

# Kinetics of High Temperature Oxidation of High Carbon Steels in Multi-component Gases Approximating Industrial Steel Reheat Furnace Atmospheres

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**Abstract**— The isothermal oxidation behaviour of some carbon steels under various experimental conditions was investigated. The composition of oxidation atmosphere used in this work was chosen to approximate atmospheres found in industrial steel billet reheat furnaces. In order to study the effect of adding each gaseous component in these atmospheres experiments were also conducted in atmospheres leading to these compositions. Since the most significant oxidation of the steel occurs at high temperatures, three temperatures of 1000°C, 1100°C and 1200°C were used in the experiments. In general, it was found that rates of oxidation in free oxygen atmospheres were higher than the rates of oxidation in nitrogen-based CO<sub>2</sub> and H<sub>2</sub>O atmospheres. For oxidation in atmospheres containing higher free oxygen content, the overall oxidation is unaffected by changing the concentration of H<sub>2</sub>O or CO<sub>2</sub>. However, oxidation rates were found to be independent of oxygen concentrations above 6 vol.% O<sub>2</sub>. Metallographic examination of the oxides layers revealed that in the presence of free oxygen, the three iron oxides, wustite FeO, magnetite Fe<sub>3</sub>O<sub>4</sub> and hematite Fe<sub>2</sub>O<sub>3</sub> were all formed. However, for oxidation in nitrogen-based CO<sub>2</sub> and H<sub>2</sub>O atmospheres only the wustite phase was present.

**Index Terms**— Oxidation, Reaction Kinetics, Reheat Furnaces, Process Modelling.

## I. INTRODUCTION

THE phenomena of scale formation (oxidation) on steel surfaces during reheating of steel stock in industrial reheat furnaces are unavoidable and difficult to control. Disadvantages of scale formation include metal consumption and scale fall out in route to rolling units, which requires clean up and may present environmental problems. Factors which affect this process include temperature, residence time in the furnace, furnace atmosphere and steel composition. During reheating in industrial furnaces, steel is passed through the furnace along which the temperature is gradually increased up to the soak zone. In there, the temperature is kept constant for thermal and chemical homogeneity of the steel. In the

reheat furnace, being direct fired using natural gas and/or fuel oil and air, the composition of the "in-furnace" atmosphere, mainly N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O and free O<sub>2</sub>, can vary dramatically. These variations are functions of the air/fuel ratio, which in turn, depends on furnace and mill operating conditions. Hence, reheating under industrial conditions is difficult to reproduce in the laboratory. As an alternative, oxidation in such conditions can be approximated from well controlled laboratory experiments [1].

The subject of high temperature oxidation of steels under different conditions has been studied extensively. The dependence of oxidation rates on temperature is well established and is known to obey an Arrhenius relationship [2]. In general, oxidation can be classified into three stages. An initial stage characterized by a linear type of oxidation, a final stage where oxidation is parabolic and an intermediate stage where a transition from linear to parabolic mechanism takes place. For oxidation of different steels in CO<sub>2</sub> and H<sub>2</sub>O atmospheres, the limiting step was found to be the rate of dissociation of CO<sub>2</sub> or H<sub>2</sub>O to oxygen and CO or H<sub>2</sub> on the oxide surface [3]-[5]. However, for oxidation in O<sub>2</sub> atmospheres, the limiting step during the initial period of oxidation was found to be the rate of oxygen transport from the gas phase to the reaction surface [6]. After the oxide layer reaches a certain thickness, oxidation follows a parabolic rate law where the rate of oxidation is controlled by the diffusion of the ionic species and vacancies through the oxide layer [3], [7], [8].

Oxidation in complex atmospheres such those exist in industrial reheat furnaces, however, received little attention. Studies showed that oxidation in multi-component gases can involve the three mechanisms of oxidation all together [9], [10].

