DOI: https://doi.org/10.53555/nnmce.v5i3.303 **Publication URL: http://nnpub.org/index.php/MCE/article/view/303**

COMPARATIVE STUDY OF HIGH TEMPERATURE OXIDATION OF MILD STEEL IN HYDROGEN, SULPHUR, AND CARBON DIOXIDE ATMOSPHERES.

Obotowo W. Obot[1]*, Chinda Believe Chibuike[2]
**[1]Department of Mechanical and Aerospace Engineering University of Uyo, Nigeria, obotowo2009@gmail.com*
[2]Department of Mechanical and Aerospace Engineering University of Uyo, Nigeria, bewise3332@yahoo.com

****Corresponding Author: -***
Email: obotowo2009@gmail.com

Abstract: -

Fabricated materials made from mild steel tend to corrode when exposed to the atmosphere overtime, and often result mostly in the complete failure of materials while in service. This research aimed at establishing the relationship between oxidation of mild steel and temperature; the comparison of oxidation of mild steel at high temperature in different atmospheres, and the calculation of the rate of oxidation of mild steel at elevated temperatures. Mild steel finds application in weldable boiler tubes and in weldable turbines requiring very high temperature for its operation, hence this research was carried out at a maximum temperature of 1000 ^{O}C and samples were pre-treated in the different atmospheres for 96 hours intervals for 480 hours. The mild steel samples used in this research were labelled samples 1 and 2 and composed 0.19875 %C and 0.19220 %C, respectively. The atmospheres in which the experiment was carried out included hydrogen, sulphur and carbon dioxide. The result of the experiment showed that the rate of oxidation of mild steel followed parabolic relationship, also the rates were different in the different atmospheres and the highest rate occurred in carbon dioxide.

Keywords: *Mild Steel, Oxidation, Aqueous Solution, Atmosphere, Weight Change.*

1.0 INTRODUCTION

Mild steel, also known as low carbon steel, is one of the classes of plain carbon steels with 0.05 - 0.25 %C. Other types of plain carbon steel include medium carbon steel with 0.3 - 0.6 %C, and high carbon steel containing 0.7% - 1.4 %C. The melting point of mild steel is 1400 ^{O}C. Mild steel is malleable, ductile, rusts readily, absorbs shocks, it is tough and elastic than wrought iron, R. K. Rajput (2004). Plain carbon steel has high fatigue strength, good yield strength, excellent thermal characteristics, and retains its property at temperatures typically found inside fire tube industrial boilers and welded turbines H. S. Bawa, (2009). Oxidation is a chemical reaction that occurs between metallic substrates and the reacting gases present in the environment due to thermodynamic instability of the substrate when exposed to these gases. The simplest oxidation reactions obey logarithmic, parabolic, or linear models, which represent limiting and ideal cases; as illustrated in Khana A. S., (2002). It is common to encounter deviations from this ideal model under real life applications, in which rate data can only be fitted by use of intermediate rate equations and/or combination of the ideal models.

1.1 Parabolic Reaction Rate

The oxidation behaviour of the majority of metals and metallic alloys follow parabolic kinetics during high temperature oxidation. The rate limiting step is the thermal diffusion of the ionic species through a compact oxide film and the driving force is the chemical potential gradient that develops across the film Kofstad, P (1966). The equation that describe parabolic kinetics is

$$X^2 = K_p t + C -------------------1.1$$

Where,

- X is the oxides thickness or mass, oxygen consumed per surface area
- K_p is the parabolic rate constant.
- t is time and C is constant

1.2 Logarithmic Reaction Rate

Logarithmic kinetics typically occurs at temperature below 400 ^{O}C and for oxide film thickness of 100nm or less. The equation for its reaction is

$$X = K_{\log} Log(t + t_0) + A ---------------1.2$$

Where,

- X is the oxides thickness or mass, oxygen consumed per surface area
- K_{log} is the logarithmic rate constant
- t and t_o are time and A is constant.

