Discussion on Steel Burning in Oxygen
(from a Steelmaking Metallurgist's Perspective)

Reference: Michael D. Lanyi[1], "**Discussion on Steel Burning in Oxygen (from a Steelmaking Metallurgist's Perspective),**" *Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Ninth Volume, ASTM STP 1395*, T. A. Steinberg, H. D. Beeson and B. E. Newton, Eds., American Society for Testing and Materials, West Conshohocken, PA, 2000.

Abstract: A fundamental understanding of iron and steel combustion in oxygen is important to the safe selection and specification of these materials for oxygen service. Much is, and should be, known on this topic -- for reactions involving iron and steel with pure oxygen have been both commercially employed and extensively researched for decades in the field of steelmaking process metallurgy. This paper takes inventory of what is generally understood by the process metallurgist concerning steel/oxygen reactions, and discusses its relevance to the topic of steel compatibility and combustion propagation in oxygen. An argument is made on the expected importance of the steel's carbon content in combustion propagation.

Keywords: oxygen, oxygen compatibility, flammability, steel, carbon, carbon monoxide, slag droplet, slag bubble, gas halo

Introduction

The topic of iron and steel combustion in oxygen continues to occupy attention for several reasons. First, steel is the most widely used material for storage and conveyance of gaseous oxygen. Most of its use occurs in conditions under which combustion is possible. Fires are rare, however, owing to strict adherence to practices and guidelines which reduce the possibility of ignition to near zero. Nevertheless, a fundamental understanding of iron and steel combustion mechanisms is desired for predicting the speed of burning, the threshold(s) of propagation, and the extent of damage should such fires be initiated.

Another reason for developing greater understanding into the mechanisms is to explain differences among different types of steels. Once insights are gained, it might be possible to safely extend the range of use in oxygen for some types of steels, with accompanying economic advantage. For example, it may be possible to safely substitute

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less expensive steel materials into valve bodies instead of more expensive materials (e.g., monel) that would be chosen with today's level of understanding for use in certain size and pressure applications.

Much is, and should be, known on this topic. First, a number of good and careful studies aimed at quantification and documentation of precise mechanisms and occurrences when iron (or steel) samples combust in oxygen have been published. Next, from a steelmaking metallurgist's point-of-view, reactions involving iron and steel with pure oxygen have been both commercially employed and extensively researched for decades now. Finally, recalling that the first commercial industrial use for pure oxygen was in oxygen cutting (by combustion) of steel, one is left to ponder: Except for perhaps more accurate quantification, what questions remain unanswered?

The purpose of this paper is to (i) look across the field of process metallurgy, (ii) take inventory of what is known and judged relevant to this topic of iron or steel combustion in oxygen, and (iii) make sure it is recognized and applied to this topic of steel combustion in oxygen and material compatibility/selection. To some, the information presented and the discussion may seem obvious. This author believes, however, that it is better to err on the side of obviousness than to either miss the opportunity to cross-fertilize with useful ideas, or to gain alternative perspective towards better understanding.

Background

There are three topic areas from "industrial steel-related process metallurgy" (let us call it) which seem relevant to iron- (or steel-) oxygen combustion:

- oxygen cutting of large steel sections (e.g., slabs blooms, billets and ingots)
- oxygen steelmaking and refining practices
- some recent studies into interactions and reaction kinetics in "direct iron ore smelting"

Each area is introduced and reviewed below. Then a short summary of some experiments reported in the literature to record and measure "rod samples burning in oxygen" is given for comparison and for the follow-on discussion.

Oxygen Cutting of Steel

In oxygen cutting (also called oxy-flame cutting), a preheat flame is directed typically to the edge, or corner of the large section of steel to be cut. Once the steel becomes locally preheated to about 870 °C (1600 °F) or higher, it is "blasted" with a stream of high purity oxygen to make the cut. The oxygen readily reacts (or "combusts") with the hot iron to produce a stream of (primarily) molten FeO and molten metal which is swept away by the flowing oxygen. The iron combusts approximately according to:

$$Fe_{(hot\ solid)} + 1/2\ O_{2\ (gas)} = FeO_{(liquid)} \qquad \Delta H^{\circ}_{298} = -63.8\ kcal/mole \qquad (1)$$

releasing a relatively large amount of heat. The enthalpy from this reaction heats and makes molten the products of combustion (FeO) so that it can flow away from the cut surface under the action of the blowing oxygen, and it heats the surrounding material so that the cut can be continued (propagated). Iron oxide in the liquid state in actuality has an indefinite stoichiometry which can vary depending on temperature (and probably pressure). The metallurgist usually refers to molten iron oxide as $Fe_{\mathbf{x}}O$ where **x** typically ranges between 0.95 - 1.0 under usual conditions. The value of ΔH°_{298} for equation (1) above is for the case where **x** equals 0.95.

