Short Communication

Weight Loss and Microstructural Studies of Stressed Mild Steel in Apple Juice

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This study investigated the effect of internal stress of mild steel on its corrosion behaviour in apple juice by weight loss and microstructural analyses. The stress in the mild steel samples was induced by heat treatment at three different austenitic temperatures of 800, 850 and 900°C, followed by rapid quenching in cold water. The analyses of the results obtained showed that the heat treatment of mild steel at different temperatures followed by cold water quenching, changed the microstructure of the mild steel. The weight loss measurements obtained were at the highest of 0.009894 g/cm^2 for the non-heat treated mild steel, 0.007831 g/cm^2 for 900°C heat treated mild steel, 0.006394 g/cm^2 for the sample heat treated at 850°C, and 0.005287 g/cm^2 for the sample heat treated at 800°C. The analyses of these results showed that the sample heat treated at 800°C was more resistant in apple juice having the lowest average corrosion rate of 53.23 μm/y. The resistance of mild steel to corrosion in this medium decreased with the increase in austenitic temperature, which is observed from corrosion rate of 53.23 μm/y for sample heat treated at 800°C, 65.05 μm/y for sample heat treated at 850°C, and 80.630 μm/y for sample heat treated at 900°C, while 99.83 μm/y is recorded for the control sample. Intergranular corrosion with traces of pitting was observed in the heat treated samples immersed in the apple juice and the acidity of the medium increased with increase in exposure time.

1. INTRODUCTION

The importance of mild steel has been established and reported in many fields. Singh et al [1] reported that mild steel is the preferred materials for many industrial applications due to its easy

availability and its excellent physical properties. Compared to wrought iron, mild steel is cheaper, stronger and more workable than cast iron. More applications of mild steel have been reported in fabrication of containers such as reaction vessels, storage tanks for industries. Mild steel also finds application for packaging in agro fluid industries, but its usage in acidic environments is restricted because of its susceptibility towards corrosion. The concentration of 20-25% of acids has been found to be most corrosive [1]. The composition of agro juice and especially the relative acidity is the most important factor that may influence the choice of this material as packaging due to corrosion attack [2].

It has been reported that apple (Malus domestica) has been the leading fruit variety according to its world production and that the most important industrial utilization of apple is the juice production [3]. The processing equipment has been identified among the sources of contaminants in apple juice production. The other contaminants being, soil, faeces, water, air, ice, handling of products, harvesting and transport [4]. The mean composition of apple juice is composed of acids such as; malic, quinic, isocitric, citric, furmaric, and shikinic [5]. The reaction of these acids with steel during processing of this agro fluid is a major cause for concern as its resulting corrosion effect could be devastating in terms of human safety, financial cost and environmental [6–7].

Corrosion involves both chemical and electrochemical reaction of a metal with its environment. This means that corrosion process requires at least two reactions namely anodic and cathodic reactions to form a current flow. The metal transfers electrons to the electrolyte and give the anodic reaction which is a chemical or electrochemical oxidation process. The various mechanisms involved in these processes have been reported by many researchers [7–8].

Stress corrosion cracking (SCC) is as an environmentally cracking of ductile material in an apparently brittle manner under tensile stress and it occurs for specific material in a specific environment [9]. The crack appearance could be transgranular, intergranular, and branched. The various factors that influence SCC have been well reported by many authors [10–15]. The combination influence of corrosive medium and tensile stress usually results to SCC on a particular metallic material. The tensile stresses may be in the form of directly applied stress or residual stress [15].

The mechanism of SCC is such that it is initiated in many ways such as; from notches created by intergranular corrosion, from pitting damage of a passive film, from pits formed by crevice corrosion or erosion corrosion, or from localized attack of slip traces on film protected surfaces [16]. The corrosion produces a surface product layer in the mechanism of film induced cleavage, which can inject cracks into the underlying metal [10]. The transgranular SCC occur by intermittent microcleavage event due to a thin film. The cleavage of transganular SCC appears to propagate discontinuously. The time between cracks growth are determined by the film formation. The film mismatch and thickness influence discontinuous cleavage crack growth [9].

Heat treatment can be used to improve some properties of steel to obtain the desirable properties such as mechanical, corrosion, electrical and magnetic [17]. This heating process also allows steel to change its microstructures and crystallographic phases which subsequently has effect on the corrosion, mechanical and electrical properties of the steel [17]. Mild steel is most frequently selected for equipment construction because it is amenable to heat treatment for varying mechanical properties [2].

