) 800°C and (c) 900°C respectively.

The specific weight change of the specimens of coated austenitic stainless steel 316L during oxidation is plotted as a function of time as shown in figure (10). Each cycle for 4h results in positive weight gain, this means that substrate appears to be fairly resistant to scale spallation even at temperature range of (700-900°C). The kinetic behavior of cyclic oxidation of the coated austenitic stainless steel 316L in air at temperature between 700-900°C follows the parabolic rate as shown in figure (10). oxidation rate coefficients are obtained and listed in table (3).

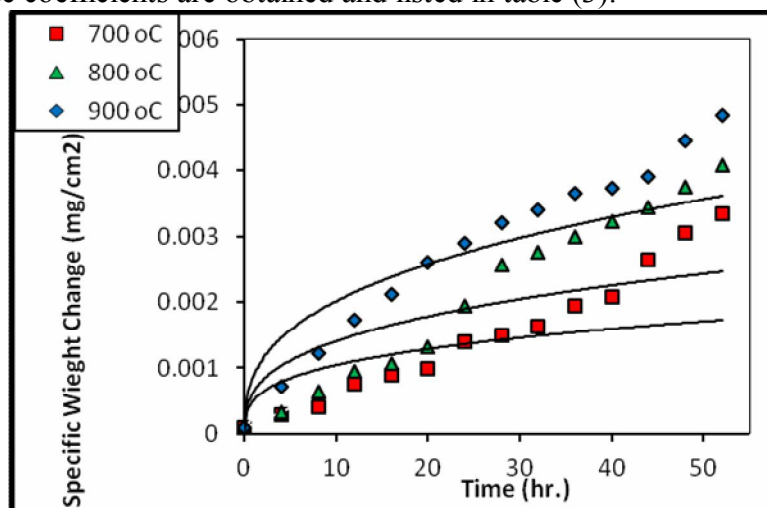


Figure (10): parabolic fitted results of weight change vs. - time plotted for coated austenitic stainless steel 316L cyclic oxidized in air at temperatures between 700 and 900°C for 52 hrs at 4hrs.

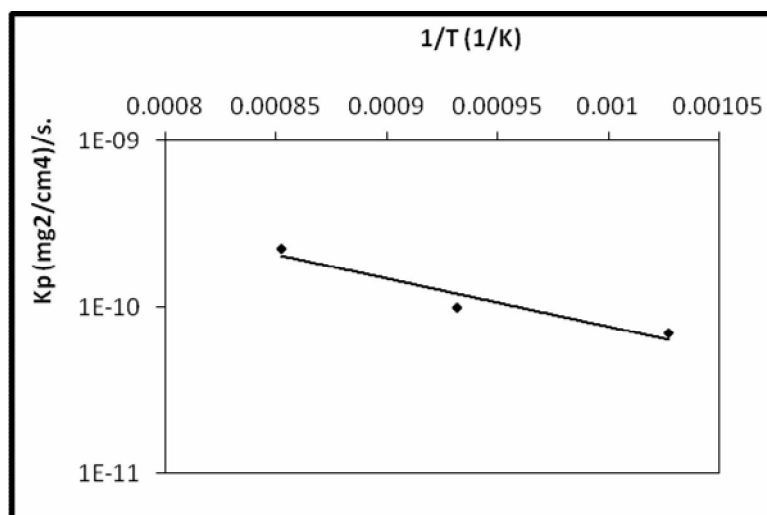


Figure (11): Plot of k_p vs. $1/T$ for coated austenitic stainless steel 316L alloy cyclic oxidized in air for 52 hrs at 4 hrs cycle.

Table (3): n values and parabolic oxidation rate constants k_p for cyclic oxidation of coated austenitic stainless steel 316L in air for 52 hrs at 4 hrs cycle.

k_p (mg ² /cm ⁴)/s.	n values	Temperature (°C)
6.94×10^{-11}	0.30	700
1.00×10^{-10}	0.33	800
2.25×10^{-10}	0.35	900