1.3 Linear Reaction Rate

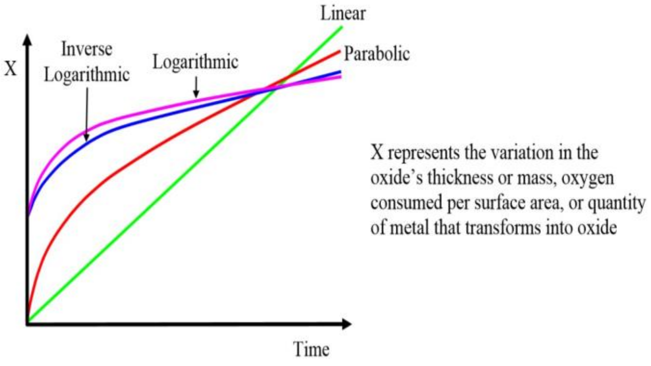
In linear kinetics, the oxidation rate is constant with time and independent of the amount of gas or metallic substrate consumed. Surface and/or phase boundary processes are the rate-limiting mechanism. The equation for linear kinetics is as follows

$$X = K_l t + C ---------------1.3$$

Where,

- X is the oxides thickness or mass, oxygen consumed per surface area
- K_l is the linear rate constant
- t is time and C is a constant

The various simple reaction rates are shown in Figure 1, where X represents the change in the parameter of interest such as the thickness of the oxide or the weight of the sample.



X represents the variation in the oxide's thickness or mass, oxygen consumed per surface area, or quantity of metal that transforms into oxide

Fig 1: Comparison of graphs of different oxidation reaction rates equations.

(Source the ASM Handbook volume 13a)

Theory of Heat Treatment of Steel

The theory of heat treatment is based on the fact that a change takes place in the internal structure of steel at specific temperature, according to Brooks, C. R. (1996). Steel in its simplest form is composed of pure iron to which a small percentage of carbon has been added. At normal temperature the steel consists of the iron, known as ferrite combined with iron carbide, which is called cementite, Porter, et al. (1992). OK Vander Voort, G. (1991) illustrated that the hard brittle iron carbide does not become fully combined with the iron however, until a temperature of approximately 800 ^{O}C is reached. If the steel is heated progressively it will be found that at this point the temperature of metal does not increase, although heat is still being added. This is owing to the fact that the increased heat is for the time being, used up in bringing about a structural and chemical change in the metal. The carbon is in fact going into what is termed as solid solution with the iron, although the steel is well below the melting point. This is termed the decalescence point or upper critical point by metallurgists. When the change has taken place, the temperature of steel begins to rise again. If the steel is removed from heat at this stage and allowed to cool, a point will again be found at which the cooling appears to be arrested, and the metal may even appear to rise slightly in temperature, this is termed recalescence point or lower critical point and indicates the metal is changing back from a solution to a mixture of iron and iron carbide. Once the change has taken place, the metal continues to cool at a normal rate. The critical points are separated by a temperature difference of 30 to 105 ^{O}C, according to the composition of the steel the recalescence point is being lower than decalescence point. The iron carbon equilibrium diagram shows the manner in which the carbon content affects the structure of steel during heat treatment. The terms on the diagram may be simply understood, pure iron ferrite and iron carbide termed cementite has already been referred to, the ferrite and cementite combine in layers and the resultant structure is termed pearlite. Micheal S. Mamlouk, and John P. Zaniewski (2011), stated that if the heating process is continued beyond the critical temperature, the pearlite dissolves to form austenite. When the steel contains 0.89% of carbon, a true pearlite structure is obtained, with less carbon some free iron remains uncombined, whereas an excess of carbon over 0.89% results in uncombined cementite. If a piece of steel is heated above its upper critical point until it becomes cherry red, i.e., its austenitic condition which is equivalent to about 900 ^{O}C, and is then plunged into cold water to cool it, the sudden cooling traps the carbon in its solid solution state and an extremely hard, needle-shaped structure known as martensite is formed, R. K. Rajput (2004).

