

Comparative Analysis of Corrosion Behavior of Martensitic and Annealed Stainless Steel in H₂SO₄ and NaOH

Oshionwu Lucky C., Idenyi N.E, Nwankwo Michael O. and Ugwu Emmanuel I.
Department of Industrial Physics, Ebonyi State University, Abakaliki Nigeria.

Luckis_Ma@yahoo.ie

Abstract

Using weight loss techniques (WLT), the comparative analysis of the corrosion characterization behavior of cast stainless steel (70.90% Fe, 19% Cr 10%Ni, 0.0% C) alloys in (0.25M- 0.5M) H₂SO₄ and NaOH has been evaluated. The cast stainless steel specimen was sectioned into three sets labeled M, A, U and machined to the same cross sectional area. M and A is subjected to a temperature of 900°C (1173K or 1652°F) where the grains forms austenitic phase which was further heat- treated to form martensitic stainless steel (M) and annealed stainless steel (A) test coupon respectively. Then, (U) is left untreated as a control test coupon sample. These preweighed test coupon samples were immersed in 0.25M and 0.5M simulated tetraoxosulphate (vi) acid (H₂SO₄) and sodium hydroxide (NaOH) respectively. The experimental process is allowed for a total of 168hr with each set withdrawn 24hr interval for weight loss analysis. The findings showed that of a passivating metals with initial steady rise in corrosion penetration rate (CPR) followed by gradual decrease in CPR which increases as molar concentration increase for the annealed specimen(A) in H₂SO₄ while the martensitic test specimen(M) is severely attacked in NaOH. The annealed specimen exhibit high passivity in H₂SO₄ with lowest CPR of 0.0071mm/yr. The severe attack of the annealed specimen is due to increase in ionization which results in redistribution of grain boundary structure.

Key words: Passivation, Corrosion kinetics, Basic Environment, Acidic Environment, Martensitic, Annealing, Weight Loss Techniques, Austenitic phase.

INTRODUCTION

In metallurgy, stainless steel is regarded as an alloy consisting majorly of iron, carbon, chromium and hence defined as a steel alloy with a minimum of 11.5 wt % chromium content (Scheil, 2006). It is believed that stainless steel does not stain, corrode or rust as ordinary steel (it is stainless) but not stain proof (Krugar, 2001) and it is useful in numerous engineering application. The unpredictable degradation these engineering material recently have been a cause for worldwide concern, consequently upon its huge financial losses (about 4-24% metal produced annually are destroyed by corrosion) and many mechanical failure results from it (Revie, 2000). Hence the recent resurgence in studying the corrossions characterization behaviour of these engineering material.

In this paper, we presents the effect of heat treatment process on the corrosion penetration rate of stainless steel with composition (70.90% Fe, 19%Cr, 10%Ni 0.08%C) which has been made martensitic and also annealed using weight loss technique (WLT). Further discussion on the x-ray diffraction analysis as well as optical micrographic analysis will be considered due to grain boundary structural analysis as a site for corrosion kinetics and dislocation movement.

MATERIALS AND METHODS

Study Area

The research: Comparative analysis of martensitic and annealed stainless steel (70.90% Fe, 19%Cr, 10%Ni 0.07%C) in acidic and basic media was carried out in Ebonyi State University Abakaliki and River State University of Science and Technology in southeastern and south-south region of Nigeria in April, 2013.

Materials and Equipments

The material used for this research work includes: cast stainless steel bar with percentage composition of (70.90% Fe, 19%Cr, 10%Ni and 0.08%C). This cast stainless steel was produced successfully at Union Founding Engineering Service, River State Nigeria. Other materials includes (0.25M, 0.5M) H₂SO₄, (0.25M, 0.5M) NaOH, Energy papers, distilled water, laboratory cylinders and beakers, record stand.

The equipments involved includes lathe machine, electronic weighing machine, vernier caliper and analytic digital weighing machine KERN 770 with serial number xx21-0014 and laboratory number EBSU/FPS/ICH/016 located in industrial Chemistry Department, Ebonyi State University, Nigeria.

