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EGGSHELL COATED GREY CAST IRON FOR CORROSION APPLICATIONS

Tuty Asma Abu Bakar*, Muhammad Fadzli Rosly, Nur Syairahtul Ain Mohamad Jafar

Faculty of Mechanical Engineering, Universiti Teknologi Malaysia 81310 UTM Johor Bahru, Johor, Malaysia

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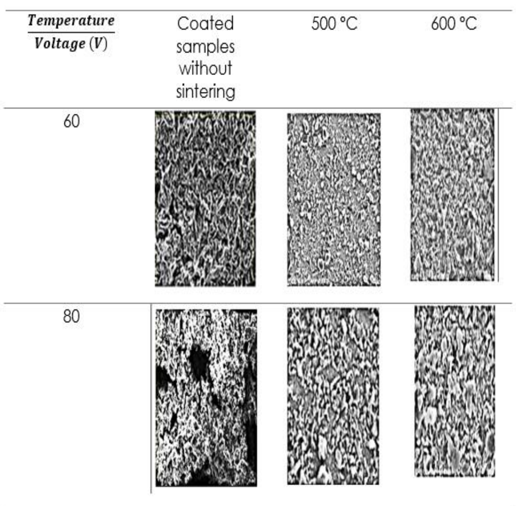
*Corresponding author
tuty@utm.my

Graphical abstract



Abstract

In many years, corrosion has been such issues for carbon steel. Eggshell waste is believed to be a potential coating material for carbon steel in many applications. This paper introduces the use of eggshell waste which contains a source of calcium carbonate as corrosion prevention coating material on the grey cast iron by utilizing electrophoretic deposition (EPD) method. Eggshell consisted of 94-95 % of calcium carbonate in the form of calcite and others. Thus, calcium carbonate precipitation can serve as naturally formed coating on the cast iron pipe and prevent diffusion of oxygen that can direct to corrosion. Besides, this method will also prevent the lengthy and complex corrosion control piping system. In this study, the eggshell has been successfully coated on the grey cast iron substrate with optimum condition of 80 V for 1 minute deposition time at the sintering temperature of 600°C. From the preliminary work, thin and uniform coating thickness were produced at 1 minute deposition time and moderate voltage values of 60 – 80V.

Keywords: Eggshell, coating, grey cast iron, calcium carbonate, sintering

1.0 INTRODUCTION

Eggshell is composed about 95% of calcium carbonate ($CaCO_3$) and the value of eggshell waste has long been underestimated because it has been considered as waste materials [1]. Recently, researcher defines the potential of eggshell as bio-filler reinforced for bio-polymer [2-4] and metal [4-5] composite. Eggshell also has been used as flame-retardant filler in intumescent coating applications [6-7], coating pigments for ink jet printing paper [8] and catalyst for biodiesel production [9]. Waste products containing eggshells specifically can be found abundantly in Malaysia from various industries. Eggshell waste is an industrial by-product, and its disposal constitutes a serious environmental hazard [10].

Carbon steel is regarded as the most widely used engineering material despite its low corrosion resistant and one of the most versatile of its usage as pipes and vessels often to transport water or submerged in water to some extend during services [11]. Internal corrosion of tuberculation is the most common type of corrosion problem faced by the water distribution system due to the excess deposited of scaling and corrosion product of tubercles inside the pipe and vessels [12].

Coatings have been established as one of the most efficient methods of reducing corrosion and the coating applied in this research is the calcium carbonate ($CaCO_3$) scale. The roles of $CaCO_3$ as protective scales for corrosion control in water distribution system evoke widespread interest. The formation of $CaCO_3$ naturally by the Ca^{2+} and HCO_3^- contain in water represents a cathodic inhibition mechanism that serves coating-like scale to protect the pipe surface from corrosion [11]. This can be achieved by the positive value of Langelier Saturation Index (LSI) by adjusting the pH, alkalinity, or calcium content of the water. LSI is a measurement of a solution's ability to dissolve or deposit $CaCO_3$. This index is not related directly to corrosion, but it is related to the deposition of the $CaCO_3$ film or scale [13]. This passive layer of $CaCO_3$ is formed naturally by the addition of lime, soda ash or caustic soda to raise the calcium content as well as the alkalinity and the pH [14]. This study has suggested the recycling of chicken eggshells that rich of $CaCO_3$ as it provides useful calcium carbonate corrosion protection coating and reduces the need of management of eggshell waste.

