

Improvement of Hot Corrosion Resistance of Austenitic Stainless Steel by Chromizing-Siliconizing

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Abstract

Simultaneous deposition of chromium and silicon by pack cementation is very effective in protecting substrates from hot corrosion and oxidation environments at high temperature. In this study, chromium and silicon were simultaneously deposited by diffusion into austenitic stainless steel 316L alloy 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 phases.

Key words: diffusion coating, pack mixture, cementation, hot corrosion, stainless steel 316L.

الخلاصة

ترسيب الكروم والسليكون بواسطة عملية السمنتة له تأثير فعال في تكوين طبقه واقية حامييه من التآكل الحار والأكسدة في أوساط تآكلييه مختلفة عند درجات حرارة عالية. في هذه الدراسة تم ترسيب الكروم والسليكون أنيا عند سطح الفولاذ الاوستنايتي باستخدام تقنية السمنتة 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: نشر طلاء، خليط حزمة، السمنتة، التآكل الساخن، الفولاذ المقاوم للصدأ.

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 stainless steels have been used in these environments; however, their corrosion resistance needs to be improved by surface modifications.

Among the various surface modification methods, pack cementation has been used for many years to enrich chromium, silicon and aluminium at the alloy surfaces. The increase in the amount of Cr in steel improves corrosion resistance; however, this has an adverse effect on mechanical properties of steel; for example, it increases the brittle transition temperature. It has been reported that the addition of Si to stainless steels could improve their high-temperature oxidation resistance (Agarwal, 2012)

Therefore, simultaneous deposition of two kinds of different elements by pack cementation is very effective in protecting substrates from hot corrosion and oxidation environments at high temperature (Nishimoto, 2003), However, a one-step process, keeping the temperature and time constant, has been used for simultaneous diffusion coating.

Chromium and silicon are simultaneously deposited into an austenitic stainless steel 316L alloy, which is used in high temperature environments, such high-temperature corrosion has occurred due to the dissolution loss of the protective oxide layer formed on the steel surface. Cr₂O₃ might be subjected to basic or acidic dissolution in the molten salt, depending on the basicity of the molten salt, whereas SiO₂ would resist basic or acidic dissolution in the molten salt. Therefore, the formation of a Si-enriched surface layer on the stainless steels was effective for enhancement of the corrosion resistance of stainless steel in the environment with the molten salt deposition due to the acceleration of SiO₂

film formation using a halide activated pack cementation in one heat treatment cycle (Fukumoto, 2012)

2. 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 in wt. %.

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

The dimensions of specimens are 20mm in diameter and 4mm in thickness with total surface area of $8.8 \times 10^4 \text{ mm}^2$, 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.

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 80mm in diameter and 140mm in height. The outer retort has a side tube through which system then 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 (1).

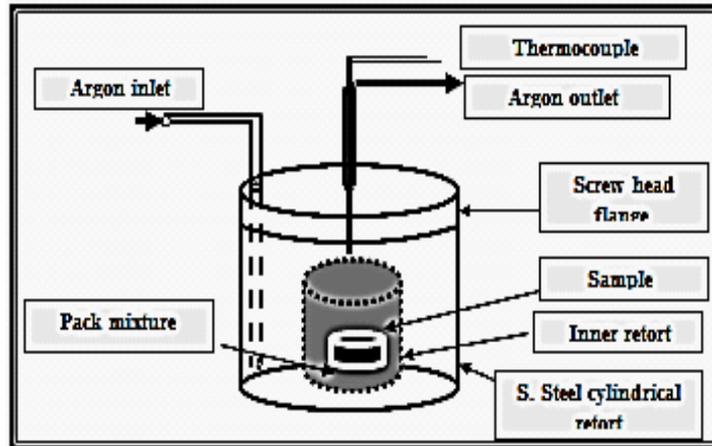


Figure (1): Schematic diagram of pack cementation apparatus.

The simultaneous chromizing and siliconizing treatments were conducted at 950°C for a constant time of 6 hrs as shown in figure (2), 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.

