Effect of Heat Treatment on Corrosion Behaviour of Austenitic Stainless Steel in Mild Acid Medium

Ayo Afolabi and Najeem Peleowo

Abstract— The effects of different tempering temperatures and heat treatment time on the corrosion resistance of austenitic stainless steel in various concentrations of oxalic acid were studied in this work, using the conventional weight loss and electrochemical measurements. Samples of a typical 304 stainless steel were tempered at 150°C, 250 and 350°C after being austenized at 1050°C for 10 minutes. These samples were then immersed in 0.5 and 1.0 M of oxalic acid and their weight losses were measured at every 5 days interval for 30 days. The results obtained show that corrosion of all ASS samples increased with an increase in tempering temperature and time. This behaviour was attributed to the precipitation of chromium carbide at the grain boundaries of these metals. Higher concentration of corrosion medium also produced more corrosion. This behaviour is further supported by the electrochemical scanning results of the samples in the same concentrations of the medium. The metallographic images of the corroded samples showed non-uniform distribution of precipitated chromium carbide at the grain boundaries.

Keywords— ASS, Corrosion, Oxalic Acid, Tempering, Temperature, Time

I. INTRODUCTION

STAINLESS steels have never been a panacea for all the corrosion problems which worry engineers and engineering structures, though when rightly applied it will result in great savings of both money and time [1]. The resistance of stainless steels is determined by its passive nature, alloy chemistry, heat treatment, precipitation morphology, kinetics and specific environment. The intactness of passive film on the surface is dependent on its stability in the medium of exposure [2 – 4]. Even though passive layer is an inexpensive means of corrosion protection, depending on the environment, it sometimes breaks down, causing severe localized corrosion attack, such as pitting, crevice, and stress corrosion cracking, leading to catastrophic failures.

Austenitic stainless steels (ASS) offer excellent corrosion resistance in many organic, acidic, industrial and marine environments. The non-magnetic properties combined with exceptionally high toughness at all temperatures make these steels an excellent selection for a wide variety of applications such as in chemical plants, industrial and maritime field [5].

As a result of these, many investigations are being carried out on these types of steels almost on a daily basis [6 – 10].

The modification of microstructures to effect changes in metallic materials is done chiefly by alloying and heat treatment [11]. Heat treatment which involves the application of heat to bring about modification in the microstructure [12] essentially alters mechanical and chemical properties based on the retained austenite, grain size and defects such as dislocation, twining, vacancies and so on. Microstructure plays an important role in the improvement of corrosion resistance of ASS. The constituents of the microstructure such as grain size, phases, precipitates and inclusions are strongly influenced by solidification rate or heat treatment. A typical 304 ASS has 18Cr8Ni and offer high creep resistance, stress-to-rupture, and tensile strength at elevated temperature.

Oxalic acid is a relatively strong organic acid being several times stronger than acetic acid. It is used in etching for metallurgical micro-examination [13] and in the refrigerator which also incorporates stainless steels. Oxalates, which are usually formed when these steels are attacked by oxalic acids, are sparingly soluble salts, hence the manner of their deposition on the steel and the adherence or otherwise of the deposit, are likely to affect considerably the further action of the acid on the steel. The above precipitates the investigation into the effect of different tempering temperatures and time on corrosion behaviour of 304 ASS in this medium. The microstructural changes that occurred at some of these tempering temperatures were also studied.

II. EXPERIMENTAL

Corrosion specimens of type AISI 304 ASS plates (20 x 20 x 3 mm) were used in this study. Its percentage chemical compositions are: 0.08C, 2.0Mn, 1.0Si, 18 – 20 Cr, 8 – 10.5 Ni, 0.045P, 0.03S, 0.0Mo, and the remaining Fe. These samples were austenitized at 1050°C for 10 minutes, then quenched in water and tempered at temperatures 150, 250, 350°C for different periods of 30, 90, and 120 minutes. The tempered test samples were totally immersed in 0.5 and 1.0 M of oxalic acid and weight loss measurement was conducted for all the samples at every five days interval for 30 days using the procedures and precautions described by Chen et al., [14], Ashassi-Sorkhabi et al., [15], Jabeera et al., [16] and Afolabi [17].

