Improvement of wear and corrosion resistance of carbon steel by hot dip aluminizing coating

Said Sifau  Musa Gaied  Musa Aburass
Higher institute of science and technology, Jadu, Libya.
Saidisifau00@gmail.com  m.gaid@yahoo.com  Mosa12131415@gmail.com

الملخص
تهدف هذه الدراسة لتحسين مقاومة البلي والتآكل للصلب الكربوني بواسطة الطلاء بالغمر على الساخن في مصهر الألومنيوم. وهي تدرس تأثير اختلاف زمن الغمر ودرجات الحرارة المختلفة على البنية المجهرية والصلادة للعينات المغطاة بالألومنيوم. تظهر النتائج أن ارتفاع درجة حرارة الانتشار ينتج سطح مسامي وأقل زمن غمر أظهر انخفاض في عمق الطبقات للحالات المدرسة. وقد أكدت الدراسات بالألمنة (Aluminizing) وجود aluminides في الطبقة السطحية، والتي يمكن أن تساهم بزيادة كبيرة في صلابة السطح. ويمكن استخدام هذه المكونات في التطبيقات الصناعية وغيرها من التطبيقات الهندسية. مقاومة البلي درست استثنائياً وتحقيق هذه المتغيرات، تم إنتاج طبقة الألومنيوم بواسطة درجات حرارة غمر مختلفة (700، 800 و 585 درجة مئوية) وزمن (15، 30، 45، 60 و 90 ثانية). التفتيش البصري (المظاهر البصرية)، قياس سمك الطلاء، صلابة الطلاء، ودرجة الخشونة، للفولاذ منخفض الكربون المصلب. أظهرت النتائج أن ظهور العديد من العيوب السطحية تحت الظروف (700، 750 درجة مئوية) وزمن 15 و 30 و 45 ثانية) على التوالي، بينما كانت النتائج جيدة في درجة 850 درجة مئوية وزمن 90 ثانية على التوالي. تزداد سماكة طبقة الطلاء والصلابة مع زيادة
Abstract:
This study aims to propose an analysis to improve wear and corrosion resistance of carbon steel by hot dip aluminizing coating. It investigates the effect of varying dip times at different diffusion temperatures on the microstructure and micro-hardness of aluminized and diffused specimens. The results show that a higher diffusion temperature yields porous surface and lower dip time showed a thin layer of case depth. Aluminized and diffused studies have confirmed the presence of aluminides in the surface layer, which could be instrumental in the significant increase in surface hardness. This could be used for components in automotive and other engineering applications. Wear resistance is considered critical. To achieve these variables, the aluminum layer coat was produced by different immersion aluminizing temperature (700, 750, 800 and 850 °C) and time (15, 30, 45, 60, 90 and 120 sec) visual inspection (visual appearance), coating thickness measurement, coating hardness, and degree of roughness, and aluminized low carbon steel. The results of appearance showed many defects on the surfaces in condition (700, 750 °C and aluminizing time 15, 30 and 45 second) respectively, while good appearance was noted in condition at aluminizing temperatures 850 °C and aluminizing time 90 &120 seconds, respectively. Coating thickness and coating hardness were increased with an
increased aluminizing temperature and time. It has also been noted that the aluminizing temperature is more effective than aluminizing time. The immersion speed is respected: while fast immersion product pulped on the surface, slow drawing shows homogeneity surface coating.

**Keywords:** Aluminizing, hot dipping, aluminizing coating, Carbon steel, Surface coatings, Corrosion resistance, Wear resistance.

1. **INTRODUCTION**

   It is widely held that most metallic surfaces, that are exposed to natural environments without protection, will react to constituents in the environment to form corrosion products. This process is affected by many variables such as composition, physical state, and surface condition of the metallic material as well as the chemical component of the surrounding medium, their phases and concentrations determine the nature of corrosion reactions. On the other hand, important variables affecting corrosion process include temperature, temperature fluctuations, movement or circulation of the medium in contact with the metal surface and impurities [1, 2]. Surface modification by coatings has become an essential step to improve the surface properties such as resistance to wear, corrosion and oxidation. Various conventional techniques are utilized for depositing the desired material onto the substrate to achieve surface modification [3-5].

   Several scholars opine that “Steel and its alloys are the most common metals that are aluminized for commercial applications” [6]. This is due not only to their excellent mechanical properties and ease of Kelvinfabrication but also to their relative cheapness.
because of the wide availability of suitable ores and the ease of extraction. However, in most environments, the corrosion resistance of iron is low compared to most other metals. This is so because of a number of factors including the ease with which cathodes reactions can proceed on its surface. This gives rise to the readiness with which concentration cells are formed and the poor protection is afforded by corrosion products \[7\].

