Elucidation on Reactions Thermodynamics and Kinetics of OFC-A of Steels

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ABSTRACT

The basic principles of Oxyfuel cutting of metals lie in rapid high-temperature oxidation of the cut metal. Considerable proportion of the published work on the subject of oxygen cutting, the details of the oxidation reaction are overlooked or confused. Most often, physical characteristics of oxidized material is attributed to that of iron rather than iron oxide. The analysis of the oxidation reactions pertinent to Oxyfuel cutting of steels has also been majorly ignored. The oxidation process of iron and steel though similar in some respects, yet, in other aspects, show significant differences. This paper presents experimental and theoretical elucidation on reactions thermodynamics and kinetics of oxyfuel cutting processes of steel. Six 10mm metallurgy steel rods of different wt% C were flame cut using different acetylene and oxygen pressures. The composition of the steel rods used ranged from 0.16 wt% C to 0.33wt% C. Acetylene pressures used ranged from 3.45×10^{-2} N.m⁻² to 5.52×10^{-2} N.m⁻², while oxygen pressure ranged from 2.76×10^{-1} N.m⁻² to 3.17×10^{-1} N.m⁻². The result shows that the cutting rates decreased with carbon content of the steel as a result of reduction of iron oxide during decarburization reactions. Theoretical models of the thermodynamics and kinetics of cutting process pertinent to steels are also discussed.

Keywords: Flame cutting, Oxyfuel, Oxyacetylene, Steel oxidation, Decarburization.

1. INTRODUCTION

OFC-A is American Welding Society (AWS) classification for oxyfuel gas cutting in which acetylene is the fuel [1]. Oxy-fuel cutting are processes that use fuel gases and oxygen to cut metals. French engineers Edmond Fouche and Charles Picard became the first to develop an oxygen-acetylene machine in 1903.

Oxy-fuel is one of the oldest welding processes, however, it is still widely used for welding pipes and tubes, as well as repair work. In the developing worlds where incesant power outage is a common phenomeneon, OFC has made arc-welding/cutting unlucrative. It is also frequently well-suited, and favored, for fabricating some types of metal-based artwork. Oxyfuel equipment is versatile, lending itself not only to some sorts of iron or steel welding but also to brazing, braze-welding, metal heating (for bending and forming), and also oxyfuel cutting. The low cost of OFC-A equipment is one of the main reasons for its use. In oxy-fuel cutting (OFC), a cutting torch is used to heat metal to kindling temperature where the metal starts to turn a cherry red. A stream of oxygen then trained on the metal combines with the metal which then flows out as an oxide slag to creat the kerf [1-3]. The cut quality depends on the torch tip size, type, and distance from the metal [1], the oxygen and preheat gas flow rates and the cutting speed. However, the kinetics of the process will also depend on the oxidation process of the cut metal.

The basic principles of Oxyfuel cutting (OFC-A) of metals, lie in rapid high-temperature oxidation of the cut metal. Considerable proportion of the published work on the subject of oxygen cutting, the details of the oxidation reaction are overlooked or confused [4]. For example, it is not uncommon for the oxidized material to be attributed with the physical characteristics of iron rather than iron oxide. The iron oxide produced as a result of oxidation by OFC-A is not clear-cut elucidated. DeGarmo [3] believes Fe_3O_4 is formed. Masachuesset Institute of Technology [5] identifies FeO, Fe₂O₃, and Fe₃O₄ as potential oxides that could be produced. The analysis of the oxidation reactions pertinent to OFC-A of steels has, also been majorly ignored. The focus of most literature has been on the Fe content of the ferrous alloy, while the other contents are ignored. The oxidation process of iron and steel though similar in some respects, yet, in other aspects, show significant differences. A practical example of this is found during the construction of the steel skeleton for a flour mill in Nigeria in 2006. It was planned that the period of execution of the job would be 6 months, based on the understanding that mild steel (0.16w%C) would be used for the steel skeleton. The cost of the project should be N15.23 million. However, the client purchased medium carbon steel (0.33wt%C). The result was that the rate of job execution was much slower than expected. The job would require about 14 months. Also more volumes of oxyfuel gases are required. The cost for labour, accommodation, feeding, transport, and rented equipments had doubled. Generally, cost became very high and over N13 million have to be added to initial N15.23 million. Definitely, there was problem. The client believed this was a gimmick by the contractor to siphon fund. The client believed 0.33wt%C steel should cut faster since it has a lower melting point.