In this study, the heat treatment of mild steel is investigated to assess its corrosion behaviour in apple juice. More is known on the SCC of mild steel in different environments, but not much is known and reported of SCC of mild steel in apple juice. This study is expected to provide information on the selection of this material for application in a typical juice processing industry to protect the integrity of this material in this medium.

2. MATERIALS AND METHOD

2.1 Mild steel sample preparation

The mild steel samples were prepared with the dimensions of 59 x 29 x 6 mm. The surfaces of the samples were prepared by mechanical grinding with SiC papers of P120, P180 and P220 grits successively to achieve a smooth mild steel surface. The polished surface was cleaned thoroughly with distilled water and acetone to expose the microstructure, remove polishing residuals and possible grease. After preparation and cleaning, the specimens were allowed to dry in air before further use.

2.2 Mild steel sample heat treatment

The samples were heated to various austenitic temperatures (800, 850 and 900°C) in an electronically controlled Lenton furnace. They were soaked at these temperatures for one hour each before being quenched in cold water to room temperature.

2.3 Weight loss technique

The corrosion of mild steel in apple juice was investigated at room temperature using weight loss measurements. The test samples were suspended in the apparatus for complete immersion in the apple juice. The exposure was observed for 45 days while the weight loss measurements took place at every three days intervals using the electronic digital weighing balance Mettler Toledo which has a sensitivity of 0.01mg and a standard deviation of ±0.02 mg. The weight loss measurements were taken using the procedures and precautions described elsewhere [18–20].

2.4 Microstructural studies

The microstructures of mild steel surfaces before and after immersion were observed using scanning electron microscope (SEM) (TESCAN). The TESCAN SEM was applied at different magnifications (from 100X to 12,000X) using secondary electron detector to obtain high quality images at voltage of 20kV electron beam energy. The SEM was coupled with energy dispersive X-ray spectroscopy (EDX) to determine the surface elements composition. The EDX was also performed on the steel samples after heating to evaluate the effect of heat treatment on their composition.

2.5 pH measurement

The pH meter (CRISON CM35) calibrated with distilled water was used to study the acidity of the corrosion medium. The pH meter was immersed in the distilled water and shaken to reach the neutral pH of 7 before subsequently immersed in the apple juice. The readings were taken at the stable points of the pH and these values were recorded at the interval of two days.

3. RESULTS AND DISCUSSION

3.1 Cumulative weight loss

Weight loss measurement has been identified as ideally good as other techniques for corrosion evaluation of metals in an immersion test [21–25]. In this investigation, the weight loss method was used to assess the corrosion of mild steel samples in apple juice medium. The weight of each of the samples was measured before immersion and then measured after three days' total immersion in the medium to obtain the weight loss. The difference in initial and final weights was used to measure the weight loss during the interval period. The weight loss measurements were analyzed at the intervals of three days for the complete period of immersion and the results were presented in the forms of cumulative weight loss and total weight loss. The cumulative weight loss per area centimeter square of non-heat treated, 800°C heat treated, 850°C heat treated, and 900°C heat treated samples are presented in the Figure 1.
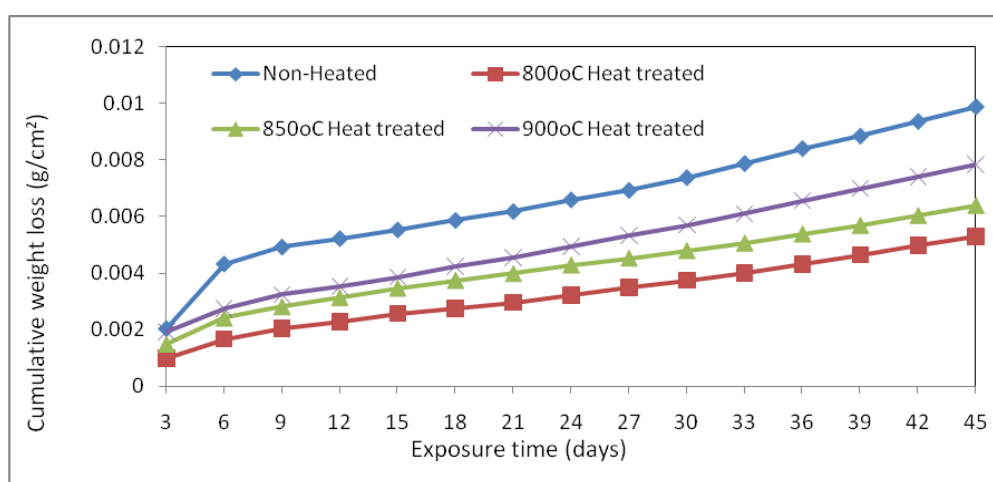

