

Effect of Tempering Temperature and Time on the Corrosion Behaviour of 304 and 316 Austenitic Stainless Steels in Oxalic Acid

Ayo S. Afolabi, Johannes H. Potgieter, Ambali S. Abdulkareem and Nonhlanhla Fungura

Abstract—The effect of different tempering temperatures and heat treatment times on the corrosion resistance of austenitic stainless steels in oxalic acid was studied in this work using conventional weight loss and electrochemical measurements. Typical 304 and 316 stainless steel samples were tempered at 150°C, 250°C and 350°C after being austenized at 1050°C for 10 minutes. These samples were then immersed in 1.0M oxalic acid and their weight losses were measured at every five days for 30 days. The results show that corrosion of both types of ASS samples increased with an increase in tempering temperature and time and this was due to the precipitation of chromium carbides at the grain boundaries of these metals. Electrochemical results also confirm that the 304 ASS is more susceptible to corrosion than 316 ASS in this medium. This is attributed to the molybdenum in the composition of the latter. The metallographic images of these samples showed non-uniform distribution of precipitated chromium carbides at the grain boundaries of these metals and unevenly distributed carbides and retained austenite phases which cause galvanic effects in the medium.

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, and the specific environment to which it is exposed. The inert nature of the passive film on the surface is dependent on its stability in the medium of exposure [2–4]. Even though a 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, which can lead 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 choice for a wide variety of applications such as chemical plants, industrial and maritime fields [5]. As a result of these, many investigations are being carried out on these types of steels on a regular 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, essentially alters mechanical and chemical properties based on the retained austenite, grain size and defects such as dislocations, twinning, 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. ASS 316 are molybdenum-bearing types of stainless steels which are more resistant to general corrosion and pitting/crevice corrosion than the conventional chromium-nickel ASS 304 (18Cr8Ni), but the latter offer higher creep, stress-to-rupture, and tensile strength at elevated temperature. In addition to excellent corrosion resistance and strength properties, the ASS 316 Cr-Ni-Mo alloys also provide the excellent fabricability and formability which are typical of the all austenitic stainless steels. Oxalic acid is a relatively strong organic acid being several times stronger than acetic acid. It is used in etching for metallurgical micro-examination [12] and in refrigerators which also incorporate 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. As there are less investigations using organic acids compared to inorganic acids and little evidence could be found in the literature on the effects of heat treatment on corrosion behaviour in organic media, the investigation into the effect of different tempering temperatures and times on corrosion properties of 304 and 316 ASS in this medium is described in this paper. The microstructural changes that occurred at some of these tempering temperatures were also studied.

II. EXPERIMENTAL

Two types of ASS, consisting of AISI 304 and 316 (20 x 20 x 3 mm) samples, were used in this study. Their nominal chemical compositions are shown in Table 1. These samples were austenized at 1050°C for 10 minutes, then quenched in water and tempered at temperatures of 150, 250, 350°C for different periods of 30, 90, and 120 minutes. The tempered test samples were totally immersed in 1.0 M of oxalic acid and

A. S. Afolabi is with the University of South Africa – Unisa, Department of Civil and Chemical Engineering, Florida Johannesburg South Africa (phone: +2711 471 3617; fax: +27 11 471 3054; e-mail: afolas@unisa.ac.za).

J. H. Potgieter, was with the University of Witwatersrand, Johannesburg South Africa and is now with Manchester Metropolitan University, Head of Chemistry and Materials Division, Manchester M1 5GD, UK (e-mail: h.potgieter@mmu.ac.uk).

A. S. Abdulkareem is with the University of South Africa – Unisa, Department of Civil and Chemical Engineering, Florida Johannesburg South Africa (e-mail: abdul@unisa.ac.za).

N. Fungura is with the University of South Africa – Unisa, Department of Civil and Chemical Engineering, Florida Johannesburg South Africa (e-mail: fungun@unisa.ac.za).

weight loss measurements were conducted for all the samples at five day intervals for 30 days using the procedures and precautions described by Chen *et al.* [13], Ashassi-Sorkhabi *et al.* [14], Jabeera *et al.* [15] and Afolabi [6].