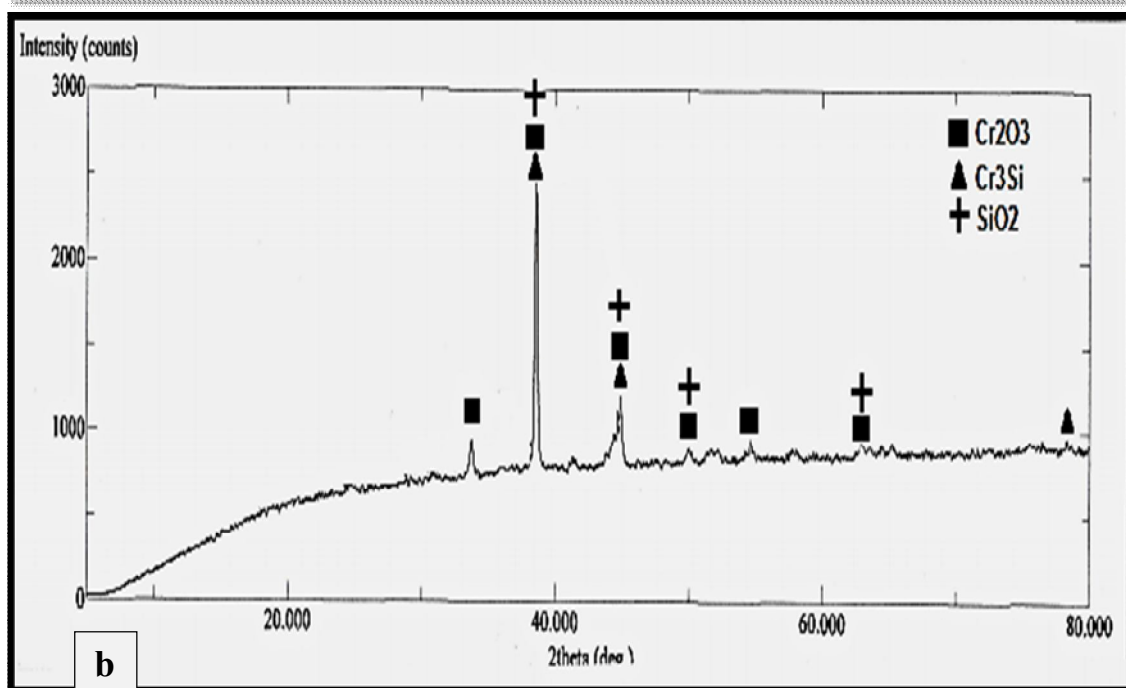
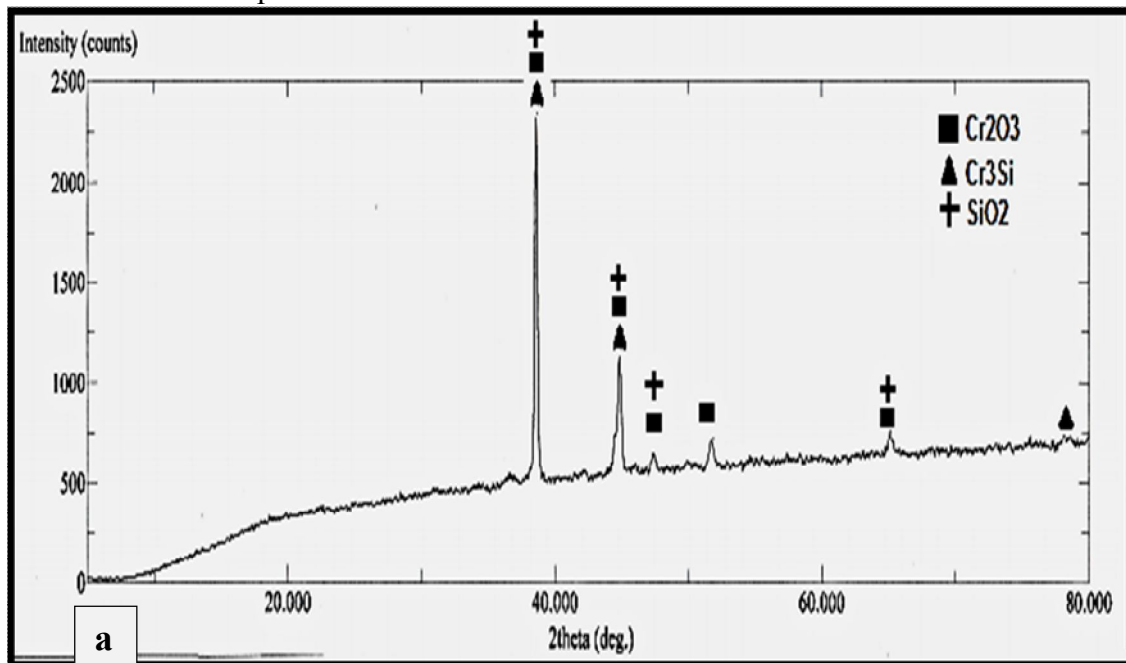
From the Plot of $\log(k_p)$ vs. $(1/T)$, the effective energy is calculated from the least square fitting ($R^2 = 0.93$) of the observed data in the temperature range from 700 to 900 °C is to be 55.336 KJ/mol. as shown in figure (11).