## II. REACTIONS KINETICS

Iron oxidizes to form three well known oxides, namely, wustite (FeO), magnetite (Fe<sub>3</sub>O<sub>4</sub>) and hematite (Fe<sub>2</sub>O<sub>3</sub>) in proportions determined by reaction kinetics, where the predominant oxide being magnetite. In general, the oxidation process can be expressed as:

$$\left(\frac{W}{A}\right)^n = k_x t \quad (1)$$

Where  $W$  and  $A$  are the sample weight (g) and surface area ( $\text{cm}^2$ ) respectively,  $k_x$  is the oxidation rate constant and  $t$  is the oxidation time (seconds). The exponential term  $n$  represents the type of oxidation mechanism. If ( $n = 1$ ), oxidation is linear with time, and if ( $n = 2$ ), the oxidation process is parabolic. Intermediate or mixed control oxidation where  $n$  is between 1 and 2 can also take place. Linear oxidation normally takes place during the initial oxidation period. During this stage, oxidation is controlled by the diffusion rate of oxygen atoms from the bulk of the gas to the reaction surface. Hence, this is the case where oxidation is a gas phase controlled process. The linear oxidation can be expressed as:

$$\left(\frac{W}{A}\right) = k_l \cdot t \quad (2)$$

where  $k_l$  is the linear oxidation rate constant ( $\text{g}/\text{cm}^2 \text{ s}$ ). The linear rate constant in the case of the oxidation of iron in oxygen-nitrogen gas mixtures is controlled by the rate of transport of oxygen molecules through the gas phase to the reaction surface [11]. The linear rate constant for oxidation in oxygen environment can be expressed as:

$$k_{l,O_2} = M_o k_{MTC} (C_{O_2}^G - C_{O_2}^*) \quad (3)$$

in which  $M_o$  is the molar mass of atomic oxygen ( $\text{g}/\text{g}\text{-mol}$ ),  $k_{MTC}$  is the mass transfer coefficient ( $\text{cm}/\text{s}$ ) and  $C_{O_2}$  is the molar concentration of oxygen in the gas mixture ( $\text{moles}/\text{cm}^3$ ), where the superscript G and \* refer to the bulk of the gas and the sample surface, respectively. The mass transfer coefficient can be obtained by solving the convective mass diffusion equation across a laminar boundary layer to the surface of a flat plate, assuming a known bulk gas velocity [12]. The final equation expressing the mass transfer coefficient,  $k_{MTC}$ , is as follows:

$$k_{MTC} = \frac{4}{3} \cdot \frac{D_{O_2}}{l} \cdot (Re)^{1/2} (Sc)^{1/3} \quad (4)$$

where  $Re$  is the dimensionless Reynolds number ( $ul/\nu$ ),  $Sc$  is the dimensionless Schmidt number ( $\nu/D_{O_2}$ ),  $M_o$  is the molar mass of atomic oxygen ( $\text{g}/\text{g}\text{-mol}$ ),  $D_{O_2}$  is the diffusion coefficient of oxygen in the binary gas mixture ( $\text{cm}^2/\text{s}$ ),  $u$  is the gas velocity past the sample surface ( $\text{cm}/\text{s}$ ),  $l$  is the length of the sample ( $\text{cm}$ ),  $\nu$  is the kinematic gas viscosity ( $\text{cm}^2/\text{s}$ ). The binary gas diffusion coefficient,  $D_{O_2}$  and the kinematic gas viscosity,  $\nu$ , were evaluated using conventional methods [13]. After the oxide layer reaches a certain thickness, between  $4 \times 10^{-3}$  mm and 0.1mm, the outward diffusion of metal ions and/or the inward diffusion of oxygen ions through the oxide layer become rate controlling [14]. This diffusion controlled process is known as parabolic oxidation where the parabolic rate constant is expressed as:

$$\left(\frac{W}{A}\right)^2 = k_p t \quad (5)$$

Where  $k_p$  is the parabolic rate constant ( $\text{g}^2/\text{cm}^4 \cdot \text{s}$ ), and  $t$  is the time in seconds. Assuming that the oxidation product is  $\text{Fe}_x\text{O}$ , the parabolic rate constant can be expressed as follows [11]:

$$k_p = 6 \frac{\rho_{\text{Fe}_x\text{O}}^2 M_o^2}{M_{\text{FeO}}^2} \cdot D_{\text{Fe}^{2+}}^* (y_{\text{FeO}/\text{Fe}_3\text{O}_4} - y_{\text{Fe}/\text{FeO}}) \quad (6)$$