TABLE I
CHEMICAL COMPOSITION OF AISI 304 AND 316 ASS SAMPLES

% Composition	304 ASS	316 ASS
C	0.08	0.08
Mn	2.00	2.00
Si	1.00	1.00
Cr	18 – 20	16 – 20
Ni	8 – 11	10 – 14
P	0.045	0.045
S	0.03	0.03
Mo	---	2 – 3
Fe	Bal.	Bal.

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 1.0 M oxalic acid at room temperature in accordance with the ASTM standards [12] for test methods and analytical procedures. The electrochemical measurements were carried out with a computer controlled potentiostat which consisted of a Ag/AgCl reference electrode (SCE) saturated in 3 M KCl salt bridge, a graphite rod counter electrode and various mounted samples of ASS as the working electrode [6,17–18]. 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 1µm diamond polished samples.

III. RESULTS AND DISCUSSION

A. Weight loss measurements

The corrosion susceptibility of 304 and 316 ASS samples in 1.0 M oxalic acid is presented in Figure 1 in terms of weight loss versus immersion time. It can be observed that 304 ASS samples show higher weight loss than 316 ASS samples throughout the exposure time studied. It can also be observed from Figure 1 that the weight loss of the 304 ASS sample increases almost linearly with time throughout the exposure period, while there seems to be some passivation occurring towards the latter days of immersion for 316 ASS sample. Stainless steels generally are known to form a thin protective layer of chromium oxide in most media [19 – 20]. These metals will behave in this manner in dilute oxalic acid due to the presence of dissolved oxygen and the weak nature of this acid. In the case of the samples under investigation, it took about twenty days of immersion in this medium before a stable protective film could be formed on the 316 ASS, while it did not seem as if film stabilization occurred on the 304 ASS throughout the exposure time studied. Hence passivation was not achieved in the case of 304 ASS exposed to the oxalic acid medium.

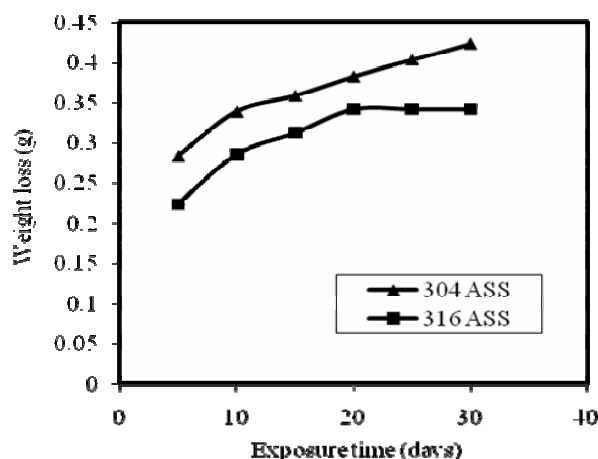


Fig. 1 Corrosion behaviour of 304 and 316 ASS in oxalic acid

Oxalic acid attacked the steel samples to form oxalate which is a sparingly soluble salt and could not form a protective layer on the steel, thereby enabling a continuous diffusion of the corrosion medium to the steel surface. This further explains why this reagent is widely used in etching for micro-examination of ASS [3,12]. Etching would have been impossible if complete passivation had been obtained during the corrosion of ASS in oxalic acid. It is suspected that the two steel samples have actually produced the usual protective chromium oxide but this film might have been too weak to ensure complete passivation on the surfaces of these ASS samples. The interaction of this chromium oxide and the oxalates on the 304 ASS sample might have led to the solubility of the product, thereby causing continuous depassivation on the steel as the exposure time progressed. In the case of 316 ASS sample, it required some period of time for the protective chromium oxide film to stabilize over the oxalate before producing passivation on the surface of this steel. This difference in corrosion behaviour of 316 ASS from 304 ASS could be attributed to the presence of molybdenum in the chemical composition of the 316 ASS samples. Molybdenum has an overall beneficial effect on the general corrosion resistance of stainless steels [21 – 22]. This element hinders the breakdown of passivity, as well as the growth kinetics of the general corrosion and it improves the corrosion resistance of stainless steels in many environments by forming Mo^{6+} oxide in the passive film, which blocks the penetration of depassivating anions or combines with cations on the surface of this steel to form molybdenum oxyhydroxide or molybdate (MoO_4^{2-}) on the active surfaces, thus blocking these surfaces during dissolution. Molybdate is insoluble and reduces the amount of free metal ions in the corrosion region, thus decreasing the diffusion of metal cations out of this region. This decrease in diffusion reduces the rate of dissolution significantly, and the reduction in free metal ions by molybdate also reduces the chances of forming any stable soluble corrosion products because the critical concentration of metal ions needed for the transition of metastable soluble corrosion products into stable ones cannot be reached. Molybdenum could also improve passivity by promoting the formation of Cr-O-OH, which even has better protective

properties than chromium oxide, and hence improve the corrosion resistance of the steel.