The kinetic behavior of cyclic oxidation of the coated system in air at temperatures between 700-900 °C follows the parabolic rate as shown in figure (10). In coated system case, oxidation rate coefficients are obtained and listed in table (3). Based on the positive specific weight change data, the coated systems of the 316L alloy appears to be fairly resistance to scale spallation even at (700-900)°C. When coated system containing Cr and Si are exposed to a high- temperature oxidation environment, Cr_2O_3 and SiO_2 scales are formed on the surface of the alloy. These scales prevent the rapid oxidation of nickel and iron in the alloy, thereby eliminating the dissolution and inward diffusion of oxygen. At temperatures higher than 900°C, the Cr_2O_3 scale, however, does not prevent the rapid oxidation of nickel and iron in the alloy due to the volatilization.

Dunning et al. (Bradya, 2014) show that, the exact mechanism by which Si enhances oxidation resistance is a matter. The effect of silicon is clearly due to the concentration of Si at the interface and is usually attributed to a layer of silica (SiO_2) adjacent to the metal. The role of Si 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 non-continuous silica layer that is reported to act as diffusion barrier to Fe and Cr reaching the oxide layer. Alloys with both Cr and Si additions have reported positive synergistic effect of the Cr and Si additions on oxidation resistance.

The phase constitution of the coatings was determined using XRD analysis. The major phases in the as-coated specimens were found to be Cr_3Si and CrSi_2 . Cyclic

oxidation between 700-900°C resulted in the formation of a continuous protective SiO_2 , Cr_3Si and Cr_2O_3 layers on the specimen surface as anticipated, its amounts increased with exposure duration. This is evident from figure (9a, 9b and 9c), which show the X-ray diffractograms of the coated system corresponding to various cyclic oxidation test temperature. In addition, no excessive scale spalling is noticed during the entire oxidation period.