where  $\rho_{\text{Fe}_x\text{O}}$  is the density of  $\text{Fe}_x\text{O}$  ( $\text{g}/\text{cm}^3$ ),  $M_o$  is the molecular weight of atomic oxygen,  $M_{\text{Fe}_x\text{O}}$  is the molecular weight of  $\text{Fe}_x\text{O}$ ,  $D_{\text{Fe}^{2+}}^*$  is the iron diffusion coefficient in iron oxide ( $\text{cm}^2/\text{s}$ ),  $y_{\text{Fe}_x\text{O}/\text{Fe}_3\text{O}_4}$  and  $y_{\text{Fe}/\text{Fe}_x\text{O}}$  are the iron ion vacancy concentrations at the  $\text{Fe}_x\text{O}/\text{Fe}_3\text{O}_4$  and  $\text{Fe}/\text{Fe}_x\text{O}$  boundaries, respectively. The vacancy concentrations are determined from the wustite/magnetite and iron/wustite phase equilibria, respectively. Values for the vacancy concentrations in the temperature range of 800 to 1100°C are presented in the study by Deich and Oeters [11]. The diffusion coefficient,  $D_{\text{Fe}^{2+}}^*$ , was determined from studies of iron diffusion using the decrease in surface activity technique for three artificially prepared iron oxides [15], and, for wustite was found to obey the following equation:

$$D_{\text{Fe}^{2+}}^* = 0.118 e^{-\frac{124,300}{RT}} \quad (7)$$

where  $R$  is the gas constant ( $\text{J}/\text{mol} \cdot \text{K}$ ) and  $T$  is the absolute temperature. Calculations using the above parabolic relations were used in studies by Yurek, et al. [16] and Garnaud et al. [17] to calculate the thickness of two layered scales,  $\text{Fe}_x\text{O}$  and  $\text{Fe}_3\text{O}_4$ . Good agreement was found between the calculated and measured values.

Since oxidation of steel in the reheat furnaces are extensive, i.e., initial oxidation rates where thin oxide layers are formed, can be ignored, and hence, parabolic rates can be considered. In evaluating the parabolic rate constant, the data collected during the first 10 minutes of oxidation was omitted. This ensures that data where oxidation is linear with time are not included in the evaluation of the parabolic rates.

### III. EXPERIMENTS

The experiments were carried out by reacting rectangular samples with compositions shown in Table I and dimensions (20mm x 10mm x 10 mm) prepared from a steel billet cross sections. A tubular vertical furnace consisting of a pure alumina process tube with an inside diameter of 25 mm was used. The furnace temperatures were chosen to be 1000°C, 1100°C and 1200°C and controlled within a  $\pm 0.2$  °C. Each experiment was performed for 90 minutes. Gases used are pre-purified nitrogen, extra dry air and carbon dioxide. The desired gas compositions were attained by adjusting the flow rate of each gas using high precision flow meters. Weight changes of the sample during oxidation and furnace temperature were digitally recorded using a high sensitivity microbalance. The experimental set up is shown in Fig. 1.

TABLE I  
CHEMICAL COMPOSITION OF INVESTIGATED  
CARBON STEELS (wt%) x 10<sup>-3</sup>.

Steel	C	Mn	P	S	Si	Cu	Ni	Cr	Mo
A	370	830	12	18	250	190	440	460	161
B	180	720	4	6	220	70	20	20	5

In industrial reheat furnaces, the composition of the furnace atmosphere depends on the magnitude of the input air/fuel ratio used. Calculated gas compositions corresponding to the combustion of natural gas with maximum, intermediate and minimum air/fuel ratios are given in Table II. The experiments were carried out with furnace atmospheres corresponding to those given in the table as well as in related binary gases of O<sub>2</sub>-N<sub>2</sub>, CO<sub>2</sub>-N<sub>2</sub> and H<sub>2</sub>O-N<sub>2</sub> leading to the final gas compositions.

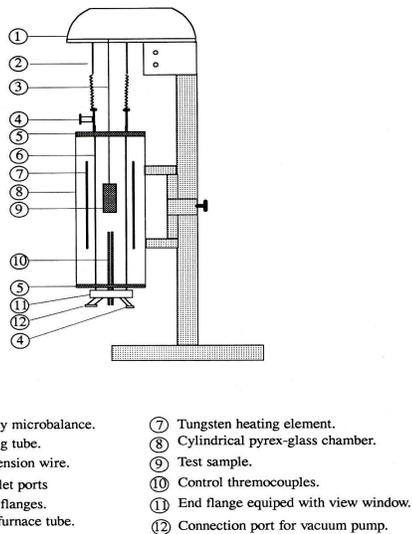


Fig. 1. Schematics of the experimental set up used for the oxidation experiments.