Aluminum coating provides steel with excellent oxidation and corrosion resistance and also with reasonable scaling resistance \[5\]. Several techniques can be used to obtain a layer of aluminium over a steel surface on a commercial scale. The most important of such techniques are electrolytic \[8, 9\], cladding\[10, 11\], pack \[12, 13\], sol-gel \[14, 15\], spray (metalizing) \[16-18\] and hot-dip aluminizing \[19-21\]. Hot dip aluminizing is one of the most widely used processes for coating steel with aluminum to increase corrosion and oxidation resistance as well as hardness \[6, 22-24\].

Most commercial hot dipped aluminum coated steel strip is produced on continuous anneal-in-line equipment similar to that used for galvanizing. The process consists essentially of three operations: surface preparation, heat treatment of the steel base, and aluminum coating. Also the conversion coatings of carbon steel is not sufficient for critical applications. Therefore, aluminizing technique is used instead of the preventing techniques which satisfies the optimum coating condition in corrosion environments \[25, 26\].

Successful application of aluminum coated steel for resistance to oxidation and corrosion at elevated temperatures depends on the physical and mechanical properties of the alloy chemical bond between the aluminum and steel. It is important also that the hot
strength of the steel is suitable for the stress and temperatures encountered [27, 28].

This study attempts to improve the surface hardness of carbon steel by surface alloying with aluminum through diffusion. It will also evaluate the optimum of the variables effecting hot dip aluminizing processes (time, temperature, speeds of drawing and emersion) to improve corrosion resistance of carbon steel. This has consistent of quality of coating of carbon steel to meet specific requirements such as degree of roughness and brightness.

2. EXPERIMENT

2.1 Materials
The low carbon steel used in this study was produced locally at Libyan steel company with chemical composition (all are in wt. %) C 0.130-0.140%, N 0.008%, P 0.006%, S 0.012, Ni 0.017%, Cr 0.028 and Si 0.100%. The Chemical Composition results were obtained by analyzing the specimens using the spectrum analysis technique, and carried out by Casting and Manufacturing Centre. The Chemical Compositions of the aluminum blocks (89% AL, 11% Si wt. %) were used to aluminize the steel.

The Chemical Composition of the aluminizing flux used ZnCl₂ 68%, NaCl 20% and NH₄Cl 12%, all are in wt. %. The temperature of the flux was kept at about 350 °C, which is higher than the melting temperature of the flux (320 °C). This flux was added to the molten aluminum bath, stirred in thoroughly and then the surface was skimmed off. The pre-immersion sample (in molten aluminium) was applied to the cleaning flux to reduce atmosphere. The Chemical Composition of cleaning flux was LiCl 44%, NaCl 30%, NaF 16.7%, and KCl 9.3% all are in wt. %.
2.2 Sample Preparation for Aluminizing

A total of 24 samples were prepared to cover the experiment variables mentioned in the previous section. All specimens were divided into 24 conditions according to their adopted type of aluminizing variables, and used in each condition of aluminizing temperature and time.

The samples chosen were cut from steel sheets about 3 mm. thick. The sample dimensions were taken as the standard corrosion coupons. (81x22x3 mm³) a hole whose radius was 2.5 mm. was drilled off near one end by using computer numerical control (CNC) machine that was used for each process, to achieve the requirements of work. These samples were mechanically and chemically cleaned as can be seen in figure 1.

![Sample shape used in this work.](image)

All samples were prepared from the actual production item and numbered (marked) for identification as test samples, based on the designation and conditions. The aluminizing temperatures are 700, 750, 800 and 850 °C; however, the aluminizing time between 15 to 120 seconds. The samples were designated based on aluminizing time, aluminizing temperature, and the sample number as illustrated in table (1). For example, the sample in the
Table 1: Sample Designation and aluminizing Conditions

<table>
<thead>
<tr>
<th>No.</th>
<th>Aluminizing Time (sec)</th>
<th>Aluminizing temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>700</td>
</tr>
<tr>
<td>1</td>
<td>15</td>
<td>A1</td>
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<tr>
<td>2</td>
<td>30</td>
<td>A2</td>
</tr>
<tr>
<td>3</td>
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<td>A3</td>
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<td>A4</td>
</tr>
<tr>
<td>5</td>
<td>90</td>
<td>A5</td>
</tr>
<tr>
<td>6</td>
<td>120</td>
<td>A6</td>
</tr>
</tbody>
</table>

2.2 Aluminizing process
The samples were mechanically cleaned by surface grinder to remove scales and flatten the surfaces, followed by aluminizing process which consists of different steps to achieve the requirements in this work. The steps are grinding, pickling, rinsing, cleaning flux, aluminizing by hot dip process (in different temperature and time), rinsing in water and drying.