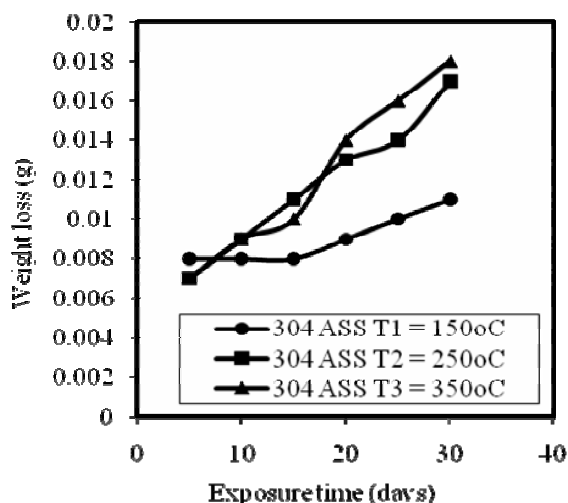


Fig. 2a Effect of tempering temperature (at time $t = 30$ mins) on corrosion behavior of 304 ASS in 1.0 M oxalic acid

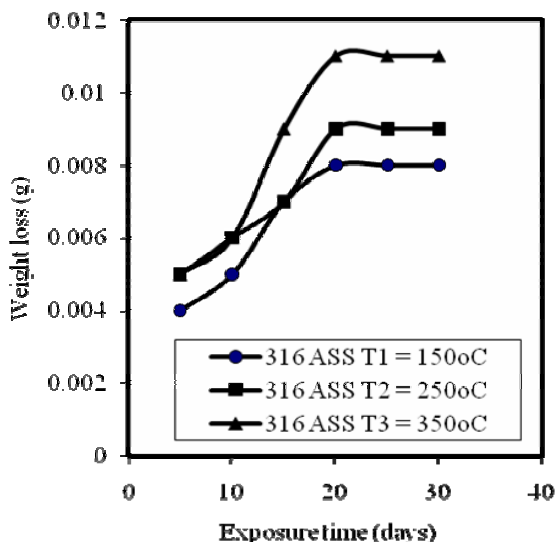


Fig. 2b Effect of tempering temperature (at time $t = 30$ mins) on corrosion behaviour of 316 Ass in 1.0 M oxalic acid

Figures 2 (a & b) show the effect of tempering temperature at time $t = 30$ minutes on corrosion behaviour of 304 and 316 ASS samples in 1.0M oxalic acid. It can be seen that the corrosion susceptibility of the 304 sample increases with increase in tempering temperatures throughout the exposure time. Similar features are noticeable at tempering times $t = 90$ and 150 minutes as shown in Figures 3 (a & b) and 4 (a & b). 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, and hence the more severe the corrosion attack by the medium. It is also evident from these figures that the longer the tempering time, the greater the corrosion susceptibility becomes on this material. On the other hand, the 316 ASS samples all show some

plateau in the weight loss after a period of twenty days, which could indicate a degree of film stability after twenty days of exposure. This behaviour is similar to what was obtain in Figure 1 and a possible cause of this behaviour could be the effect of molybdenum in the composition of the metal (which has been previously described). However, the corrosion susceptibility is higher in the heat treated samples as compared to the as-received samples.