TABLE II  
CALCULATED GAS COMPOSITIONS RESULTING FROM THE  
COMBUSTION OF NATURAL GAS WITH DIFFERENT AIR/FUEL  
RATIOS (vol.%).

Atmosphere		Air/gas Ratio	H <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>
I	Low	10	20	3	10	bal.
II	Intermediate	14	15	5	8	bal.
III	High	37	7	15	3	bal.

#### IV. RESULTS AND DISCUSSION OF RESULTS

Because of the large number of experiments conducted in this work only few results representative experiments will be presented. The experiments were performed in single gas atmosphere, binary gases and finally ternary gases representing those found in industrial steel reheat furnace atmospheres shown in Table 2. The purpose for this strategy is to investigate the effect of single gases and relate that to the more complex multi-component gases. In general, the two

factors defining the shape of the sample weight change curves during oxidation are the weight gain due to oxygen pick-up (oxidation) and weight loss due to carbon diffusion out of the sample surface (decarburization). If decarburization is predominant a weight loss is observed, however, if oxidation is predominant a weight gain is observed

#### A. Effect of Temperature

Experiments were carried out first in nitrogen-based oxygen atmospheres in the three temperatures of 1000°C 1100°C and 1200°C where oxygen was maintained at 6 vol.% during these experiments. Typical samples weight change curves during oxidation of the two carbon steels are shown in Figs. 2 and 3. As it is well known, oxidation was highly a function of temperature, however, some differences of oxidation behaviour at the three temperatures can be seen. At the lower temperatures rates of oxidation followed approximately linear type of oxidation mechanism throughout the oxidation process, especially at the temperature of 1000°C. This behaviour is a result of the controlling mechanism of oxidation. That is, since the oxide layer is very thin and provided no significant resistance to the transport of oxygen/iron ion to the reaction surface, the rate of the chemical reaction at the steel surface is controlling and hence rates of oxidation exhibited a linear behaviour. For oxidation at 1200 °C, and after a short period of time lasting about 10 minutes, where oxidation rates followed a linear rate law as described above, the oxide layer reached a thickness after which the oxidation process became controlled by the solid state diffusion of the oxidizing species through the scale layer. In this case, oxidation was independent of furnace atmosphere composition. This behavior was observed for the rest of the experiments where oxidation was conducted at different atmospheres on the two steels.

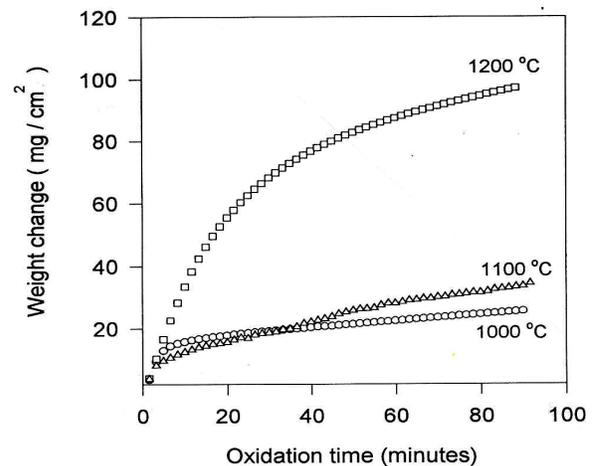


Fig. 2. Weight change curves for oxidation of 0.18 wt.% steel.

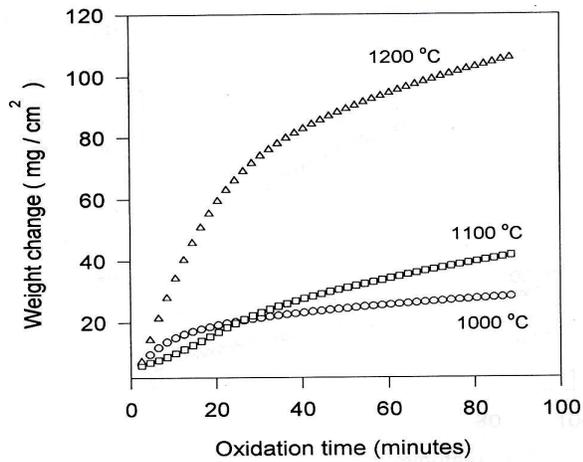


Fig. 3. Weight change curves for oxidation of 0.32 wt.%C steel.

