Surface Modification of the Improved Stainless Steel Alloy AISI-304 and the Use of Diffusion Coating and a Study of Its Efficiency in Resistivity Hot Corrosion in an Atmosphere of Sodium Chloride Vapor NaCl and Sodium SulfateNa₂SO₄

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Abstract:
This research aims to modify the components of stainless steel alloy by the method of surface engineering through the single diffusion coating technique in order to obtain new alloys with high efficiency in resisting harsh environmental conditions. Steam a mixture of sodium chloride (NaCl) and sodium sulfate (Na₂SO₄) at a temperature of 900 °C and then compare it with the base alloy. The results showed that the alloys produced in this way are very efficient. The results showed that the aluminum coating showed high efficiency in resisting oxidation and provided better protection for a longer time compared to the uncoated alloy due to the Al₂O₃ oxide crust layer formed with high adhesion as well as the aluminum-rich phases, whether the phases were nickel-aluminum or iron-aluminum. The results also showed that the thickness of the coating and the weight gain of the alloy is subject to the parabola relationship with time.

Key words: Diffusion coating, High temperature oxidation, Hot corrosion, Parabola relationship, Surface engineering.

Introduction:
The engineering designs used in high temperatures and various harsh conditions must possess a high resistance to these media for the purpose of performing the work for which they were made, taking into account the acceptable economic costs. It has become possible to test some improved alloys (Superalloys) in resistance to heat and oxidation in harsh conditions that have become commonplace in many industrial applications, especially in gas turbine engines in electrical stations, jet engines, rocket engines, internal combustion engines, spacecraft engines and other uses ¹,². The problem of corrosion is one of the biggest problems that the industry suffers from wherever it is found, and it affects the metal parts as a result of the interaction of the metal surface with the medium in it, which leads to the collapse and failure of these parts. In the state in which it was before the corrosion occurred, in other words, this reaction takes place spontaneously between the surface of the metal and the medium, leading to the release of energy ³⁻⁶.

In addition, there is a reaction called an electrochemical reaction, and this does not happen except when the medium in which the metal is a conductor of electricity, that is, an (electrolyte). Between this surface and some gaseous elements in the middle, such as oxygen and sulfur, this type of failure usually occurs at high temperatures and is known as corrosion at high temperatures ⁷. As for the oxidation process, which is a type of corrosion, if the union is between the surface of the metal and oxygen, and a malfunction may occur as a result of the friction force, then this is called failure or corrosion and not corrosion, because the cause is purely mechanical and not chemical ⁸. And the mechanical force is sometimes a catalyst factor in some media for the occurrence of electrochemical corrosion, as in some types of corrosion such as stress and corrosion ⁹.

Diffusion:
The atoms in solids are in constant motion around their positions in the lattice, so a number of atoms gain enough energy and jump to the adjacent
site. This random movement is called diffusion\textsuperscript{10}, and it requires two conditions in the atom to make this movement:

First: the presence of an empty neighboring site.
Second: the atom must have enough energy to break bonds with its neighboring atoms\textsuperscript{11}. Diffusion is one of the basic processes in materials, and this random movement may occur singly or collectively for a large number or a few atoms\textsuperscript{12, 13}.

Diffusion occurs when there is a gradient in the chemical composition or a change in concentration, and with an increase in temperature, the speed of diffusion increases as the amplitude of vibrations increases, and thus the rate of migration of atoms increases, accompanied by the formation of gaps and changes in dimensions\textsuperscript{14}. It is worth noting that the aluminumization process of the steel and the oxidation processes are governed by the diffusion process of atoms or ions through the surface layer\textsuperscript{15}. In general, propagation can be classified into two types\textsuperscript{13}:

- stable diffusion.
- unstable diffusion.

practical part:
Samples were prepared from AISI 304L Stainless Steel, as shown in Table 1, with different dimensions and sizes. The sample was thoroughly cleaned, as the preparation process is one of the necessary means for the coating process.