2.0 Materials and Methods

Sample 1 was polished by filing and mechanically cut into 16mm thickness and 30mm long, it is cylindrical in shape. Sample 2 which has the shape of a cuboid was also cut mechanically into dimensions of 40mm length by 30mm width by 3.5mm thickness, this was made possible with the help of a hacksaw, and samples were griped in a vice while cutting operation was going on. Samples were first drilled with a drilling machine using 2.5mm drill bit. Electronic weighing balance Model MSa 225S was used to weigh the samples and then stored in a desiccator. Electric furnace was used to heat the steel samples to 800 ^{O}C and 1000 ^{O}C only. A pair of tongs was used to remove samples from electric furnace. 60 samples comprising 30 pieces of sample 1 and 30 pieces of sample 2 were used in the experiment. A set of samples were analysed in the Defence Industries Corporation of Nigeria (DICON), a research and development centre in Kaduna. The result of the chemical composition is shown in Table 1.

Table 1: Chemical composition of samples

Element	Symbol	Content	
		Sample 1	Sample 2
Carbon	C	0.19875	0.19220
Silicon	Si	0.18670	0.15592
Iron	Fe	98.12502	98.15511
Copper	Cu	0.00331	0.00772
Manganese	Mn	1.03600	1.03621
Phosphorus	P	0.04012	0.02819
Lead	Pb		
Sulphur	S	0.05029	0.04232
Nitrogen	N	0.01100	0.01100
Molybdenum	Mo	0.26512	0.26950
Tin	Sn	0.02118	0.01142
Titanium	Ti	0.01715	0.01922
Cobalt	Co	0.01240	0.01448
Zinc	Zn	0.00340	0.00340
Nickel	Ni	0.02956	0.05331

Tap water and aqueous solution of sulphur and calcium carbonate prepared with 100 grammes of sulphur and calcium carbonate with 1000 cm^{3} of deionized water were used in this experiment. Samples 1 and 2 were first weighed and then pre-treated by allowing them in these solutions and used at 96hours, 192hours, 288hours, 384hours and 480hours. Upon treatment, atmospheres of hydrogen (H_2), sulphur(S) and carbon dioxide (CO_2) were created, hence these equations from Osei Yaw Ababio, (2000).

$$3Fe_{(s)} + 4H_2O_{(g)} \rightarrow Fe_3O_{4(s)} + 4H_{2(g)} \text{-----------------} 2.1$$
$$Fe_{(s)} + S_{(s)} \rightarrow FeS_{(s)} \text{-------------------------} 2.2$$
$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \text{---------------------} 2.3$$

After pre-treatment of samples for 96 hours in hydrogen atmosphere; samples 1 and 2 were heated to 800^{O}C, allowed to cool in the furnace and weighed again, its weight differential was recorded. A fresh set of samples of 1 and 2 heated to 1000 ^{O}C was subjected through the above procedure. Similarly, the procedure above using two sets of samples for sulphur and carbon dioxide atmospheres.

3.0 Results and Discussions

The results of passing mild steel samples 1 and 2 through hydrogen atmosphere at 800 ^{O}C are presented in Tables 2 and 3, also the results of exposing these samples in hydrogen atmosphere at 1000 ^{O}C are presented in Figures 2 and 3. Similarly, the results of passing these samples through sulphur atmosphere at 800 ^{O}C and 1000 ^{O}C are presented in Tables 4 and 5, and Figures 4 and 5, respectively. Finally, the results of passing same samples through carbon dioxide atmosphere at 800 ^{O}C and 1000 ^{O}C are presented in Tables 6 and 7, and Figures 6 and 7, respectively.

Table 2: Oxidation of mild steel sample 1 in hydrogen atmosphere at 800 ^{O}C

Times (hours)	Initial weight (g)	Final weight (g)	Weight Change (g)
96	44.15	44.15	0.00
192	44.15	44.15	0.00
288	45.00	45.05	0.05
384	45.00	45.05	0.05
480	45.00	45.00	0.00

Table 3: Oxidation of mild steel sample 2 in hydrogen atmosphere at 800 ^{O}C

Times (hours)	Initial Weight (g)	Final Weight (g)	Weight Change (g)
96	31.10	31.20	0.10
192	31.10	31.15	0.10
288	31.50	31.60	0.10
384	31.50	31.55	0.05
480	31.50	31.50	0.00