If more than stoichiometric quantities of oxygen are supplied to the iron being cut (the usual case), there is the possibility for the molten FeO to react and solidify to higher forms of oxides (Fe_3O_4 and Fe_2O_3) according to:

$$FeO + 1/6\ O_2 = 1/3\ Fe_3O_4 \qquad \Delta H^{\circ}_{298} = -25.5\ kcal/mole_{\ (FeO\ further\ oxidized)} \qquad (2)$$

or

$$FeO + 1/4\ O_2 = 1/2\ Fe_2O_3 \qquad \Delta H^{\circ}_{298} = -34.6\ kcal/mole_{\ (FeO\ further\ oxidized)} \qquad (3)$$

with additional releases of enthalpy. These "additional oxidations" of the iron to Fe_3O_4 and Fe_2O_3 occur from either (i) 'more-than-stoichiometric amounts' of oxygen being dissolved into the molten FeO by the high partial pressure of gaseous oxygen surrounding the liquid FeO (which pushes the oxygen concentration in the molten FeO towards saturation), or by (ii) excess free oxygen in the gas phase combining and reacting with the ejected and cooling FeO as it solidifies. It seems reasonable to presume that both mechanisms will occur. The final products of iron cutting can be a mixture of all three of these oxides together with some melted but un-oxidized iron that was also produced by the intense heat release of the above oxidation reactions. Material discharged from the "kerf" (i.e., the slit or the notch) of oxygen cutting is reported to consist of about two-thirds iron oxide and one-third un-oxidized iron that was melted and carried out of the kerf by the stream of unused oxygen.

In oxygen cutting of steel, both the speed and quality of cut are usually important. Quality is usually related to the cleanliness (lack of adhering oxide) and straightness of the surface and edges of the cut. A slower cutting speed usually results in a higher quality cut. Also, it has long been known that the purity of oxygen greatly influences the speed at which a given piece of steel can be cut. Even a few percent of non-oxidizing gas species (i.e., N_2, Ar, or CO) in the oxygen can have a dramatic influence on the maximum speed at which a cut can be smoothly continued (Fig. 1). A decrease of only one percent in oxygen purity is known to reduce the maximum obtainable cutting speed

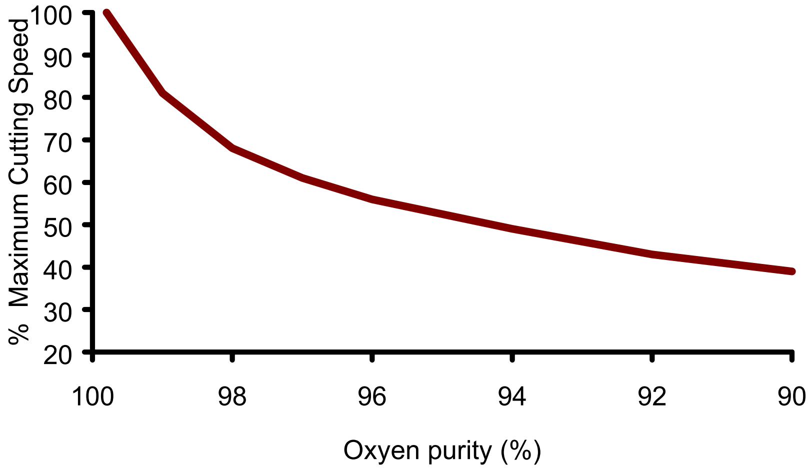


Fig. 1—*Steel cutting speed as a function of oxygen purity*

by about 15%. The presumed reason for this influence is: When gaseous impurities are present in the oxygen, they become momentarily concentrated and "left behind" at the cut interface when the oxygen is consumed. It is postulated that this concentrated boundary layer of non-oxidizing gaseous species interferes (slows) the delivery of additional oxygen molecules which must diffuse across this boundary layer of impurity species to the hot iron interface. The speed at which the steel can be cut is thus retarded.

The explanation given above is further corroborated by experience in cutting cast irons. Cast iron with its high carbon content is resistant to regular oxygen cutting. This is generally known and logically explained by the creation and release of CO and CO_2 gaseous species immediately in the vicinity of the cut interface which then interfere with the cutting operation in essentially the same manner as impurity gas species in the supplied oxygen would. The local generation of CO and CO_2 gas species contributes to an impurity-ladened gas boundary layer through which the oxygen atoms must diffuse to react with the iron. This, together with a more viscous, "sticky", or refractory slag containing oxides of silica from dissolved silicon typically present in large concentration in cast irons, both work to make these cast irons, and other high alloy steels, difficult to cut. The increase in cutting difficulty with increasing carbon, once it is quantified and understood, might prove useful to oxygen piping designers who wish less combustible metals of construction.

Difficult-to-cut iron alloys (e.g., cast irons and stainless steels) can however be successfully cut with the addition of supplemental iron powder to the oxygen stream. This iron powder acts in two regards: First, it is a fuel which combusts to increase the heat input rate to speed and perpetuate the cutting action on difficult to cut alloys. Second, the liquid FeO created acts to fluidize and dilute any of the more refractory (i.e., higher melting point) oxides (e.g., SiO_2, Cr_2O_3) which would tend to form, stick, and not flow from the cut face of the higher alloy iron attempting to be cut. By intensifying the heat generation, and forming and adding fluidizing liquid FeO to the kerf stream (through oxidation of added iron powder) steels that cannot be cut with pure oxygen are, in fact, cut.

Oxygen Steelmaking

In oxygen steelmaking, molten "hot metal" (that is, carbon-saturated iron containing around 4¼% C, plus dissolved silicon, manganese, and other elements) is obtained from a blast furnace and charged into a pear-shaped converter called a Basic Oxygen Furnace (BOF). Here the typically 250 tons of carbon-saturated molten iron is blown with about 600 normal cubic meters (~22,000 standard cubic feet) per minute of essentially pure oxygen at supersonic velocities. The reactions and mixing are intense. Oxygen reacts with the dissolved silicon, dissolved manganese, and the iron itself to make a liquid FeO-containing slag. The oxygen also reacts with the dissolved carbon to liberate CO gas and thereby decarburize the iron - a main objective in steelmaking.

