Effect Of Temperature On Oxidation Kinetics Of Mild Steel

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Abstract: This research "Effect of temperature on oxidation kinetics of mild steel" was aimed at establishing the relationship between oxidation of mild steel with temperature and make comparison of oxidation of mild steel with temperature in different atmosphere. Fabricated materials made from mild steel tends to corrode when exposed to the atmosphere overtime, this tendency of the materials to corrode results mostly in complete failure of the materials while in service. Mild steel find applications in weldable boiler tubes and in weldable turbine requiring very high temperature for its operation, hence this research was studied with maximum temperature of 1000^oC. This research was studied using the method thermogravimetry analysis and it employed two samples of mild steel labelled sample 1 and sample 2 composed of 0.19875%C and 0.19220%C respectively. The atmospheres in which the research was carried out include air, oxygen and sulphur. The result of the investigations revealed that the oxidation of mild steel behaved differently with atmospheres, the calculated rate of oxidation showed that oxidation of mild steel with atmosphere of oxygen was higher than that of sulphur and in air.

Keywords: mild steel, oxidation, atmosphere, weight change.

I. INTRODUCTION

Plain carbon steel is a metal alloy which primarily consists of iron and carbon. Carbon steel is the most widely used kind of steel. The properties of carbon steel depend primarily on the amount of carbon it contains. Carbon steel is classified into three namely Low Carbon Steel (Mild Steel) containing 0.05% - 0.25%C, medium carbon steel containing 0.3% - 0.6%C, and high carbon steel containing 0.7% - 1.4%C.[1] Plain carbon steels are generally used in boiler system in which its operation requires very high temperature. 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.[2]

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 most common reacting gas is oxygen and the by-product is oxides. The reaction rate and the oxidation behaviour depend on many factors that can result in a complex reaction behaviour in which several mechanisms are simultaneously active; in general these factors are

✓ Composition, pre-treatment and surface area of the substrate
✓ Gas composition and partial pressure of the environment
✓ Temperature
✓ Time

Depending on the combination of these factors, the reaction can be slow to a point that the substrate is virtually un-attacked, or it can be fast leading to eventual component failure. The last case is usually detrimental for high temperature applications for oxidation rate increase with temperature.

The general equation that describes the chemical reaction between the metallic substrate and oxygen to form oxide is written as[3]

$$aM + \left(\frac{b}{2}\right)0_2 \Rightarrow M_20_2 \ ------------- Equation \ \ 1.1$$

Where M and O represent the metal and oxygen respectively

a- The number of moles of the metal
b- The number of moles of oxygen

The onset of oxidation occurs with the adsorption of oxygen on the substrate surface which dissolves and diffuses into the substrate as the reaction proceeds. This leads to the

formation of an oxide compound on the surface as a layer or separate nuclei. The parameters that influence the process and initial oxide formation are crystal defects and orientation at the surface, surface finish, and impurities in the substrate and gaseous environment. Once a continuous oxide film has covered the surface, the reaction continuous via solid state diffusion of the reacting species through the oxide film. One of the reacting species is metallic ions which are termed anions and have a positive charge. The driving force for the transport of the reacting species depends on the thickness of the oxide film. For thin film, the driving force may be an electric field in or across the film with the addition of electron transport. If the layer is thick, the driving force may be a chemical potential gradient across the film as in the oxidation process in fig 1.1

Depending on the oxidizing environment and the substrate, the oxide film may consist of a single oxide layer or of multiple oxide layers, in which the layers may be porous or compact. A compact oxide film tends to have a protective nature, which serves as a diffusion barrier between the reacting species and thus limits the reaction process. At higher temperature, the oxide film may volatize and/or melt, which may lead to catastrophic failure. [4]
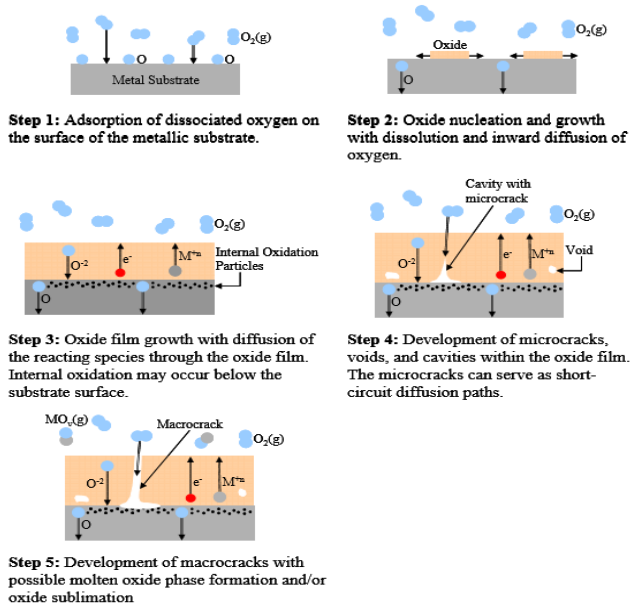