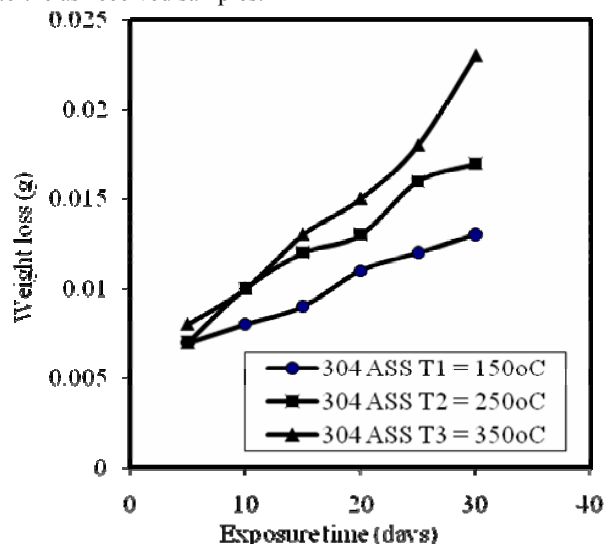


Fig. 3a Effect of tempering temperature (at time $t = 90$ mins) on corrosion behaviour of 304 ASS in 1.0 M oxalic acid

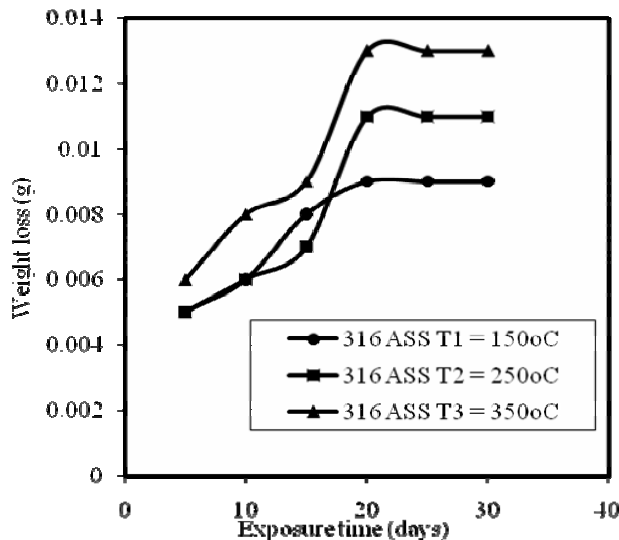


Fig. 3b Effect of tempering temperature (at time $t = 90$ mins) on corrosion behaviour of 316 ASS in 1.0 M oxalic acid

It is known that the high tempering temperature range (usually between 400°C and 700°C) of most stainless steels leads to sensitization [22 – 23], which in turn leads to precipitation of chromium carbide at the grain boundaries of these steels.

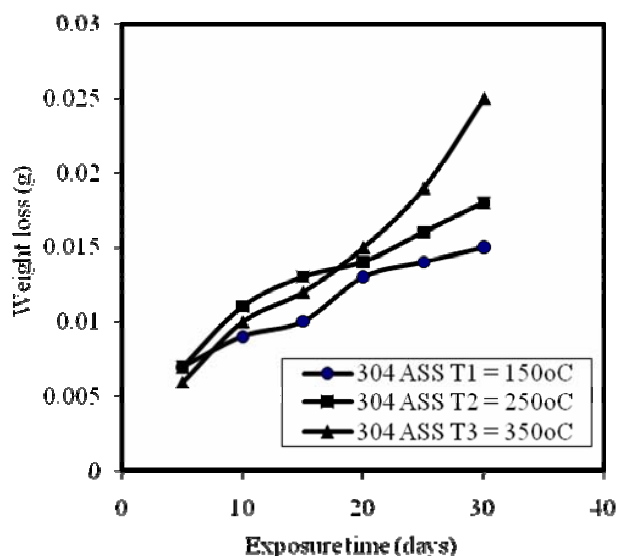


Fig. 4a Effect of tempering temperature (at time $t = 120$ mins) on corrosion behaviour of 304 ASS in 1.0 M oxalic acid