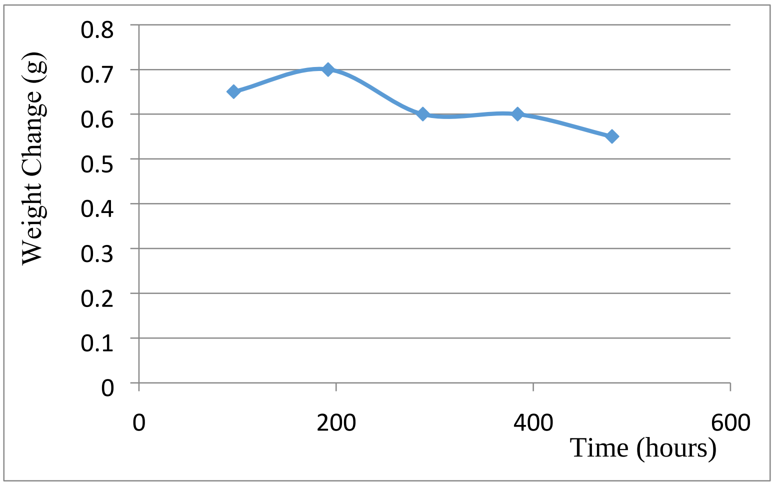


Fig 2: Oxidation of mild steel sample 1 in hydrogen atmosphere at 1000 ^{O}C

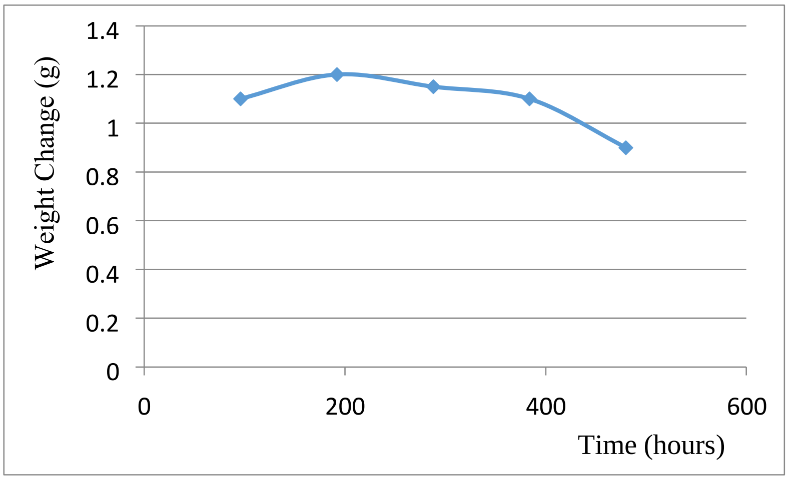


Fig 3: Oxidation of mild steel sample 2 in hydrogen atmosphere at 1000 ^{O}C

Table 4: Oxidation of mild steel sample 1 in sulphur atmosphere at 800 ^{O}C

Time (hours)	Initial Weight (g)	Final Weight (g)	Weight Change (g)
96	43.65	43.65	0.00
192	43.60	43.45	-0.15
288	43.80	43.60	-0.20
384	44.00	43.70	-0.30
480	44.20	43.90	-0.30

Table 5: Oxidation of mild steel sample 2 in sulphur atmosphere at 800 ^{O}C

Time (hours)	Initial Weight (g)	Final Weight (g)	Weight Change (g)
96	31.45	31.45	0.00
192	31.65	31.60	-0.10
288	31.70	31.40	-0.30
384	31.75	31.55	-0.25
480	31.95	31.65	-0.30

