Hydrothermal blackening on AISI 4140 steel with and without hydrazine hydrate

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Abstract. The blackening coating is a conversion coating with the black colour of crystallised magnetite (Fe₃O₄) on the surface of steel. The coating is to be soaked with oil or wax to prevent the corrosive environment. Recently, the technique to synthesise the black coating, hydrothermal method is introduced. In the synthesis process, hydrazine hydrate (N₂H₄·H₂O) is often recommended as a catalyst but it is also reported toxicity. In this work, AISI 4140 was hydrothermally immersed in the FeSO₄·7H₂O added NaOH solution with and without addition of hydrazine hydrate. During the process, the temperature and pressure of the chamber were controlled at 140°C and 2 bar, respectively. To confirm the formation of Fe₃O₄, the samples were characterised by SEM and XRD. These results showed that the coatings were composed of octahedron morphology in all conditions and the thicknesses of the coating with hydrazine hydrate concentration of 0.0, 0.1, and 0.5M were 7.05, 9.25, and 8.75 µm, respectively. With hydrazine hydrate, the Fe₃O₄ layer can be easily formed. However, the results of the oxalic acid spot test and potentiodynamic polarisation indicated the equivalence in quality of the coating, despite the absence of hydrazine hydrate.

1. Introduction

Blackening is a process to convert the surface of steel to be the crystallised magnetite (Fe₃O₄) of which the aesthetic black colour is shown. The oxide surface is expected to be passive and prevents the steel substrate from the corrosive environment. In general usage, oil or wax is further applied to the coating to enhance the corrosion resistance [1]. To dates blackening practically exhibits effectiveness in various applications with low cost and long life time of service.

The conventional blackening process is done in hot alkaline consisted sodium hydroxide (NaOH) with temperature range of 140-150°C. Some oxidizing agents, such as sodium nitrite (NaNO₂) and sodium nitrate (NaNO₃) are added in the solution to accelerate the chemical conversion and lower the process temperature [1]. Recently, the mixing solution which consisted ferrous sulphate hydrate (FeSO₄·7H₂O), NaOH and hydrazine hydrate (N₂H₄·H₂O) has been proposed for blackening, and the higher pressure than the atmospheric pressure is applied to lower the concentration of the chemicals in the solution [2, 3]. This blackening is called the hydrothermal method.
Nevertheless, according to the material safety data sheets, most of the oxidizing agents such as NaNO₂, NaNO₃, and N₂H₂·H₂O are harmful, especially in vapour phase they tend to be toxic. Therefore, the solutions which comprised ferrous sulphate hydrate (FeSO₄·7H₂O), NaOH with or without hydrazine hydrate were studied for the hydrothermal blackening in order to reduce the usage of hydrazine hydrate. The formation of magnetite on a steel substrate with and without N₂H₂·H₂O was analysed by microstructural characterisation. Lastly, to assure the quality of the black coating, the corrosion behaviours in terms of the oxalic acid spot test and potentiodynamic polarisation were investigated.

2. Material and experimental producer

For study of the magnetite formation, AISI 4140 steel of which the chemical composition was Fe with 0.43C-0.22Mn-0.82Si-0.20 Mo-0.006 P in wt.% was used as a substrate for blackening. The sample size was 3.0x1.2 cm² prepared from a 2-mm thick steel sheet by laser cutting. Each sample was perforated a hole with a diameter of 3 mm on the center top for suspension as immersed into the process solution. Before blackening, surface finishing of all samples was done by grinding with SiC sandpapers up to 1,000-grit number. Then the samples were cleaned in acetone with an ultrasonic bath and dried in air.