The overall goal of this study is to investigate the effectiveness of the eggshell powder coating on the grey cast iron by using EPD method. The optimum condition of EPD such as the deposition voltage and deposition time are investigated. The effect of the sintering temperature on the coated sample are also studied. The characterization of the eggshell powder, the grey cast iron and the coated samples before and after the sintering process are investigated by XRF, XRD and SEM. The best deposition voltage and deposition time of the samples are selected and then will undergo the sintering process with sintering temperatures of 500 and 600°C to investigate the effect of the sintering on the coated substrates.

2.0 METHODOLOGY

This section discussed on the research experimental work conducted in laboratory.

2.1 Eggshell Powder Preparation

Empty chicken eggshell was collected from the bakery and washed with tap water. The eggshells then were boiled for half an hour and dried under the sunlight. The clean eggshells were then crushed and grinded first using dry blender followed by pulveriser machine with speed of 11000 rpm for 1 minute into very fine powder. The eggshell powders then were sieved to obtain the average size range of 45 µm and sintered/heated inside oven at 110 °C for half an hour to remove odor and contamination. The eggshell powder then was characterized by X-Ray Fluorescence (XRF) to determine their elemental composition.

2.2 Grey Cast Iron Substrate Preparation

Grey cast iron substrates were cut from plate into small rectangular plate sample with dimension of 30 mm x 10 mm with thickness of 3 mm by using EDM wire cutting machine. The substrates then were grinded with abrasive silicon carbide papers (120, 400, 800, 1000 grit) to remove all corrosion product on the surface and maintain the surface roughness average of 0.15 µm. The substrate then was covered with oil before being coated to avoid corrosion.

2.3 Suspension Preparation

Stable suspension for EPD was prepared by adding 10g of eggshell powder into 200 ml of ethanol with addition of 2 drops of nitric acid, HNO_3. The solution was then continuously stirred overnight (24 hours) using magnetic stirrer to ensure homogeneous distribution of constituting particles.

2.4 Electrophoretic Deposition (EPD) Coating

The coating process started with the deposition of eggshell powders on the substrates at room temperature on cathode region using the deposition voltage parameters of 20, 40, 60, 80, and 100V for deposition time, 1 minute. Besides, graphite plate was set as the anode and the distance between the electrodes was approximately 2 cm to avoid the contact between them and to get the proper coating afterwards. Thus, these variations in the voltage deposition parameter were chosen to permit wisdom into the optimum conditions yielding free-crack and better surface morphology of the coating. Finally, the coating methodology was repeated by using different parameter which the deposition time of EPD coating for 2 and 3 minutes.

The coating was deposited at deposition voltage of 20-120V with 1-3 minutes deposition time. The best deposition voltage range was found at 20-100V. The effect of sintering temperatures at 500 and 600°C for 1 hour on the coated samples were investigated. The coated sample before and after the sintering process were characterized their surface morphology by using SEM.

3.0 RESULT AND DISCUSSION

3.1 Characterization of the Eggshell Powder

The average size and zeta potential was determined by using the Malvern Nanoparticles ZSP machine. As for the average size of the eggshell particles after sieved were at average of 43.5 µm. Zeta potential of the eggshell powder were also measured to enable the eggshell suspension coated on the substrates surface. Zeta potential is the voltage value occurring between the surface of a solid particle immersed in a conducting liquid. Hence, this parameter is essential to determine either ethanol is the suitable dispersion medium eggshell powder and the possibility to be coated using electrophoretic deposition coating. Therefore, the zeta potential of eggshell with dispersion medium solvent using ethanol at room temperature is -24.6 mV. In XRF analysis, the eggshell powder used was approximately 1.5 g for the elemental analysis before coating process with respect to oxygen content. Therefore, from the result shown in Table 1, high levels of calcium (Ca) and oxygen (O) with other small amount of other elements such as magnesium (Mg), sulphur (S), phosphorus (P) and vice versa with respect to oxygen. Based on this result, CaO has shown up to 70% of the overall chemical composition of eggshell powder before coating process. Hence, this result also proved the eggshell contained $CaCO_3$.