Figure 1: Oxidation reaction between a metallic substrate and oxygen. Figure based on Kofstad [2, 3] and the ASM Hand book volume 13a[6]

II. OXIDATION OF STEEL

Douglass and Rizzo-Assunco studied the isothermal oxidation of a Fe-19.6c-14Mn alloy in air for 24hours in the temperature range from 700^oC - $1000^\circ C$ and observed that the general oxidation curves were parabolic,[5] but true parabolic behaviour was not observed due to the simultaneous formation of several oxides as the protective oxide was forming. Hoelzer et al., observed that the oxidation of ODS Fe-Cr stainless steel resembled parabolic kinetics when investigating the oxide films formed in lab air for 10000 hours at $700^\circ C$, $800^\circ C$ and $900^\circ C$.[6] During the investigation on the oxidation of stabilized Ferritic Fe-Cr stainless steels with different chromium content in water vapour, Henry et al., observed that parabolic kinetics were followed when the sample were oxidized in Ar$+15\%$ at $900^\circ C$ up to 400hours.[7] Brylewski et al. investigated the oxidation kinetics of DIN 50049 in air from $750^\circ C$ to $900^\circ C$ from 70 to 480hours and observed parabolic oxidation over the studied temperature range.[8] Other researches have observed non parabolic kinetics or even change in behavior during an oxidation scan. Saeki et al., studied the oxidation of 430 stainless steel with different manganese content in 0.165 atm O_2-N_2 at $1000^\circ C$ from 0 to 1800seconds and observed that the oxidation rates did not follow parabolic kinetics.[9] This was also observed by Vosson et al., when studying the limits of oxidation resistance in dry lab air of different types of stainless steels at $650^\circ C$ for 30 seconds to 3000hours.[10] When investigating the composition, structure, and thickness of oxide film formed on MANET I when exposed to various oxidizing condition for different exposure times. Iordanova et al., observed that a simple kinetics law was not followed during the entire process for samples oxidized in air at $600^\circ C$ up to 2hours and at room temperature up to 1450 hours.[11]

III. 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. It is first drilled with a drilling machine using 2.5mm drill bit. Electronic weighing balance was used to weigh the samples and then stored in a desiccator to prevent corrosion when not in used. Electric Furnace was used to heat the steel samples to desired temperature. 30 samples of mild steel comprising of 15 samples of sample 1 and 15 samples of sample 2 were used in this experiment.

Suspected samples of commercial mild steel labelled sample 1 and sample 2 were tested in Defence Industries Corporation of Nigeria (DICON) a research and development centre in Kaduna. The result of the chemical composition is shown in table 1

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

Table 1: Chemical composition of samples

In this study, the following atmospheres were created, these are; (i) Oxygen (O) (ii) Sulphur (S) and (iii) air. These atmosphere were created by application of heat to 20grammes of the solid compounds of the following; Calcium oxide (CaO), Sulphur powder (S), and furnace air.

Sample 1 is first weighed and recorded and heated in oxygen atmosphere to temperature of $200°C$ and weighed again. The difference in weight is calculated. Another sample 1 is weighed again and heated in oxygen atmosphere to temperature of $400°C$ and weighed again.