Sample Preparation

The cast stainless steel bar is thoroughly cleaned with energy paper of different grit size to avoid surface pitting and remove carbonize layer. Using lathe machine, the sample is machine to a sizeable dimension and subsequently cut into a coupon samples with dimension range of 25.1mm x 24.1mm x 10mm and specific surface area of 22.78cm². A groove is drilled on both sides of the specimen to allow for string suspension with regards to the ASTM immersion standard specification.

Preparation of Test Environment

Basically, the environment for this research work includes; Acidic and basic environment of different concentration prepared from its stock. The (0.25M and 0.5M) H_2SO_4 is produce from its stock solution with 98% purity assay while the NaOH is produce from its stock of 46% purity assay.

Measurement and Weighing

Using vernier caliper, the dimensions of the test specimen were measured as 25.1mm x 24.1mm x 10mm while the specific area is calculated using the formula

$$S_a = 2[(xy + xz + yz) - \pi r^2 h] \quad (1)$$

where h is height of groove, r is radius of groove, S_a is specific area, x , y and z are length, width and thickness respectively. Using analytic digital weighing machine prior to immersion, the initial weights of the test coupons is ascertain.

Design Setup and Procedure

The test coupons are divided into three groups which comprises of 6 test specimen each. The first group is allowed as a control sample. The remaining two groups are subjected to a temperature of 900°C where austenitic phase are formed. One group are withdrawn and quenched in distilled water rapidly to produce martensitic specimen (M) while the second group is allowed to be furnace cooled to produce the annealed specimen (A) (Ashby, 2007, Antropov, 1975). One test coupons from each of these groups is immersed in a solution of H_2SO_4 and NaOH of different concentration with exposure time of 168hr. Then, one test coupon in each set are withdrawn, washed with acetone and dried at 24hr interval. Prior to corrosion penetration rate analysis, the digital analytic weighing machine is used to determine the final weight. The degree of corrosion progress is conveniently evaluated using the corrosion penetration rate expressed in miles/year or mm/yr and its mathematical computation is based on the formula.

$$CPR = \frac{k(W_i - W_f)}{PA(\Delta t)} \quad (2)$$

where W_a and W_b are initial and final weight respectively, while t , ρ and A are exposure time, density and area respectively. K is a constant with a value of 87.6mm/yr (callister, 1997, Idenyi et al, 2006 Landrum, 1990).

RESULTS AND DISCUSSION

The results of the experiment shown in the tables below, are in conformity with those of passivating metal but are more pronounced on some of the heat treated specimen as discussed below.
Observation in 0.25M H_2SO_4 and 0.5M H_2SO_4

A perusal at the corrosion penetration rate data in table 1-2 reviews weight loss which increases with time in the stainless steel alloy. This trend is in conformity with the fact that the degradation of materials in acidic environment has direct consequence on the media concentration (callister, 1997). However, the overall trend of the corrosion profile clearly depicts that of passivating metal subjected to simulated environment. In this case, the drift shows an initial increase in corrosion rate which depict the active region of the stainless steel until a limit is attained where passivation phenomenon sets in leading to a gradual decline in corrosion rate as exposure time increases (passive region attained). Hence in the solution of 0.25M H_2SO_4 , was observed that the annealed specimen (A) exhibit high passivity with the lowest corrosion penetration rate of 0.007mm/yr while the control sample has the highest corrosion penetration rate of 0.0450mm/yr. the annealed specimen (A) witness the lowest CPR due to the compact nature of the grain boundaries as a result of heat treatment as well as media saturation. In the same vein, the annealed specimen witnesses high passivity in 0.5M H_2SO_4 and low corrosion penetration rate (CPR) while the martensitic specimen witness sharp increase in penetration rate due to it initial active state.