For blackening, the hydrothermal blackening solution was based on 0.1M ferrous sulphate (FeSO₄·7H₂O), 1.0M sodium hydroxide (NaOH) and hydrazine hydrate (N₂H₂·H₂O). The effect of hydrazine hydrate was investigated by varying the concentration of hydrazine hydrate to be 0.0, 0.1, and 0.5M. Those three conditions of reagents were dissolved in deionised water with magnetic stirring. After completing the solution, the steel samples were suspended and immersed in the blackening bath and they were subjected in an autoclave chamber. The temperatures and pressure of the autoclave were controlled at 140°C and 2 bar, respectively. The coating time is 30 min for all samples.

After blackening, the samples were investigated on characterisation and corrosion resistance. For the characterisation, the surface and cross-sectional morphology were analysed using a scanning electron microscopy (SEM), JEOL JSM-7800F. An X-ray diffractometer (XRD), D8 Discovery, Bruker, with Cu Kα (α = 1.5406 Å) radiation was performed to identify the oxide phases formed on the steel surface. The diffraction angles measured from the studied samples was matched with the standard XRD patterns summarised by the International Centre for Diffraction Data (ICDD).

The standard MIL-DTL-13924D test or the oxalic acid spot test was performed after blackening to guage the surface quality of blackening steel in acid media. The samples with the size of 4.0x3.5 cm² were introduced. This test was done by 3 drops (0.2 mL) of a 5% oxalic acid solution dropped on surface of blackening steel. The reacted surface with oxalic acid can be observed after 5 min then it will be rinsed and compared. Then the potentiodynamic polarisation testing was performed to confirm the corrosion resistance at room temperature in 3.5% NaCl solution. The apparatus was the Potentiostat-Galvanostat (PGSTAT 302 N). A three-electrode cell configuration was used and consisted a platinum counter electrode, a Ag/AgCl reference electrode and a sample with a surface area of 4.56 cm² as the working electrode. All electrodes were placed parallel. Prior to the measurement, the samples were immersed in the 3.5% NaCl solution for 30 min to measure the open circuit potential (Ecorr). The polarisation curves of samples were measured in a scan rate of 1 mVs⁻¹ with the potential range from –0.5 V to 0.5 V with respecting to Ecorr.
3. Results and discussion

3.1 Characterisation of blackening steel

Figure 1 depicts the XRD patterns of the blackening coating of the steel as prepared by hydrothermal process with different hydrazine hydrate concentrations of 0.0, 0.1 and 0.5M. Only the XRD peaks of iron as AISI 4140 steel and magnetite (Fe₃O₄) were dominantly found. All conditions of blackening steel, the peaks can be readily indexed to cubic Fe with the lattice constant a=2.87Å, which agrees with the standard pattern ICDD 87-0721. These peaks of Fe correspond to plans (110), (200) and (211). Beside the peaks of Fe, the peaks of magnetite can be defined to cubic Fe₃O₄ with the lattice constant a=8.38Å as referring to ICDD 88-0866. The major peak of Fe₃O₄ in this work is at (311) plan which is similar to the previously studies on hydrothermal synthesis of magnetite powder and coatings on steel substrates [2,4,5]. Therefore, the blackening coating of Fe₃O₄ can be formed in various conditions.

To observe morphology of blackening steel, SEM images of surfaces and cross-section of the magnetite coating (the left and right columns) samples with 0.0 M (first row), 0.1 M (second row) and 0.5 M (third rows) of hydrazine hydrate were shown in figure 2. The formed Fe₃O₄ crystallite on steel was able to be detected as octahedron morphology in all concentrations of hydrazine hydrate. The thicknesses of the coatings with 0.0, 0.1, and 0.5M hydrazine hydrate were 7.05±0.28, 9.25±0.62, and 8.75±0.47 µm, respectively, in figure 2 (the right column). The Fe₃O₄ sub-layers composed of smaller and bigger crystallite sizes at the inner layer and the outer layer (at the surface) as shown in figure 2 (SEM images at high magnitude in the left column). Zhu et al [6] and later Chandra-ambohn et al [3] reported that the inner submicron grain and the outer large grain of Fe₃O₄ were formed by the reaction between Fe(II) and Fe(III) with hydrazine hydrate in hydrothermal basic solution. Despite the absence of hydrazine hydrate, Fe₃O₄ layer with the appropriate thickness and grain size can be formed in the present study.

