The Oxidation and Reduction Behavior of Metal Surface in a Flame*

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We examined the possibility that indirect heating by radiant tubes in a continuous annealing process in the steel industry may be replaced with direct flame heating without the oxidation of metal surfaces. Energy and capital savings are expected as a result of this new-concept technology. The possibility of its practical application has been proved although the successful operating conditions are sensitive to the controlling factors. To realize this concept, the residual oxygen concentration in a flame must be lower than 0.1% (v/v), and the volume ratios of CO/CO₂ and H₂/H₂O in the flame should be over 0.4 and 0.09, respectively.

Key Words: Energy Saving, Annealing Process, Oxidation, Reduction

1. Introduction

Substantial energy saving has been achieved in the steel industry since the energy crisis in 1973, and the batch treatment in the annealing process of cold mills has been replaced with a continuous annealing line.

In the continuous annealing process, radiant tubes in an inert or reducing atmosphere have been employed to heat steel strip to avoid surface oxidation. This indirect heating method suffers from its low thermal and space efficiencies because the maximum operating temperature is restricted due to the short durability of the radiant tube. If direct flame heating of the steel strip without surface oxidation were to become possible, a remarkable contribution to the efficient utilization of thermal energy would be

achieved⁽¹⁾.

The objectives of the present study are to observe the oxidation/ reduction behavior of metal surfaces during direct heating by a laminar flat flame and a turbulent jet flame, and to elucidate the controlling factors and design parameters for the nonoxidizing direct flame heating technology.

2. Experimental Apparatus and Procedure

It seems essential to elucidate the oxidizing behavior of flames under simplified circumstances where the interaction between flow and combustion is eliminated. To realize such a circumstance, we employed a laminar flat flame.

Figure 1 shows the experimental setup for the laminar flat flame. A laminar flat flame was stabilized at the stagnation region, where the combustible mixture issuing from a converging 21-mm-diameter nozzle impinged onto the bottom surface of a water-cooled rotatable drum (60 mm O.D.), on which a sample steel plate to be heated was attached. The distance between the nozzle and the drum was 30 mm. A surrounding stream of nitrogen was added to extinguish the attached flame to the nozzle rim as well as

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to stabilize the flapping of the flat flame. A sample plate, on the back of which a thermocouple was welded to monitor its temperature, was fixed to the drum.

The steel plate, which was kept at the top of the drum being exposed to a nitrogen jet, was suddenly brought into the flame to be heated by rotating the drum. The drum was returned to the initial position to cool the plate down by the nitrogen jet when the plate temperature reached the specified value. Pure methane or a mixture of carbon monoxide and a trace of hydrogen were used as the fuel.

The gas temperature was measured using a silica-coated Pt/Pt-13% Rh thermocouple of 50- μm -diameter wire. Radiation and conduction losses were not corrected.

Figure 2 illustrates another heating device adopting a turbulent jet burner. Burnt gases produced at the porous-metal burner flowed up through a ceramic

Fig. 1 Flat flame burner and heating device for a sample plate

Fig. 2 Porous burner and heating device for a sample plate

tunnel 28 mm in diameter. Two types of porous-metal burner were prepared to change the pressure drop through the burner. A steel plate can be inserted into or withdrawn from the flame through any hole at cross sections at $h=40, 80, 120$, and 160 mm by a pneumatic-driven cylinder, as shown in Fig. 2. The nominal velocity of the jet was 10 to 12 m/s. A city-gas (88% methane) was used as the fuel. With this rig, the steel plate can be heated up to 750°C in several seconds, one order faster than the case of the laminar flat flame heating. The plate was cooled by a nitrogen jet to avoid oxidation.

A steel sheet to be used for car bodies was cut to 80 mm $\times$ 10 mm and used as a test piece. Thicknesses of 0.6 and 0.8 mm were selected to change the heating rate. An alumel-chromel thermocouple was welded to detect the plate temperature at the center of the plate. The oxidized layer thickness was measured at the same point.