The path to oxidation of these elements (carbon, silicon, etc.) during steel refining is to blow oxygen into the iron solution to the point where its concentration in the melt exceeds the equilibrium level allowed by the particular impurity of interest. The dissolved oxygen and the dissolved impurity element then combine to form CO gas (in the case of carbon) or liquid silica (in the case of silicon). Since the solubility of both of these species ($CO_{\text{(gas)}}$ and $SiO_{2\,\text{(liquid)}}$) is very limited in molten iron, they quickly nucleate their separate phases, coagulate, consolidate, and are floated-out by the intense stirring action of the process.

Also, during the intense oxygen blow of steelmaking, some of the molten iron is itself oxidized to FeO which then becomes intensely mixed with the molten metal into an emulsion and can react with the dissolved impurities in the molten iron directly according to:

$$Fe_{\text{(molten)}} + \tfrac{1}{2}\, O_{2\,\text{(gas)}} = FeO_{\text{(liquid slag)}} \quad (4)$$

$$FeO_{\text{(liquid slag)}} + \underline{C}_{\text{(dissolved in the molten iron solution)}} = CO_{\text{(gas)}} + Fe_{\text{(molten)}} \quad (5)$$

$$2FeO_{\text{(liquid slag)}} + \underline{Si}_{\text{(dissolved in the molten iron solution)}} = SiO_{2\,\text{(liquid)}} + Fe_{\text{(molten)}} \quad (6)$$

These oxidation reactions are highly exothermic. The heat released from oxidation of silicon and other impurities, together with the enthalpy from oxidation of iron itself, is used to increase the temperature of the steel for downstream casting and transfer operations, or to melt-in additional cold scrap to increase the size of the "melt".

CO_2 is never produced within the bath of a steelmaking vessel except in trace quantities. CO_2 (if it ever is formed) is quickly turned into CO by reaction with any remaining dissolved carbon in the steel according to:

$$CO_2 + \underline{C} \rightarrow 2\,CO \tag{7}$$

Furthermore, if there is no dissolved carbon remaining after oxidation of the molten steel, CO_2 is reduced to CO by the oxidation of iron itself according to:

$$CO_2 + Fe \rightarrow FeO + CO \tag{8}$$

Thus CO_2 is an oxidant at steelmaking temperatures. The equilibrium product of reaction for oxidation of iron, or carbon dissolved in iron, by CO_2 is strongly towards CO, with trace quantity of CO_2 according to the Gibbs Free Energy calculations.

Oxygen compatibility practitioners should further note that carbon acts as a reducing agent to FeO according to equation (5), and is another factor which can slow (or interfere) with iron oxidation.

During the steelmaking process, some of the iron can itself become "burned" or oxidized to the point where it adds to the percentage of molten iron oxide in the liquid slag phase which co-exists in the furnace with the metal. If the steelmaker makes a mistake and fails to stop the oxygen "blow" at the desired "end-point" of impurity oxidation, the oxidation of iron can become excessive. This will show up as a measurable yield loss of iron to the slag, giving predictable, calculable, higher concentrations of molten iron oxide (FeO) in slag. To the steelmaker, there is no mystery about what happens when iron burns. Once the carbon is gone (oxidized to CO), any additional oxygen combines with the iron to produce FeO into the slag.

Recent Study Involving Reactions Between FeO-containing Slags and Carbon-containing Molten Iron Droplets

A recent and important topic of study in iron and steelmaking process metallurgy has been the rate of reaction between (a) FeO in molten slags, and (b) carbon-containing molten iron drops. In oxygen steelmaking, the reaction is responsible for decarburization (as described above). In recent years, there has been renewed interest in understanding and quantifying the kinetics of this reaction because of the role it plays in the newly developing "bath smelting" processes for direct ironmaking. Here, iron ore, oxygen, and coal are fed directly to a molten metal- and molten slag-filled reactor to produce the molten iron "hot metal" in one step -- thereby replacing the separate and traditional steps of first turning coal into coke in coke ovens, then charging coke together with ore in a hot air blast furnace to produce the iron.

