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Behavioral Corrosion Mechanism of Cold Worked Mild Caron Steel Immersed in Various Acidic Environments

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Abstract **Original Research Article**

This research work investigated the corrosion rate of cold worked mild carbon steel in Hydrochloric acid, Nitric acid, Acetic acid, Hydrogen tetraoxosulphate (VI) acid, and phosphorus acid, to determine the corrosivity of each of the acids, and susceptibility cold worked mild steel to corrosion in the used environment, using weight loss measurement approach. The coupons were measured prior to immersion and different weight measurement taken at interval of 24 hours, over the period of 168 hours. The difference in weight between the original weight and the weight at each 24 hour interval (weight loss), was estimated and used for calculating the corrosion rates. The results obtained showed that t HNO_3 is more aggressive in all the five acids considered.

Keywords: Cold work, mild carbon steel, weight loss, corrosion rate, acidic environment.

INTRODUCTION

Mild carbon steel is a vital material in the construction and fabrication industry [1-2]. It is extensively used in chemical and allied industries for the handling of acid, alkalis and salt solutions [3]. The good properties of mild carbon steel include [4-5]: its ultimate strength which is somewhere in the region of 29-30 ton per in^2, a modulus of elasticity about 13,000-13,500 ton per in^2, a yield strength of 15-16 tons per in^2, very ductile, relatively cheapness of production, high mechanical properties, ease of cold working and ability to be hot worked without loss of mechanical properties. Its major disadvantage is that, it re quires efficient protection to prevent corrosion [6].

The mild carbon steel has a chemical composition mainly iron with the addition of small percentages of other materials, principally carbon and manganese [2, 7]. The percentage of carbon is usually somewhere about 0.2% and in modern steels, the manganese content is not less than 2.5 times the carbon content [8]. Impurities such as sulphur and phosphorus are kept at a low level, usually 0.0055 for each. The addition of carbon and manganese is responsible for the superior mechanical properties of mild steel as compares with iron [8].

Cold working is a permanent plastic deformation of a metal at a temperature below its recrystallization point or annealing temperature, that is, any form of mechanical deformation processing carried out on a material below its recrystallization temperature. It is low enough to produce strain hardening. It is usually, but not necessary, conducted at room temperature. It is also referred to cold forming or cold forging.

Cold working process involves the alteration of the shape or size of a metal by plastic deformation. Processes include rolling, drawing, pressing, spinning, extruding and heading [9]. It is carried out below the recrystallization point usually at room temperature. Hardness and tensile strength are increased with the degree of cold work, whilst ductility and impact values lowered. The cold rolling and cold drawing of steel significant improves surface finish [10].

During cold working the crystal structure becomes broken up and distorted, and then the materials become strained or work-hardened. Cold working increases the mechanical strength which makes the material harder but more brittle. Its electrical resistivity also increases. However the metal becomes so hard that further attempt at cold working would result in fracture of the material.

In the industry cold working is a common practice. However, a cold work material might be affected in corrosion environment. The aim of this work is to investigate the general corrosion behavior and mechanism on cold worked in various acidic solution environments which include: hydrochloric acid, acetic acid, hydrogen tetraoxosulphate vl acid, and phosphoric acid with concentration varying from 0.5-2.5 mol per dm^3 at room temperature and at fixed time intervals. The objective of this work is to determine the rate of corrosion from weight loss measurement.

MATERIALS AND METHOD

The mild carbon steel used in this research work was obtained from Vinupet Steel Company, Warri, and Delta State. The elemental percentage composition was carried out at Delta State Company Limited, Ovian-Aladja, and Delta State.

The experiment involved the use of 25 pieces of cold worked mild steel coupons immersed in various environment of acidic solution. The corrosion environment used includes:

- Hydrochloric acid (HCl) of molar mass 36.5g, percentage purity 36%, specific gravity 1.17, and relative density of 1.17g/ml or 1170g/l
- Nitric acid (HNO_3) of molar mass of 63.01g/mol, percentage purity 68%, specific gravity 1.42 and relative density 1420g/L
- Acetic acid (CH_3COOH) of molar mass 60.05g/mol, percentage purity 99.7%, specific gravity 1.04, relative density 1040g/L
- Phosphoric acid (H_3SO_4) of molar mass of 98.0g, percentage purity 85%, specific gravity 1.685g/mol or 1685g/L and
- V. Hydrogen tetraoxosulphate VI acid (H_2SO_4) of molar mass 98g/mol, percentage purity 98%, specific gravity 1.305, relative density 1830.5g/L.

