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A Brief Study of Steel Combustion Using Quick-Frozen Test Specimens[2]

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ABSTRACT: Iron and steel combustion models are of both theoretical and practical interest. A brief effort to capture "excess oxygen" in quick-frozen slag of burning carbon steel has led to an apparently new and significantly different combustion model hypothesis, and speculation about its key features is offered. This model suggests a burning steel droplet might comprise an oxide bubble, spherical molten steel core and a gas-filled annulus. Based on these results, several published theories such as the presence of large-scale excess oxygen in the slag of burning steel, the argument that burning steel droplets are well mixed, that detached slag droplets are largely oxides of iron are questioned, and other model features in the literature are critiqued.

KEY WORDS: oxygen, flammability, fire, metals, iron.

Steel, in particular carbon steel, which is principally iron, is doubtless the most widely used material by weight in oxygen service. Most of this service is mundane: miles of pipeline. Nonetheless steel combustion is significant, because most of these pipelines are operated in a condition in which combustion is possible, and the main defense against fires is through ignition prevention. A body of experience that is massive justifies this continued practice. However, there are frequently new applications arising for which the existing experience may not be applicable. Among them are increasing numbers of applications in which new domains of pressure and temperature are involved or where oxygen enrichment is being used and for which an understanding of the threshold at which the metal will not burn is desirable. Indeed, ASTM Committee G-4 is considering tests of stainless steel next year (1996) to increase its domain of use.

Theories on steel and/or iron combustion have been published, including many data, some empirical correlation's, and some hypothesis. However, the ignition and burning of metals is very system dependent, the experimental database is not large, and there is not a

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consensus on steel combustion mechanisms. Some interpretations of observations are diametrical. Further, not every study is rigorous in specifying whether the metal was an iron (in gray, ductile, or, malleable form), whether it was a carbon steel, or what the contents were of potentially critical constituents such as carbon, silicon, and nonmetallic inclusions.

This paper takes a somewhat different approach to the study of steel combustion. It sought to observe carbon steel combustion in a "personal" fashion, working very closely with the specimens, especially during ignition. Steel combustion was visually observed at close quarters and photographed at low pressure in glass tubes. Importantly, test specimens and combustion droplets were quick frozen in liquid nitrogen or water, and unexpected results occurred. A limited amount of analytical testing with SEM and other methods was also accomplished. These data were then fit to a new model of steel combustion centered on the presence of an oxide bubble and an annular gas-filled space between the bubble wall and a molten-metal droplet at the bubble's center. This hypothesis is apparently new and could not be explored in more than brief detail in the present program. It is offered here for examination and debate in the research community. The case for this new model is not compelling, however, in view of the new experimental results, neither are the cases for existing models.

Clearly, there are several perspectives, and the definitive combustion model is not yet obvious. However, these data should stimulate thought among the workers in this field. Hopefully the prospects will narrow as the bodies of observations are reconciled, and a better ability to predict and cope with steel hazards should emerge.

Existing Observations and Theory

Upward Combustion Exhibits Droplets

As steel rods burn upward in oxygen in normal gravity, a series of droplets form, grow and fall away [*1*]. The rate of propagation of combustion is cyclic with the droplets [*2*]. The rate is greatest just after a droplet has fallen [*2-4*]. These rates are typically reported as the regression rates of the interface between the rod and the tops of the droplets [*2,4*]. When extinguishment occurs, it most often occurs just after a droplet has detached, leaving little remaining slag on the rod [*5*]. The combustion of vertical rods, 0.094-in (2.4-mm) in diameter in atmospheric pressure oxygen is exhibited in Fig. 1; These views are at about 0.3-second intervals and are from the present work.

Burning Rate Depends on System Parameters.

Early papers indicate fine wires exhibited a square-root-of-pressure influence on the combustion rate for small changes in pressure [*1*]. However, these data also showed a region in which the influence of pressure was relatively flat that was attributed to a mechanism shift. Later data [*5*] have shown a somewhat less significant effect of pressure for specimens of much larger diameter. Specimen regression rate has been inverse to cross section [*1,6*]. Oxygen concentration has had a monotonic influence on regression rate, and the rate has increased dramatically as trace diluents have been removed [*7,8*].