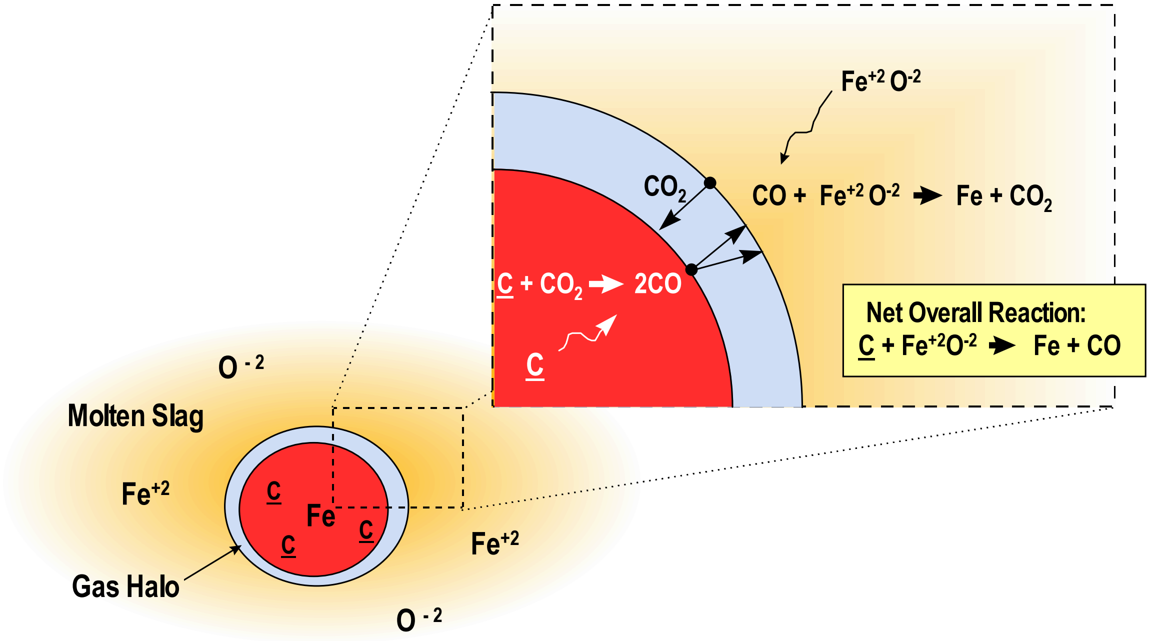


Fig. 2—*Model for reaction between carbon-containing iron droplet and FeO-containing molten slag across the gas halo*

In iron-bath smelting, the ore dissolves into the liquid slag to add to and increase the FeO content of the slag. Metallic iron is then "reduced" from the slag (i.e., the liquid FeO is stripped of its oxygen) by reaction with both (i) carbon dissolved in the carbon-containing molten iron droplets held in a slag/metal emulsion created by the intensely blown oxygen, and (ii) solid coal char particles coming from the coal. It is estimated that approximately half of the iron reduction occurs by each. Knowing the kinetics and limitations on each of these reactions is important to sizing the vessels and estimating possible productivity. It is for this reason the subject has been studied.

A study by Mulholland et al. [*1*] using X-ray fluoroscopy of the reaction between carbon-containing iron droplets and FeO-containing slags showed the existence of a "gas halo" around the metal droplet as it reacted with the slag. Others [*2,3*] made similar observations and measured rates of reaction. Based on these studies, it is generally agreed the reaction between FeO in the slag with carbon-containing iron droplets occurs across a CO-CO_2 gas halo. In a more recent study by Min and Fruehan [*4*], the CO gas generation around the molten metal droplet was carefully measured (with a gas mass flow meter) and observed (with X-ray fluoroscopy videotape) as it interacted with the molten slag phase. From these measurements and observations, Min and Fruehan were able to determine the rates of reaction for various slag and droplet compositions, and to identify the rate controlling steps for reaction kinetics. Their explanation, and model, has two separate reactions, at two separate reaction sites, with CO_2 gas acting as the oxygen transport across a CO-CO_2 gas halo as shown in Fig. 2. In actuality, there will be five steps involved in this reduction reaction:

1. Mass transfer of Fe^{+2} and O^{-2} ions in the molten slag
2. Reaction at the slag/gas halo interface:

$$FeO_{(slag)} + CO_{(gas)} = Fe_{(liq.)} + CO_{2\ (gas)} \tag{9}$$

3. Gas diffusion of CO_2 giving oxygen transport across the gas halo
4. Reaction at the gas/metal interface:

$$CO_{2\ (gas)} + C_{(dissolved\ in\ the\ iron\ drop)} = 2\ CO_{(gas)} \tag{10}$$

5. Mass transfer (diffusion) of carbon in the molten iron drop

Net reaction:

$$FeO_{(slag)} + C_{(dissolved\ in\ the\ iron\ drop)} = Fe\ (liq.) + CO_{(gas)} \tag{11}$$

Depending on factors such as the sulfur content of the metal, different steps in this net reaction can become rate controlling. At higher sulfur concentration in the metal (i.e., >0.01 wt.% $\underline{S}$), the rate of reaction is controlled by reaction at the gas metal interface. (Sulfur is "surface-active" and limits this reaction). At low residual sulfur levels in the metal (i.e., 0.002 wt.% $\underline{S}$), the rate is controlled by mass transfer across the gas halo and diffusion of the reactant species in the liquids. Regardless of what controls, it is clear that the gas halo develops, and this important observation needs to be considered any time one has a situation with molten carbon-containing iron in contact (or surrounded) with molten FeO-containing slags.

Previous Rod-burning Studies

Several recent studies examined the upward burning of iron or steel rods in oxygen. It is generally recognized and accepted that when small-diameter steel rods are burned in oxygen in normal gravity, a slag droplet forms on the bottom that grows as the combustion proceeds upward until it detaches and falls away under gravity [*5*]. A new droplet cycle then begins and the process repeats. The rate of propagation is cyclic with the droplets, and is greatest just after a droplet has fallen [*6,7*]. In a 1992 paper by Steinberg et al. [*8*], results are presented from burning 3.2 mm diameter rods of vacuum processed iron of 99.954% Fe (minimum) in 6.9 MPa (1000 psi) pressure oxygen. In these experiments, very careful measurements were made of the temperature and pressure in the test chamber while the sample rod burning event was photographed at 0.15 second intervals. These measurements and observations enabled the researchers to calculate a gas-phase oxygen balance and the quantity of iron combusted over time. By comparing (1) the calculated amount of oxygen consumed from the chamber atmosphere to (2) the stoichiometric amount required for oxide production, these researchers concluded "During combustion… there is excess oxygen above the stoichiometric requirement for oxide production in the molten ball." Then, citing evidence from quenched samples, these researchers note a "core of pure metal (liquid) within the combusting mass" consisting of the metal and the liquid oxide. They suggest the iron core remains attached to the rod, and the periodic droplets falling from the sample consist primarily of liquid oxide. Their unfiltered temperature measurements show periodic pulses every 0.45 s corresponding to higher temperature radiation coming from accelerated reaction at the exposed iron - iron oxide interface during drop detachment. From all of this they conclude that "the excess oxygen and the presence of the well-defined iron core suggests that the rate limiting step is the kinetic reaction at the iron core - iron oxide interface." Finally, Steinberg presents evidence of oxygen outgassing from the dropped and cooling slag. The final solidified oxide was analyzed to be a mixture of magnetite (Fe_3O_4) and hematite (Fe_2O_3).