The concentrations vary from 0.5 to 2.5 moles per dm^3. The method employed for this research was simply the weight loss method, which involve the difference in weight of the coupon before and after exposure to the various corrosion medium at a given time interval and at room temperature. Different tags were used to ensure that the experiment was not mixed-up. To aid the process in observing the corrosion behavior on cold mild steel, the following equipment and apparatus were used:

Hacksaw

This tool enabled the cutting exercise.

Vice

This device aids the positioning of the flat steel bar prior to cutting.

Drilling Machine

This allows for hole to be drilled enabling a hold-point on the coupon.

pH Paper

This enables the acidity and the basicity of the solution to be known.

Volumetric Flask

Used to hold the corrosive solution in which the coupon is immersed.

Beakers

It was used for measuring of the solutions.

Vernier Calliper

It was used to measure the dimensions and thickness of the coupon.

Nylon Thread

This was used to aid the suspension of the coupons in the solutions.

Mettler PM II Sensitive Balance

It was used to measure the variation in weight of the coupon at different stages.

Coupons Preparation

The flat steel bar of about 1500mm x 20mm was cold worked using three-high rolling mill machine to plastically deform the metal into a cylindrical shape, this was manually done.

Preparation of Coupon to Size

The 1500mm x 20mm (flat steel bar) was cut into 50mm x 19.5mm for ease of experiment, producing 25 sets of coupon. This was achieved by clamping the 1500mm x 20mm flat steel bar into a vice and then using hacksaw to cut the desired dimensions. After which a hole of 4mm diameter was drilled on each coupon using an electrically operated drilling machine with 4mm diameter drilling bit. The drilled hole is to aid the suspension of the coupons in different acidic environment using nylon thread. No further preparation or treatment was given to the coupon except being washed in distilled water as shown in figure 1 below.

Fig-1: Steel bar Specimens

Preparation of Standard Corrosion Solution

The various stock solution used for the experiment were prepared using Equation (1) to Equation (3).

Amount of stock solution in g/dm^3 = percentage purity x relative density/100 (1)

Number of moles = mass of substance in g per dm^3/molar mass in g per (2)

After knowing the concentration of the stock solution, the volume of the stock solution required to prepare each of the environment was calculated using the dilution formula as shown in Equation (3).

$V_1M_1=V_2M_2$ (3)

Where,

M_1 = Concentration of stock solution

V_1 = Volume of stock solution required to make environment.

M_2 = Concentration of environment to be prepared.

V_2 = Volume of environment to be prepared

For HCL acid

Molar mass of HCL = 36.5g

Percentage purity = 36%

Specific gravity = 1.17

Relative density = 1.17g/ml or 1170g/L

To calculate the amount of the stock solution:

Percentage purity x relative density

= 36/100 x 1170 = 421.2g/L

Amount of stock in mol/dm^3 = 11.54MHCL

Thus, 36% of hydrochloric acid contains 11.54M of undiluted HCL

For concentration of 0.5MHCL using the dilution formula

$V_1 = M_2V_2/M_1$

$M_1 = 11.53$

$M_2 = 0.5$

V_2 = 200ml

V_1 = ?

Hence, V_1 = 0.5x200/11.53 = 8.67ml

Then, Volume of distilled water, 200ml – 8.67ml = 191.33ml

Thus, 8.67ml of concentrated HCl acid was dissolved into 19.33ml of distilled water to give an environment of 200ml to 0.5M.

Same procedures were adopted for all reagents used. Table1 shows the volume of the stock solution (acid) required to prepare each concentration of the different environment.