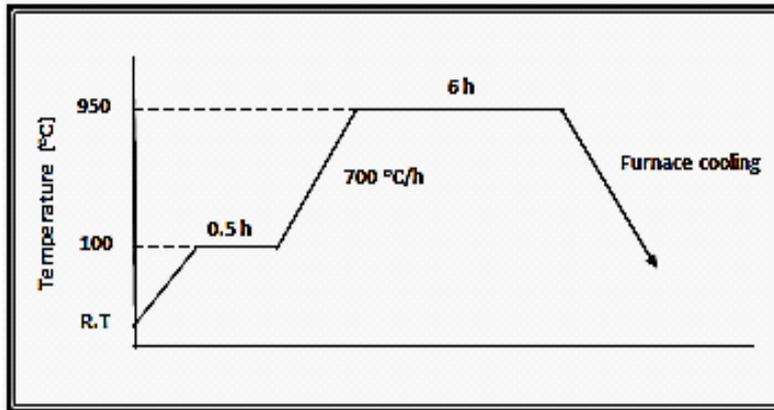


Figure (2): Heating cycle for one step pack cementation process.

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 (3). 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.

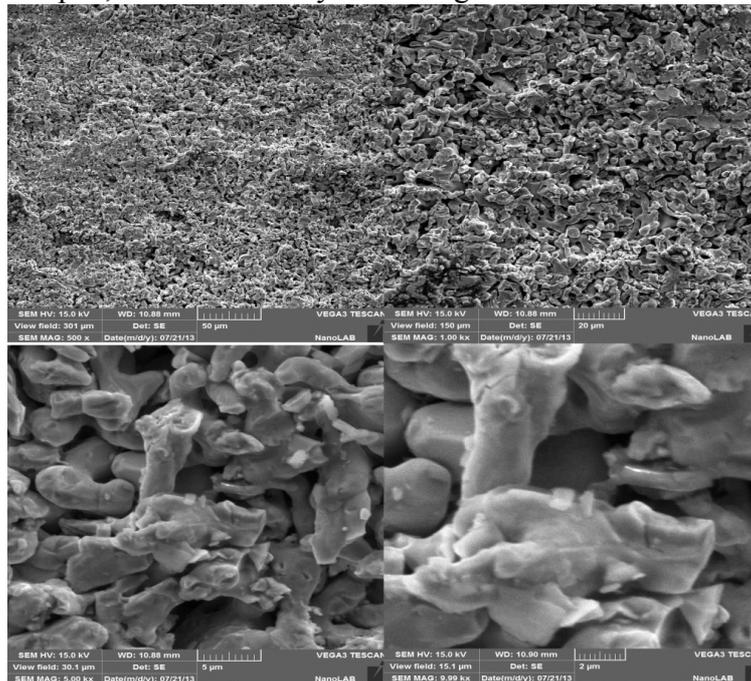


Figure (3): SEM image of austenitic stainless steel 316L in the as coated.

3. 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. Austenitic stainless steel with and without

chromium-silicon diffusion, coating specimens were used for hot corrosion experiments. Specimens were deposited with NaCl/Na₂SO₄ concentrations (50/50 wt. %), 100wt. % NaCl and 100wt. % Na₂SO₄ until a total coating weight of 2 mg/cm² was reached. The specimens were measured and weighed first, then placed on a hot plate heated to 250°C. An air gun sprayed one of the three saturated aqueous –salt solutions in an air mist, and a coat of fine salt particles formed on the specimen's surface after the mist settled and the water evaporated. The process was repeated until the dry particles were deposited up to 2 mg/cm². Hot corrosion test was performed in a static air at 850°C for 52hrs at 13 cycles in furnace. After testing the specimens were cleaned in an ultrasonic bath, first in distilled water and then in ethanol. They were then weighed on a digital balance to determine the change in weight.

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 (Fredriksson, 2013):

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

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(4), 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 Cr₂O₃ 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 (Volinsky, 2013)

The oxidation kinetics of uncoated austenitic stainless steel 316L alloy oxidized with 100 wt.% NaCl, 100 wt.% Na₂SO₄ and (50 wt.% NaCl + 50 wt.% Na₂SO₄) deposits at 850°C for 52hrs at 4hrs cycle is plotted of specific weight change vs. time and shown in figure (4).