Table 1. Composition of Stainless Steel Alloy (AISI 304L)

<table>
<thead>
<tr>
<th>Component</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>Ni</th>
<th>S</th>
<th>Si</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt%</td>
<td>0.0</td>
<td>2.0</td>
<td>0.04</td>
<td>10.5</td>
<td>0.03</td>
<td>1.0</td>
<td>19.5</td>
<td>BA</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>L</td>
</tr>
</tbody>
</table>

The materials and equipment used
1. A mixture of pure aluminum powder, ammonium chloride powder NHCl as an activator, and pure aluminum oxide Al\textsubscript{2}O\textsubscript{3} to prevent clumping of the mixture, with the following weight percentages 25\%, 5\% and 70\% for each of Al, NH\textsubscript{4}Cl and Al\textsubscript{2}O\textsubscript{3} respectively\textsuperscript{16}.
2. A tube made of heat-resistant alumina, open at one end and closed at the other.
3. Accuracy Sensitive Electric Scale 0.0001 gm.
4. X-ray diffraction machine.
5. Optical microscope equipped with a camera.
6. vacuum pump.
7. temperature controlled.
8. grinding machine.
9. Electric ovens with a temperature of 1150 °C.
10. Microscope type (AHSLER Type V-Testor 2) to measure the thickness of the coating.
11. Thickness measuring device (AMSLER Type V- Testor 2).
12. Temperature controller type.
13. Scanning electron microscope device.

Sample preparation for coating
The process of preparing samples for coating is one of the necessary and very important means for the success of the coating process. After the alloy cutting process, the preparation process of the samples was carried out in several stages, as the smoothing and polishing process of the samples was carried out to remove the oxides on the surface using smoothing paper made of silicon carbide with different smoothness degrees starting from 270 and passing through 400, 600, 1000 and 1200 until reaching Final Class 2000, the samples were washed with warm water and washing powder, then with methanol to remove suspended fats, then with acetone for quick drying, then with distilled water, all to obtain a suitable surface for the coating process\textsuperscript{14}.

Coating Processes
The prepared samples were coated using the cementing method, which is one of the diffusion coating methods. This method was used to coat all samples prepared in this research. Cement pulp contains pure aluminum powder 25\% and is used as a source of paint and aluminum chloride powder 5\% as a material. An activator that transfers aluminum from the mixture to the sample to be coated, and the rest of the powder is alumina Al\textsubscript{2}O\textsubscript{3} and is used as a substance that prevents the mixture from clumping. It is entered into a vacuum electric furnace, and the coating process was carried out at a temperature of 1000 °C for several samples and at times 2, 4, 6 and 8 hours and for one stage, and it is called the single coating system. Fig. 1 shows a schematic diagram of the coating process using a vacuum furnace.
Figure 1. A schematic diagram showing the coating process in an electric furnace.

Hot Corrosion
The hot corrosion process in which the metal is converted from its transitional (free) form to its stable transitional form, that is, the opposite of the basic reaction for extracting minerals because most metals are extracted from their ores by supplying them with a certain amount of energy, as they are in the single state at higher energy levels. From the federal form, according to the thermodynamic second law, the last case is a return to the lowest possible energy level, that is, to return to the federal form again, and this process is called hot corrosion.

Hot Corrosion Testing
The hot corrosion test was carried out in the furnace manufactured for this purpose by the method of periodic oxidation or thermal cycles at a temperature of 900 ºC as in Fig. 2 and under normal atmospheric pressure. The duration of each cycle was five hours and in an atmosphere of a mixture of sodium sulfate vapor and sodium chloride by using a beaker containing a mixture of sodium sulfate and sodium chloride with a liter of water and placing it on the heater until it reaches the boiling point, and thus the vapor of the mixture moves into the oven at a degree 900 ºC in order to test the behavior of the uncoated and coated samples with the types of coatings used.

Ordinary aluminum paint (Pack Cementation), which is over four periods of time.

Microscopy
Samples were allocated for microscopic examination after the completion of the coating operations, where cold basing operations were carried out on them and the smoothing and polishing process was conducted on them, then a microscopic examination was conducted to determine the thickness of the coating and the structures that appeared as a result of the coating. As for the display process (Etching) It was done by using the revealing solution, which is a solution of ferric chloride FeCl₃ (5gm) and hydrochloric acid HCl (50mL) and distilled water 100 mm. And to reduce hot corrosion and oxidation, which is followed in our research, this is the simple alumina coating, or what is known as diffusion coating.
Results and discussion:

Single phase aluminum coating at 1000°C for the alloy. The aluminum gained (Uptake) resulting from the aluminumization process increases with time according to the parabola relationship as shown in Fig. 3, which indicates that the diffusion process governs the coating process \(^{25}\) and Fig. 4 shows the relationship of the thickness of the resulting coating as a function of time, which also obeys the law of parabola. Table. 2 includes the weight gain and thickness rates for four periods of 8, 6, 4, 2 hours at a temperature of 1000 °C.