Table-1: Volume of the Stock Solution (Acid) required preparing each Concentration of the different Environment

Concentration (M)	Volume of acids used (cm^3)				
	H_2SO_4	HCl	HNO_3	CH_3COOH	H_3PO_4
0.5	8.67	6.53	5.79	6.84	5.46
1.0	17.35	13.05	11.58	13.69	10.92
1.5	26.02	19.58	17.37	20.53	16.38
2.0	34.69	26.11	23.16	27.38	21.85
2.5	43.37	32.64	28.95	34.22	37.31

Experimental Procedures

After preparing the various stock solutions, fifty (50) sets of clean beakers were tagged with the name of the various acids, with CW, denoting cold worked specimen. Each of five (5) corrosion environment having ten (10) beakers each, five of which is for cold worked specimen, with various concentration ranging from 0.5M to 2.5M. Prior to immersion, the approximate pH value of each solution was taken, using a pH meter, and the value recorded. The specimens were properly washed with distilled water, dried with clean piece of cloth, and then the initial weight was taken, using the Meter PM II Sensitive Digital weigh balance, and then recorded. Total immersion in 200ml test solution of the specimens into the various environment, was aided with the use of a nylon rope tied to a clean to a clean flattened steel rod of about 3mm diameter, placed on top of each beaker, for support as shown in figure 2 below.

Fig-2: Experimental Set up

RESULTS AND DISCUSSION

The mild steel material elemental composition from the spark test analysis result is as follow; 0.15%C, 0.22% Si, 0.5% Mn, 0.66%P, 0.057%S, 0.02%Mo, 0.25% Cr, 0.1%Ni, 0.26%0.009%V, 0.001%Al, 0.021%Sn, 0.001%Ti and 98.34%Fe. Table 2 Table 6 shows the weight in grams (g) obtained from the measurement taken at twenty four (24) hours intervals.

Table-2: Weight (g) of Cold Worked Coupons in Hydrochloric Acid (HCL) Environment

Time (hrs.)	Concentrations (M)				
	0.5M	1.0M	1.5M	2.0M	2.5M
Wi	18.2847	18.0496	17.8735	17.7044	18.1717
24hrs.	18.1706	17.8851	17.6139	17.382	17.8116
48hrs.	18.0807	17.7561	17.5497	17.297	17.605
72hrs.	18.0007	17.657	17.3255	17.0119	17.298
96hrs.	17.8962	17.4087	17.0379	16.7324	16.7754
120hrs.	17.646	17.1924	16.7221	16.0795	16.3787
144hrs.	17.5485	16.9149	16.4184	15.7005	15.8943
168hrs.	17.4509	16.7374	16.2147	16.1215	15.4009

Table-3: Weight (g) of Cold Worked Coupons in Nitric Acid (HNO_3) Environment

Time (hrs.)	Concentrations (M)				
	0.5M	1.0M	1.5M	2.0M	2.5M
Wi	18.3432	18.2542	18.2289	18.7698	18.3904
24hrs.	16.6399	14.3821	11.654	10.7968	10.0893
48hrs.	15.9995	14.1878	11.4681	10.2728	9.5347
72hrs.	15.7591	13.6935	11.0822	9.9487	8.9874
96hrs.	15.427	13.5897	10.8793	9.6246	7.9021
120hrs.	15.2713	13.4835	10.5811	9.0362	7.423
144hrs.	15.1828	12.2852	10.3613	8.6489	7.0237
168hrs.	15.1828	12.7869	9.5415	8.2616	6.4244

Table-4: Weight (g) of Cold Worked Coupons in Acetic Acid (CH_3COOH) Environment

Time (hrs.)	**Concentrations (M)**				
	0.5M	1.0M	1.5M	2.0M	2.5M
Wi	17.6871	18.4322	18.3568	18.1569	18.5254
24hrs.	17.6065	18.3511	18.2683	18.0631	18.4223
48hrs.	17.5859	18.3302	18.2409	18.0275	18.3807
72hrs.	17.5652	18.3093	18.2235	18.0028	18.3591
96hrs.	17.5484	18.2874	18.1879	17.9716	18.3115
120hrs.	17.5268	18.2713	18.1707	17.9632	18.2904
144hrs.	17.5045	18.2486	18.157	17.9384	18.273
168hrs.	17.4822	18.2258	18.1193	17.9136	18.2455