The standard method of measuring the oxidized layer thickness is not applicable because the layer is far thinner than one micron, so we employed an ion mass analyzer (IMA) for this purpose. When an Ar-ion beam is focused on a steel plate, a hole is gradually bored through the plate, emitting ionized iron or ferrous ions. Since the intensity of ion emission is higher for the ferrous oxide in the oxidized layer than for the nonoxidized iron body, the boring time of the oxidized layer can be determined by the change in the level of emission intensity. We defined the boring time, τ_A , as the intersection of the two tangent lines as illustrated in the time record of emission intensity in Fig. 3. τ_A can be related to the actual thickness, δ_{ox} , measured by a surface roughness tester, though the accuracy of this method is insufficient in the range of the oxidized layer thickness. The value, τ_A , therefore, was adopted as the scale of the oxidized layer thickness in the present experiment.

Fig. 3 Definition of IMA boring time of an oxidized layer

3. Results and Discussion

3.1 Direct heating by a laminar flat flame

Figure 4 exhibits the change in oxidized layer thickness in terms of heating duration changing the equivalence ratio of the methane-air mixture from 0.8 to 1.15. The oxidized layer thickness, δ_{ox} , measured by a surface roughness tester is also shown as the ordinate to indicate the correlation with boring time, τ_A . The flame number denoted in the figure corresponds to that in Table 1.

Oxidation proceeded rapidly with heating time in the case of fuel-lean flame ($\phi_{CH_4}=0.8$), while the growth rate of the oxidized layer thickness decreased with heating time on the fuel-rich side. Comparing Figs. 4(a) and (b) to see the effect of the heating rate, the growth of the oxidized layer was slow for the slow heating rate, that is, for the thicker plate.

Not only the plate temperatures are unknown in Fig. 4 but also the flame temperature actually varies with the equivalence ratio. The same data were rearranged in Fig. 5 in terms of plate temperature. A similar tendency was seen for $\phi_{CH_4}=1.05$ and 1.15, that is, the oxidized layer grew linearly with the plate

temperature. For $\phi_{CH_4}=0.8$, oxidation proceeded as for fuel-rich cases below 500°C, but an intense increase with the plate temperature was seen thereafter although the rate of temperature rise decreased. The oxidized layer thickness in terms of plate temperature was almost identical for the two plate thicknesses, although a slight difference was recognized for the cases of $\phi_{CH_4}=0.8$ in Figs. 5(a) and (b). This suggests that the plate temperature more significantly affected the growth of oxidized layer than did the heating duration. Steel plates of 0.8 mm thickness were used thereafter.

In order to study the effect of the burnt gas compositions, carbon monoxide flames with small hydrogen addition were used in subsequent experiments. Considerable oxidation was observed in Fig 6 despite a slightly fuel-rich flame of $\phi_{CO}=1.2$. However, oxidation was still noticeable for $\phi_{CO}=2.0$, and the oxidized thickness was thicker than the allowable limit of "nonoxidized" surface (<10 nm), which indicates strong oxidation by carbon dioxide at high temperatures.

Once a thick oxidized layer had formed, it was not reduced again in flames. When an extremely fuel

Fig. 4 Effect of heating duration on oxidation (CH_4)

Fig. 5 Effect of steel plate temperature on oxidation (CH_4)

Table 1 Equilibrium compositions of combustion products

No	Equiv. ratio	Fuel	H ₂ addition	Temp.	O ₂	CO	CO ₂	H ₂	H ₂ O	CO/CO ₂	H ₂ /H ₂ O
1	$\phi_{\text{CH}_4}=0.8$	2.4 l/min	0 l/min	1000 K	0.039	≈ 0	0.077	≈ 0	0.155	≈ 0	≈ 0
2	$\phi_{\text{CH}_4}=1.05$	3.1	↑	↑	≈ 0	0.005	0.093	0.014	0.183	0.052	0.076
3	$\phi_{\text{CH}_4}=1.15$	1.9	↑	↑	≈ 0	0.015	0.090	0.040	0.169	0.163	0.236
4	$\phi_{\text{CO}}=1.2$	7.5	0.05	↑	≈ 0	0.064	0.322	6×10^{-4}	0.002	0.199	0.289
5	$\phi_{\text{CO}}=1.2$	7.5	0.35	↑	≈ 0	0.075	0.306	0.005	0.013	0.244	0.352
6	$\phi_{\text{CO}}=2.0$	12.6	0.05	↑	≈ 0	0.258	0.256	0.001	8×10^{-4}	1.010	1.457
7	$\phi_{\text{CO}}=2.0$	12.6	0.35	↑	≈ 0	0.260	0.248	0.008	0.006	1.049	1.513
8	$\phi_{\text{CO}}=4.0$	12.6	0.10	900	≈ 0	0.507	0.168	0.004	0.001	3.033	4.375
9	$\phi_{\text{CO}}=4.0$	12.6	0.35	↑	≈ 0	0.504	0.163	0.015	0.003	3.093	4.461