![Figure 1. XRD patterns of the blackening steel with different of hydrazine hydrate concentration](image-url)

The grain sizes of the outer Fe₃O₄ layers produced by all conditions were evaluated using SEM images and the Image J software; furthermore the Debye-Scherer equation was used to compare the results. According to the Debye-Scherer equation, the crystallite grain size (D) of the Fe₃O₄ can be estimated as:
\[ D = \frac{k\lambda}{\beta \cos \theta} \]  

Where, \( k \) is a constant that has a value of 0.94, \( \lambda \) is the wavelength of the X-ray radiation (1.5406 Å), \( \beta \) is the full-width of half-maximum intensity of the peak, and \( \theta \) is the diffraction angle. From the preferred (311) diffraction peaks and the measured outer large grains of Fe$_3$O$_4$ layer, the grain size of crystallite Fe$_3$O$_4$ prepared by various hydrazine hydrate concentrations were shown in figure 3. The results indicated that the crystallite grain size of the Fe$_3$O$_4$ decreased with an increase 0.1 M to 0.5 M in the hydrazine hydrates. This result was related with Yan et al. for synthesis Fe$_3$O$_4$ nanoparticles which reported that the excess hydroxide ions generated from N$_2$H$_4$·H$_2$O were absorbed on the surface and underwent the nucleation. The repulsive force between hydroxide ions can inhibit the growth of crystal grains [7].

![Figure 2. Surfaces and cross-section of the magnetite coating (left and right column) samples with 0.0 M (first row), 0.1 M (second row) and 0.5 M (third rows) of hydrazine hydrate](image-url)
The possible mechanism of Fe₃O₄ formation was proposed in this experiment [8]. A hydrazine hydrate (N₂H₄·H₂O) was a reducing agent.

\[ \text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 \]  
(2)

\[ \text{Fe(OH)}_2 + \text{N₂H₄} + 4\text{H₂O} \rightarrow 2\text{Fe(OH)}_3 + 2\text{NH}_4\text{OH} \]  
(3)

\[ 2\text{Fe(OH)}_3 + \text{Fe(OH)}_2 \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H₂O} \]  
(4)

According to reactions (2), (3) and (4), Fe(OH)₂ contributed Fe(II) which was an iron source (ferrous sulphate) in the alkalescent aqueous media, and it was further oxidised into Fe(OH)₃ in the presence of hydrazine hydrate. Under hydrothermal treatment at 140°C and 2 bar, Fe(OH)₂ and Fe(OH)₃ were oxidised to form the Fe₃O₄ phase. Therefore, Fe₃O₄ crystal nucleus was increasingly formed on the surface of the AISI 4140 steel with submicron size. Then, the crystal nucleus of magnetite grew well at the outer layer. Finally, at the outer surface of the crystallite began to grow and the large size was obtained [6]. Although one condition in the present experiment, the coating was formed without hydrazine hydrate, the Fe₃O₄ layer can be formed. Following reaction (3), the formation of Fe(OH)₃ cannot occur. Also, reaction (4) was reduced to the Schikorr reaction (reaction 5) [9].

\[ \text{Fe(OH)}_2 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + \text{H}_2 \]  
(5)

As mentioned in above the results, from increased thickness of magnetite in present work, it can implied that hydrazine hydrate can increase the nucleation rate as it is a stronger reducing agent than sodium hydroxide. When the concentration of hydrazine hydrate was raised to 0.5M, the nucleation rate is dramatically contributed to Fe₃O₄ crystallite forming on surface of steel with a low growth rate, thus the inner later became submicron crystallite. Compared with the condition without hydrazine hydrate, the crystalline grain size of the 0.1M condition were larger than the others, because possibly the growth of the submicron crystallite was more dominant than nucleation.