Table-5: Weight (g) of Cold Worked Coupons in phosphoric Acid (H_3PO_4) Environment

Time (hrs.)	**Concentrations (M)**				
	0.5M	1.0M	1.5M	2.0M	2.5M
Wi	18.2602	18.3466	18.0722	17.8402	18.2308
24hrs.	18.1683	18.232	17.9402	17.6774	18.1198
48hrs.	18.1213	18.212	17.9168	17.662	18.0317
72hrs.	18.0743	18.1479	17.8633	17.6265	17.9993
96hrs.	18.0123	18.081	17.7047	17.5592	17.9396
120hrs.	17.9483	18.0021	17.7953	18.2392	17.999
144hrs.	17.9483	17.6413	18.1707	17.4692	17.8284
168hrs.	17.8254	1709109	17.5996	17.3367	17.5548

Table-6: Weight (g) of Cold Worked Coupons in Hydrogen Tetraoxosulphate (VI) Acid (H_2SO_4) Environment

Time (hrs.)	Concentrations (M)				
	0.5M	1.0M	1.5M	2.0M	2.5M
Wi	18.0903	18.159	18.7216	18.1082	18.4389
24hrs.	17.9803	17.9899	18.5237	17.9066	18.2186
48hrs.	17.9172	17.8895	18.4199	17.7717	18.0330
72hrs.	17.8441	17.8291	18.276	17.6968	17.6473
96hrs.	17.7128	17.7331	18.1399	17.4973	17.1739
120hrs.	17.6356	17.6523	18.0939	17.1077	16.7954
144hrs.	17.5383	17.5081	17.9546	16.8114	16.4510
168hrs.	17.4209	17.4038	17.3252	16.5151	16.1066

From the measured weight presented in Tables 2 to Table 6 above, the weight loss of coupons was calculated which is the difference between the original weight before immersion and the weight after immersion at a given time. Tables 7 to Table represent the weight loss for the various environments.

Table-7: Weight Loss (mg) of Cold Worked Coupons in HCL Environment

Time (hrs.)	Concentrations (M)				
	0.5M	1.0M	1.5M	2.0M	2.5M
24hrs.	0.1141	0.1645	0.2596	0.3224	0.3601
48hrs.	0.204	0.2935	0.3238	0.4074	0.5667
72hrs.	0.284	0.3926	0.548	0.6925	0.8734
96hrs.	0.3885	0.6409	0.8356	0.972	1.3693
120hrs.	0.6387	0.8572	1.1514	1.6249	1.793
144hrs.	0.7362	1.1347	1.4551	2.0039	2.2774
168hrs.	0.8338	1.1322	1.6588	2.5829	2.7618

Table-8: Weight Loss (mg) of Cold Coupons in HNO_3 Environment

Time (hrs.)	Concentrations (M)				
	0.5M	1.0M	1.5M	2.0M	2.5M
24hrs.	1.7033	3.8721	6.5749	7.973	8.3011
48hrs.	2.3437	4.0664	6.7608	8.497	8.8557
72hrs.	2.5841	4.5607	7.1467	8.8211	9.403
96hrs.	2.9162	4.6645	7.3496	9.1452	10.4883
120hrs.	3.0719	4.7707	7.6478	9.7336	10.9674
144hrs.	3.1161	4.969	7.8676	10.1209	11.3667
168hrs.	3.6104	5.4673	8.6874	10.5082	11.966

Table-9: Weight (mg) Loss of Cold Worked Coupons in CH_3COOH Environment

Time (hrs.)	Concentrations (M)				
	0.5M	1.0M	1.5M	2.0M	2.5M
24hrs.	0.806	0.8011	0.0885	0.0938	0.1031
48hrs.	0.1012	0.102	0.1159	0.1294	0.1447
72hrs.	0.1219	0.1229	0.1333	0.1541	0.1663
96hrs.	0.1387	0.1448	0.1689	0.1853	0.2139
120hrs.	0.1603	0.1609	0.1816	0.1937	0.235
144hrs.	0.1826	0.1836	0.1998	0.2185	0.2524
168hrs.	0.2049	0.2064	0.2375	0.2433	0.2799