(a) Effect of plate temperature
 (b) Effect of heating duration
 Fig. 6 Effect of steel plate temperature and heating duration on oxidation (CO + H₂)

Fig. 7 Temperature distribution adjacent of flame and steel plate ($\phi_{\text{CH}_4}=1.05$)

-rich mixture ($\phi_{\text{CO}}=4.0$) was used, the cessation of oxidation or reduction of the oxidized layer was observed and a nonoxidized surface was obtained, as shown in Figs. 6(a) and (b). A small addition of hydrogen was also found to be effective in reducing the oxidation rate. However, the flame temperature was not high enough to heat the steel plates up to 700°C. Furthermore, from the energy-saving point of view, such an extremely fuel-rich mixture would not be acceptable in practice.

In the present experiments, the laminar flat flame was used to provide relatively simple conditions. In the boundary layer on a steel plate, a moderate temperature gradient was formed as shown in Fig. 7. It was, therefore, expected that the burnt gases in the vicinity of the plate would be in chemical equilibrium.

Calculations of chemical equilibrium for the above flames were made, assuming that the gases burned at a slightly higher temperature (727°C) than the specified plate temperature (700°C) were in contact with the steel plate, although 627°C was assumed for the flames of $\phi_{\text{CO}}=4.0$. Table 1 shows the calculated equilibrium compositions for nine experimental flame conditions. More oxidation was observed for carbon-monoxide flame of $\phi_{\text{CO}}=1.2$ than methane flame of $\phi_{\text{CH}_4}=1.15$ in the experiment. However, the calculated reduction indices CO/CO₂ and H₂/H₂O were higher but H₂O of the oxidizer was lower for $\phi_{\text{CO}}=1.2$, which is contradictory. The reason is ascribed to the difference in CO₂ concentration acting as an oxidizer in high temperatures. The resultant ratios of CO/CO₂ and H₂/H₂O in Table 1 were plotted in the oxidation/reduction domain diagrams for the pure gas mixtures of CO-CO₂ and H₂-H₂O in Fig. 8⁽²⁾. The upper side of the curve in each figure corresponds to a domain of reduction atmosphere. Only the ratios for flames 8 and 9 are in the reduction-possible domain, which explains the experimental phenomena. Taking the experimental results and calculated equilibrium compositions into consideration, it is conjectured that the high ratios of CO/CO₂ and H₂/H₂O in burnt gases play an important role in the oxidation process of a metal

surface. Extremely fuel-rich laminar flames, however, are not suitable for the nonoxidizing direct flame heating because the high ratios of CO/CO_2 and $\text{H}_2/\text{H}_2\text{O}$ are incompatible with the high flame temperature.

3.2 Direct heating by a turbulent jet flame

A steel strip is heated to 750°C in the annealing process. Figure 9 shows the effect of the equivalence ratio on oxidation, where the oxidized layer thickness, δ_{ox} , or the boring time, τ_a , is plotted versus surface temperature. Oxidation proceeded rapidly with the temperature rise of a steel plate for near-stoichiometric mixtures, but for richer mixtures, slight oxidation proceeded with the initial temperature rise ($400\sim 600^\circ\text{C}$) and distinct reduction occurred there-

Fig. 8 Oxidation/reduction domain of gas mixtures in terms of gas composition ratios and steel plate temperature, and points corresponding to the tested flame conditions

Fig. 9 Effect of equivalence ratio and steel plate temperature on oxidation ($h=160$ mm, burner A)

after at higher temperatures. The observed thicknesses for the cases richer than $\phi_{13A}=1.17$ were acceptable as the "nonoxidized" surface (<10 nm).