2.3 Sample characterising examination
The specimens used for measuring the coating thickness and micro-hardness were small sections mounted in order to permit convenient handling during grinding and polishing. The surface of the mounting samples is ground using emery papers of various
grades of fineness and polished by cloth fibers supported on lapping wheel. When the surface becomes flashing, it is then cleaned by water and alcohol and carefully dried to be clearly visible under the microstructure examination and the micro-hardness tester. The measurement methods were carried out to study the main variables of hot dip aluminizing on low carbon steel (temperature and time of aluminizing).

2.3.1 Visual examination
At the end of each experiment, the samples were taken from the molten bath, and visually inspected, photographed and reported for discussion. All these specifications were according to International Standards for Organization (ISO) \[29\].

2.3.2 Coating thickness measurements
A metallurgical microscope (S.E.M) scan electron microscope type signal (S.E.I) detector was used in the laboratory for measuring the thickness of the intermetallic layer. Then, a microstructure of samples was examined under 500 X magnification coatings, applied by hot dip aluminizing. This is designed to protect the iron and steel products against corrosion. The length of time of corrosion protection by such coatings (whether light or dark grey) is approximately proportional to the coating thickness. For extremely aggressive conditions and/or an exceptionally long service life, thicker coatings, than those specified here, may be required. The thickness of intermetallic layer for each sample is measured in the laboratory. The average of 3 readings were taken for each thickness measurement.
2.3.3 Scanning Electron Microscopes Examination

To scan specimen surface and to image one point at each time, a focused beam of electrons has been used for the examination of such factors. Morphology analysis of coated samples was performed using scanning electron microscope.

2.3.4 Microhardness measurements

The general specifications of this equipment are to measure the microhardness of metals under operating loads ranging from 5 to 1000 gm. The magnifications of the microscope are 600 x (40 x objective, 15x Eyepiece) and 90 X (6X objective, 15X Eyepiece), measurements Eyepiece graduation 1 u (0.001mm) and guaranteed accuracy 0.5u (0.005 mm). The types of indenters are Diamond Pyramid Hardness (DPH) and Knoop hardness numbers (KHN). A range of light loads using a diamond indenter to make an indentation was specified by the microhardness test procedure. It is then measured and converted to a hardness value. This work is carried out according to standards[30].

3 Results and Discussion
3.1 Visual inspection

Through aluminizing process which was conducted on the samples, as explained in the experiment, under aluminizing temperature between 700, 750, 800 and 850 °C, with varying aluminizing time 15,30,60,90 and 120 seconds. The test samples were taken out from the bath and rinsing in water, and dried at room temperature, then immediately visually inspected and photographed. Presence of aluminizing coating, clear change in appearance between the sample and remarks where then reported for further discussion for each group.

Samples A1, A2 and A3 of group A was aluminizing at 15, 30 and 45 sec, and showed poor layers formed of aluminum coating on
surface. Also, the dark spots were visible to naked eye, and the samples A4, A5 and A6 got aluminized at time 60, 90 and 120 sec, and showed the layer formed and the brightness start present. Samples 1, 2 and 3 of group B and C were aluminizing at 15, 30, 45 sec showed uncoated area, and non-uniformly colored and some of smuts on its surface, as can be seen in the above samples. While samples B4, B5, B6, C4 and C5 show dull luster appearance and low degree of brightness on its surface, sample C6 was seen as more bright and more uniform. On the other hand, regarding the results of group D that are aluminized at 850 °C and various aluminizing time, the sample showed a change in its surface coating, compared to the first steps to light and more light-grey without any defected surface.

The Sample D1 illustrates the change in color and brightness compared to the other surfaces in the first tree conditions in same time which is more uninformative and no uncoated area no defect appear. The Sample D2 which aluminizes at 850 °C for 30 sec showed more uniformity of appearance in its surface with other samples in same immersion time, also it has light silver color. As can be seen in figure 2, sample D3, i.e., the surface sample, has some slouches on the end. Sample D4, in figure 2, showed less uniformity with dark silver color. Continuous and free from uncoated area was seen. Sample D5 was dull luster darker. Sample D6 aluminizing at 850 °C for 120 sec showed more uniformity of appearance in its surface than other samples in same immersion time, also it has light silver color, and more homogeneity in surface coating. That means the better condition was seen from visual examination.
Figure 2 Results of steel strips coating on surface hot-dipped aluminizing for each group at different temperatures: group (A) 700 °C, group (B) 750 °C, group (C) 800 °C and group (D) 850 °C. The immersing time in molten aluminum for each group was 15, 30, 45, 60, 90 and 120 sec respectively.