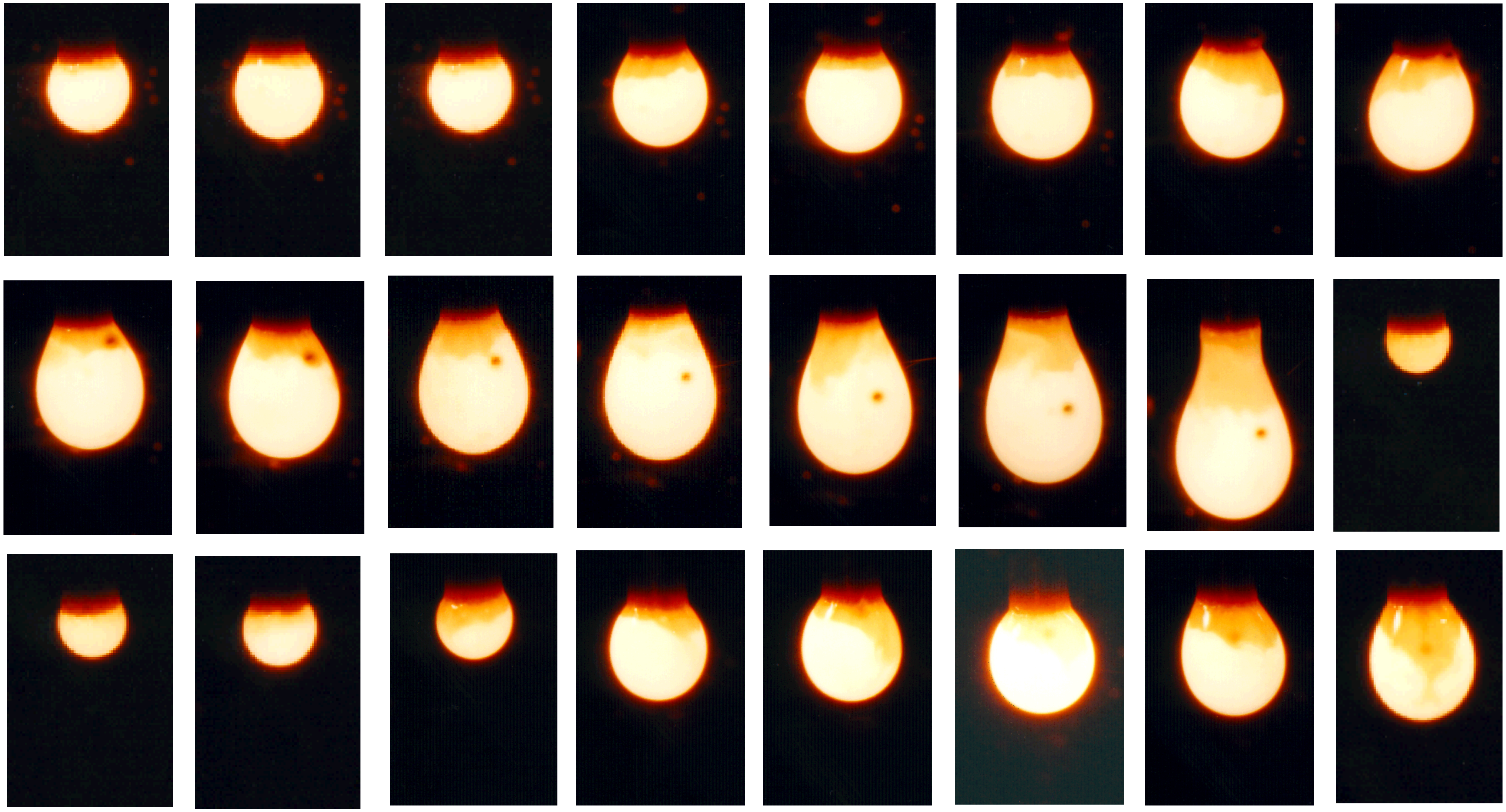

FIG. 1—*Droplet Growth mid-cycle to mid-cycle. Views are at about 0.3-second intervals.*

Combustion limits

Sufficient diluent in mixture with oxygen has affected the combustion of steel. Trace amounts of diluent [*7,8*] dramatically reduced the rate at which steel burns. At higher levels of diluents [*9*] combustion was thwarted. Combustion limits have widened as temperature or pressure increased [*9*].