Table 2. Details of weight gain and coating thickness ratios (alluminization only) for AISI304 single-stage at 1000 °C

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Coating Time (h)</th>
<th>Av. Thickness of Coating (µm)</th>
<th>Av. Weight gain (gm/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Outer layer</td>
<td>Interdiffusion zone</td>
<td>Inner layer</td>
</tr>
<tr>
<td>1000</td>
<td>2</td>
<td>70</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>133</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>139</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>144</td>
<td>12</td>
</tr>
</tbody>
</table>

The microscopic examination of the coating after 6hr also showed the presence of two regions, the outer region containing dark structures, which may be secondary phases, and the inner region having light-colored structures, somewhat narrow and a little thick at the bottom, i.e. the interfacial region. This is known as the diffusive exchange zone \(^{26, 27}\).

It is also noted that the microscopic structure of the resulting coatings with the four time periods is similar, and is characterized by the presence of more than one phase in the coating layer, and the outer coating layer consists of phases rich in aluminum. It is also characterized by the presence of carbide deposits of different colors, dark brown, light brown, and light yellow, which are affected by the type of rendering solution used.

It must be remembered that the alloy used in the research is iron-based, and its coating with aluminum leads to the formation of one of the phases of intermediate compounds (iron-aluminum), and this has already happened. The results of XRD analysis revealed many complications in terms of the number of resulting phases, but they confirmed the formation of The aluminum-rich phase \(\text{Fe}_2\text{Al}_5\) is mainly in the coatings produced after the 4 times 2; 4; 6 and 8 hours, and this indicates that the primary phase formed

It does not change with the increase in the coating time, but only changes with the change in temperature, the concentration of the powder coating or the composition of the base alloy, and this has been confirmed by recent research \(^{28, 29}\).
Figure 5. Microstructure of the samples coated with a single-phase (alluminization only) at a temperature 1000 °C for 2 and 8 hour periods

Table 3 shows the results of the X-ray diffraction analysis of the coated sample for a period of 8 hours as was shown from the diffraction model, Fig.6, the appearance of peaks of intermediate compounds belonging to phases (iron - aluminum) such as FeAl, which appeared mainly and Fe₄Al₃ with strong peaks, but there are a number of weak peaks that indicate the existence of what is believed to exist. It is the phase Al₂Cr, and the analysis confirmed the presence of peaks for intermediate compounds belonging to (aluminum - nickel) such as NiAl and NiAl₃, and by returning to the phase diagrams for both systems (iron - aluminum), and (aluminum - nickel), Fig.6, we find that such phases are possible to form at this temperature.

Table 3. X-ray examination results (XRD) for a sample coated at 1000 °C for 8 hours.

<table>
<thead>
<tr>
<th>Phase type</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeAl</td>
<td>Vs</td>
</tr>
<tr>
<td>Fe₄Al₃</td>
<td>Vs</td>
</tr>
<tr>
<td>NiAl</td>
<td>S</td>
</tr>
<tr>
<td>NiAl₃</td>
<td>S</td>
</tr>
<tr>
<td>Al₂Cr</td>
<td>Vw</td>
</tr>
<tr>
<td>Vs = very strong</td>
<td>W = weak</td>
</tr>
<tr>
<td>S = strong</td>
<td>Vw = very weak</td>
</tr>
</tbody>
</table>

The results of the analysis of the electronic scanner device (SEM-EDS) for the coating layer with a magnification of 500nm, and as shown in Fig. 7, showed a homogeneous spread of aluminum, which covers the coating layer almost, and this is confirmed by Fig. 8, spectroscopic analysis of the EDS, as we note that there is There are many peaks for the elements, including aluminum, iron and chromium, and the highest intensity of these peaks is the element aluminum, which represents the basic element for the coating layer, and this is what appeared in the data of Table.3 for quantitative and qualitative analysis by the scanning electronic device (SEM-EDS), as the percentage of aluminum was equal to 28.02 wt% and iron 12.72 wt%, and this supports the analysis of XRD spectrum in obtaining the intermediate compounds of iron - aluminum, as well as obtaining some intermediate compounds of chromium - aluminum, with a weight ratio of 3.43 wt% of chromium.

Figure 6. X-ray diffraction plot of a sample coated with aluminum at 1000 °C for 8 hours
Figure 7. Microscopic structure by scanning electron device (SEM) of austenitic stainless steel (AISI-304) alloy coated with single aluminum for 6hr at 1000 °C.

Table 4. Details the weight and qualitative ratios of austenitic stainless steel alloy (AISI-304) coated with single aluminum for a period of 6hrs at a temperature of 1000 °C.