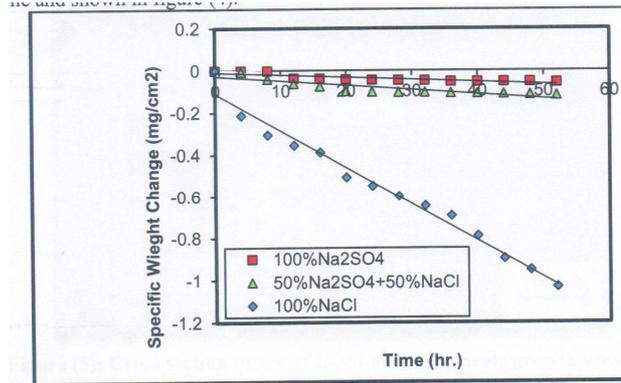


Figure (4): Linear fitted results of specific weight change vs. - time plotted for uncoated austenitic stainless steel 316L cyclic oxidized with 100% Na₂SO₄, 100% NaCl, and (50%Na₂SO₄ + 50%NaCl) deposits at 850 °C for 52hrs at 4hrs cycle.

In cyclic hot corrosion test using 100% Na₂SO₄, 100% NaCl and (50 / 50 wt. % and 0 / 100 wt. %) Na₂SO₄ / NaCl deposit exhibit clearly gradual weight-loss rate as a function of time due to Cr depletion, values of n and k are shown in Table (2):

Table 2: n values and oxidation rate coefficients k for cyclic hot corrosion test of uncoated austenitic stainless steel 316L in various NaCl/Na₂SO₄ concentrations at 850°C for 52hrs at 4hrs cycle

Linear rates of specific weight change (k_L) (mg/cm ²)/s.	n values	Salt composition
-48.6×10^{-7}	1	NaCl
-3.05×10^{-7}	1	Na ₂ SO ₄
-5.83×10^{-7}	1	50%NaCl+50%Na ₂ SO ₄

The kinetic behavior of an uncoated austenitic stainless steel 316L oxidized with 100% NaCl, 100% Na₂SO₄ and 50%NaCl+50%Na₂SO₄ follows a linear rate law (the value of n = 1). In the linear rate law, the reactions occurring at the alloy / scale interface are fast and, in general, attention can be turned to the processes occurring at the scale/deposit interface. This indicates that a surface reaction is the rate-determining step.

Figure (5) shows that, the hot corrosion behavior changes drastically in the presence of sodium chloride. Extensive cracking and spalling was observed in all tests. At the same temperature and time exposure, the corrosion rate of uncoated austenitic stainless steel 316L alloy oxidized with 100% NaCl in several times greater than that in pure Na₂SO₄ and 50%NaCl+50%Na₂SO₄.

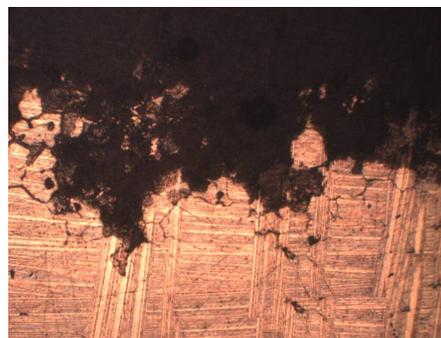
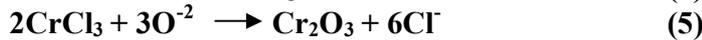


Figure (5): Cross section image of LOM of surface scale growth uncoated stainless steel 316L alloy oxidized with 100% NaCl deposits at 850°C for 52hrs at 4hrs cycle.

The chlorine generated by the dissociation of NaCl reacts with alloying elements such as chromium, tungsten and titanium and forms highly volatile metal chlorides which diffuse out of the scale reacting with oxygen present near the scale by releasing chlorine and forming a discontinuous non adherent, and loose oxide scale. The reaction of chlorine with Cr, Ti, and W present in the protective oxide scale to form metal chlorides having high vapor pressures causes cracking and spallation of the protective oxide scale on the surface of the alloy and, hence, the corrosion rate is appreciably high. The various reactions involved are (Chaia, 2013):



However, when compared with all the experimental data, the uncoated austenitic stainless steel 316L alloy deposited with 100% NaCl reveals the most severe corrosion attack, and this attack increased as the NaCl content increased in the salt mixtures from 50/50 wt. % NaCl / Na₂SO₄ to 100 wt. % NaCl deposits. Na₂SO₄ is not as detrimental as NaCl to the corrosion resistance of uncoated austenitic stainless steel 316L alloy during exposure at 850 °C to cyclic oxidation test for 52hrs at 4hrs cycle.

In this study, and according to the XRD analysis shown in figure (6), the thick scale formed due to hot corrosion test consisted mainly of (Cr₂O₃), NiO and Ni-Cr-Fe but chlorides or chlorine produced by oxychlorination were not detected by X-Ray diffraction analysis probably due to its volatility. The accelerated oxidation was than caused by the oxychlorination preventing the formation of a continuous chromia scale.