Electrochemical test samples were prepared with dimensions of 10 X 10 mm and mounted with resin. The mounted samples were polished using 600 grit silicon carbide
grinding paper to give uniformly smooth surfaces. The electrochemical tests were conducted using a conventional air-tight 3-electrode cell with 0.5 and 1.0 M oxalic acid at room temperature in accordance with the ASTM standards [18] for test methods and analytical procedures. The electrochemical measurements were carried out with a computer controlled potentiostat which consisted of a saturated calomel reference electrode (SCE) saturated in 3.0 M KCl salt bridge, a graphite rod counter electrode and various mounted samples of ASS as the working electrode [4,19 – 20]. The potentiodynamic tests were conducted using a potential sweep rate of 0.5 mV/s and a scanning range between -1 to 2 V. The metallographic examination of the corroded samples was carried out using an optical microscope on the transversely prepared surfaces of the 1 μm diamond polished samples.

III. RESULTS AND DISCUSSION

The corrosion behaviour of the ASS sample in 0.5 and 1.0 M oxalic acid is presented in Figure 1 in terms of weight loss versus immersion time. It can be observed from the Figure that the weight loss of the samples slightly increases with increase in exposure period. This indicates slight dissolution of this material in this medium during this period. A closer look at the two curves shows that the weight loss is slightly more pronounced in 1.0 M medium than in 0.5 M. This is similar to the findings of Hausmann [21] and Afolabi and Fasuba [22] that most metallic materials are more susceptible to corrosion at higher concentration of corrosion medium.

Fig. 1 Corrosion behaviour of ASS in oxalic acid

The behaviour of this material in oxalic acid was expected to be mild due to the weak nature of this acid and passivating ability of stainless steel in most media. It can however be observed that slight passivation of this material was obtained between fifteenth and twentieth day of exposure in both concentrations of oxalic medium. Oxalic acid attacked the steel sample to form oxalate which is a sparingly soluble salt and could not form a protective layer on the steel thereby enable continuous diffusion of the corrosion medium into the steel surface. The normal protective chromium oxide which was formed on the steel surface is responsible for the little passivation observed during the exposure period. This further explains why this reagent is widely used in etching for micro-

examination of ASS [3, 13]. Etching would have been difficult if not impossible if complete passivation have been obtained during the corrosion of ASS in oxalic acid.

Fig. 2 Effect of tempering temperature (at t = 30 mins) on corrosion behaviour of ASS in oxalic acid

Fig. 2 shows the effect of tempering temperature at time t = 30 minutes on corrosion behaviour of 304 ASS in 1.0 M oxalic acid. It can be seen that the corrosion susceptibility of the material increases with increase in tempering temperatures. Similar feature is noticeable at tempering time t = 90 and 150 minutes as shown in Figs 3 and 4. This may be attributed to precipitation of chromium carbide at the grain boundaries of this medium which eventually become susceptible to attack by the corrosion medium. The higher the tempering temperature the more the chromium carbide precipitated at the grain boundaries hence the more the corrosion attack by the medium. As it is also evident from Figs 3 and 4, that the more the tempering time the more the precipitation at the grain boundaries, consequently the more the corrosion susceptibility on the material.