<table>
<thead>
<tr>
<th>Elt</th>
<th>Line</th>
<th>Int</th>
<th>Error</th>
<th>K</th>
<th>Kr</th>
<th>W%</th>
<th>A%</th>
<th>ZAF</th>
<th>Pk</th>
<th>LConf</th>
<th>HConf</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Ka</td>
<td>66.1</td>
<td>159.114</td>
<td>0.0088</td>
<td>0.0068</td>
<td>6.10</td>
<td>18.08</td>
<td>0.1109</td>
<td>52.56</td>
<td>5.82</td>
<td>6.37</td>
</tr>
<tr>
<td>F</td>
<td>Ka</td>
<td>0.0</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.00</td>
<td>0.00</td>
<td>0.2351</td>
<td>97.68</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Ni</td>
<td>Ka</td>
<td>74.9</td>
<td>159.114</td>
<td>0.0103</td>
<td>0.0079</td>
<td>5.14</td>
<td>9.08</td>
<td>0.1545</td>
<td>49.90</td>
<td>4.93</td>
<td>5.36</td>
</tr>
<tr>
<td>Al</td>
<td>Ka</td>
<td>129.0</td>
<td>598.733</td>
<td>0.0185</td>
<td>0.0143</td>
<td>3.01</td>
<td>3.97</td>
<td>0.4740</td>
<td>29.53</td>
<td>2.91</td>
<td>3.10</td>
</tr>
<tr>
<td>Si</td>
<td>Ka</td>
<td>194.3</td>
<td>598.733</td>
<td>0.0283</td>
<td>0.0218</td>
<td>2.70</td>
<td>4.56</td>
<td>0.6060</td>
<td>36.08</td>
<td>3.50</td>
<td>3.69</td>
</tr>
<tr>
<td>P</td>
<td>Ka</td>
<td>126.5</td>
<td>598.733</td>
<td>0.0187</td>
<td>0.0144</td>
<td>2.12</td>
<td>2.43</td>
<td>0.6818</td>
<td>19.98</td>
<td>2.05</td>
<td>2.18</td>
</tr>
<tr>
<td>S</td>
<td>Ka</td>
<td>1246.4</td>
<td>598.733</td>
<td>0.1879</td>
<td>0.1446</td>
<td>18.50</td>
<td>20.55</td>
<td>0.7816</td>
<td>33.62</td>
<td>18.31</td>
<td>18.69</td>
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<tr>
<td>Cl</td>
<td>Ka</td>
<td>116.2</td>
<td>598.733</td>
<td>0.0178</td>
<td>0.0137</td>
<td>1.92</td>
<td>1.93</td>
<td>0.7162</td>
<td>6.86</td>
<td>1.85</td>
<td>1.98</td>
</tr>
<tr>
<td>Ca</td>
<td>Ka</td>
<td>154.2</td>
<td>83.3317</td>
<td>0.0251</td>
<td>0.0193</td>
<td>2.07</td>
<td>1.84</td>
<td>0.9320</td>
<td>9.37</td>
<td>2.01</td>
<td>2.14</td>
</tr>
<tr>
<td>Y</td>
<td>Ka</td>
<td>195.4</td>
<td>83.3317</td>
<td>0.0332</td>
<td>0.0256</td>
<td>3.65</td>
<td>2.05</td>
<td>0.9291</td>
<td>10.83</td>
<td>2.68</td>
<td>2.83</td>
</tr>
<tr>
<td>Cr</td>
<td>Ka</td>
<td>786.6</td>
<td>83.3317</td>
<td>0.1401</td>
<td>0.1078</td>
<td>11.13</td>
<td>7.62</td>
<td>0.9683</td>
<td>33.50</td>
<td>10.98</td>
<td>11.27</td>
</tr>
<tr>
<td>Mn</td>
<td>Ka</td>
<td>403.1</td>
<td>83.3317</td>
<td>0.0735</td>
<td>0.0565</td>
<td>6.24</td>
<td>4.05</td>
<td>0.9060</td>
<td>20.69</td>
<td>6.13</td>
<td>6.35</td>
</tr>
<tr>
<td>Fe</td>
<td>Ka</td>
<td>2276.4</td>
<td>83.3317</td>
<td>0.4251</td>
<td>0.3271</td>
<td>36.33</td>
<td>23.17</td>
<td>0.9003</td>
<td>98.60</td>
<td>36.1</td>
<td>36.61</td>
</tr>
<tr>
<td>Co</td>
<td>Ka</td>
<td>65.8</td>
<td>83.3317</td>
<td>0.0126</td>
<td>0.0097</td>
<td>1.10</td>
<td>0.66</td>
<td>0.8810</td>
<td>8.17</td>
<td>1.05</td>
<td>1.15</td>
</tr>
</tbody>
</table>