The specified requirements for appearance in aluminizing coating on low carbon steel lie in being continuous, free from gross imperfection, free from sharp points, free from uncoated areas, relatively smooth, uniform in texture and distributed. The above remarks are important visual examination for hot dip aluminizing
products. The results that have been taken for samples after aluminizing process within different temperature and time showed poor coating on their surface. This is so because the temperature is below the minimum recommended temperature which doesn’t reflect the reaction that occurs on the interface between the steel and molten aluminum and which reflects formation of the diffusion layers.

3.2 Coating thickness measurements
During the aluminizing by hot dipping, diffusion between the aluminum bath and the steel sheet brought about an intermetallic reaction. The phases that are formed within the intermetallic layer as well as their thicknesses are important to determine the behavior of the coating. Moreover, hot dipping was conducted in a commercial purity aluminum bath and used low carbon steel sheets [4]. The temperatures used for hot dipping were 700, 750, 800 and 850°C and the immersion times were 15, 30, 60, 90 and 120 sec. The results indicate that the thickness of the intermetallic layer increases with increasing bath temperature and immersion time. The coating thicknesses were monitored by the condition of the surface and speed of immersion and withdrew the sample from the bath as well as the aluminizing time and temperature. The adhesion of aluminum to low carbon steel as substrate metal varies with the type and thickness of the coating. The large thicknesses have coarse grains of crystal, which form weak bonds to the substrate.

Results of samples showed poorer quality of coating thickness that was aluminized by immersed molten aluminum at 700 and 750 °C, due to the poor aluminizing coating.
Table 2  The thickness of diffusion layer as a function of dipping time

<table>
<thead>
<tr>
<th>Exposure Temperature °C</th>
<th>Exposure Time in sec</th>
<th>Average thickness of diffusion layer in µm</th>
</tr>
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<tbody>
<tr>
<td>700</td>
<td>15</td>
<td>25.7</td>
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<tr>
<td></td>
<td>30</td>
<td>34.8</td>
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<td>42.2</td>
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<tr>
<td></td>
<td>90</td>
<td>66.6</td>
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<tr>
<td></td>
<td>120</td>
<td>115.6</td>
</tr>
<tr>
<td>750</td>
<td>15</td>
<td>31.4</td>
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<tr>
<td></td>
<td>30</td>
<td>37.3</td>
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<tr>
<td></td>
<td>60</td>
<td>49.6</td>
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<td>800</td>
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<td></td>
<td>30</td>
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<td>45</td>
<td>59.7</td>
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<td>114.4</td>
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<td></td>
<td>120</td>
<td>128.8</td>
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</tbody>
</table>

The coating thickness increases as the aluminizing temperature and time increase. Moreover, the sample aluminized was affected by temperature at about 800 and 850 °C, at time 90 and 120 sec having thick layers, and good adhesion between aluminum and steel, being satisfactory thick. In other words, the trend of this data approached to the standards and specifications.

3.3 Scan Electron microscope examination

When solid iron is in contact with molten aluminum, inter-diffusion of Fe and Al takes place at the interface, resulting in the
formation of a diffusion layer in each of the two metals. The two metals rise in the iron content of the aluminum, Fe-Al alloys is formed. Based on the binary phase diagram [31]. According to this diagram, the expected phases are FeAl₃, Fe₂Al₅, FeAl₂, Fe₄Al₅ and Fe₃Al [32-35].

During a short initial period of immersion, the temperature in the near vicinity of the specimen drops, as a result of which the compound formed ceases to grow into the melt and is more or less arrested on the specimen surface. At the same time, a solid solution of aluminum rapidly is formed in the iron. A weak adhesion but in another type the fine surface produced by fine-grain coating results from diffusion of the aluminum in steel surface to produce compounds of aluminum and ferrous. The FeₙAlₘ phase formed during the reaction between molten aluminum and solid iron occurs in the form of tongue-shaped areas. This was found to be true in this investigation as demonstrated in figure (4 a, b).

Figure (4) Optical light micrographs of FeₙAlₘ phase forming during the reaction between molten aluminum and solid iron occurs in the form of tongue-shaped areas: (a) sample D5 at 850°C and 90 sec (b) sample D6 at 850 °C and 120 sec.
The result of diffusion layer is invariably serrated on the iron side when the basis has bcc-Fe lattice, but it has straight boundaries when the reaction is between aluminum and iron in the form of FCC-Fe or an alloy containing such iron. Since aluminizing temperatures used were lower than that temperature at which the -phase of such steel is stable, the straight boundaries were not observed.