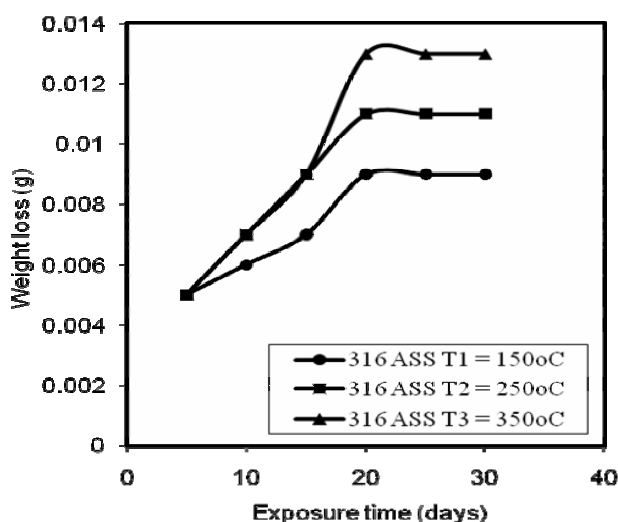


Fig. 4b Effect of tempering temperature (at time $t = 120$ mins) on corrosion behaviour of 316 ASS in 1.0 M oxalic acid

This precipitation increased within the tempering temperature and holding time studied, hence leading to corrosion of these samples in oxalic acid [3]. This phenomenon is in contrary to the findings of Lim *et al.* [23], where longer holding times produced sensitization recovery of 403 ferritic stainless steel. This “healing of sensitized stainless steel” seems to be possible only at high tempering temperature and much longer holding time.

B. Electrochemical measurement

Table II (a & b) shows the comparative potentiodynamic results of the 304 and 316 ASS samples immersed in 1.0 M oxalic acid at different tempering temperatures and times. It is evident from this table that the corrosion rates of 304 ASS samples are higher than 316 ASS samples at all the temperatures studied. This trend of results is also similar to the weight loss results discussed in section 3.1. It can also be seen

from the table that corrosion current (I_{corr}) values in 304 ASS is greater than those in 316 ASS and as these values increase, E_{corr} tend to move to more negative values, indicating that dissolution of these metals takes place with increase in tempering temperatures and exposure time.

TABLE 2A

POTENTIODYNAMIC RESULTS OF THE 304 ASS IN 1.0 M OXALIC ACID

Temp (°C)	Time (hrs)	304 ASS		
		Ecorr	Icorr	Corr rate
0	0	-0.357	7.02E-06	8.15E-02
1050	60	-0.349	1.89E-08	2.49E-04
150	30	-0.282	1.85E-06	2.42E-02
150	90	-0.285	2.60E-06	2.51E-02
150	120	-0.289	3.04E-06	3.05E-02
250	30	-0.275	1.89E-06	2.26E-02
250	90	-0.291	1.93E-06	2.62E-02
250	120	-0.295	5.14E-06	5.97E-02
350	30	-0.282	2.19E-06	2.56E-02
350	90	-0.279	4.84E-06	5.62E-02
350	120	-0.297	6.21E-06	6.88E-02

TABLE 2B

POTENTIODYNAMIC RESULTS OF THE 316 ASS IN 1.0 M OXALIC ACID

Temp (°C)	Time (hrs)	316 ASS		
		Ecorr	Icorr	Corr rate (mm/yr)
0	0	-0.286	3.84E-06	4.46E-02
1050	60	-0.228	1.95E-08	2.26E-04
150	30	-0.248	2.11E-10	2.45E-06
150	90	-0.253	2.50E-10	2.85E-06
150	120	-0.319	2.75E-10	3.17E-06
250	30	-0.325	2.10E-10	3.41E-06
250	90	-0.329	4.70E-10	5.46E-06
250	120	-0.331	7.82E-09	9.08E-05
350	30	-0.345	1.33E-08	1.54E-04
350	90	-0.354	2.24E-08	2.44E-04
350	120	-0.361	3.38E-08	3.61E-04

C. Microstructural examination

Figures 5 - 6 show the typical microstructures examinations of 304 and 316 ASS samples before and after immersion in the corrosion medium. It can be seen that the as-received samples have fairly homogeneous constituents which are evenly distributed within the matrix of the metal. These constituents are known to include carbon, chromium among other elements, which are soluble in the austenite phase and therefore homogeneously distributed within the matrices of this phase until these metals were heated to an austenitic region and held for a specified period of time. The rapid cooling has caused an imbalance in the composition of the austenite phase which led to retained austenite within the matrices of the metals due to fast transformation of the metal constituents. The solubility of carbon in these metals decreased drastically during the fast cooling and resulted in the precipitation of carbide.