Table 1: CPR Computed data in solution of 0.25m H₂SO₄

Conc.	Code	Exposure Time (hr)	Initial wt(g)	Final wt (g)	wt. diff (g)	CPR (mm/yr)
0.25MH ₂ SO ₄	M ₁₁	24	5.6123	5.5571	0.0552	0.0071
	M ₁₂	48	5.5571	5.1315	0.4256	0.0273
	M ₁₃	72	5.1315	4.6507	0.4808	0.0205
	M ₁₄	96	4.6507	4.1147	0.5360	0.0172
	M ₁₅	120	4.1147	3.5233	0.5914	0.0152
	M ₁₆	144	3.5233	2.8772	0.6461	0.0138
	M ₁₇	168	2.8772	2.1756	0.7016	0.0126
0.25MH ₂ SO ₄	A ₁₁	24	4.5912	4.5560	0.3520	0.0045
	A ₁₂	48	4.5560	4.4829	0.0731	0.0047
	A ₁₃	72	4.4829	4.3773	0.1056	0.0045
	A ₁₄	96	4.3773	4.2356	0.1417	0.0046
	A ₁₅	120	4.2356	4.0594	0.1762	0.0045
	A ₁₆	144	4.0594	3.7073	0.3521	0.0075
	A ₁₇	168	3.7073	3.3198	0.3875	0.071
0.25M H ₂ SO ₄	U ₁₁	24	5.8952	5.8120	0.0832	0.0107
	U ₁₂	48	5.8120	5.1109	0.7011	0.0450
	U ₁₃	72	5.1109	4.3746	0.7363	0.0315
	U ₁₄	96	4.3746	3.6023	0.7723	0.0240
	U ₁₅	120	3.6023	2.7958	0.8065	0.0207
	U ₁₆	144	2.7958	1.9537	0.8421	0.0180
	U ₁₇	168	1.9537	1.0764	0.8773	0.0161

Table 2: CPR Computed data in solution of 0.5M H₂SO₄

Conc.	Code	Exposure Time (hr)	Initial wt(g)	Final wt (g)	wt. diff (g)	CPR (mm/yr)
0.5MH ₂ SO ₄	M ₂₁	24	6.7132	5.8119	0.9013	0.1157
	M ₂₂	48	5.8119	5.6768	0.1351	0.0087
	M ₂₃	72	5.6768	5.4067	0.2701	0.0116
	M ₂₄	96	5.4067	5.0015	0.4052	0.0130
	M ₂₅	120	5.0015	4.4612	0.5403	0.0139
	M ₂₆	144	4.4612	3.7868	0.6744	0.0144
	M ₂₇	168	3.7868	2.9773	0.8095	0.0148
0.5MH ₂ SO ₄	A ₂₁	24	4.7895	4.7114	0.0781	0.0100
	A ₂₂	48	4.7114	4.6080	0.1034	0.0066
	A ₂₃	72	4.6080	4.4791	0.1289	0.0055
	A ₂₄	96	4.4791	4.3250	0.1541	0.0049
	A ₂₅	120	4.3250	4.1458	0.1795	0.0046
	A ₂₆	144	4.1458	3.9410	0.2048	0.0044
	A ₂₇	168	3.9410	3.7103	0.2307	0.0042
0.5MH ₂ SO ₄	U ₂₁	24	5.8679	5.3266	0.5413	0.0695
	U ₂₂	48	5.3266	4.7600	0.5666	0.0363
	U ₂₃	72	4.7600	4.1683	0.5917	0.0253
	U ₂₄	96	4.1683	3.5511	0.6172	0.0198
	U ₂₅	120	3.5511	2.9083	0.6428	0.0165
	U ₂₆	144	2.9083	2.2388	0.6695	0.0143
	U ₂₇	168	2.2388	1.5451	0.6937	0.0127

Table 3: CPR Computed data in solution of 0.25M NaOH

Conc.	Code	Exposure Time (hr)	Initial wt(g)	Final wt (g)	wt. diff (g)	CPR (mm/yr)
0.25MNaOH	M ₃₁	24	5.5917	5.5666	0.0251	0.00322
	M ₃₂	48	5.5666	5.5162	0.0504	0.00324
	M ₃₃	72	5.5162	5.4407	0.0755	0.00323
	M ₃₄	96	5.4407	5.3364	0.1043	0.00335
	M ₃₅	120	5.3364	5.2109	0.1255	0.00322
	M ₃₆	144	5.2119	5.0600	0.1509	0.00322
	M ₃₇	168	5.0600	4.8837	0.1763	0.00323
0.25MNaOH	A ₃₁	24	5.8712	5.8299	0.0413	0.0053
	A ₃₂	48	5.8299	5.7476	0.0823	0.0053
	A ₃₃	72	5.7476	5.6235	0.1241	0.0053
	A ₃₄	96	5.6235	5.1223	0.5012	0.0161
	A ₃₅	120	5.1223	4.5798	0.5425	0.0139
	A ₃₆	144	4.5798	3.9959	0.5839	0.0125
	A ₃₇	168	3.9959	3.3701	0.6258	0.0115
0.25MNaOH	U ₃₁	24	5.3527	5.2782	0.0345	0.00443
	U ₃₂	48	5.2782	5.2089	0.0693	0.00445
	U ₃₃	72	5.2089	5.1052	0.1037	0.00444
	U ₃₄	96	5.1052	4.9661	0.1391	0.00446
	U ₃₅	120	4.9661	4.7735	0.1726	0.00443
	U ₃₆	144	4.7735	4.5864	0.2071	0.00443
	U ₃₇	168	4.5864	4.3447	0.2417	0.00443