3.4 Microstructure examination

For microstructure examination, the microscopic cross-section method could be used. However, it should be noted that this method is not appropriate for routine use on large or expensive articles for being destructive. It also relates only to a single line giving a simple visual picture of the line to be examined.

Figure (5) Cross-section microstructure of aluminized layer at: (a) 700 °C and 30 sec (b) 750 °C and 45 sec (c) 800 °C and 90 sec and (d) 850 °C and 120 sec.
Various views have been expressed on the composition of FeₐAlₘ, considering it to be FeAl₃. The brittleness of the diffusion layer was ascribed to the presence of FeAl₃. In case of low-carbon steel, FeAl₃ or Fe₂Al₅ is the principal compound; the composition of the diffusion layer corresponds to Fe₂Al₅, and micro-hardness was about 900. For this purpose, the thickness of the diffusion layer was measured as a function of dipping time while the dipping temperature was kept constant at one of the following temperatures, 700, 750, 800 and 850 °C, as shown in figure (5a to 5d). However, the relation between diffusion layer thickness and time is linear.

3.5 Micro-hardness measurements

The Al content in an aluminized sample normally decreases from the outer surface inwards. All the intermetallic compounds predicted by the phase diagram may be present. However, the amount of each phase may not be substantial to show its characteristic micro-hardness as example sample A1 at 700°C and 15 as can be seen in figure 6. On the other hand, aluminizing at 850°C for 120 sec indicates that Fe₂Al₅ is present in substantial amount near the surface of the specimen.

Figure (6) Sample A1 Hardness distribution from surface to steel substrate immersed
As Figure 6 illustrates, in the case of dipped condition, the surface hardness of aluminized layer was found to be low, i.e. around 50-200 HV. It is also clear that the surface hardness of the low carbon steel increased to a maximum of 1000 HV after the diffusion process was completed. This is due to the pick-up process of aluminum during aluminizing and formation of Fe-Al complex layer during diffusion. The lower dip time (15, 30 sec) sample yielded the increased hardness at the near surfaces whereas the high dip time extended its increased hardness towards the core material. The specimen dipped for 90 and 120 sec showed the increased hardness case depth of about 200 μ from the surface. However, at high temperature diffusion 850°C, the surface showed the non-porous structure, probably arising from the oxidation. At higher diffusion temperature of 850 °C, the case depth was found to be high due to the non-porous layer. At lower diffusion temperature 750 °C, the case depth was around 170-190 μ with less porous layer. The specimens aluminized at 800 and 850°C may be chosen as a diffusion temperature and 120 sec as a dip, considering a non-porous surface and the increased case depth.

The thickness along with aluminum content in the Fe–Al alloy layer after etching the samples of the aluminized steel. The microstructure of the Fe–Al alloy layer and the base metal have been vividly displayed [36]. This analysis supports analysis conducted by [36] in which the thickness of the Fe–Al alloy layer on the surface of the hot dip aluminized steel was about 140 μm. The present analysis also supports [36] in that “The variation of the micro-hardness value in the Fe–Al alloy layer was large” which indicates “that the phase structure and performance in the
Fe–Al alloy layer also varied accordingly”. A micro-hardness test has been used to measure The Fe–Al alloy layer’s micro-hardness from surface to the inside. The results obtained from this test showed that the micro-hardness was lower (HV 130 ~ 250), and the sub-surface layer’s micro-hardness was higher (about HV490 ~ 860) [36].

4. CONCLUSIONS
To conclude, the study at hand proposes an analysis to improve the wear and corrosion resistance of carbon steel by hot dip aluminizing coating. The surface of steel base was modified through diffusion of aluminum by hot dip aluminized, for improving wear and corrosion resistance. The results obtained allow to propose the optimum variables, hot dip aluminizing temperature and time that can be applied on the surface of low carbon steel. The results were satisfactory in aluminized time and temperature at 850 °C and time 90 and 120 sec with no effect as pitting or scratches appearing on surface of coating. However, in another condition there was some damaged area on surface. That is to say, the reaction between the molten aluminum and substrate doesn’t occur. The aluminum-iron alloys are particularly hard areas which can be subjected to severe abrasion. Areas under coarse gravel are subjected to severe erosion by impact and abrasion. The good bond between aluminum coatings and steel (particularly in hot dip aluminizing where there is an alloying reaction) helps to limit such effects. On the other hand, the produced hot dip aluminizing layer has a range of coating thickness depending on the aluminizing time and temperature. This allows to propose the optimum variables depending on the need of applications.