This procedure is repeated for temperatures of $600°C$, $800°C$, and $1000°C$ respectively. The whole experiment is repeated with sample 1 in atmosphere of sulphur, and in air. The weight of the samples at each stage of the experiment is monitored. Also sample 2 is weighed and recorded and then heated in oxygen atmosphere to temperature of $200°C$ and weighed again. Another sample 2 is weighed at room temperature and then heated in oxygen atmosphere to temperature of $400°C$ and weighed again. This procedure is repeated for temperatures of $600°C$, $800°C$, and $1000°C$ respectively. The weight of the samples is recorded at each stage of the experiment.
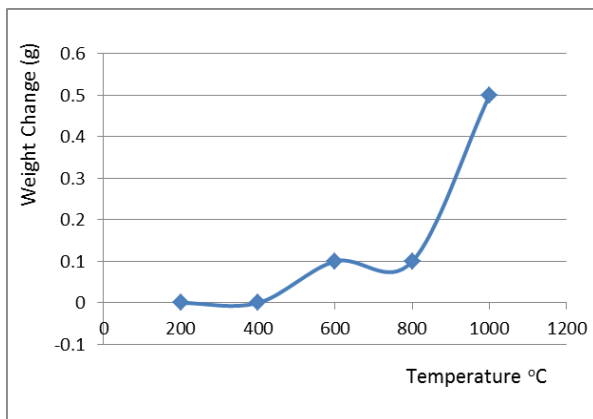
IV. RESULTS AND DISCUSSION

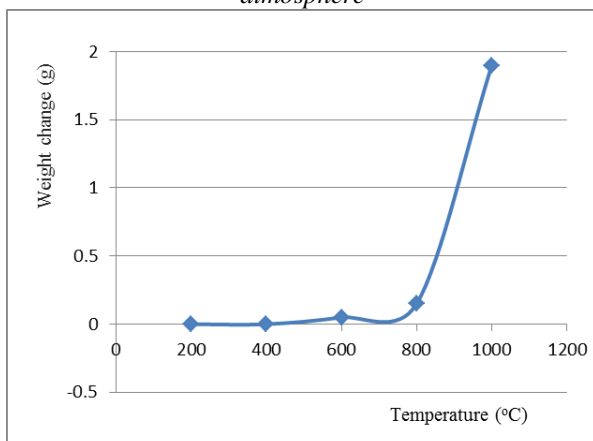*Figure 2: Oxidation of mild steel of sample 1 in oxygen atmosphere*

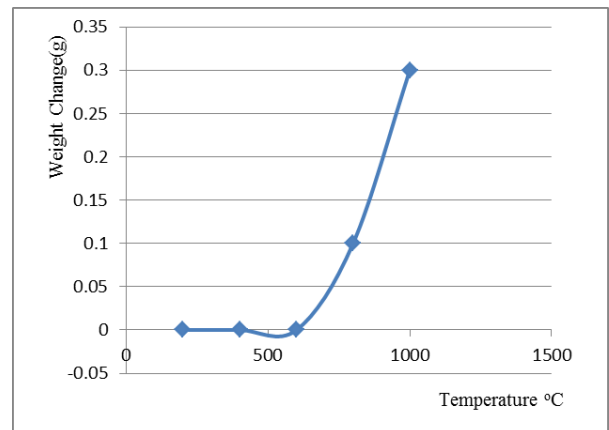*Figure 3: Oxidation of mild steel of sample 2 in oxygen atmosphere*

Figure 4: Oxidation of mild steel of sample 1 in sulphur atmosphere
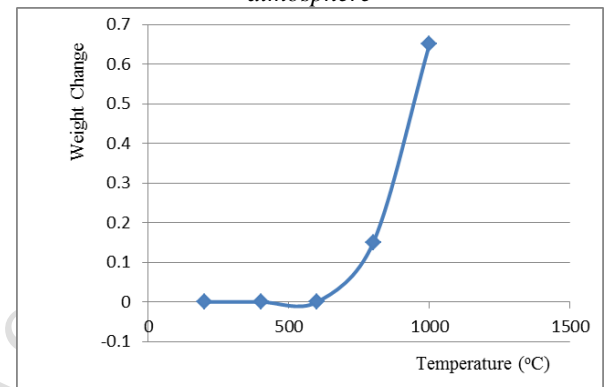

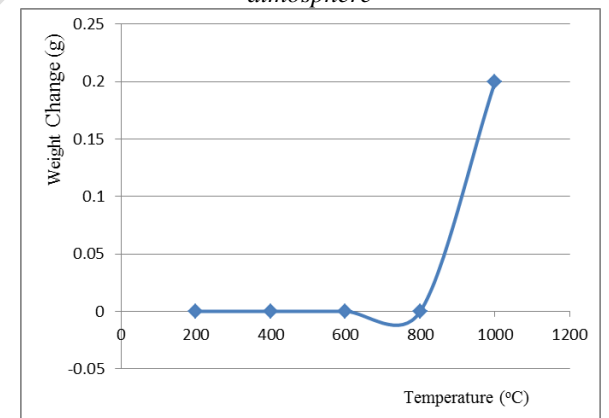*Figure 5: Oxidation of mild steel of sample 2 in sulphur atmosphere*