Table 4.4 CPR Computed data in solution of 0.5M NaOH

Conc.	Code	Exposure Time (hr)	Initial wt(g)	Final wt (g)	wt. diff (g)	CPR (mm/yr)
0.5MNaOH	M ₄₁	24	5.2093	5.1780	0.0313	0.00171
	M ₄₂	48	5.1780	5.1154	0.0626	0.00402
	M ₄₃	72	5.1154	5.0215	0.0939	0.00402
	M ₄₄	96	5.0215	4.8964	0.1251	0.00402
	M ₄₅	120	4.8964	4.7402	0.1562	0.00401
	M ₄₆	144	4.7462	4.5525	0.1877	0.00402
	M ₄₇	168	4.5525	4.3337	0.2188	0.00401
0.5MNaOH	A ₄₁	24	6.7852	6.7321	0.0531	0.0068
	A ₄₂	48	6.7321	6.6258	0.1063	0.0068
	A ₄₃	72	6.6258	5.9246	0.7012	0.0300
	A ₄₄	96	5.9256	5.1703	0.7543	0.0242
	A ₄₅	120	5.1703	4.3628	0.8075	0.0207
	A ₄₆	144	4.3628	3.5027	0.8601	0.0184
	A ₄₇	168	3.5027	2.5886	0.9141	0.0163
0.5MNaOH	U ₄₁	24	5.2751	5.2339	0.0412	0.00529
	U ₄₂	48	5.2339	5.1515	0.0824	0.00529
	U ₄₃	72	5.1515	5.0274	0.1241	0.00531
	U ₄₄	96	5.0274	4.8625	0.1649	0.00529
	U ₄₅	120	4.8625	4.6562	0.2063	0.00529
	U ₄₆	144	4.6562	4.4087	0.2475	0.0053
	U ₄₇	168	4.4087	4.1203	0.2884	0.00529