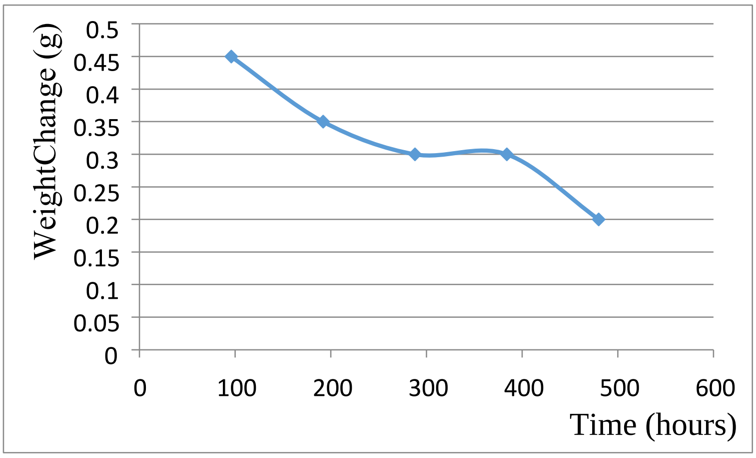


Fig 4: Oxidation of mild steel sample 1 in sulphur atmosphere at 1000 ^{O}C

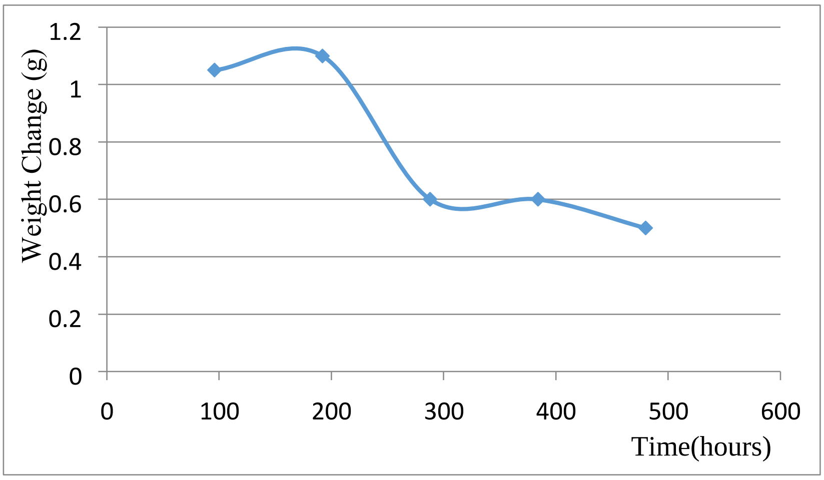


Fig 5: Oxidation of mild steel sample 2 in sulphur atmosphere at 1000 ^{O}C

Table 6: Oxidation of mild steel sample 1 in carbon dioxide atmosphere at 800 ^{O}C

Time (hours)	Initial Weight (g)	Final Weight (g)	Weight Change (g)
96	40.85	40.85	0.00
192	40.85	40.85	0.00
288	41.35	41.40	0.05
384	41.45	41.50	0.05
480	42.75	42.80	0.05

Table 7: Oxidation of mild steel sample 2 in carbon dioxide atmosphere at 800 ^{O}C

Time (hours)	Initial Weight (g)	Final Weight (g)	Weight Change(g)
96	30.45	30.45	0.00
192	30.55	30.60	0.05
288	30.70	30.75	0.05
384	30.80	30.85	0.05
480	30.85	30.95	0.10

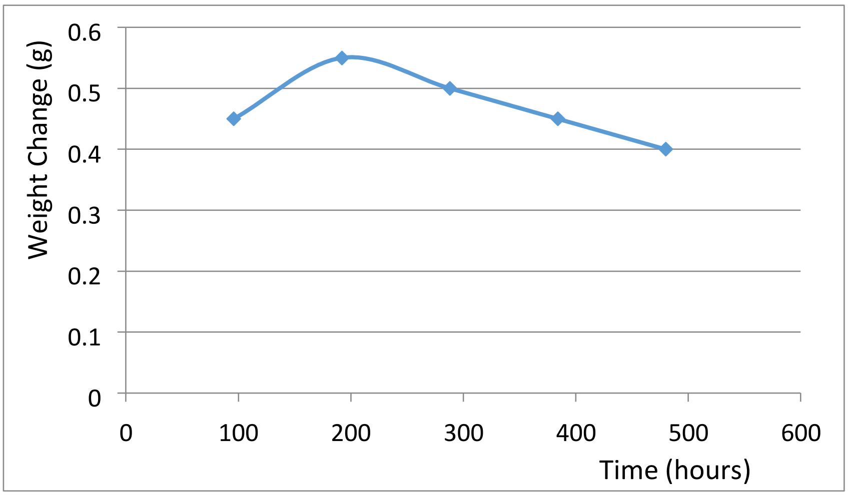


Fig 6: Oxidation of mild steel sample 1 in carbon dioxide atmosphere at 1000 ^{O}C