Figure 1. Cumulative weight losses Vs exposure time for mild steel in apple juice

From Figure 1, it can be observed that the sample heat treated at 800°C has the highest corrosion resistant in this medium since the lowest weight was lost during the exposure period. This is followed successively by the samples heat treated at 850°C, 900°C, and lastly the control sample. The general observation on these results is an evident increase of weight loss with exposure time and a similar progression pathway of cumulative weight losses for all the samples with increase in exposure

time. The reason for the constant difference in cumulative weight loss from the start until the end could be the difference in composition and structure generated by the different heat treatment.

3.2 Corrosion rate

The corrosion rate assists field engineers, scientists to envisage the lifetime of many metallic components in service. The corrosion rate of a metallic material is evaluated by considering its density, equivalent weight and the area of exposed material. The corrosion rate was calculated using equation (1) [26].

$$R_{corr} = 10^4 \frac{ML}{\rho \; x \; A \; x \; t}$$

(1)

where; Rcorr = corrosion rate μm/y, ML = mass loss g, A = area of specimen, cm^2, t = time of exposure year, ρ = density of specimen, g/cm^3.

The corrosion rates of different mild steel samples were calculated at different intervals of exposure time and the data obtained were plotted in Figure 2.
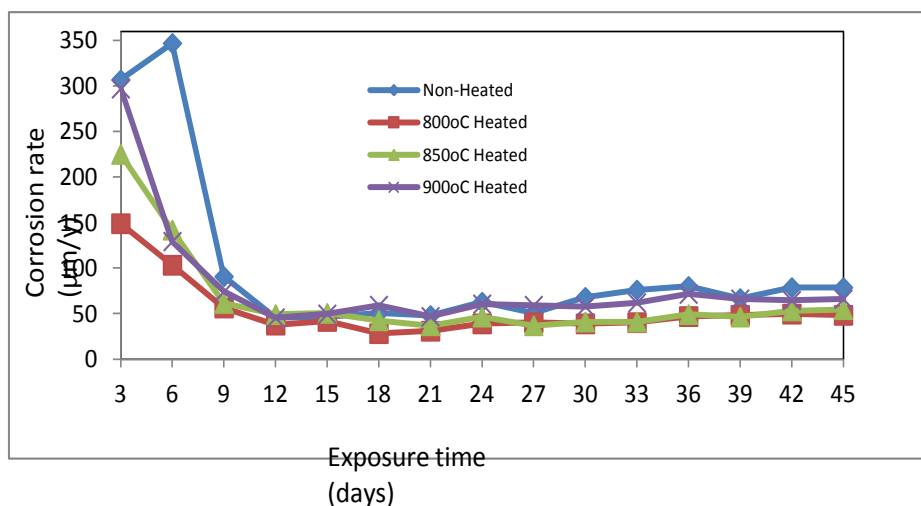

Figure 2. Corrosion of mild steel samples Vs exposure time in apple juice medium

The corrosion kinetics of mild steel samples in apple juice as observed from Figure 2 is composed of two phases. The first phase was the initiation phase which is characterized by a strong linear decrease in corrosion rate, which started from the beginning of exposure time until the about 9th day of exposure. The reason for this decrease in corrosion rate can be attributed to the formation of a passive film on the surface of mild steel which displayed a protective layer that slowed down the corrosion rate.
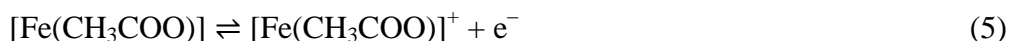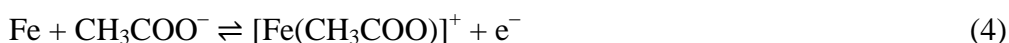
The mechanism of mild steel dissolution in a typical organic acid (such as acetic acid) follows a direct reduction of this acid at the metal surface and reduction of the hydrogen ions, of which the rate of the dissolution of this metal at the anodic site depends on the cathodic reaction, which can be summarized as shown in equations 1 – 3 [27 – 30].