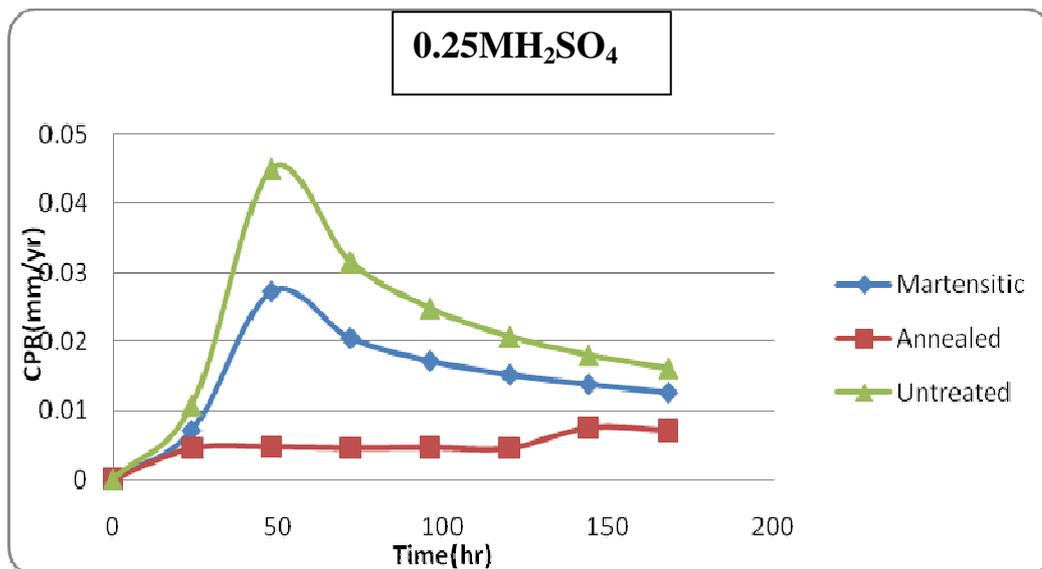


Fig1.1 Graph of CPR vs Time for 0.25MH₂SO₄

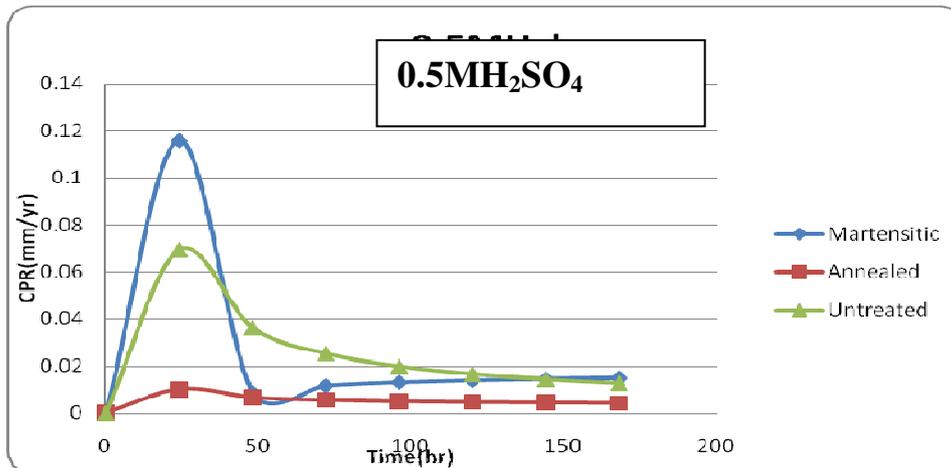


Fig1.2 Graph of CPR vs Time for **0.5MH₂SO₄**

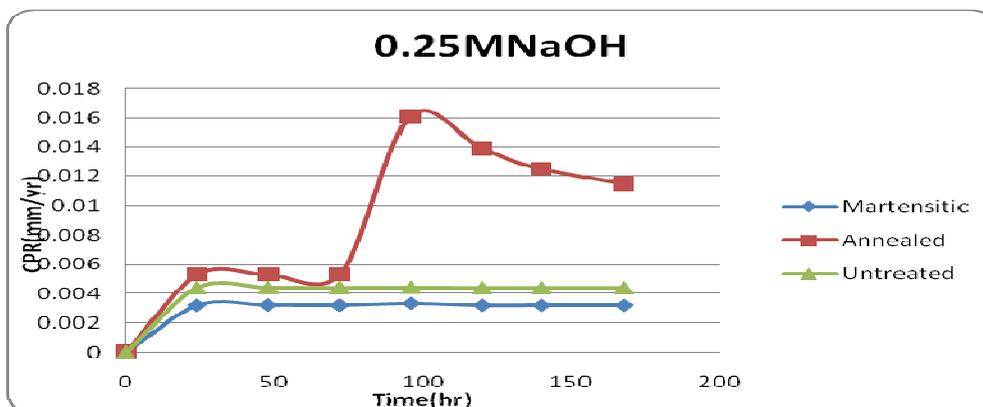


Fig1.3 Graph of CPR vs Time for **0.25MNaOH**

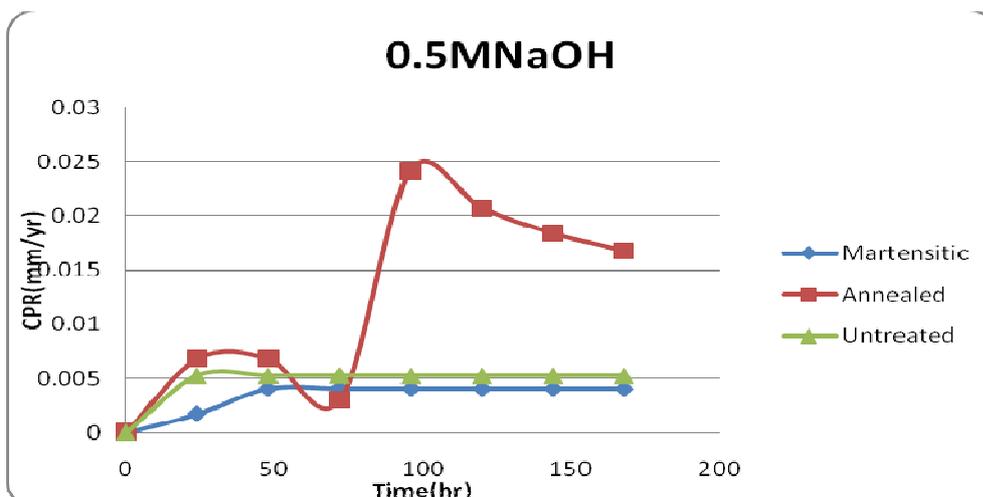


Fig1.4 Graph of CPR vs Time for **0.5MNaOH**

Comparatively, the corrosion penetration rate data from Table 3-4 shows a significant drift from those of table 1-2. The annealed specimen (A) exhibit high corrosion penetration rate (CPR) of 0.0161mm/yr in an basic environment of **0.25M NaOH** as compared to the martensitic and untreated stainless steel test coupons. This is basically consequence of higher oxygen diffusion rate and ionization which depicts a higher corrosion rate

profile as compared to lower ionized H_2SO_4 acidic environment. Furthermore, the electrical conductivity of the simulated environment is reduced which progressively leads to decline in diffusion rate of the soluble oxygen enriched media and hence a drastic reduction in corrosion kinetics due to immobility of current carrying ions. The martensitic specimen (M) in solution of 0.25M H_2SO_4 was observed to have the lowest penetration rate due to formation of passive thin film that inhibits further corrosion process. In the same vein, the corrosion penetration rate data from Table 3-4 reviews that the annealed specimen follows the trend of a passivating metal with noticeable pitting corrosion and intergranular attack.

CONCLUSION

The comparative analysis of corrosion behaviour of martensitic and annealed cast stainless steel in (0.25M-0.5M) H_2SO_4 and (0.25M-0.5M) NaOH have been successfully carried out using weight loss techniques (WLT). In general, it can easily be inferred that the phenomenon of passivation is predominant in the various media concentrations for both the acidic and basic media. The effect