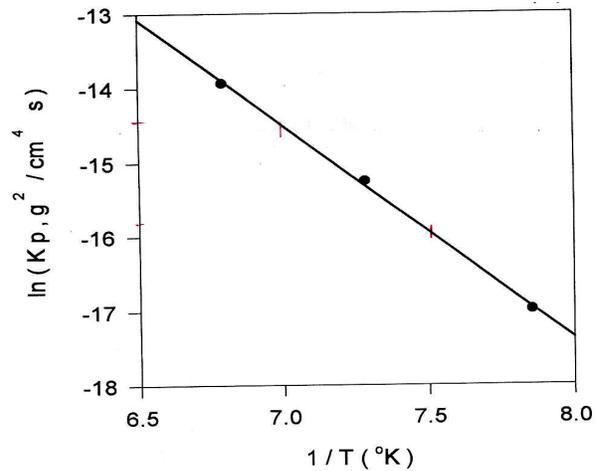


Fig. 4. Arrhenius plot for oxidation of 0.18 wt.%C steel.

### B. Oxidation Rate Constant

The rates of oxidation of the two steels can be best compared by looking at their oxidation rate constants. The parabolic rate constants for oxidation of the two steels can be obtained from the analysis of the weight gain data during oxidation and are given in Table III. From this data is clear that rate of oxidation for the two carbon steels at different temperatures are quite similar and differ only by about 15% at the most. The similarity in oxidation behaviour can be also illustrated by comparing the reaction activation energies obtained from the Arrhenius plots shown in Figs. 4 & 5.

TABLE III  
MEASURED PARABOLIC RATE CONSTANTS FOR OXIDATION OF THE TWO STEELS IN AN ATMOSPHERE OF 6 VOL.% O<sub>2</sub>

Temperature, °C	$k_p$ (g <sup>2</sup> /cm <sup>4</sup> s)	
	0.18 wt.%C	0.32 wt.%C
1000	$4.2 \times 10^{-8}$	$5.1 \times 10^{-8}$
1100	$2.38 \times 10^{-7}$	$3.75 \times 10^{-7}$
1200	$8.87 \times 10^{-7}$	$1.12 \times 10^{-6}$

For oxidation of the 0.18wt.%C the activation energy was found to be (238 kJ) and that for oxidation of the 0.32wt.%C was (242 kJ), both indicative of a parabolic rate type of oxidation mechanism. From this data the parabolic rate constant over the temperature range 1000 to 1200°C for the 0.18wt.%C and 0.32wt.%C, respectively, can be expressed as:

$$k_p = 256.21 e^{-\frac{238179}{RT}} \left( \frac{g^2}{cm^4 s} \right) \quad (8)$$

$$k_p = 486.8 e^{-\frac{242128}{RT}} \left( \frac{g^2}{cm^4 s} \right) \quad (9)$$

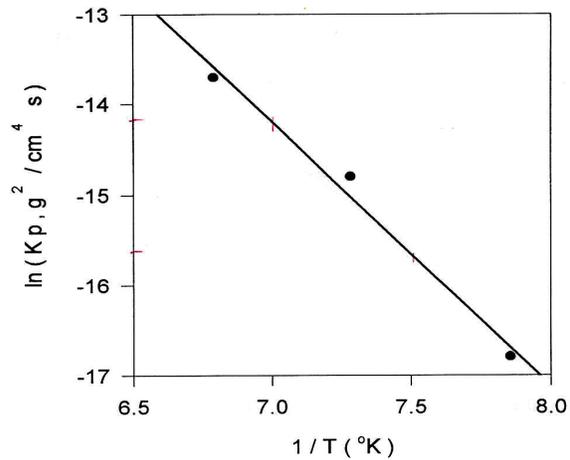


Fig. 5. Arrhenius plot for oxidation of 0.32 wt.%C steel.