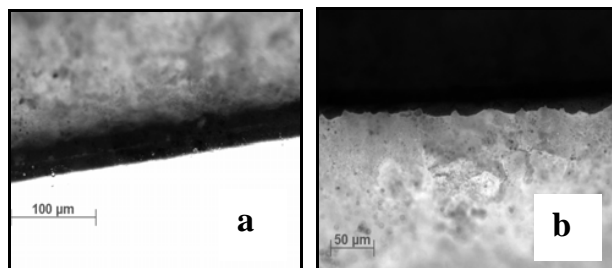


Fig. 5 Micrographic images of ASS samples tempered at 150°C for 150 minutes (a) before and (b) after immersion in 0.5 M oxalic acid

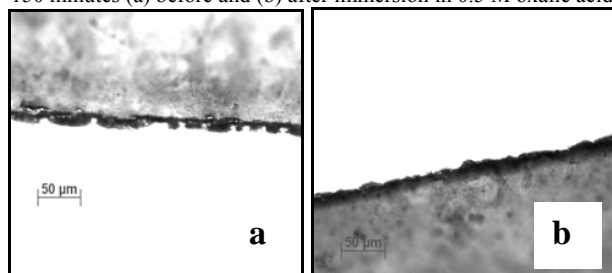


Fig. 6 Micrographic images of 316 ASS samples tempered at 150°C for 150 minutes (a) before and (b) after immersion in 0.5 M oxalic acid

The constituents of these metals were expected to be relocated to their preferred (normal) sites when tempered at the tempering temperatures (150 – 350°C) was employed. However, some of the carbides were trapped inside the austenite phase, possibly due to low tempering temperatures and/or short tempering period employed. The presence of these two inhomogeneous phases could have resulted in a small galvanic effect in the corrosion medium and which might have led to the selective distribution of the carbide phase. This phenomenon has therefore led to a decrease in the general corrosion resistance of the steel sample when immersed in the oxalic acid.

IV. CONCLUSIONS

Based on the comparison 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 heat treatment time on corrosion behaviour of 304 and 316 ASS in oxalic acid.

- (i) The corrosion rate increases with increasing tempering temperature and heat treatment time for both the 304 and the 316 ASS samples. This is attributable to the carbide precipitation at the grain boundaries of these metals.
- (ii) The corrosion susceptibility of the 316 ASS sample is lower than that of the 304 ASS sample due to the molybdenum in the composition of the former.
- (iii) The tempered microstructure consists mainly of unevenly distributed phases of carbide and retained austenite which can cause a galvanic effect when immersed in the oxalic acid medium.