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \tag{1}$$

$$2HAc + 2e^- \rightleftharpoons H_{2(g)} + 2Ac^-_{(aq)} \tag{2}$$

Hence, the anodic reaction involves the dissolution of the metal at the in order to balance the charge as shown in equation (3):

$$Fe_{(s)} \rightleftharpoons Fe^{2+}_{(aq)} + 2e^- \tag{3}$$

In a more precise mechanism, the dissolution of the mild steel in the acetic acid and consequent formation of the protective film on the surface of the metal may be summarized as shown in the equations 4 – 6 [45 xx]

$$Fe + CH_3COO^- \rightleftharpoons [Fe(CH_3COO)]^+ + e^- \tag{4}$$

$$[Fe(CH_3COO)] \rightleftharpoons [Fe(CH_3COO)]^+ + e^- \tag{5}$$

$$[Fe(CH_3COO)]^+ + H^+ \rightleftharpoons Fe^{2+} + CH_3COOH \tag{6}$$

The dissociation of the acetic acid is reduced appreciably and hence sufficient number of H^+ is not available for the last reaction (equation 6) to proceed in significant manner and the salt film remains intact on the surface which led to passivity which is thus an adherent, non-porous and protective film on the metal substrate [1, 7, 31].

The second phase is the propagation phase which is characterized by a slightly constant corrosion rate, which started from the 12th day and progressed until the end of exposure. For example, the corrosion rate of the sample heat treated at 800°C started at a value of 148.97 μm/y on the third day of exposure and was 56.37 μm/y at ninth day, with a decrease of about 62.2% during this period. From day 12 until the end of 45 days, the corrosion rate was at an average of 40.82 μm/y (±12.6 μm/y). The initiation stage of material decomposition plays a special role since the corrosion starts generally on weakest locations which can be, the surface defects, the grain boundaries, the segregations or inclusions. The corrosion resistance of many industrially used alloys with passive system is the result of the formation of a stable surface of oxide layer films [6].

3.3 Average corrosion rate

The average corrosion rates of the samples in apple juice during the exposure period are presented in Figure 3. It can be observed from the Figure that the lowest average corrosion rate of about 53.23 μm/y is observed for the sample heat treated at 800°C. The highest average corrosion rate of 99.84 μm/y is observed for the control sample and this is followed by 80.63 μm/y for the sample heat treated at 900°C, 65.05 μm/y for the sample heat treated at 850°C and lastly 53.23 μm/y for the sample heat treated at 800°C.
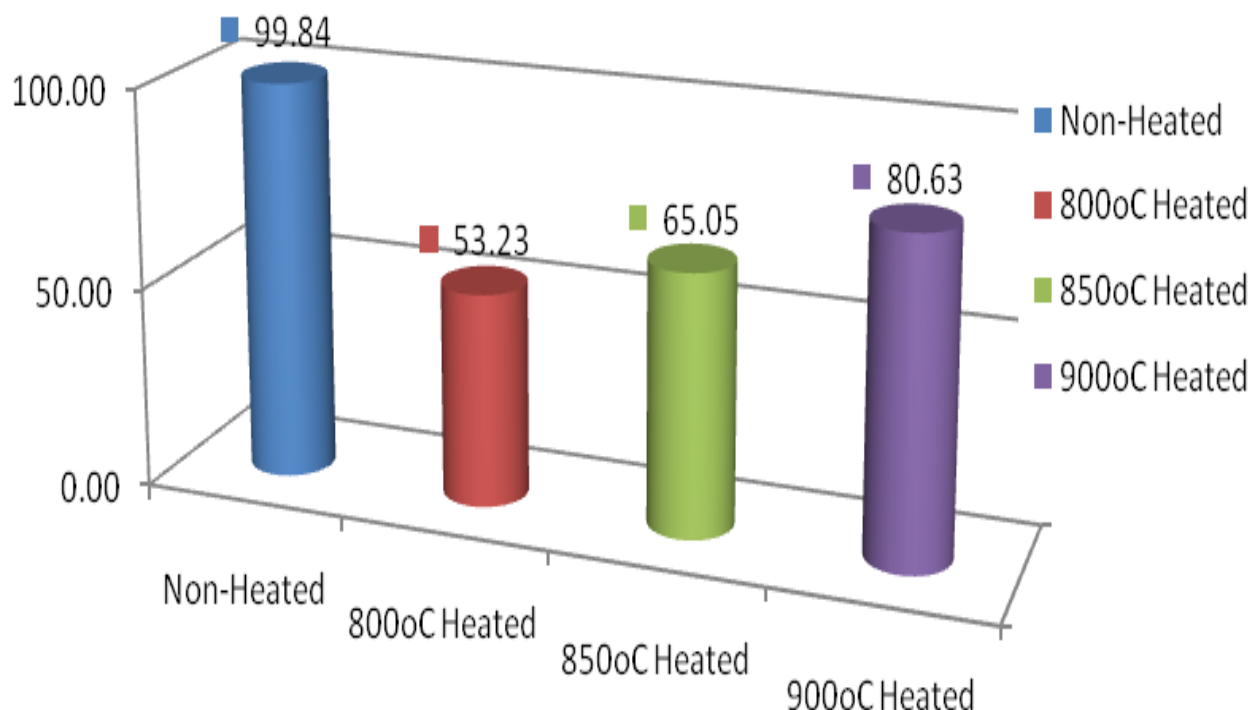
Figure 3. Average corrosion rates of mild steel during exposure period