Table 1 XRF results of percentage of mass of elements ratio to oxygen of eggshell powder prepared for coating process

Elements ratio of oxygen	Mass %
CaO	71.00
O	27.3
Al_2O_3	0.093
SO_3	0.45
K_2O	0.061
MgO	0.79
P_2O_5	0.28

XRD pattern of the eggshell powder is shown in Figure 1. From the result, the distinctive peaks indicated a characteristic crystalline mineral phase of calcium carbonate in the form of calcite. The major peak was observed at 29.5° with hkl miller indices of (104). Hence, as for the XRD lines are intercepted each other among theoretical and experimental, then the eggshell was proved due to high amount of the calcite.

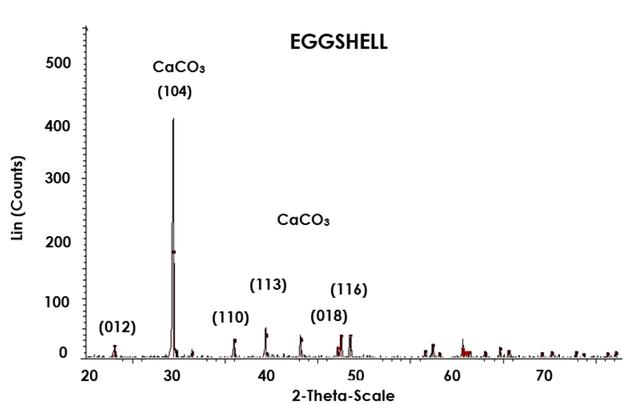


Figure 1 The XRD pattern of eggshell powder used for coating iron substrates

3.2 Characterization of the Grey Cast Iron Substrates

Basically, grey cast iron contains small, interconnected graphite flakes and have many clusters or eutectic cells of interconnected graphite flakes [17]. Therefore, the comparison between theory micrograph of the grey cast iron and the grey cast iron used in this research are shown in Figure 2. Hence, the substrate used in this research has been proved as grey cast iron due to present of the graphite flakes in the microstructure of the substrate.

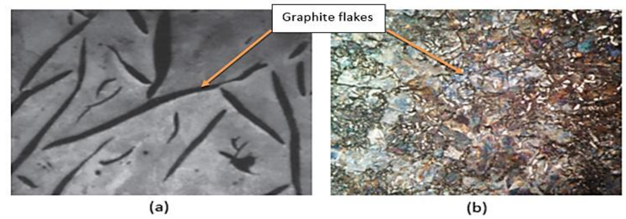


Figure 2 SEM micrograph of the grey cast iron by theoretical [17] (a) and by experiments (b)

3.3 Effect of Deposition Process Parameters on Coating Morphology

The effect of deposition voltage and deposition time were investigated. Figure 3 indicates the full results impact of deposition voltage and deposition time on the quality of eggshell coating on the grey cast iron substrate.