These results were further supported by the calculations and experimental work reported in a more recent paper by Steinberg et al. [*9*] where they calculate molar ratios of oxygen:iron in the molten oxide mass to range from 1.6 to as high as 2.2. By comparison, stoichiometric Fe_2O_3 and Fe_3O_4 would have molar ratios of 1.5 and 1.33, respectively.

Werley [*10*] examined and has reported on the upward burning of 2.4 mm mild steel welding rods in atmospheric pressure oxygen. The burning in atmospheric press oxygen is a major departure in practice from most (perhaps all?) other experiments of this type. These rather simple and somewhat crude experiments reveal some additional occurrences which should be considered when steel (an alloy with other constituent elements; primarily carbon) combusts in oxygen. (Mild steel welding rods contain typically between 0.06-0.09 wt.% C and from 0.15 to 0.30 wt.% Si.) In Werley's experiments, falling droplets from the burning rod were caught and quick-frozen in either water or liquid nitrogen. In some cases, the end of the burning rod itself was quenched (dipped into liquid nitrogen or water) and frozen. In other cases, the burning rod end would be extinguished and slow-quenched in flowing argon. The resulting specimens were collected, sectioned, examined, and in some cases analyzed. In addition, Werley photographed (as others had) the rod burning sequence at approximately 0.3 s intervals.

The main finding from the Werley experiments was that the oxide phase surrounding the burning end of the rod did not always appear as a single molten liquid droplet as he expected; rather in many cases it appeared to be an oxide "bubble" (perhaps gas-filled to make it somewhat like a "balloon") which surrounded - but was physically separated from - the end of the rod which had been burning. From the droplets quenched in water, Werley reports being able to usually recover "shell structure droplets containing a single loose pellet of iron metal." He also noted visual observation of an apparent annulus when attempting to reignite the end of the rod with an oxy-acetylene torch after the specimen had been unexpectedly extinguished. Still further evidence of this "balloon-like" structure, or behavior, comes from his photographic record. In several of his photographic sequences, Werley notes a sudden expansion or "droplet-volume increases" of the slag droplet to where its volume after "inflation" might be as large as

2.5 to 3 times the volume before the event. Also, when droplets - still attached to the end of the burning rod - were quenched in water, Werley described that "the slag fractured and broke away, often revealing a thin-skinned oxide bubble and exposing a large spherical core with a surface that resembled that of a bearing ball."

Werley presents many speculations on the cause of this structure. No further work was done by Werley to resolve the issue. The value of this work (in this author's opinion) is not in these discussions of speculations, but rather in the clear descriptions, sample dissection, and photographic evidence of his observations.

Discussion

In all cases described in the Background section above, we have comparable (if not the same) system developed, namely:

- molten iron (or iron alloy),
- in close physical contact with molten FeO (or FeO-containing) slag phase,
- at high temperature above the melting point of iron,
- where excess oxygen is available,
- and oxygen transport and the heat flow situation can be important.

The same physical and thermo-chemical principles must apply. Thus, we can draw from one experience (or knowledge area) to explain the other. Out of this above juxtaposition, a number of points arise that this metallurgist feels compelled to emphasize:

1. *Without question, the products of iron combustion in oxygen are liquid iron oxide and liquid iron. That is, iron (steel) burns in the liquid phase, not the vapor phase.*

When steel burns, the source of heat is the iron oxidation reaction giving about 64 kcal per g•mole of iron consumed in the reaction. The possible uses for this heat are:

- raising the temperature of the resultant oxide itself (first expected use),
- for conduction into and raising the temperature of the underlying, as-of-yet-unoxidized substrate material (also obviously happens),
- heating of the surroundings (by radiation and convection).

According to this author, a reasonable estimate of the relative proportions of heat use in each of the three bulleted uses might be 50%/30%/20%, respectively. The actual ratios of partitioning this heat among the three uses could be different, but the argument to be put forth (next) remains the same. Considering the temperature versus enthalpy