Burning Produces Little Smoke and Dust

In comparison to metals like aluminum, the burning of many steels, in particular carbon steel, specimens in normal gravity has produced relatively little smoke and dust [*10*]. The burning droplet's surface could be viewed and photographed with relative ease. This is in stark contrast to aluminum combustion in which a cloud of smoke and dust has obscured direct vision. This is one of the features that is used to infer the combustion is not with the iron in the vapor state but rather with the oxygen entering or reacting into the liquid.

Combustion Temperatures are High

Early efforts to measure or to estimate the surface temperature of the droplets of burning steel have yielded values of about 3000 K [*11*]. A new paper [*12*] measures droplet temperatures in 1.6 MPa oxygen in the range 2500-3800 K with the temperature at the low end of the range just after droplet detachment and increasing with droplet size.

Oxygen Diffusion

Oxygen diffusion as a factor limiting the reaction rate of steel has been suggested but most recently was disputed as the principal limit [*13*].

Diluents

The diluents nitrogen and argon have exhibited major effects on the burning rate of steel but have shown relatively small differences in their effects on the threshold for steel combustion [*5,7-9*]. This is contrary to the effects of these diluents on aluminum combustion in which trace levels alter the threshold greatly despite the fact that reaction of nitrogen occurs with aluminum [*14*]. Diluents in the gas phase are believed to interfere with transport of the oxygen to the metal by accumulating near the droplet surface as the oxygen is consumed or dissolved. The possibility of diluents being dissolved into the steel slag does not appear to have been suggested nor evaluated to date, although the potential presence of "permanent gases" has been cited in the combustion of small aluminum particles [*15*].

Reaction Site

Reactions of some metals have been postulated to occur in the gas phase (vapor-phase combustion), at the surface of the metal-gas interface (surface burning), and within the interior of the molten slag (liquid-phase combustion) [*16*]. Some have suggested the site might shift during combustion or that mixed modes might occur [*17,18*]. For the most part, there is consensus that iron combustion does not occur principally in the vapor phase at typical test conditions [*16,17,19*], but it may not be precluded under all conditions .

Similarly, there is little doubt that at lower temperatures, the reaction is on and near the surface. Solid iron rusts near room temperature to produce a surface layer of predominantly Fe_2O_3 oxide with no significant mobility of oxygen into the interior or iron to the atmosphere. At higher temperature, the surface layer that results is largely Fe_3O_4.

Subsequent to ignition, however, there is controversy about whether the predominant effect in iron combustion is the arrival of oxygen molecules at the surface of molten iron/oxide, reacting there, and then diffusing into the interior of the melt as oxide, or whether there can be a potentially large population of oxygen (called “excess oxygen”) within the molten slag that reacts with iron [*20,13,21*].

Molten Slag Composition is Ultimately FeO and Fe

There is strong argument that during combustion, within steel droplets, the principal Fe species present should be Fe and FeO [*13*]. Measurements and estimates of the droplet temperature indicate it is above the decomposition temperature of the other stable oxides of iron (Fe_2O_3 and Fe_3O_4). These other oxides might form early on, but as the temperature escalates, a shift to the FeO is likely.

Droplets are Well-Mixed (Slag Dynamics)

The behavior of the surface of the molten slag attached to a burning specimen has been used to draw several inferences.

The slag surface has exhibited substantial activity. Sato [*10*] has observed locations that become bright near the bottom, and the bright spots move upward towards the rod. This dynamic behavior has been used to infer that the slag is well mixed and approximately uniform. The mixing has been attributed to surface-tension gradients within the slag [*22*]. The present author is unaware of any previous effort to assess the mixing that would result simply from diffusion at the extreme temperatures of combustion.

The Melt Contains “Excess” Oxygen

Hirano et al. [*20*], Steinberg et al. [*13*], Benz et al. [*3*] and Dreizin and Trunov [*21*] are among those who have proposed that there is oxygen present in the burning slag of iron or various other metals that is available for reaction (e.g., as a solute). Within the author’s knowledge, Hirano et al. is to earliest paper to make this assertion regarding rod combustion. It was apparently based upon the Fe:O ratio of wuestite ($Fe_{0.95}O$) which was the oxide they cited in their droplets. They calculated the size of the molten droplets