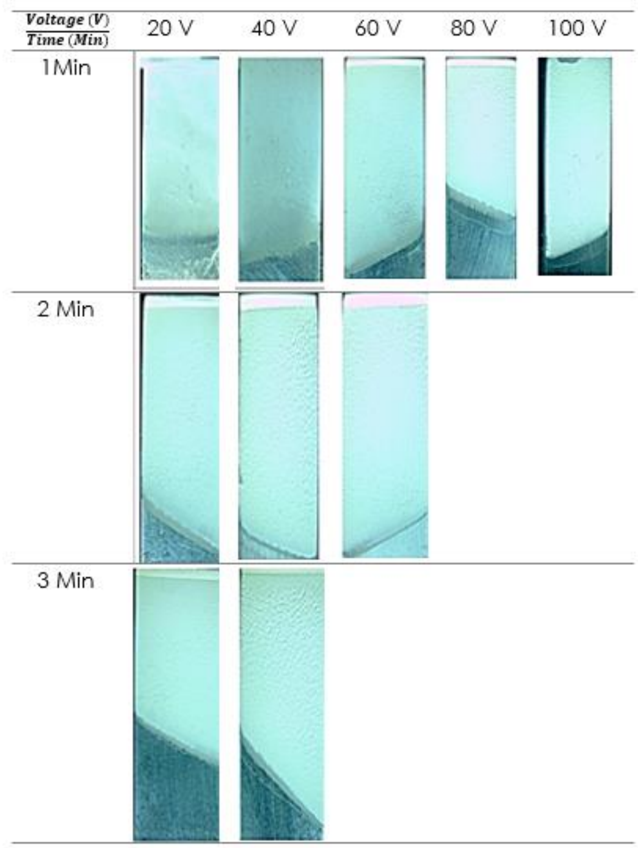


Figure 3 Effect of deposition voltage and deposition time on the eggshell coating onto grey cast iron substrates

From the previous study, the moderate voltage used during the deposition coating is ranged between 40 – 100 V/cm, it produced more uniform coating and for the higher voltage relatively more than 100 V/cm, it deteriorated the quality of the coating. This is due to higher deposition voltage may lead the particles to move fast and have no time to sit in their best positions to form a closed-packed structure [16]. As from the results in Figure 3, referring to the deposition time 1 minute, the deposition voltage which carried out at 20 V resulted in a very thin and uneven coating on the substrates. Meanwhile, increasing the deposition voltage indicated in thin and more uniform coating. When the voltage increasing more than 100 V resulted in thick, uneven, non-adhesive and deteriorated the quality of the deposition coating. This is due to the probability of the turbulence may occur in the suspension and distracted the coating process.

From previous findings, the quality of the coating has decreased when the deposition time increases which lead to produce very thick coating even using low deposition voltage and causing non-adhesive and non-uniform coating. Ultimately, this condition happened due to lateral motion of the particles once deposited is limited on the surface of the already deposited layer [16]. Therefore, by referring to the research, for the deposition time 1 minute, the eggshell coating thickness indicated thin and even. On the other hand, for 2 minutes deposition time, for the first 20V of the deposition coating is still uniform however increasing the deposition voltage resulted in the coating quality deterioration. For further investigation, the coating is also deteriorated by 3 minutes deposition time as shown in Table 2.

The surface morphology of the deposition coating was shown in Table 2 and it is proved the deposition coating can be easily modified by either adjusting the voltage or the deposition time. As a justification, a combination of both essential parameters which are deposition voltage and deposition time can be applied not only to enhance a desired thickness with uniform deposition besides assisted to achieve optimum adhesion. Hence, based on the results, the best deposition time of 1 minute and deposition voltage of 60 and 80V were selected for further studies on the effect of sintering temperature on the microstructure and composition of eggshell coating on the grey cast iron substrate.

3.4 Effect of the Sintering Process Parameter on the Uncoated and Coated Samples

Figure 4 shows the comparison of the microstructure between unsintered and sintered samples. Two best deposited samples are selected based on the best deposited voltage which are 60 and 80 V and the best deposition time is 1 minute. In Table 2, it was clearly shown the reduction of porosity after sintering process at the temperatures of 500°C and 600°C.

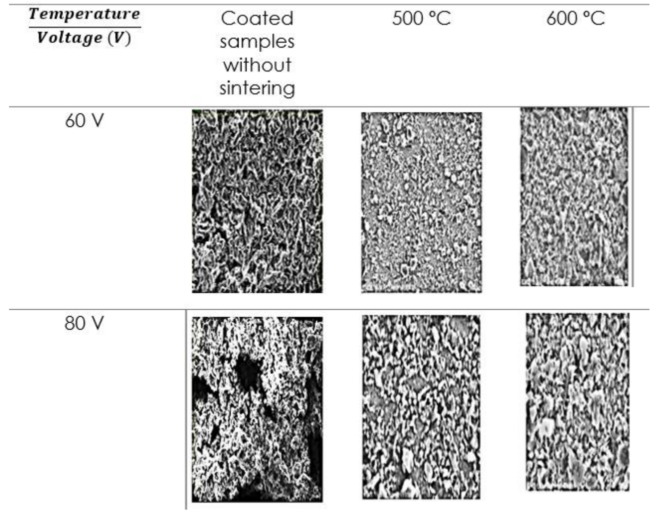


Figure 4 SEM micrograph of the coated samples at sintering temperatures of 500 °C and 600 °C (500X magnification)

In general, no crack was found in the microstructure of all samples, indicating that the mismatch in thermal expansion between eggshell coating and grey cast iron substrate during the heating and cooling was well tolerated, essentially because of the small particle size used in average 45 µm. The densification of the eggshell coatings also is well performed with the increasing of sintering temperature (Table 3). From the results, it was indicated that the eggshell was deposited in irregular circular form and good coverage over the entire surface and the level of porosity also were reduced for the sintered samples as compared to the unsintered sample.