of heat treatment on the cast stainless steel (annealed and martensitic) has resulted in the reduction to the extent of passivation especially in the annealed specimen. This factor may be attributed to the compact nature of the grain boundaries as a result of redistribution in the grain boundaries as well as slip dislocation movement of grains. Furthermore, it becomes obvious that an acidic environment (H_2SO_4) of (0.25-0.5) molar concentration has adverse effect on cast stainless steel (70.90% Cr, 10%Ni 0.08% $^{\circ}C$) product which can be controlled by heat treatment process. In the same vein, a basic environment (NaOH) of (0.25-0.5) molar concentration has less severe effect on stainless steel specimen with composition (70.90% Fe, 19Cr, 10% Ni, 0.08% $^{\circ}C$) which can be controlled by heat treatment process as observed above. However, this research is inconclusive as further research will be conducted on the x-ray diffraction analysis as well as optical micrographic analysis to ascertain the grain boundary structural analysis as a site for corrosion kinetics and dislocation movement.

REFERENCES

- Ashby, M.D, (2007). Engineering of Material Plus-Kent Publisher Ram Nagar, New Delhi-110055, Fourth Edition.
- Antropov, L.I (1975). Theoretical Electrochemistry, Mir Publisher, Moscow.
- Callister W.D, 1997. Materials Science and Engineering. John Wiley and Sons Inc., New York.
- Idenyi N.E., C.E Ekuma and I.O Owate, 2006. The influence of alloy composition on the passivation layer characteristics of al-2n alloy systems. Proceedings of Materials Science and Technology 2006 meeting and Exhibition Cincinnati, Ohio, USA (October 15th -9th).
- Kruger, J. (2001). Electrochemistry of Corrosion, John Hopkins University Baltimore, MD 21218,USA.
- Reive R.W, 2000. Uhlig's Corrosion Handbook. John Wiley and Sons, New York, USA.
- Scheil A. (2006), American Iron and Steel Institute (AISI)