Fig. 3 Effect of tempering temperature (at t = 90 mins) on corrosion behaviour of 304 ASS in 1.0 M oxalic acid

It is known that high tempering temperature range (usually between 400°C and 700°C) of most stainless steels leads to sensitization [23 – 25] which in turn leads to precipitation of
chromium carbide at the grain boundaries of these steels. However, ASS samples used in this study were sensitized at lower tempering temperature range of 150 and 350°C. This phenomenon could be attributed to the absence of molybdenum in the chemical composition of these ASS samples. Molybdenum has an overall beneficial effect on the general corrosion resistance of stainless steels [25–26]. This element hinders the breakdown of passivity by pitting, as well as the growth kinetics of pitting. It also improves the pitting resistance of stainless steels in many environments by forming Mo6+ oxide in the passive film, which blocks the penetration of depassivating anions or combines with cations in the pits to form molybdenum oxyhydroxide or molybdate (MoO42-) at the active surface sites, thus blocking the active sites during dissolution.

Molybdate is insoluble and reduces the amount of free metal ions in the pit solution, thus decreasing the diffusion of metal cations out of the pit. This decrease in diffusion reduces the rate of dissolution significantly, resulting in a decrease in the size of the pits. The reduction in free metal ions in the pit by molybdate also reduces the chances of forming stable pits because the critical concentration of metal ions needed for the transition of metastable pits into stable pits cannot be built. Molybdenum could also improve passivity by promoting the formation of Cr-O-OH (which has better protective properties than even chromium oxide) and hence improve the corrosion resistance of the steel.

The lack of passivating properties of molybdenum in the composition of ASS could have allowed sensitization to occur at low tempering temperature under study thus enabled precipitation of carbide at the grain boundaries of the ASS samples. This precipitation increased within the tempering temperature and holding time studied and hence weight loss of these samples take place in the oxalic medium [3, 24]. This phenomenon is in contrary to the findings of Lim et al., [24] where longer holding time produced sensitization recovery of 403 stainless steel. This “healing of sensitized stainless steel” seems to be possible only at high tempering temperature and much longer holding time.

The potentiodynamic test result of the sample is shown in Figs. 5 and 6. This trend of result is also similar to the weight loss results previously discussed. It can be seen from the Figures that corrosion current (Icorr) increases and Ecorr moves in a more negative direction with an increase in tempering temperatures and exposure time.

Fig. 4 Effect of tempering temperature (at time t = 150 mins) on corrosion behaviour of 304 ASS in 1.0 M oxalic acid

Fig. 5: Potentiodynamic plot of ASS sample at different tempering times and tempering temperature of (a) 150°C and (b) 250°C

Fig. 7 shows the typical microstructural examination of ASS sample before and after immersion in the corrosion medium. It can be seen that the as-received sample has a homogeneous constituents which are evenly distributed within the matrix of the metal. These constituents are known to be ferrite and austenite phases which are in homogeneous phase until this metal is heated to an austenitic region and holding it for a period of time under studied. However, the rapid cooling has caused imbalance in the ferrite – austenite phases which led to retained austenite within the metal matrix due to fast transformation of the metal constituents.
The constituents of these two phases were expected to be relocated to their preferred (normal) sites when tempered at the tempering temperatures (150 – 350°C) employed. However, some of the ferrite were trapped inside the austenite phase due to low tempering temperatures and short tempering period employed. According to Synnios (1990), this presence of two phases produces a galvanic effect between both phases and the selective distribution of the ferrite phase take place so that a decrease in the ferrite phase may increase the galvanic effect due to the increase in the cathodic area (austenite) in comparison with the anodic one (ferrite). This phenomenon leads to decrease in the general corrosion resistance of the steel sample when immersed in the oxalic acid.

IV. CONCLUSIONS

Based on the analyses of the results obtained and the observations made during the course of this work, the following conclusions can be made on the effect of tempering temperature and time on corrosion behaviour of 304 in oxalic acid.

(i) The corrosion rate of the 304 ASS sample increases with increasing tempering temperature and time in both concentrations of the oxalic acid used. This is attributable to the carbide precipitation at the grain boundaries due to lack molybdenum in the composition of the ASS sample.

(ii) The tempered microstructure consists mainly of ferrite and retained austenite which causes galvanic effect and leads decrease in potential with increase in tempering temperature and time.

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial supports of the National Research Foundation (NRF) and University of South Africa.

REFERENCES