![Crystallite size as a function of hydrazine hydrate concentration on blackening steel](image)

**Figure 3.** The Crystallite size as a function of hydrazine hydrate concentration on blackening steel

### 3.2 The oxalic acid spot test

To examine the quality of blackening coating in acid media, figure 4 displays the surface of the magnetite coatings on steel after the oxalic acid spot testing. On the report of MIL-DTL-13924D standard, a remained black colour at the centre of the samples with some or small white stains border
indicates a good quality of the coating. In all condition, the blackening coatings were qualified in this test. Some or small white stain border appeared from oxalic acid exposure on the magnetite layer. Therefore, all conditions of blackening process provide good acidic corrosive resistance.

![Figure 4](image)

**Figure 4.** Surface of the magnetite coating on steel after the oxalic acid spot testing

### 3.3 Potentiodynamic polarisation test

The polarization curves of the magnetite coatings in 3.5% NaCl solution are showed in figure 5. The Tafel extrapolation method was used to determine the corrosion potentials ($E_{corr}$) and corrosion current densities ($i_{corr}$). The corrosion potentials of the coatings produced by hydrazine hydrate concentrations of 0.0, 0.1, and 0.5 M were -0.478, -0.507 and -0.483 V vs. Ag/AgCl, respectively. These values were closed to other reports which were -0.505 V \[2\]. Additionally, the values of the corrosion current densities were 1.48x10$^{-5}$, 1.58x10$^{-5}$ and 1.74x10$^{-5}$ A cm$^{-2}$ in 0.0, 0.1, and 0.5 M of hydrazine hydrate, sequentially. After the potentiodynamic polarisation test, the blackening samples were remained black colour without the deterioration due to NaCl solution. From this point, it ensures that the polarisation plot was applied the Fe$_3$O$_4$ layer, not the steel substrate. The insignificant difference of corrosion current densities indicated that changing the concentration of hydrazine hydrate does not affect to the corrosion rate. Although, the corrosion potentials were slight different due to the steady-state potential of Fe$_3$O$_4$ layer with high to low magnetite thicknesses respecting 0.1, 0.5 and 0.0 M of hydrazine hydrate concentration. According to Ohm’s law in equation (6), steady-state potential of Fe$_3$O$_4$ layer was provided as:

$$E_{Fe_3O_4,\text{steady-state}} = \parallel E_{corr} \parallel = i_{corr} \rho \zeta$$

Where, $\rho$ and $\zeta$ are the electrical resistivity and the thickness of magnetite, sequentially. Therefore, as the thickness of magnetite increases, the steady-state potential of the Fe$_3$O$_4$ layer will shift to a more negative potential or higher absolute potential.
4. Conclusion
The AISI 4140 steel was blackened by the hydrothermal process using NaOH solution with varying 0.0, 0.1, and 0.5 M of the hydrazine hydrate at 140°C and 2 bar for 30 min. The results of XRD and SEM confirmed the coating layers of Fe₃O₄ with octahedron morphology forming on the surface of the steel substrates in all blackening conditions. The grains of Fe₃O₄ were composed of two layers: one was micron ordered crystallite at the outer surface and the other was submicron grain at the inner surface. The blackening coating with hydrazine hydrate was thicker than the condition without hydrazine hydrate due to the acceleration of the nucleation rate affected by hydrazine hydrate. The acceleration of nucleation gives rise to the inner fine grain of Fe₃O₄. Among the blackening conditions, with 0.1M N₂H₄·H₂O the growth step of the outer Fe₃O₄ crystallites was more dominant than the nucleation step. Therefore, the outer large crystallites of blackening steel were obtained. The oxalic acid spot test and potentiodynamic polarisation provided the results showing good corrosive resistance of the blackening coating steel, despite the absence of hydrazine hydrate.

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