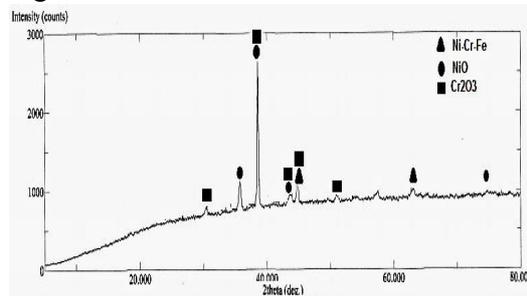


Figure (6): Diffractograms from the surface of austenitic stainless steel 316L specimen cyclic oxidized with 100% NaCl deposits at 850°C, for 52hrs at 4hrs cycle.

Figure (7) shows the LOM images of the uncoated austenitic stainless steel 316L alloy deposited with 100% Na₂SO₄ and exposed to cyclic oxidation at 850°C for 52hrs at 4hrs cycle. One can conclude from figures (4, 5 and 7) that Na₂SO₄ is not as detrimental as NaCl to the hot corrosion resistance of uncoated austenitic stainless steel 316L alloy under the same conditions.

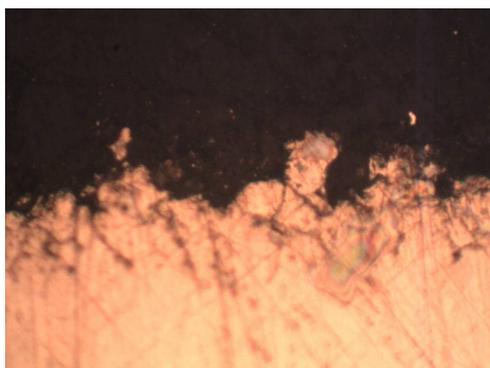


Figure (7): Cross section image of LOM of uncoated austenitic stainless steel 316L alloy cyclic oxidized with 100% Na₂SO₄ deposits at 850°C for 52hrs at 4hrs cycle.

Furthermore, the corrosion rate of the Na₂SO₄ induced hot corrosion is parabolic rate. This is probably due to the formation of easy diffusion paths in the metal sulphides formed at the scale / alloy interface. No phases containing Na or S were found by XRD analysis. It was observed that in the presence of 100% Na₂SO₄ deposits and after cyclic oxidation at 850°C for 52hrs at 4hrs cycle, the scale remains primarily Cr₂O₃, NiO and Ni-Cr-Fe (see figure 8).

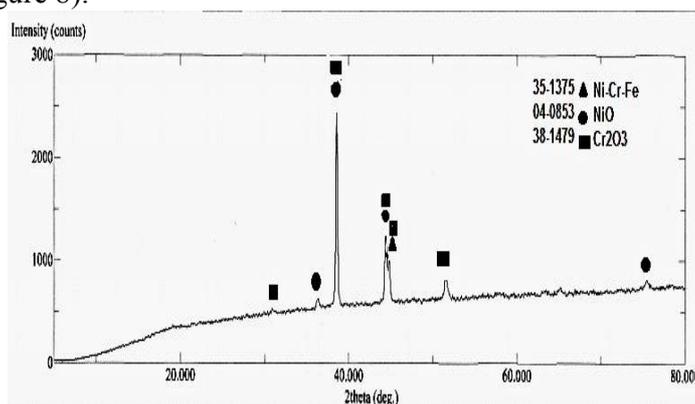


Figure (8): Diffractograms from the surface of uncoated austenitic stainless steel 316L specimen cyclic oxidized with 100% Na₂SO₄ deposits at 850°C, for 52hrs at 4hrs cycle.

While metal sulphides produced by Na₂SO₄ decomposition were not detected by X-ray diffraction analysis probably due to lower sulphides concentration at the surface of tested specimen

Figure (9) shows a cross section of uncoated austenitic stainless steel 316L alloy surface deposited with (50 wt. % Na₂SO₄ + 50 wt. % NaCl) and exposed to cyclic oxidation test at 850°C for 52hrs at 4hrs cycle. A scale may be non-protective due to the volatility of the oxide. Scales may initially be protective, but become non-protective due to a variety of factors, one of them, which is the most widespread being mechanical failure because of the inability of the scale, often at a critical thickness, to relieve the stresses produced in the growing scale, or especially sulphide commonly with high molar volume (Walston, 2004).