Table 2 and Figure 5 show the EDX results of elemental composition of eggshell coating before the sintering process and Table 3 and Figure 6 show the EDX results of elemental composition of eggshell after the sintering process. It was proved that the highest elements present were calcium and oxygen which are complementary to EDX results before the coating process.

Table 2 Chemical composition of the eggshell coating (80V, 1 minute) before sintering samples

Element	Mass (%)	Mass Norm (%)	Atomic (%)
Calcium (Ca)	11.23	46.44	25.23
Carbon (C)	9.54	39.42	53.65
Iron (Fe)	2.65	20.96	19.88
Carbon (C)	0.77	3.17	1.24

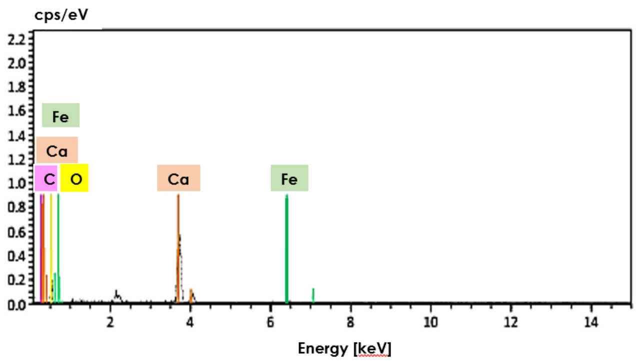


Figure 5 EDX spectra of the elements in eggshell coating (80V, 1 minute) before sintering process

Table 3 Chemical composition of the eggshell coating (80V, 1 minute) after sintering samples

Element	Mass (%)	Mass Norm (%)	Atomic (%)
Calcium (Ca)	19.20	52.16	61.70
Carbon (C)	11.90	32.33	15.27
Iron (Fe)	5.21	14.16	22.31
Carbon (C)	0.28	0.75	0.26

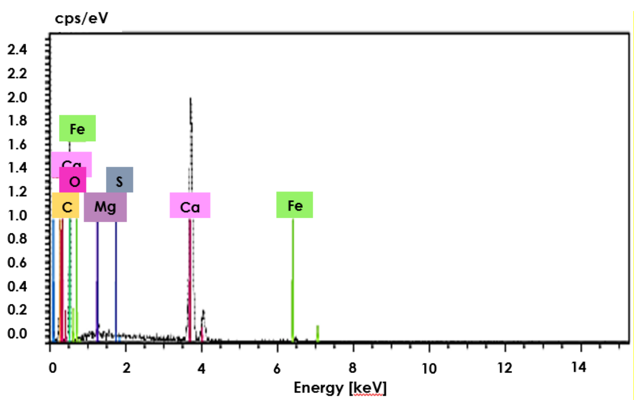


Figure 6 EDX spectra of the elements in the eggshell coating (80V, 1 minute) after sintering process

The results of EDX analysis of all samples showing the presence of mainly calcium, oxygen, with some magnesium, phosphorus, potassium constituents in coating surface which indicate there were no changes in element constituents before and after the sintering process. Therefore, there was no effect/changes on the chemical composition of the eggshell powder used in the research by the deposition voltage or by the sintering temperature. It also found that no impurity present on the surface coating except the reduction in the percentage composition of the constituent elements.

4.0 CONCLUSIONS

It can be concluded that the eggshell prepared for the coating purpose contained a high amount of calcium carbonate and was successfully coated on the grey cast iron substrates by using the EPD method. From the investigation on the effect of the deposition voltage and time on the coating morphology, the quality of the coating was decreased with the increasing of the deposition time but not voltage. The investigation on the effect of the sintering temperature on the coated samples showed the densification of the eggshell coating increased as sintering temperature increased.

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