It can also be inferred from the Figure that the sample heat treated at 800°C displays more passive behaviour than other samples and this can be attributed to the composition and structure modification because of the specific heat treatment at 800°C. The comparison of average corrosion rate showed that, the sample heat treated at 850°C is 1.2 times higher than the sample heat treated at 800°C, while the sample heat treated at 900°C is 1.5 times higher than the 800°C heat treated sample, and the control sample is 1.9 times higher than the 800°C heat treated sample.

3.4 Microstructural analyses of the samples

The effects of heat treatment on the microstructures of the samples were studied using the SEM analysis (Figure 4). It was observed that the morphologies of the mild steel samples changed with the increase of heat treatment temperatures. Some grains are noticed within structures of the samples as the austenitic temperature increased. This significantly alters the orientation of the grains in these samples and it was expected that this change will affect the corrosion behaviour of these samples when immersed in the juice medium.

The SEM images of the control sample mild steel before immersion was observed and presented in the Figure 4 (a). From this image, it can be seen that there is uniform distribution of the phases present in the microstructures of the steel sample. The grain boundaries are even hardly visible due to homogeneity of the constituents in the material. The SEM image of the mild steel sample heat treated at the 800°C is shown in Figure 4(b).
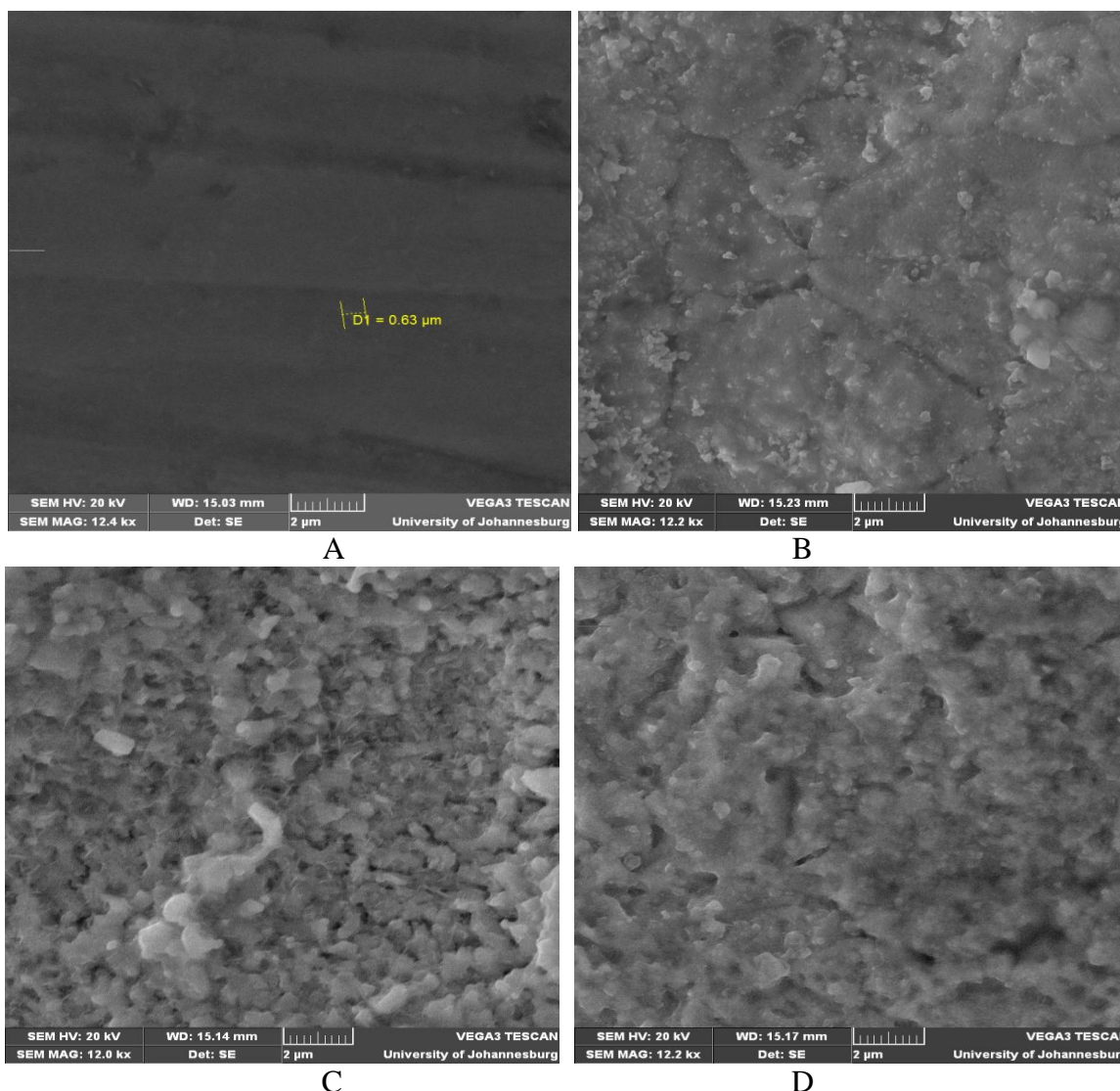
Figure 4. SEM images of (a) control sample (b) sample heat treated at 800°C (c) sample heat treated at 850°C (d) sample heat treated at 900°C before immersion in apple juice.

This Figure reveals visible phases present in the steel and cracks are clearly visible along the grain boundaries of the sample. This is an indication that the heat treat this sample was subjected to has created some internal stresses which have caused cracks within the phases of the material. The quenching heat treatment process actually caused the formation of scattered grain particles which spread through in transgranular and intergranular spaces of the materials. More cracks are conspicuously visible in samples heat treated at 850°C and 900°C as shown in the images in Figures 4 (c & d).

The SEM microstructural analysis of the samples were also examined after immersion in apple juice for 45 days to study the dissolution or resistance of these samples in the corrosive medium. Figure 5 shows the SEM images of mild steel samples after immersion in apple juice for 45 days. From the Figure, it can be seen that passive layer films are observed for all SEM images. This passive layer films appear whitish in colour and cover the corrosion surfaces of the samples. The passive layer observed on the surface of these samples is due to the oxidative reaction. The oxidation occurred first