Fig. 9, shows the oxidation and hot corrosion of the single aluminum alloy coating for the periods of time hr 2, 4, 6, 8 and from the observation of the time chart with the change of weight, we note the continuation of the weight stability and the approximate non-decrease especially for the coating for a period of hr (6, 8) Until after the 200 hr and the tests showed that the coating layer, especially at 8 hr, proved good efficiency in resisting hot corrosion, and this indicates that the protective oxide crust Al₂O₃ did not fall off and that it had good adhesion. As for the other coating hours, the weight started to decrease slightly with the cycles Thermal and to the end of exposure compared with the uncoated alloy, which collapsed after the first hours of the thermal cycles. As for the painted alloy, the slight decrease in weight is due to the formation of the unstable oxide Al₂O₃, which is formed during the transitional oxidation before the formation of the protective oxide crust Al₂O₃ which was formed during the thermal cycles, and the rates of weight loss were not more than 0.1657 gm. After more than 200 hr have passed, and the laboratory test indicated that the model still had good adhesion.
Conclusions:
In this research, a new alloy was produced that differs from the parent alloy by adding the element Aluminum to its surface components through surface engineering and by a diffusion coating method. By studying the kinetics of oxidation and hot corrosion of the Aluminizing sample for the time periods of 2, 4, 6, 8, hours, it was found that the best model is the Aluminizing model at the time of 8 hours, as it was highly efficient in resisting oxidation and corrosion Heat, at high temperatures and in an atmosphere containing the vapor of a mixture of sodium chloride and sodium sulfate. By monitoring the weight loss, this model continued to maintain its weight for a very long time, lasting up to 200 hours, compared to the rest of the models. As for the Aluminizing model for a period of 6 hours, it was less efficient than the first, but it is also considered to be highly efficient, and then a time of 4 hours and 2 hours, respectively.

Overall, for the above, this modified alloy is considered an alloy with very high efficiency in resisting the harsh operating conditions of engineering equipment and can be used in equipment used in gas turbine and power plants.

Acknowledgement:
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Authors' declaration:
-Conflicts of Interest: None.
-We hereby confirm that all the Figures and Tables in the manuscript are ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.
-Ethical Clearance: The project was approved by the local ethical committee in department of Environmental Engineering, University of Mosul.

Authors' contributions statement:
T. M., designed the study. He conducted research experiments and data analysis. T. M. and M. A. contributed to the design and implementation of research and analysis from the results and writing the manuscript.

Reference:


التعديل السطحي لسبيكة الفولاذ المقاوم للصدأ AISI-304 كفاءتها في مقاومة التآكل الحر في جو بخار كلوريد الصوديوم (NaCl) وكبريتات الصوديوم (Na2SO4) واستخدام الطلاء الانتشاري ودراسة كفاءتها في مقاومة التآكل الحر في جو بخار كلوريد الصوديوم (NaCl) وكبريتات الصوديوم (Na2SO4).

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الخلاصة:
يهدف هذا البحث إلى تحديد مكونات سبيكة الفولاذ المقاوم للصدأ بطريقة هندسة السطح من خلال تقنية الطلاء الانتشاري المنفرد بغية الحصول على سبائك جديدة ذات كفاءة عالية في مقاومة الظروف الاحترافية. وفي هذا البحث استخدمنا اختبار قاسي لهذه السبائك المنتجة وهو عملية التآكسد في درجات حرارة عالية وفي جو بخار خليط من كلوريد الصوديوم (NaCl) وكبريتات الصوديوم (Na2SO4) في درجة حرارة 900 °C. ومن ثم مقارنتها مع السبيكة الأساسية. وقد أظهرت النتائج أن السبائك المنتجة بهذه الطريقة ذات كفاءة عالية جداً. وعملت هذه الطلاء بحسب نمط الطلاء اللون االألمنة أظهر كفاءة عالية في مقاومة التآكسد ووفر حماية أفضل ولوقت أطول للمقارنة مع السبيكة غير المطلية التي تكون ذات الاحترافية. وقد اظهرت هذه الطلاء ازتيأض جودة الطلاء الحديدي، وكذلك اظهرت النتائج ان سمك الطلاء والوزن المكتسب للسبيكة يخضع لعلاقة قطعية مع الزمن.

الكلمات المفتاحية: الطلاء الانتشاري، الاصدأ في درجات الحرارة عالية، التآكسد الحديدي، علاقة القطع المكافئ، هندسة السطح.