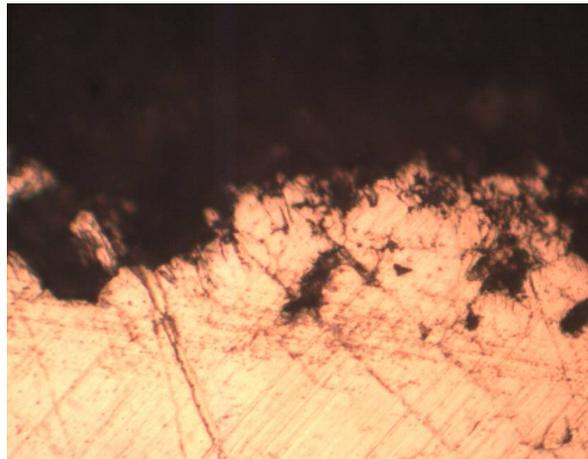


Figure (9): Cross section image of LOM of uncoated austenitic stainless steel 316L alloy cyclic oxidized with (50%Na₂SO₄ + 50%NaCl) deposits at 850°C for 52hrs at 4hrs cycle.

The major phases formed at the surface of uncoated austenitic stainless steel 316L deposited with (50% NaCl and 50% Na₂SO₄) exposed at 850°C for 52hrs at 4hrs cycle were NiO, Cr₂O₃, and Ni-Cr-Fe as shown in figure (10). The metal sulphides and / or chlorides, which expected to appear, did not detect by XRD analysis probably because of the lower concentration of sulphides and / or chlorides content in the outer scale layer. The obtained value is in a good agreement with data from Gatea et. al. (Abbass, 2009)

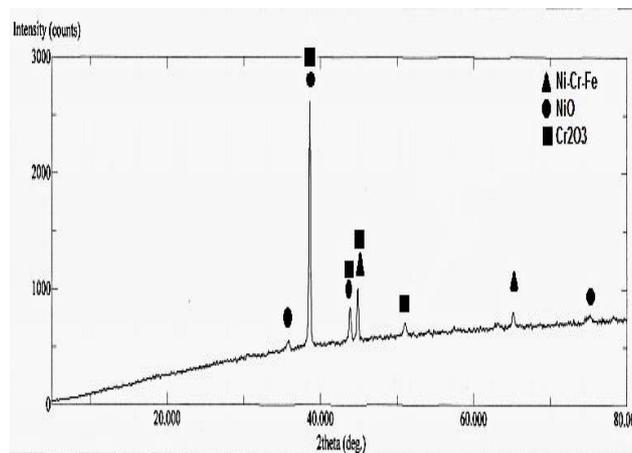


Figure (10): Diffractograms from the surface of austenitic stainless steel 316L specimen cyclic oxidized with (50%Na₂SO₄ + 50%NaCl) deposits at 850°C, for 52hrs at 4hrs cycle.

5. Conclusion

The chromizing-siliconizing diffusion coated 316L alloy substrate revealed good cyclic hot corrosion resistance compared with uncoated 316L at the same identified conditions as a result of the major phase that exist in the coated-layer is CrSi₂. The oxidation rate of uncoated austenitic stainless steel 316L deposited with 100wt.%NaCl, 100wt.%Na₂SO₄ and 50wt.%NaCl+ 50wt.%Na₂SO₄ follow nearly linear oxidation rate coefficient (k_L) value is found to be equal to -5.833×10^{-7} (mg/cm²)/s for 100wt.%NaCl, -3.055×10^{-7} (mg/cm²)/s for 100wt.%Na₂SO₄ and -4.861×10^{-6} (mg/cm²)/s for

50wt.%NaCl+50wt.%Na₂SO₄. Whereas the corrosion rates of diffusion coated 316L substrate deposited with 100% Na₂SO₄ and with (50% NaCl + 50% Na₂SO₄) follow nearly parabolic kinetics, corrosion rates are ($k_p = 5.136 \times 10^{-9}$ and 1.078×10^{-7} (mg²/cm⁴)/s) respectively and the corrosion rate of diffusion coated 316L substrate deposited with 100% NaCl is linear. The linear oxidation rate coefficient k_L value is found to be equal to 1.305×10^{-6} (mg/cm²)/s.

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