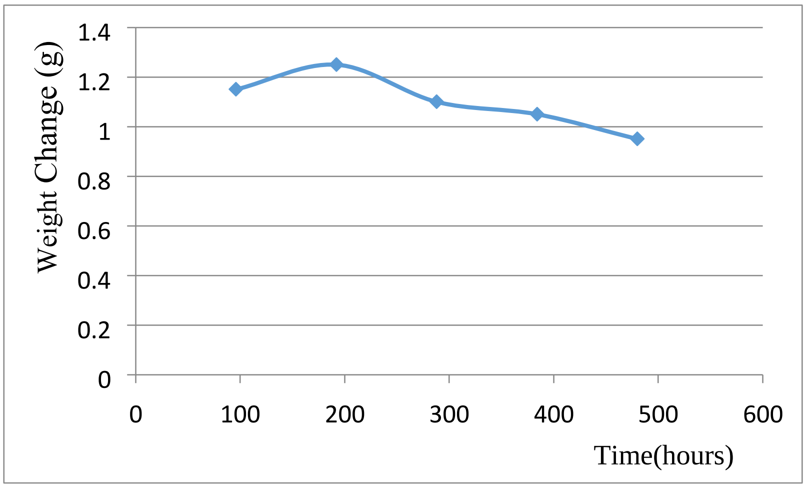


Fig 7: Oxidation of mild steel sample 2 in carbon dioxide atmosphere at 1000 ^{O}C

Calculation of rate of oxidation of mild steel samples

Oxidation of mild steel at high temperature followed parabolic relationship, hence parabolic reaction rate equation:

$$X^{n} = K_{p}t + C\text{-----------------}3.1$$

Where,
X - is the oxide thickness or mass oxygen consumed per surface area
K_p- is the parabolic rate constant
t - is the time and C is a constant
The equation can be further expressed as

$$\left(\frac{W}{A}\right)^{n} = K_{p}t\text{---------------}3.2$$

Where,
W and A are the sample weight (g) and surface area (cm^2), respectively. Oxidation follows parabolic relationship at high temperature, with exponential term (n=2), therefore the rate of oxidation is calculated for temperature 1000 ^{O}C.
Area of sample 1 (cylindrical shape) is given as A = $2\pi r^2 + 2\pi rh$

Given $r = \frac{D}{2} = \frac{1.6}{2}$ cm = 0.8
Height (h) = 3cm

$\therefore$ Area $= 2 \times \frac{22}{7} \times 0.8^2 + 2 \times \frac{22}{7} \times 0.8 \times 3 = \underline{19\text{cm}^2}$

Area of sample 2 (cuboid shape) is given as
A = 2(LW) + 2(hL) + 2(hW)
= 2(5×3) + 2(5× 0.35) + 2(3 × 0.35)
= $\underline{35.6\text{cm}^2}$
The time used in this experiment was 3hours (10800s). Calculated values are presented in Tables 8, 9 and 10.

Table 8: Calculated Rate of Oxidation of Samples in Hydrogen Atmosphere at 1000 ^{O}C

Time (Hours)	Rate of oxidation of mild steel kp (g^2/cm^{4}s)	
	Sample 1	Sample 2
96	1.084×10^{-7}	8.791×10^{-8}
192	1.257×10^{-7}	1.052×10^{-7}
288	9.234×10^{-8}	9.662×10^{-8}
384	9.234×10^{-8}	8.791×10^{-8}
480	7.759×10^{-8}	5.918×10^{-8}

Table 9: Calculated Rate of Oxidation of Samples in Sulphur Atmosphere at 1000 ^{O}C

Time (Hours)	Rate of oxidation of mild steel of samples kp (g^2/cm^4s)	
	Sample 1	Sample 2
96	5.194×10^{-8}	8.055×10^{-8}
192	3.142×10^{-8}	8.840×10^{-8}
288	2.308×10^{-8}	2.630×10^{-8}
384	2.308×10^{-8}	2.630×10^{-8}
480	1.026×10^{-8}	1.826×10^{-8}