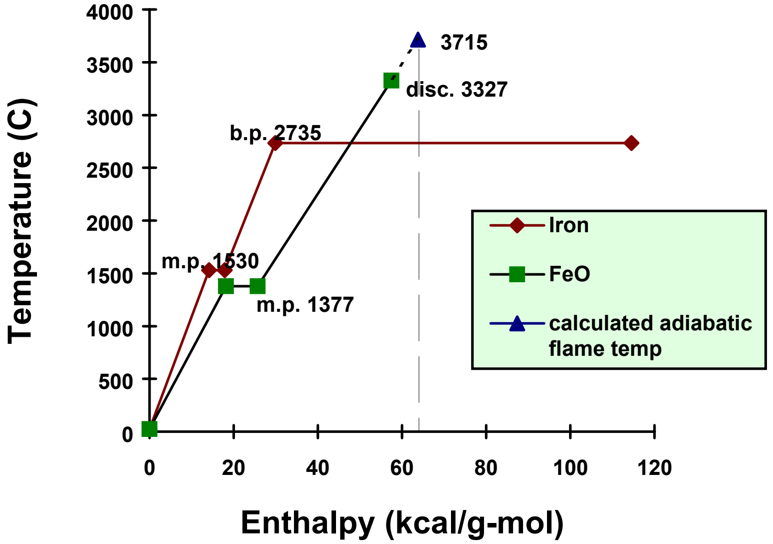


Fig. 3—*Temperature rise versus enthalpy for iron and FeO*

curves for iron and iron oxide (Fig. 3), and knowing that we have only about 64 kcal per mole to distribute over the two phases, and knowing from experience (and careful examination of evidence) that indeed some of the underlying unreacted iron (or steel) becomes melted, one quickly finds that there is insufficient enthalpy to consider temperatures higher than those necessary for liquid phases. Moreover, if the steelmaker (as described in the Background section) can inject pure oxygen into already superheated molten iron on a massive scale and detect no material losses due to vapor phase generation, we can rule out the possibility of producing a vapor phase when combusting ambient temperature iron with ambient temperature oxygen.

2. *Nature and behavior of the liquid iron oxide from iron combustion can be likened to - and has great similarity to - slags in metallurgical processes.*

Molten metallurgical slags are ionic in nature consisting of both simple and complex ions with no definite stoichiometric composition in the liquid state. When silica is present (the usual case in steelmaking slags), silica tetrahedra $(SiO_4)^{-4}$ connect together at the corners to form rings, or chains -- with cations of other oxides randomly distributed in the interstices. Oxides which form anion complexes in the melt (e.g., silica, alumina) are called acidic oxides and work to strengthen and lengthen the chains. Oxides such as CaO, MgO, and FeO work to break down the chains and are said to be basic. Nearly pure molten iron oxide would expected to be very fluid with very high ion mobility. In chemical reactions, slags behave more like a chemical electrolyte than a melted compound in terms of specie transport. This means we should expect oxygen transport through molten FeO (and FeO-containing) slag to be very rapid. From a metallurgical process experience, it is indeed viewed this way.

Since molten FeO or molten metallurgical slags have no definite stoichiometry, they by definition have a range of O^{-2} ion solubility. Oxygen ion solubility under high oxygen pressure would (and should) expected to be higher than under low pressure according to Le Chatelier's principle. Thus, these slags might rightfully be viewed at certain times, or in certain circumstances, as a source-supply, or reservoir, for oxygen to a reaction site.

The physical nature of FeO-containing slags are that they are very wetting, fluid, and chemically-aggressive in comparison to other slags. FeO slags wet steel, and they wet and dissolve almost any refractory oxide. The flow properties of metallurgical slags (i.e., viscosity and surface tension) are known to be a strong function of temperature and composition (particularly FeO content).

When slags cool, they may nucleate and solidify to stable or metastable crystalline phase(s); or they may transform to a glass depending on composition, viscosity [=f(composition)], and cooling rate. Generally, the higher the slag fluidity, the greater the tendency to nucleate crystals. High FeO slags almost always yield some crystalline structure. When crystalline solidification occurs, atoms align to a fixed geometric arrangement and molar ratio causing segregation and rejection of non-stoichiometric solute elements. It is this feature which this author believes is responsible for the "out gassing" of oxygen which Steinberg measures to occur at the end of iron combustion experiments under high oxygen pressure during slag cooldown.

3. *While the rate of steel burning is influenced by several factors (for example oxygen purity mentioned earlier) it is also largely dependent and affected by heat flow processes, and factors which affect heat transfer.*

Previous studies at Air Products on how to improve cutting speeds when lower purity oxygen is the only oxygen available, have brought to light another important principle - that of heat transfer during cutting. With somewhat lower purity oxygen (e.g., 95%), losses in cutting speed could be regained by inclining the cutting torch from the usual vertical position, to one where the top part of the cut would precede the now trailing lower discharge part of the cut. Comparison of this "inclined cutting" to normal vertical cutting is depicted in Fig. 4. With inclination, the hot liquid iron oxide being generated during the cutting operation would "roll down" the face of the cut; have better contact with the underlying base material; and transfer more of its heat to the workpiece being cut. Inclination cutting therefore enabled greater heat "recapture" by the workpiece so that cutting speed lost from lower purity oxygen could be compensated (regained) by the influence of greater heat conduction from the hot oxide to the base material. More simply, inclined cutting increases heat transfer which compensates for higher inert build-