In this present paper, a description of the mechanism of interactions of the different phases involved in the reactions of slag forming process when steel is cut is provided. The role of carbon in this process is elucidated. Theoretical models of the thermodynamics and kinetics of cutting process pertinent to steels are also discussed. Similar theoretical models have been applied in laser-oxygen assisted cutting [6-15].

2. METHODOLOGY

The hot-rolled 10mm metallurgy steel rods that were used in this study were procured from the Universal Steel Rolling Mill, Ogba-Ikeja, Lagos, Nigeria. These were cut into 0.2m long specimen. The compositions of the steel rods are given in Table 1.

SN	Alloying elements (wt%)										
	С	Si	S	Р	Mn	Ni	Cr	Мо	V	W	Fe
1.	0.16	0.18	0.0589	0.0288	0.6440	0.1030	0.1244	0.0114	0.0010	0.0007	Rest
2.	0.18	0.22	0.0410	0.0237	0.7160	0.1100	0.1250	0.0220	0.0020	0.0030	Rest
3.	0.25	0.15	0.0510	0.0419	0.3658	0.01034	0.0889	0.0177	0.0003	0.0032	Rest
4.	0.28	0.18	0.0523	0.0275	0.6247	0.1170	0.1306	0.0141	0.0013	0.0035	Rest
5.	0.32	0.18	0.0576	0.0367	0.6494	0.01064	0.1550	0.0141	0.0024	0.0037	Rest
6.	0.33	0.31	0.052	0.0274	0.7523	0.1110	0.1750	0.0170	0.0030	0.0040	Rest

Table 1: Composition of steels used.

At the required pressures, cutting torch is used to heat the steel rods surface to kindling temperature where the steel rods starts to turn a cherry red. Oxygen is then released by depressing the oxygen lever to react with the metal which then flows out of the cut (kerf) as an oxide slag. The time taken to cut the rods is noted and recorded using a stop watch. The cutting rate is calculated by finding the ratio of the diameter of rod to the total time taken i.e.:

Cutting rate = Diameter of rod / total time of cut

3. RESULTS AND DISCUSSION

Figures 1, 2, 3 and 4 show the variations of cutting rates with carbon contents at different acetylene and oxygen pressures. From Fig. 1, the cutting rate was a maximum of 2.02 mm/min at $5.52 \times 10^{-2} \text{ N.m}^{-2}$ acetylene pressure and $3.17 \times 10^{-1} \text{ N.m}^{-2}$ oxygen pressure. A minimum of 1.02 mm/min. was achieved at $5.52 \times 10^{-2} \text{ N.m}^{-2}$ acetylene pressure and $2.76 \times 10^{-1} \text{ N.m}^{-2}$ oxygen pressure. In Fig. 2, a maximum of 1.90 mm/min was achieved at $4.83 \times 10^{-2} \text{ N.m}^{-2}$ acetylene pressure and $3.17 \times 10^{-1} \text{ N.m}^{-2}$ oxygen pressure for 0.16 wt% C steel. The minimum of 0.91 mm/min was achieved for 0.33 wt% C steel at $4.83 \times 10^{-2} \text{ N.m}^{-2}$ acetylene pressure and $2.76 \times 10^{-1} \text{ N.m}^{-2}$ oxygen pressure. Figure 3 shows that the maximum cutting rate is 1.82 mm/min for 0.16 wt% C steel at $4.14 \times 10^{-2} \text{ N.m}^{-2}$ acetylene and $3.17 \times 10^{-1} \text{ N.m}^{-2}$ oxygen pressure. The minimum is 0.80 mm/min for 0.33 wt% C steel at $4.14 \times 10^{-2} \text{ N.m}^{-2}$ acetylene pressure and $2.76 \times 10^{-1} \text{ N.m}^{-2}$ oxygen pressure. Figure 4 has maximum cutting rate of 1.70 mm/min. at $3.45 \times 10^{-2} \text{ N.m}^{-2}$ acetylene pressure for 0.16 wt% C steel. The minimum of 0.70 mm/min. was achieved at 0.33 wt% C steel at $3.45 \times 10^{-2} \text{ N.m}^{-2}$ acetylene and $2.76 \times 10^{-1} \text{ N.m}^{-2}$ oxygen pressure. Figure 4 has maximum cutting rate of 1.70 mm/min. at $3.45 \times 10^{-2} \text{ N.m}^{-2}$ acetylene pressure for 0.16 wt% C steel. The minimum of 0.70 mm/min. was achieved at 0.33 wt% C steel at $3.45 \times 10^{-2} \text{ N.m}^{-2}$ acetylene and $2.76 \times 10^{-1} \text{ N.m}^{-2}$ oxygen pressure. Figure 4 has maximum cutting rate of 1.70 mm/min. was achieved at 0.33 wt% C steel at $3.45 \times 10^{-2} \text{ N.m}^{-2}$ acetylene and $2.76 \times 10^{-1} \text{ N.m}^{-2}$ oxygen pressure. Figure 4 has maximum cutting rate of 1.70 mm/min. was achieved at 0.33 wt% C steel at $3.45 \times 10^{-2} \text{ N.m}^{-2}$ acetylene and $2.76 \times 10^{-1} \text{ N.m$

 10^{-1} N.m⁻² oxygen pressure. Generally, the trend shows a decrease in cutting rates with increase in carbon content.