Table 10: Calculated Rate of Oxidation of Samples in Carbon dioxide Atmosphere at 1000 ^{O}C

Time (Hours)	Rate of oxidation of mild steel of samples kp (g^2/cm^4s)	
	Sample 1	Sample 2
96	5.194×10^{-8}	9.662×10^{-8}
192	7.759×10^{-8}	1.142×10^{-7}
288	6.412×10^{-8}	8.840×10^{-8}
384	5.194×10^{-8}	8.055×10^{-8}
480	4.104×10^{-8}	6.594×10^{-8}

4.0 Discussion of Results

Oxidation at 800 ^{O}C was relatively insignificant and inconsistent with maximum weight gain of only 0.1g, in hydrogen and carbon dioxide atmospheres, however in sulphur atmosphere at 800 ^{O}C, tarnishing of samples was observed resulting in weight loss. Considerable high rate of oxidation of samples was observed at 1000 ^{O}C in hydrogen, sulphur and carbon dioxide atmospheres. Oxidation was recorded with weight gain and maximum rate of oxidation was observed at 192 hours in all the atmospheres. The rate of oxidation of samples was higher at the beginning of the experiment at 96hours and 192 hours pre-treatment of samples in all the atmospheres and slightly reduced with time. The rate of oxidation of samples was maximum in carbon dioxide atmosphere with weight gain of 1.25 g while, the least record of oxidation was in sulphur atmosphere with weight gain of 0.2 g. The oxidation of sample 1 and sample 2 behaved alike in a particular atmosphere but the rate of oxidation of sample 2 was always higher than sample 1. Surfaces of samples were stained with brownish rust at temperature of 800 ^{O}C in sulphur and carbon dioxide atmospheres but at temperature of 1000 ^{O}C, surfaces of samples were smooth in all the atmospheres.At 800 ^{O}C the rate of oxidation of samples was not calculated, this is because the results of the change in weight was insignificant, hence rate of oxidation at 1000 ^{O}C was only calculated in hydrogen, sulphur, and carbon dioxide atmospheres.

6.0 Conclusions

1) The rate of oxidation of mild steel followed parabolic relationship and the highest rate occurred in carbon dioxide atmosphere, at equal treatments and conditions.
2) Exposed surface area of mild steel affected the rate of its oxidation; sample 2 with more exposed surface area recorded higher rate of oxidation in all the atmospheres.
3) Oxidation of mild steel behaved alike in a particular atmosphere, but its rate of oxidation increased with an increase in temperature.

References

[1].Brooks, C. R., (1996) *Principles of the Heat Treatment of Plain Carbon and Low Alloy Steels*, ASM International, Materials Park, OH,

[2].H. S. Bawa (2009) *Workshop Practice*, published by Tata MC Graw-Hill Publishing Company Limited, New Delhi

[3].Khana A. S., (2002) *Introduction to High Temperature Oxidation and Corrosion*, Materials Park, Ohio ASM International.

[4].Kofstad, P (1966) *High Temperature Oxidation of Metals*, New York, John Wiley and Sons Inc

[5].Micheal S. Mamlouk, John P. Zaniewski (2011). *Materials For Civil and Construction Engineers.* Third Edition by Pearson Education Inc. Publishing as Prentice Hall,Upper Saddle River New Jessey PP 505-507

[6].OK Vander Voort, G. (1991), *Atlas of Time–Temperature Diagrams for Irons and Steels*, ASM International, Materials Park, OH.

[7].Osei Yaw Abiobio (2000) *New school chemistry, senior secondary edition series* published by African-FEP publishers limited, book house trust; 1 african-FEP drive, PMB 1639, Onitsha Nigeria p441

[8].Porter, D.A. and K. E. Easterling, (1992) *Phase Transformations in Metals and Alloys*, Chapman and Hall, New York

[9].R. K. Rajput (2004) *Material science and engineering* 3rd *ed*. published by S. K. Kataria & sons, 4760-61/23, Ansaria road, Daryaganj, New Delhi- 110002 p 317