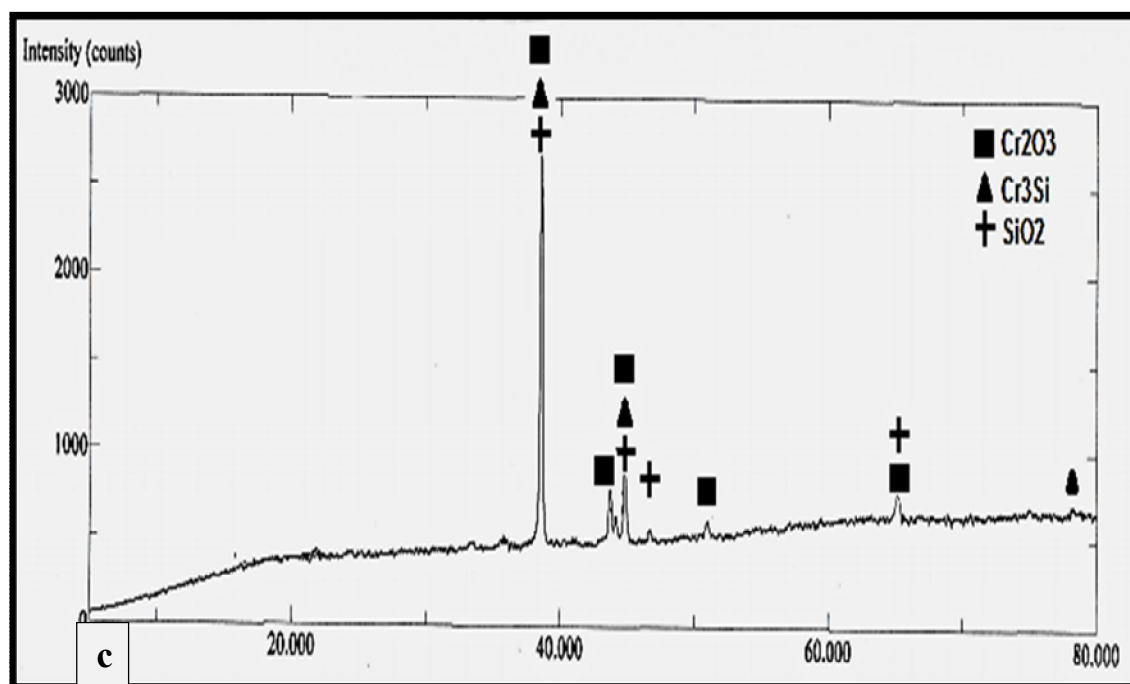


Figure (9) Diffractograms from the surface of coated 316L alloy after cyclic oxidation in air at (a) 700°C, (b) 800°C and (c) 900°C respectively.

4. Conclusion

From the isothermal oxidation tests in air at temperatures 700 to 900 °C; both the coated and uncoated austenitic stainless steel 316L exhibit parabolic oxidation rate and no oxide spalling was found over the period of oxidation but the chromizing-siliconizing diffusion coated 316L substrate revealed good cyclic oxidation resistance compared with uncoated 316L at the same identified conditions as a result of the major phase that exist in the coated-layer is CrSi_2 .

5. Reference

- Agarwal, R., "Recent Advances in Aircraft Technology", pp. 76-96.
- Bianco, R., Harper M. A. and Rapp, R. A., 1991, "Codeposition of Elements in Diffusion Coatings by the Halide-Activated Pack Cementation Method" Department of Materials Science and Engineering.
- Bieraggi, B., 2005, "Comments on Growth Rates of Alumina Scales on Fe-Cr-Al Alloys", *Oxidation of Metals*, Vol.64, No.516, pp. 397-403.
- Brady, G. S. , Cluster, H. R. , and Vaccari, J. A. , 2012, "Materials handbook" 50th edition, (2000).
- Bradya, M. P. , Magee, N , J., Yamamoto, Y., Helmick, D. and Wang, L. , 2014, "Co-optimization of wrought alumina-forming austenitic stainless steel composition ranges for high-temperature creep and oxidation/corrosion resistance", *Materials Science & Engineering*, 590, pp. 101–115.
- Duran, B., Çakmakçı, I., Bereket, G., 2013, "Role of supporting electrolyte on the corrosion performance of poly (carbazole) films deposited on stainless steel", *Corrosion Science* 77 pp. 194–201.
- Hatab, K. , 2004, "Effect of environments on oxidation behaviour of Inconel Alloy 600", *The Department of Production Engineering and Metallurgy, University of Technology*.
- Palcut, M., Mikkelsen, L., Neufeld, K., Chen, M., Knibbe, R., and Hendriksen, P. V., 2012, "Improved oxidation resistance of ferritic steels with LSM coating for

- high temperature electrochemical applications", International Journal of Hydrogen Energy, Vol. 37, Issue 9, pp. 8087-8094.
- Park, H. H., Lee, K. T. and Shin, H. S., 1998, "Simultaneous Chromizing-Aluminizing Diffusion Coating of Austenitic Stainless Steel by a Two-Step CVD Process", Oxidation of Metals, Vol.50, NO. 516, Nos. 5/6, pp. 377-386.
- Rapp, R. A., 1992, "Codeposition of Chromium and Silicon onto Iron-Base Alloys via Pack Cementation" Department of Materials Science and Engineering, the Ohio State University.
- Rohr, V., 2005, "Developpement De Revetements Pour Les Aciers D'echangeurs Thermiques Et Amelioration De Leur Resistance A La Corrosion En Environnement Simulant Les Fumees De Combustion De Charbon ", These, Institut National Polytechnique De, Toulouse.
- Zhang, K., Liu, M. M. , Liu, S. L. , Sun, C. and Wang, F. H. , 2011, "Hot corrosion behaviour of a cobalt-base super-alloy K40S with and without NiCrAlYSi coating", Corrosion Science 53 pp. 1990–1998.