at the surface of mild steel and the resulting metal oxide scales forms a barrier, which restrict further oxidation as observed in the SEM images in the Figures [1,31].
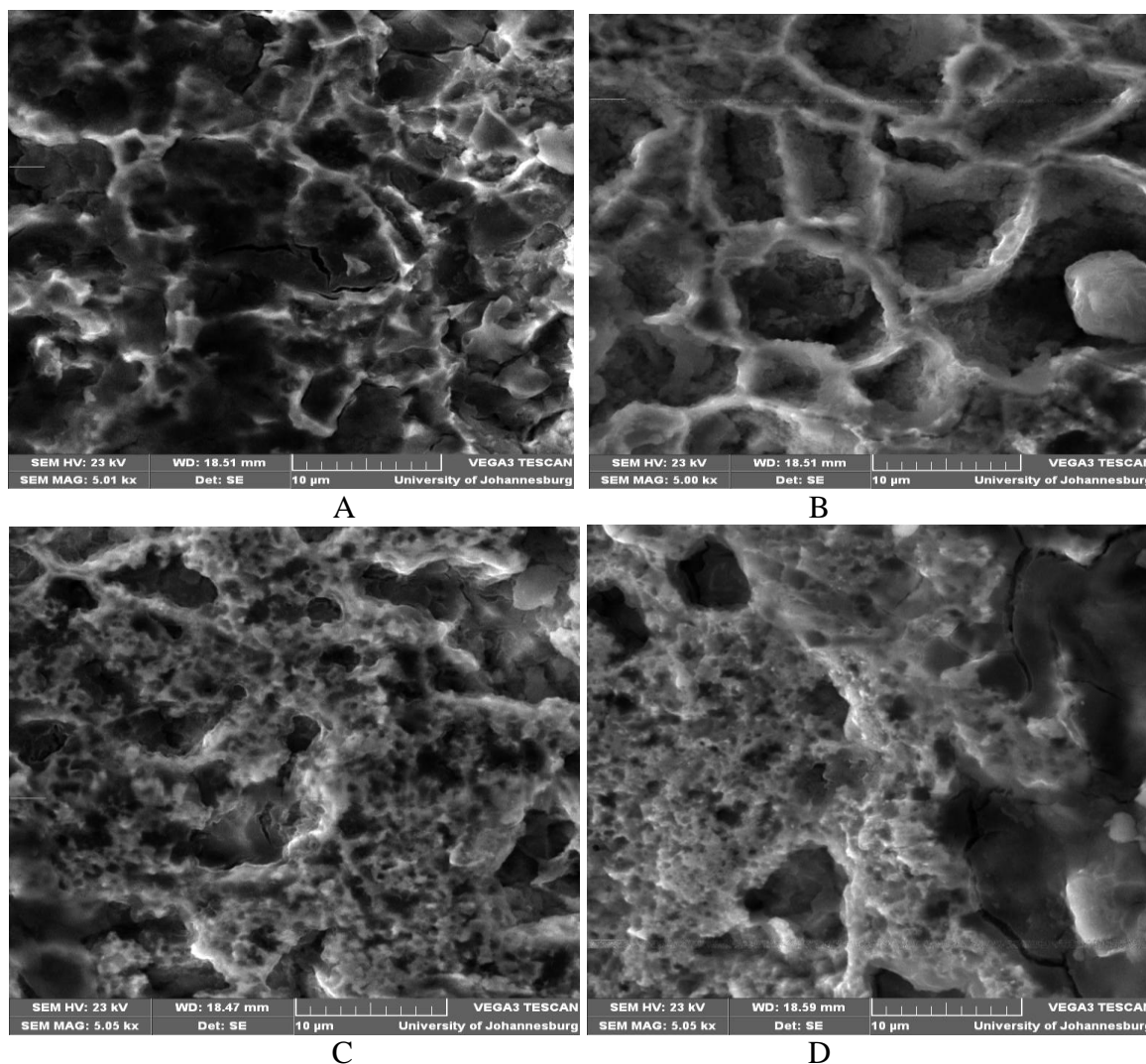

Figure 5. SEM images of (a) control sample (b) sample heat treated at 800°C (c) sample heat treated at 850°C (d) sample heat treated at 900°C after of immersion in apple juice.

It can be observed that the control mild steel sample shows less protective passive layer film than other samples, and this indicates that the corrosion attack is more in this sample as corroborated in Figure 1. It can also be seen that thicker passive layer films were observed on heat treated samples which indicates that these samples show more resistance to corrosion in this medium. The behaviour is also evident in the weight loss results shown in Figure 1. The possible reason for this behaviour can be attributed to the fact that at higher austenitic temperature, the material became harder and brittle thus became more resistance to dissolution in this medium. It means that quenching this mild steel sample at higher austenitic temperatures actually increased the corrosion resistance of this material in this medium.

Quenching is known to be a hardening process which produces martensitic structure with brittle nature. This structure has been known to be inert to some mild corrosive media and in this study, the apple medium contains mild organic acid (acetic acid) which is not strong enough to dissolve this

structure during the immersion period studied. A more careful observation is the fact that, the little attack observed in these samples occurred across the grain boundaries of these samples, which indicates that the corrosion is transgranular in nature. Some holes are however observed at the surfaces of the passive films of the samples heat treated at 850°C and 900°C, which might have occurred due to breakdown of the passive layers and might lead to pitting after further immersion in this medium.