Table-10: Weight (mg) Loss of Cold Worked Coupons in H_3PO_4 Environment

Time (hrs.)	Concentrations (M)				
	0.5M	1.0M	1.5M	2.0M	2.5M
24hrs.	0.0919	0.1146	0.132	0.1628	0.187
48hrs.	0.1389	0.1466	0.1554	0.1782	0.1991
72hrs.	0.1859	0.1987	0.2089	0.2737	0.2315
96hrs.	0.2479	0.2545	0.2769	0.289	0.2912
120hrs.	0.2603	0.2609	0.2816	0.2937	0.335
144hrs.	0.3119	0.3445	0.3675	0.371	0.4034
168hrs.	0.4348	0.4357	0.4726	0.5035	0.6746

Table-11: Weight (mg) Loss of Cold Worked Coupons in H_2SO_4 Environment

Time (hrs.)	Concentrations (M)				
	0.5M	1.0M	1.5M	2.0M	2.5M
24hrs.	0.1100	0.1691	0.1979	0.2016	0.2203
48hrs.	0.1731	0.1695	0.3017	0.3365	0.4059
72hrs.	0.2462	0.3299	0.4456	0.4114	0.7916
96hrs.	0.3775	0.4259	0.2817	0.6109	1.265
120hrs.	0.4547	0.5067	0.6277	1.0005	1.6435
144hrs.	0.5520	0.6509	0.3675	1.2968	1.9879
168hrs.	0.6694	0.7554	1.3964	1.5931	2.3323

Coupon Total Surface Area

The total surface area of the coupon was calculated using the formula stated below owing to its geometry as shown below;

$A = 2(LW + Wt + Lt)$ (1)

where,
A = Total surface area of the coupon,
L = Length of Coupon
W = Width of coupon
t = thickness of coupon, and

The coupons used for the research were of the following dimension:
L = 50millimeter (mm) = 1.960 inches (in)
W = 19.5mm = 0.768in
T = 2.5mm = 0.098in

Therefore;
$A = 2[(1.969 \times 0.768) + (0.768 \times 0.098) + (1.969 \times 0.098)]$
A = 3.561 sq. inch
Density of mild steel = 7.85g/cm_3

Considering the hot worked coupon in 0.5M HCl environment at 24h, the corrosion rate was calculated as follows

Weight loss = 0.01098g = 109.8mg
Substituting into "CR" formula,

$$CR = \frac{534 \times 109.8}{7.85 \times 3.561 \times 24} = 87.4 \text{ mpy}$$

Figure 1 and Table 12 show the corrosion rates calculated for the various weight loss. The calculated weight loss obtained for cold worked coupons, increases with increasing acid concentration for all five acids as reflected in the normalized graph, indicating accelerated behavior for the metal dissolution. This result is expected because, with increasing acid concentration, both acidity and CI – ion concentration were increased too. It could be seen that the weight loss of cold HNO3 and HCl were higher and this was as the results of the acid concentration. The observed increase in corrosion rate of the cold worked coupons can be attributed to segregation of carbon, or nitrogen atoms at imperfection site produced by plastic deformation, and the higher residual stresses, or energy produced in the material by cold working.

Comparing the corrosion rate of the coupons at different environment shown that HNO_3 proved to be more aggressive, followed by HCL, and H_2SO_4 as while CH_3COOH, proved to be the least aggressive acid among the five acids used for the research for both the hot worked and cold worked coupons.