Figure 1: Variation of cutting rates with carbon content at $5.52 \times 10^{-2} \text{ N.m}^{-2}$ acetylene pressure.



Figure 2: Variation of cutting rates with carbon content at 4.83 x 10^{-2} N.m⁻² acetylene pressure.



Figure 3: Variation of cutting rates with carbon content at $4.14 \times 10^{-2} \text{ N.m}^{-2}$ acetylene pressure.



Figure 4: Variation of cutting rates with carbon content at $3.45 \times 10^{-2} \text{ N.m}^{-2}$ acetylene pressure.

3.1 Metal Oxidation Process

Generally, during hot rolling process, an oxide scale layer always develops at the metal surface. Oxidation of steel at temperatures higher than 843K leads to three different iron oxide layers: wustite (FeO), magnetite (Fe₃O₄) and hematite (Fe₂O₃), in oxygen content increasing order, going from substrate to free surface. Below 843K, only the last two are thermodynamically stable [16]. According to the literature, the relative thickness fractions of

these layers between 973K and 1473K are 95% wustite, 4% magnetite and 1% hematite at equilibrium [16, 17], although this balance can vary from one case to another. Depending on temperature, time, atmosphere conditions and steel chemistry, energy barriers develop, which must be overcome for an oxide to grow [16].

Kinetics of oxidation reactions of metals at high temperatures, are generally assumed to be controlled by the rates of mass transport of reactants and products in the gas-slag interface, slag-metal interface and slag phases [18]. The passage of oxygen from the gaseous phase through the slag to the metal is generally believed to be as illustrated below Fig. 5 and 6.



Figure 5: Pattern of interactions during flame cutting



Figure 6: Reactions of slag forming process

However, Schwerdtfeger and Prange [19] have shown that slag-metal reactions involving iron and/or silicon under industrial process conditions are very unlikely controlled by the transfer kinetics of the reaction. Besides, whatever the means oxidation is being achieved, cutting by OFC-A is achieved by melting of the slag. The cutting rate in OFC-A will depend significantly on the rate of slag formation. Any reaction that retards formation of slag affects the cutting rate. FeO is a significant proportion of products of oxidation. When ferrous metals are cut by OFC-A, the process becomes one of rapid oxidation i.e. burning [1, 3, 5, 20]. The retardation to the formation of FeO affects the cutting rate. Reactions below (equations 12 to 14) are unfavourable to the formation of FeO.

$$FeO + C \rightarrow Fe + CO$$
 (12)

$$FeO + CO \rightarrow Fe + CO_2$$
 (13)

$$CO_2 + C \rightarrow 2CO$$
 (14)

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Min et al [21] and Kudrin [22] confirm reaction between iron oxide (FeO) and carbon (C), while Min and Freuhan [23], Dogan [24] and Mori [18] elucidated on the reactions between iron oxide and carbon monoxide (CO), carbon monoxide and carbon.

Generally, high carbon steels are more difficult to flame cut because of the reactions between carbon, carbon monoxide and iron oxide [5, 25].

3.2 Thermodynamics of OFC-A of Steels

The general equation used to calculate ΔG (the change in Gibbs free energy) is :

$$\Delta G = \Delta H - T \Delta S \tag{15}$$

where ΔH is the enthalpy, i.e. the heat energy evolved by the reaction, T is the temperature in K and ΔS is the change in entropy. Equation (15) above shows the temperature dependence of ΔG , ΔH is also temperature dependent, as shown in the equation below:

$$\Delta H_{T2} = \Delta H_{T1} + \int_{T_1}^{T_2} C_p dT$$
 (16)

where C_p is the specific heat capacity at constant pressure.