REFERENCES

- [1] Monypenny, J.H.G. (1951) *Stainless iron and steel*, Chapman and Hall Ltd. London, pp 50,162-173, 228-237.
- [2] Pandey, J. L., Singh, I. and Singh, M. N. (1997) Electrochemical corrosion behaviour of heat treated AISI 304 austenitic stainless steel in inorganic acid mixture. *Anti-Corrosion Methods and Materials* Vol. 44, No1, pp 6 – 9.
- [3] Matula, M., Hyspecka, L., Svoboda, M., Vodarek, V., Dagbert, C., Galland, J., Stonawska, Z. and Tuma, L. (2001) Intergranular corrosion of AISI 316L steel. *Materials Characterization* Vol. 46, pp 203 – 210.
- [4] Aydogdu, G. H. and Aydinol, M. K. (2006): Determination of susceptibility to intergranular corrosion and electrochemical reactivation behaviour of AISI 316L type stainless steel. *Corrosion Science* Vol. 48, pp 3565 – 3583.
- [5] Tsay, L.W., Yu, S.C., Chyou, S. D. and Lin, D.Y. (2007): A comparison of hydrogen embrittlement susceptibility of two austenitic stainless steel welds. *Corrosion Science* Vol. 49, pp 4028 – 4039.
- [6] Matula M, Dagbert C, Hyspecka L, Galland J, Martinakova I. (2000) Detection of sensitization to intergranular corrosion in AISI 316L stainless steel: electrochemical potentiokinetic reactivation tests. *Proc Int Conf Eurocorr*, London, September 10–14.
- [7] Betova, I., Bojinov, M., Kinnunen, P., Pohjanne, P. and Saario, T. (2002) Influence of the electrolyte composition and temperature on the transpassive dissolution of austenitic stainless steels in simulated bleaching solutions. *Electrochimica Acta* Vol. 47, pp 3335 – 3349.
- [8] Galal, A., Atta, N. F. and Al-Hassan, M. H. S. (2005): Effect of some thiophene derivatives on the electrochemical behaviour of AISI 316 austenitic stainless steel in acidic solutions containing chloride ions. I Molecular structure and inhibition efficiency relationship. *Materials Chemistry and Physics* Vol. 89, pp 38 – 48.
- [9] Girija, S., Kamachi Mudali, U., Khatak, H.S. and Raj, B. (2007): The application of electrochemical noise resistance to evaluate the corrosion resistance of AISI type 304 SS in nitric acid. *Corrosion Science* Vol. 49, pp 4051– 4068.
- [10] Frangini, S. and Loreti, S. (2007): The role of alkaline-earth additives on the molten carbonate corrosion of 316L stainless steel. *Corrosion Science* Vol. 49, pp 3969 – 3987.
- [11] Kamma, C. M. (1993): Design of Microstructure in mild Steel by thermochemical treatment. *Proceedings of Nigerian Metallurgical Society*. Vol. 11, pp 8-18.
- [12] ASTM A 262 – 90 (1992) Standard practices for detecting susceptibility to intergranular attack in austenitic stainless steels. *Annual Book of ASTM Standards 1990: Section 3. Metals test methods and analytical procedures: Vol. 03.02. Wear and erosion. Metal corrosion*. Philadelphia, PA: ASTM, 1992.
- [13] Chen, X. H., Chen, C. S., Xiao, H. N., Cheng, F. Q., Zhang, G. and Yi, G. J. (2005): Corrosion behaviour of carbon nanotubes-Ni composite coating. *Journal of Surface and Coating Technology* Vol. 191, pp 351-356.
- [14] Ashassi-Sorkhabi, H., Ghalebsaz-Jeddi, N., Hashemzadeh, F. and Jahani, H. (2006): Corrosion Inhibition of Carbon Steel in Hydrochloric Acid by Some Polyethylene Glycols. *Electrochimica Acta* Vol. 51, pp 3848-3854.
- [15] Jabeera, B. Shibli, S. M. A. and Anirudhan, T. S. (2006): Synergistic Inhibitive Effect of Tartarate and Tunstate in Preventing Steel Corrosion in Aqueous Media. *Journal of Surface Science* Vol. 252, pp 3520-3524.
- [16] Afolabi, A. S. (2007): Corrosion and stress corrosion behaviours of low and medium carbon steels in agro-fluid media. *Leonardo Electronic Journal of Practices and technologies*. Vol. 10, pp 55 – 66.
- [17] Pohjanne, P. (1997): *Corrosion/97*, NACE international, Houston, Paper no 376.
- [18] Casales, M., Salinas-Bravo, V. M., Martinez-Villafane, A. and Gonzalex, R. (2002): Effect of heat treatment on the stress corrosion cracking of alloy 690. *Journal of Materials Science and Engineering A* Vol. 332, pp 223 – 230.
- [19] Okamoto, G. (1973) Passive film of 18–8 stainless steel structure and its function. *Corrosion Science* Vol. 13, p 471.
- [20] Igual, M. A., Garcia, A. J., Lopez, N. S., Guinon, J. L. and Perez, H. V. (2004): Corrosion studies of austenitic and duplex stainless steels in aqueous lithium bromide solution at different temperatures. *Corrosion Science* Vol. 46, pp 2955 – 2974.
- [21] Ilevbare, G.O. and Burstein, G.T. (2001): The role of alloyed molybdenum in the inhibition of pitting corrosion in stainless steels. *Corrosion Science* Vol. 43, pp 485-513.
- [22] Qin, B., Wang, Z. Y. and Sun, Q. S. (2007) Effect of tempering temperature on properties of 00Cr16Ni5Mo Stainless steel. *Materials Characterization*. Article in press.
- [23] Lim, L. C., Lai, M. O. and Ma, J. (1993) Tempering of AISI 403 stainless steel. *Materials Science and Engineering* Vol. A171, pp 13 – 19.