### C. Comparison of Oxidation in the Three Atmospheres

The oxidation experiments have shown that in atmospheres containing 3 and 5% O<sub>2</sub> are fairly similar. However, oxidation in atmosphere III, where the free oxygen content is 15 vol. %, is different. This difference is seen during the initial period of oxidation where the rates were much higher. The initial rate of oxidation is a gas phase transport control and is highly dependent on oxygen concentration in the gas. In general, furnace atmospheres containing higher levels of free oxygen, the overall oxidation is unaffected by changing the concentrations of CO<sub>2</sub> and H<sub>2</sub>O.

### D. Metallographic Examination

The phase composition of oxide layers after oxidation of the samples at different conditions was examined using electron microprobe. It was found that oxidation in atmospheres containing higher levels of free oxygen produced oxide layers which consisted of the three phases, wustite FeO, magnetite Fe<sub>3</sub>O<sub>4</sub> and a very small layer of hematite Fe<sub>2</sub>O<sub>3</sub>. However,

oxidation in the atmosphere containing 3 vol.% O<sub>2</sub> only wustite and magnetite were present. Shown in Fig. 6 is a microstructure of 0.72 wt.%C steel which exhibited similar structure of the two carbon steels being presented in this article. For comparison purposes, the microstructure of the oxides produced in an actual reheat furnace was also examined, Fig. 7. In this case, the microstructure consisted mainly of wustite with the presence of a thin layer of magnetite.

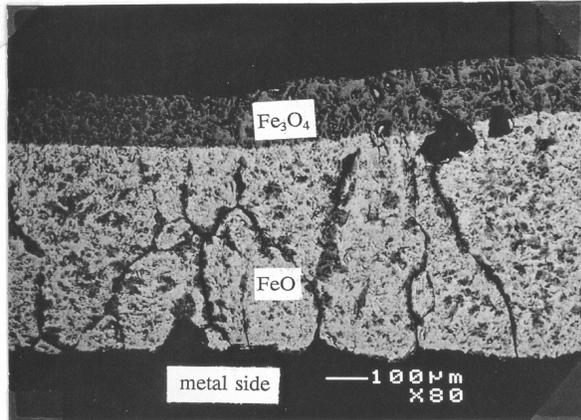


Fig. 6. Oxides microstructure of a (similar) 0.72wt.C after oxidation in the Laboratory.

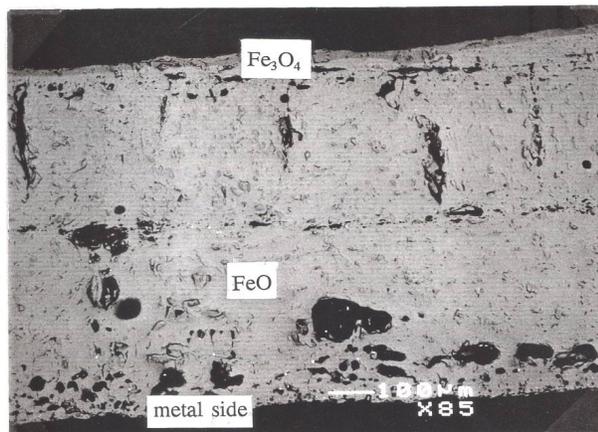


Fig. 7. Oxides microstructure of a 0.72wt.C after oxidation in the industrial reheat furnace.

## V. CONCLUSIONS

This work showed that the overall isothermal oxidation of high carbon steel in multi-component nitrogen based atmospheres (O<sub>2</sub>-CO<sub>2</sub>-H<sub>2</sub>O) was oxygen and temperature dependent. At higher temperature, i.e., 1200°C, oxidation rates increase with increasing oxygen content up to about 6 vol.%, beyond which no increase in oxidation rates was observed. Oxidation in atmospheres containing free oxygen exhibited a parabolic type of oxidation behaviour. However, oxidation in CO<sub>2</sub> and H<sub>2</sub>O nitrogen based atmospheres followed a linear rate law and was mainly temperature dependent. In the quaternary atmospheres, the most important component contributing to higher initial oxidation

rates was the free oxygen. The higher the carbon content the lower the overall oxidation of the steel, especially at high temperatures. To control scaling rates of the carbon steels studied this required control of the level of free oxygen in the furnace atmosphere.

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