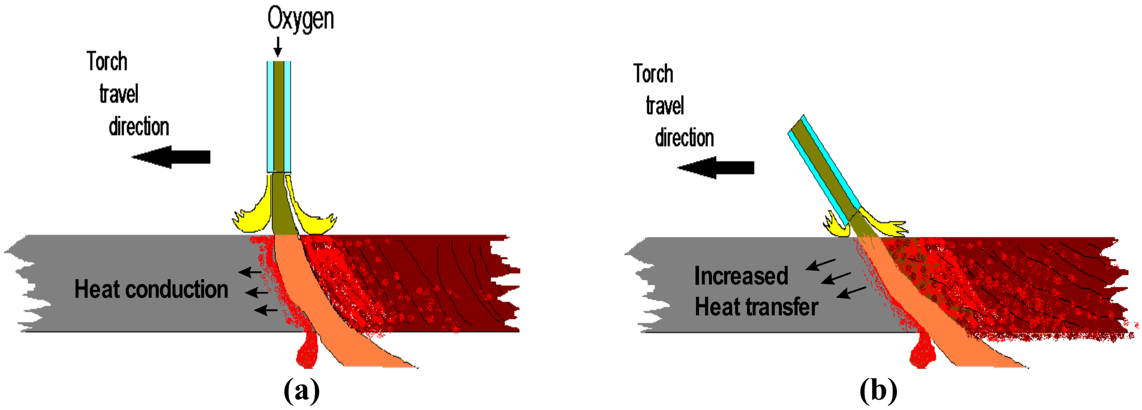


Fig. 4—*Comparison of normal (a) to inclined (b) oxygen cutting of steel*

ups (from less pure oxygen) in the gaseous boundary layer next to the cutting face. This practice of inclined torch angle might have been a good idea in practice if it were not for the fact that it (of necessity) leads to greater amounts of adhered oxide synonymous with poor quality cuts -- a serious unwanted side effect. But the results show the importance of heat transfer in perpetuating an iron cutting (burning) reaction.

Similar arguments can be made to explain the differences in combustion rates of rod burning experiments conducted in micro- and normal-gravity experiments. In micro-gravity, combustion rates of burning rod specimens are higher than in normal gravity because the heat source (supplied by the hot molten FeO) is allowed to wet, stay in contact, and provide its heat to a greater surface area portion of the burning rod. Moreover, rapid spreading and thinning of the molten FeO slag phase in micro-gravity delivers soluble oxygen to the iron initially, then provides "not much" of a barrier to oxygen transport later (since it is thinned). In comparison, in normal gravity with a rod burning upward, the molten slag accumulates at the lower end where it cannot supply heat except to the very end portion of the rod and to the surroundings. As the FeO slag ball accumulates, grows in thickness, and perhaps begins to become more viscous on the outside surface due to radiation heat losses, it may even start to impede oxygen delivery to the combustion site. Eventually, gravity overpowers surface tension, and the accumulated ball of slag falls away taking with it its storehouse of enthalpy which otherwise might have been used to sustain the combustion. Once it falls away, newly forming FeO creates and supplies the heat needed to momentarily accelerate the combustion process, and then the cycle repeats. If, however, the oxidation of the iron remaining at the rod end is insufficient to overcome the combined heat losses (due to radiation, conduction up the rod, and convection) at the moment of slag ball detachment, the combustion process becomes extinguished.

4. *Combustion propagation rates of steel in oxygen should also be a function of the steel's carbon content.*

The carbon-containing steel burning situation is essentially the same as that which occurs in the steelmaking process refining reactions, i.e., that which was described by Min and Fruehan [*4*]. In both cases we have molten iron with some amount of dissolved carbon present in initial direct physical contact with a FeO-containing slag phase. We know from steelmaking metallurgy principles that there are equilibriums, with published equilibrium constants [*11*], for the reactions between molten FeO and molten iron with dissolved oxygen according to:

$$\mathrm{Fe_xO}\ \text{(liquid)} = x\,\mathrm{Fe}\ \text{(liquid)} + \underline{\mathrm{O}}\ \text{(wt. \%)} \qquad (12)$$

$$\log k\ \text{(at 1 atm.)} = -6372 / T(\mathrm{K}) + 2.73$$

(where x is not a constant due to the ionic nature of the iron oxide. It may however be taken as very nearly equal to one for approximate calculations)

and between dissolved oxygen and dissolved carbon in the iron according to:

$$\underline{\mathrm{C}}\ \text{(dissolved in Fe)} + \underline{\mathrm{O}}\ \text{(dissolved in Fe)} = \mathrm{CO}\ \text{(gas)} \qquad (13)$$

$$\log k\ \text{(at 1 atm.)} = 1168 / T(\mathrm{K}) + 2.07$$

This means - as oxygen is supplied (dissolved) into the molten iron by equilibrium with the FeO - the oxygen will eventually reach a saturation point in equilibrium with the dissolved carbon present, and CO (gas) will tend to nucleate. Typically one needs a supersaturation, or net driving force, for this to occur. As more and more iron becomes oxidized to FeO in the steel rod burning case, both the carbon and oxygen in the remaining molten iron become enriched. At some point just beyond saturation, the CO "halo", or the Werley observed "annulus", becomes formed (and the Werley droplet inflates). The presumed sequence of events is depicted in Fig. 5. Compare this with the actual sectioned quick-frozen burning rod specimen of Werley in Fig. 6.

Notice that the CO(gas) must nucleate against the ambient pressure. If the system pressure is elevated, the frequency, or severity of the inflations will likely be suppressed.