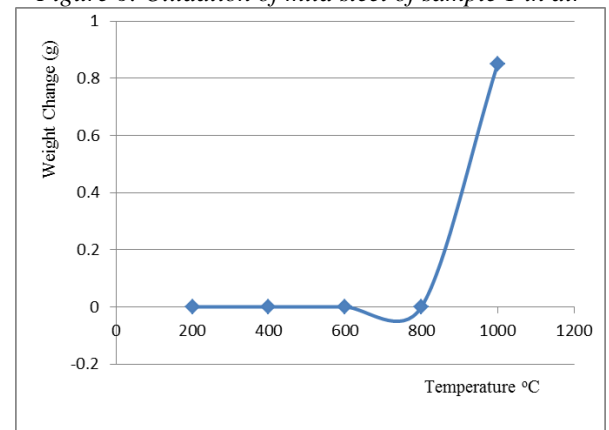*Figure 6: Oxidation of mild steel of sample 1 in air*

Figure 7: Oxidation of mild steel of sample 2 in air

CALCULATED RATE OF OXIDATION OF MILD STEEL SAMPLES

Oxidation of mild steel at high temperature followed parabolic relationship,[12] hence from parabolic reaction rate equation

$$X^n = k_p t + C$$

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

$$\left(\frac{W}{A}\right)^n = K_p t$$

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 800°C and 1000°C.

Area of sample 1 (cylinder) is given as A = $2\pi r^2 + 2\pi r h$

Given r = $\frac{D}{2}$ = $\frac{1.6}{2}$cm = 0.8

Height (h) = 3cm

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

Area of sample 2 (cuboid) is given as

A = 2(LW) + 2(hL) + 2(hW)

= 2(5×3) + 2(5× 0.35) + 2(3 × 0.35)

= $\underline{35.6cm^2}$

The time used in this experiment 2hours 30minutes (9000s) for temperature of 800°C and 3hours (10800s) for temperature of 1000°C. Computing these values in the formula, the results of the calculated values are tabulated in table 2 and 3

Atmospheres	Rate of oxidation of mild steel of sample 1 k_p (g^2/cm^{4}s)	
	800°C	1000°C
Oxygen	3.078 x 10^{-9}	6.412 x 10^{-8}
Sulphur	3.078 x 10^{-9}	2.308 x 10^{-8}
Air	-	1.026 x 10^{-8}

Table 2: Calculated rate of oxidation of mild steel of sample 1

Atmospheres	Rate of oxidation of mild steel of sample 2 k_p (g^2/cm^{4}s)	
	800°C	1000°C
Oxygen	1.973 x 10^{-9}	2.637 x 10^{-7}
Sulphur	1.973 x 10^{-9}	3.087 x 10^{-8}
Air	-	5.279 x 10^{-8}

Table 2: Calculated rate of oxidation of mild steel of sample 2

V. DISCUSSION OF RESULTS

From the results of the experiment carried out in this study; oxidation of mild steel of both sample 1 and sample 2 was recorded with weight gain. In oxygen atmosphere from fig 2 and fig 3 the effect of oxidation was not felt up to temperature of 400°C, hence the weight change was zero, but from temperature of 600°C an increase in weight was recorded therefore its oxidation was seen at this temperature.

For atmosphere of sulphur, oxidation was recorded at temperature of 800°C while oxidation in air was only seen at temperature of 1000°C. The rate of oxidation of mild steel was highest with atmosphere of oxygen than atmosphere of sulphur and in air.

Oxidation of sample 1 and sample 2 in a particular atmosphere behaved alike but oxidation of sample 2 showed higher oxidation than sample 1 in each atmosphere, this is because sample 2 has more surface area than sample 1.

VI. CONCLUSION

Effect of temperature on oxidation kinetics of mild steel was studied and the following conclusions were drawn
- Oxidation of mild steel was only recorded at high temperature; from temperature of 600°C, its relationship therefore followed parabolic kinetics.
- The rate of oxidation of mild steel increases with an increase in temperature irrespective of the atmospheres: oxygen, sulphur and air.
- The weight gain in oxygen atmosphere is more than that for sulphur and in air, hence mild steel exhibit higher oxidation in the atmosphere of oxygen.

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