The corresponding local gas compositions associated with the change in oxidized layer thickness are shown in Fig. 10(a). The "nonoxidized" surface required local gas compositions to be such that the residual oxygen concentrations would be lower than 0.1% by volume and the ratios of $\text{H}_2/\text{H}_2\text{O}$ and CO/CO_2 would be over 0.085 and 0.4, respectively, as far as the stable species were concerned. Figure 10(b) shows the results for the other porous-metal burner B, and the "nonoxidized" surface was obtained above $\phi_{13A}=1.10$. Accordingly, it is understood that oxidation does not depend on the equivalence ratio of the mixture supplied. The compositions at $\phi_{13A}=1.10$ were $\text{O}_2=0.1\%$, $\text{H}_2/\text{H}_2\text{O}=0.135$ and $\text{CO}/\text{CO}_2=0.4$.

To examine the effects of local gas composition on the oxidation behavior, carbon monoxide was added to city-gas/air flames. The boring time and the change in local gas compositions versus flow rate of added CO or total equivalence ratio are shown in Fig. 11. The addition of CO to the mixture of constant equivalence ratio, $\phi_{13A}=1.05$, decreased the oxidized layer thickness, and the "nonoxidized" surface was obtained above CO flow rate of 5 l/min, the total equivalence ratio, ϕ_t , of which was 1.22. For the case of $\phi_{13A}=1.15$ (Fig. 11(b)), the nonoxidizing limit was 1.2 l/min of CO addition and $\phi_t=1.19$. The critical compositions for nonoxidation derived from the results in Figs. 10 and 11 were $\text{O}_2<0.1\%$, $\text{H}_2/\text{H}_2\text{O}>0.09$ and $\text{CO}/\text{CO}_2>0.4$.

Fig. 10 Oxidized layer thickness and local gas compositions versus equivalence ratio ($h=160$ mm)

Fig. 11 Effect of CO addition on oxidation ($h=160$ mm, burner A)

Judging from the variation in the oxidized layer thickness, the total equivalence ratio cannot be related to the oxidizing behavior. Instead, the acceptable conditions for the nonoxidizing direct flame heating are given by the combination of local gas compositions, especially the residual oxygen concentration and the ratios of H_2/H_2O and CO/CO_2 . However, a chemical equilibrium interpretation seems to be insufficient to explain the experiments because the equilibrium compositions of $H_2/H_2O=0.09$ and $CO/CO_2=0.4$ correspond to the oxidizing domain in Fig. 8. Fluctuations in temperature and species concentrations or nonequilibrium compositions may play an important role in the oxidation/reduction behavior of metal surfaces.

4. Conclusions

Not only the low concentration of residual oxygen but also the presence of considerably high concentrations of H_2 and CO are essential for the nonoxidizing direct flame heating because the residual oxygen

and carbon dioxide in combustion products act as strong oxidizers. However, we cannot expect such compositional equilibrium in the fuel-rich mixtures usually used in industries. In this respect, laminar flat flames are not suitable for the present purpose because near equilibrium burnt gases are in contact with a metal surface.

It has been shown experimentally that the nonoxidizing direct flame heating to the necessary temperature is possible by a turbulent jet flame in which species in various combustion stages are considered to impinge onto metal surfaces, although the optimum conditions are sensitive to design parameters and operating conditions. In respect to stable species, the critical condition suggested by the experiments is that the residual oxygen concentration must be lower than 0.1% by volume, and at the same time the ratios of H_2/H_2O and CO/CO_2 in a burnt gas should be over 0.09 and 0.4, respectively.

The impingement of a turbulent flame onto the metal surface is believed to be essential for establishing favorable conditions. Fluctuations in temperature and species concentrations or nonequilibrium kinetics are necessary to understand the oxidation/reduction behavior of metal surfaces in a flame.

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