During OFC-A, cutting flame only heats the metal to start the process; further heat is provided by the burning metal. It is generally agreed that the exothermic reaction of oxygen with the cut metal provides a considerable thermal input. The maximum reaction temperature of the process will consist of the sum of the heat by the flame and that of the exothermic reaction of oxygen with the cut metal. The steel flame cutting process consists of reactions as follows:

$$[C] + 2[O] \rightarrow CO_2 \qquad \qquad \Delta H_2 = q_2 \qquad (18)$$

$$[C] + [O] \rightarrow CO \qquad \qquad \Delta H_3 = q_3 \tag{19}$$

While the heat by the flame is expressed as:

 $C_2H_2 + O_2 \rightarrow 2CO + H_2 \qquad \Delta H_4 = q_4 \qquad (20)$

$$4CO + 2/3 H_2 + O_2 \rightarrow 4/3CO_2 + 2/3H_2O \qquad \Delta H_5 = q_5$$
 (21)

The total heat liberated by the OFC-A process of steel is given as the sum of heat of equations (17), (18), (19) and those of equations (20) and (21). The maximum heat input is given as:

$$Q = q_1 + q_2 + q_3 + q_4 + q_5$$
(22)

The relationship between the maximum heat input and maximum reaction temperature (T_m) is expressed thus:

$$Q = \int_{298}^{T_m} \sum n_i C_{p(product)} dT$$
(23)

Where Cp is the specific heat capacity of products at constant pressure, n_i is the mole fractions of component i in the product. Thus;

$$Q = \int_{298}^{T_m} (n_{FeO} \cdot C_{p(FeO)} \cdot dT + n_{CO_2} \cdot C_{p(CO_2)} \cdot dT + n_{CO} C_{p(CO)} dT + n_{H_2} C_{p(H_2)} dT + n_{H_2O} C_{p(H_2O)} dT)$$
(24)

$$C_{p(CO2)} = 44.14 + 9.04 \text{ x } 10^{-3}\text{T} - 8.58 \text{ x } 10^{5}\text{T}^{-2} \text{ J/K/mol}$$
(25)

$$C_{p(CO)} = 28.45 + 4.184 \times 10^{-3} \text{T} - 0.46 \times 10^{5} \text{T}^{-2} \text{ J/K/mol}$$
(26)

$$C_{p(H2O)} = 30.0 + 10.71 \text{ x } 10^{-3} \text{T} - 0.33 \text{ x } 10^{5} \text{T}^{-2} \text{ J/K/mol}$$
(27)

$$C_{p(H2)} = 15.02 + 6.09 \text{ x } 10^{-3} \text{T} - 1.2 \text{ x } 10^{5} \text{T}^{-2} \text{ J/K/mol}$$
(28)

$$C_{p(FeO)} = 43.18 + 6.86 \text{ x } 10^{-3} \text{T} - 1.15 \text{ x } 10^{5} \text{T}^{-2} \text{ J/K/mol}$$
(29)

The total value of Q depends on the ratios of n_{FeO} : n_{CO2} : n_{CO} . This ratio is a function of concentration and activity of carbon and oxygen. Kudrin [22] and Bigeyev [27] showed that there is increased tendency for formation of carbon dioxide at lower carbon concentrations. Since $C_{p(CO2)}$ is about twice the value of $C_{p(CO)}$, higher values of n_{CO2} : n_{CO} will give higher heat input. Also, cutting rate has been shown to increase with temperature [4]. This is illustrated in Fig. 4. The energy available as heat from the FeO oxidation reaction at atmospheric pressure suddenly rises in energy evolved above the boiling point of iron (T_b ; 3330K). The reactions extinct at the dissociation temperature T_d which is 3660K (see Fig 5).



Figure 7: A typical relationship between cut front temperature and cutting rate [4, 27].



Figure 8: Variation of enthalpy and Gibbs free energy with temperature for FeO oxidation reaction at atmospheric pressure [4].

Although the thermal energy generated by the oxidation reaction rises by approximately 350 kJ/mol (from 250 to 600) at the onset of boiling[4], the latent heat of boiling iron (347 kJ/mol) almost exactly matches this rise. Thus, if there is no increase in the proportion of iron oxidized there will be no net increase to the thermal input to the cutting process. The decarburization process retards iron oxidation, thereby reducing the proportion of iron oxidized per time. Generally, high carbon steels are more difficult to flame cut because of the reactions between carbon, carbon monoxide and iron oxide [5, 25].

4. CONCLUSION

Generally, the cutting rates decreased with carbon content of the steel. At the same oxygen pressure, cutting rates have decreased up till about 65 pct with increase in carbon content of about 0.17 wt%. The reason for the observed trend being the retardation to the formation of FeO by decarburization reactions between iron oxide (FeO) and carbon (C), iron oxide and carbon monoxide (CO), carbon monoxide and carbon.

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