It is important to recognize that in steel or ironmaking processes, the FeO concentration in the slag is rarely over 50%; typically 10-30%. In steel combustion problems, the FeO content of the slag is nearly 100%. This gives a large driving force for oxygen to dissolve into the liquid iron droplet. Thus, while the situations are all similar, relative mass quantities of the reacting species need to be taken into consideration if one wants to predict the quantity of CO (gas) which will form. But one thing is clear--if carbon is present as a dissolved element in the iron, any reaction of this iron with oxygen will result in a drive towards the formation of carbon monoxide as

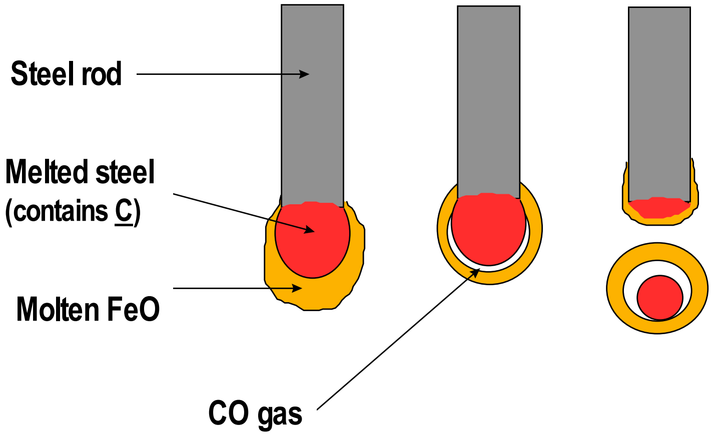
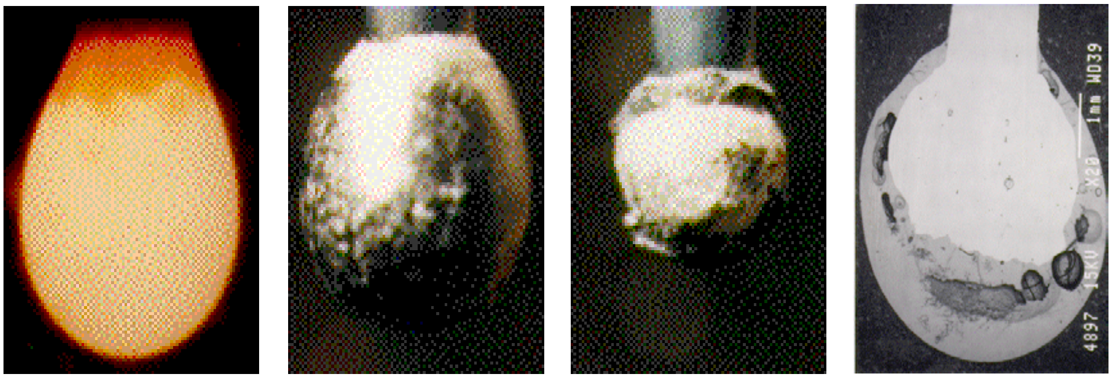


Fig. 5—*Presumed sequence of events during* ***steel*** *(with carbon) rod burning*

dictated by chemical reaction thermodynamics. Physical appearance of gaseous bubbles is then a function of nucleation and CO diffusion kinetics, CO gas solubility in the liquid phases present, CO mass availability from the system, and system pressure (following Le Chatelier's principle).

We can reasonably project that all of the following factors will contribute towards the tendency for CO bubble nucleation, and coalescence of these bubbles into gas halos:

- higher levels of carbon in the steel being reacted
- lower system pressures
- presence of other dissolved surface active elements (e.g., sulfur) which lower the interfacial tension between the molten iron and slag,



(a) Before quench

(b) After quench

(c) Slag removed

(d) Different specimen (quenched and sectioned)

Fig. 6—*Corresponding burning, quenched and section steel rod burning samples (from Werley [10])*

- any physical or geometrical arrangements which enhance "mass accumulation" of molten iron droplets surrounded by a molten slag phase.

The sudden inflations observed and reported by Werley in his experiments can now be explained. These simply correspond to that point at which the saturation (or "overpressure") of nascent CO bubbles (i) overcame the nucleation barrier, (ii) formed at the molten iron/molten slag interface, and (iii) grew against the ambient pressure to relieve the pent-up saturation. This can occur (and has been observed) as either the rod continues to burn (supplying more CO), or as a quenched droplet cools (decreasing the CO solubility). In both instances, a supersaturation of CO is being created: either by the additional reaction of oxygen with carbon as the rod burns, or by decreasing solubility for dissolved carbon in the presence of dissolved oxygen as a molten steel droplet (and slag) cools. Once the supersaturation becomes large enough to overcome the nucleation barrier associated with creation of new surfaces, the bubble nucleates. This naturally occurs at a an interface where the interfacial energy requirement (i.e., the energy required to create new interfaces) is compensated by the partial elimination of some existing interface (i.e., that between the slag and metal). Once nucleated, a CO bubble provides an easy "dumping ground" for any further CO which can form. Thus bubbles grow and coalesce into a halo, or annulus.

The presence of the CO gas-filled annulus is an important factor affecting steel combustion propagation from two aspects. Gas halos set up an additional obstacle to:

a) oxygen transport to the molten and burning iron core
b) heat transfer (as it was earlier described to be important)

Hence, carbon content of the steel should be expected to be an important influence on the propagation of combustion with steel in oxygen. It should be investigated (possibly used to benefit) in material specification for oxygen compatibility.

Conclusions

- Iron and steel combustion mechanisms are reasonably explained and understood by principles from steelmaking process metallurgy.

- The carbon content of steel could become an important factor in determining steel compatibility in oxygen service with higher carbon levels tending towards inhibiting combustion propagation. Service pressure may be an important determining factor on its influence. Probably, this is a fruitful area for further investigation.

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