3.5 pH analysis of the samples

The pH values of the apple juice of the heat treated samples during the immersion period were recorded. Figure 6 shows the plot of the pH data versus the exposure time incorporating the average pH.
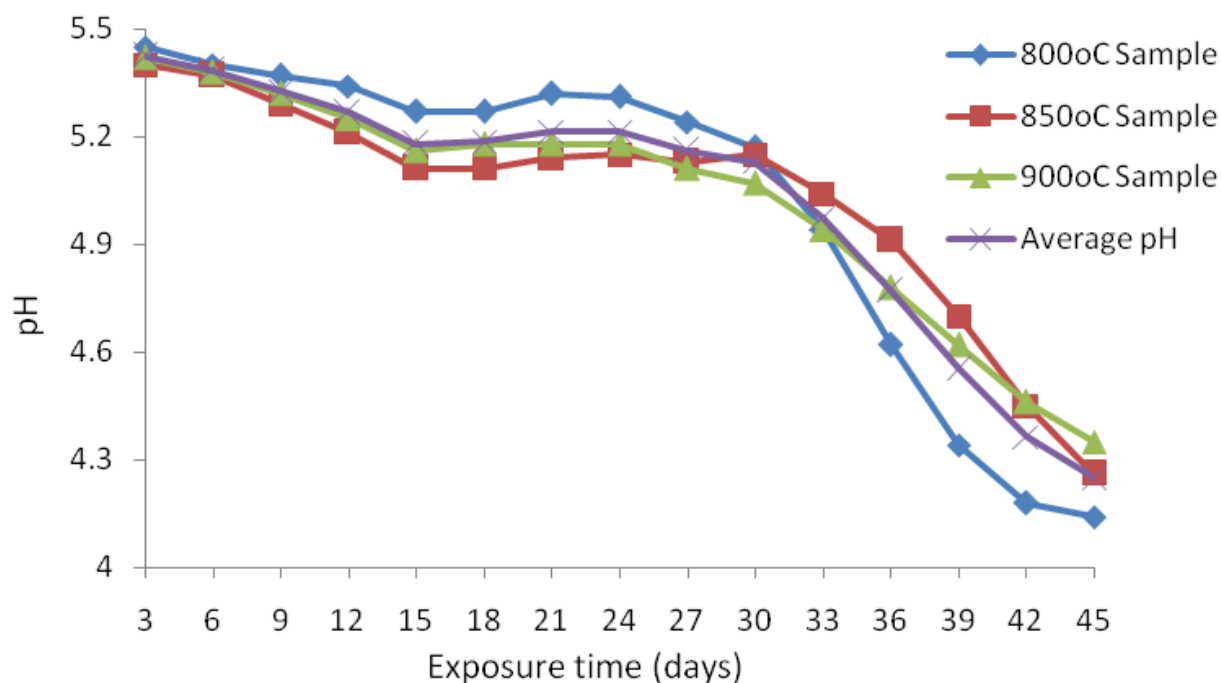

Figure 6. pH variations of heat treated mild steel samples with exposure time.

It can be seen from this Figure that a decrease of pH is observed from the average value of 5.42 at the start of exposure period to an average of 4.25 at the end of immersion period. This decrease showed that the solution became more acidic as the exposure time increases which can be traced to breakdown of the protective films on the samples and resulted to some pitting at further immersion in the medium. This behaviour is more pronounced in samples heat treated at 850°C and 900°C austenitic temperatures which is further confirmed in the SEM images in Figure 4 (c & d).

4. CONCLUSIONS

The corrosion behaviour of pre-stressed mild steel immersed in apple juice was investigated in this study by weight loss measurement and microstructural analysis. The analyses of the results

obtained showed that the water quenched mild steel samples showed significant changes in their microstructures. The mild steel heat treated at 800°C was found to be more corrosion resistant with a average corrosion rate of 53.23 μm/y than all other samples which had successively; 65.05 μm/y for the 850°C heat treated, 80.62 μm/y for the 900°C heat treated, and 99.84 μm/y for the non-heat treated mild steel samples. Thus, these results indicate that heat treatment of this steel samples increased their corrosion resistance in apple juice. The optimum corrosion reduction was obtained in the sample heat treated at 800°C. Intergranular corrosion with traces of pitting were observed in the heat treated samples immersed in the apple juice medium while the acidity of this medium increased with increase in exposure time.

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