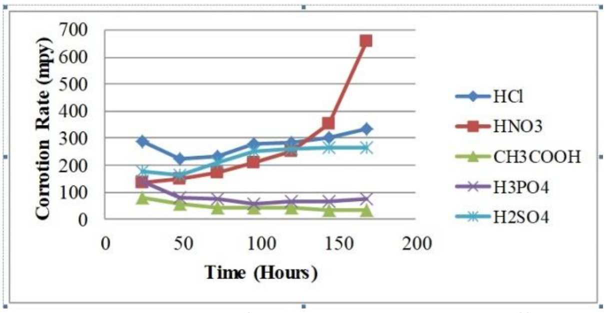

Fig-1: Corrosion Rate of Cold Worked Coupons at Different Environment

Table-12: Corrosion Rate of Cold Worked Coupons at Different Environment

	Concentrations of Acid				
Duration (Hrs.)	0.5M	1.0M	1.5M	2.0M	2.5M
24	286.6	136.06	82.1	140.9	175.3
48	225.2	150.79	57.6	79.2	161.5
72	231.7	174.59	44.1	74.7	210
96	277.8	208.71	42.6	57.9	251.7
120	285.4	249.48	42.6	64.1	261.6
144	302.1	352.44	33.5	64.9	263.7
168	336.8	660.73	31.8	76.9	265.2

CONCLUSIONS

This study investigated the corrosion behavior of mild steels in different acidic environment (HCl, HNO_3, CH_3COOH, H_3SO_4, and H_2SO_4). The results obtained revealed that corrosion rates increased with increased in acid concentration. It was observed that nitric acid (HNO_3) prove to be a more corrosive acid among five acids considered in this research work. This was followed by hydrochloric acid (HCL), hydrogen tetraoxosulphate (VI) acid (H_2SO_4) and phosphoric acid (H_3PO_4). However, acetic acid (CH_3COOH) proved to be the least corrosive acid. Visual inspection of the coupons after immersion in the various acidic solution environments of different concentrations showed general and pitting corrosion, and the latter became more pronounced at higher level of the various acidic solution environment concentrations.

RECOMMENDATION

Based on the corrosion behavior of cold work mild steel in various acidic environments, further research work should be conducted to determine the effect of temperature change on the corrosion rate of cold worked mild steel.

REFERENCES

1. Onyekpe B. The Essentials of Metallurgy and Materials in Engineering. 2002.
2. Abdulkhaleq LG. The inhibitive effect of Eucalyptus camaldulenis leaves extracts on the corrosion of low carbon steel in HCl. J. Eng. Dev. 2013;17(3):1555-69.
3. International Journal of Advances in Scientific Research and Engineering (ijasre). 2018; 4(12)
4. Afolabi AS. Corrosion and stress corrosion behaviors of low and medium carbon steels in agro-fluid media. Leonardo Electronic Journal of Practices and Technologies. 2007 Jan;10:55-66.
5. Noor EA, Al-Moubaraki AH. Corrosion behavior of mild steel in hydrochloric acid solutions. Int. J. Electrochem. Sci. 2008 Jul 1;3(1):806-18.
6. Mathina A, Rajalakshmi R. Corrosion inhibitor on of Mild steel in acid Medium using Canna indica as Green corrosion Inhibitor. RASAYAN Journal Chemistry. 2016;9(1):56-66.
7. Akeer E, Brown B, Nesic S. The influence of mild steel metallurgy on the initiation of localized CO2 corrosion in flowing conditions. CORROSION/2013, paper. 2013 Mar 17;2383.
8. Adedayo AV, Ibitoye SA, Oyetoyan OA. Annealing heat treatment effects on steel welds. Journal of minerals and materials characterization and Engineering. 2010 Jun 20;9(06):547.
9. Aramide FO, Olorunniwo EO, Atanda PO, Borode JO. Corrosion Characteristics of Ascast Ductile Iron in Lime Juice. Journal of Minerals and Materials Characterization and Engineering. 2010 Oct 20;9(10):867.
10. Kamachi UM. “Corrosion Science and Technology: Mechanism, Mitigation and Monitoring, Mumbai”, narosa publishing house
11. Callister DW. “Materials Science and Engineering”: An Introduction, 7th Edition, John Wiley and Sons Incorporation, UK
12. Daramola OO, Adewuyi BO, Oladele IO. Corrosion behaviour of heat treated rolled medium carbon steel in marine environment. Journal of Minerals and Materials Characterization and Engineering. 2011 Aug 10;10(10):888.
13. Oyejide JO, Orhorhoro EK, Ogie AN, Idi US. Investigation of the effect of annealing on the corrosion resistance of medium carbon steel in sea water. Journal of Emerging Trends in Engineering and Applied Sciences. 2017 Oct 2;8(5):219-24.