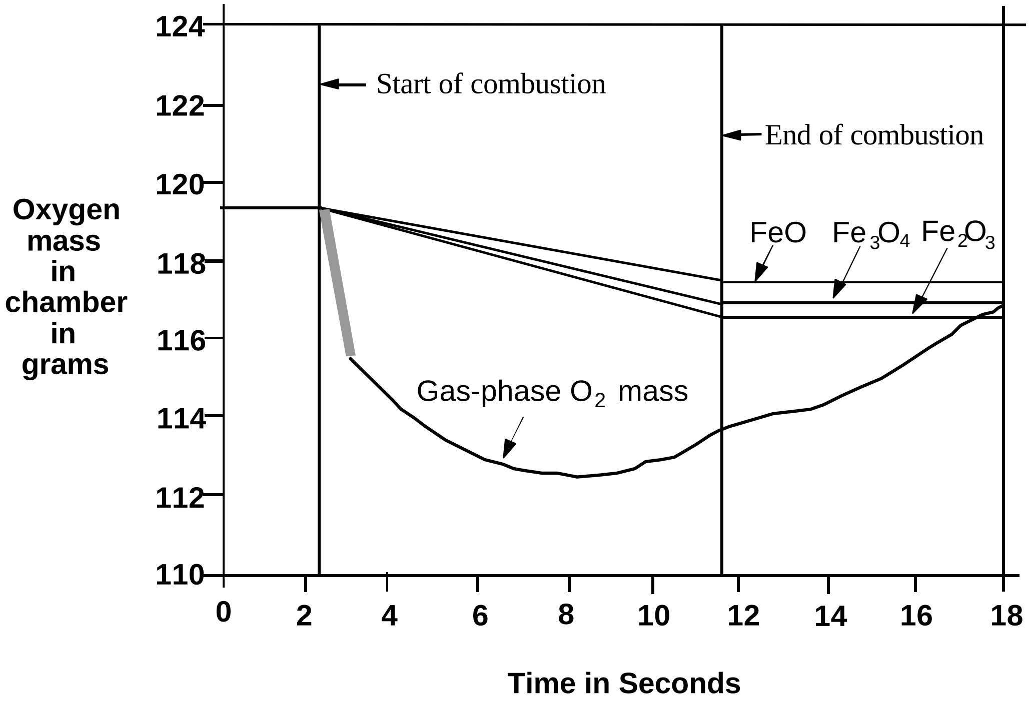

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FIG. 2—*Oxygen mass profile per Steinberg et al.* [*13*].

as three times the size of the metal that produced them. In a later paper, Benz et al [*3*], noted that the size of a liquid droplet on stainless steel appeared 2.5 times greater than they predicted for a molten metal and metal oxide. The extra size was attributed to extra oxygen dissolved in the liquid.

Further, Steinberg et al. [*13*] also suspect that far greater than the amount of oxygen necessary for stoichiometric formation of the most stable oxides is present in the slag of iron during much of the combustion. Their 1992 paper implies that the excess may be massive, and this datum led them to conclude that the reaction-rate limiting feature is neither mass transfer nor absorption of oxygen (diffusion of gaseous oxygen to the liquid), but rather the kinetic reaction at the interface between regions of molten-iron and oxygen-containing molten iron-oxide within the slag. Fig. 2 (based on data taken from the latter paper) suggests the capacity of the molten slag may be impressive. Note that at the seven-second point, the gaseous oxygen inventory appears reduced from an initial 119-g level to about 112-g, a net 7-g reduction, while the amount of oxygen needed to react the molten fraction of iron at that time would be only about 1.4-g (for Fe_2O_3) and 0.9-g (for FeO). This suggests that the "excess oxygen" (oxygen beyond that needed for reaction) in the slag would be nearly seven-fold stoichiometric relative to FeO and four-fold relative to Fe_2O_3. Total oxygen in the mixture would be approximately eight-fold stoichiometric (for Fe_2O_3) and five-fold stoichiometric (for FeO).

Attached Droplets are "Largely" Reacted

Benz et al. [*3*] mathematically analyzed the reaction on stainless steel rods and infer that small attached droplets on small diameter rods, 0.051 cm, are completely reacted to oxide. Attached droplets on larger rods, 0.32-0.64 cm, were expected to be about 70% reacted.

Slag Releases Oxygen Upon Cooling

Steinberg et al. [*13*] infer that as the slag from the combustion of iron cools, the FeO reacts with the "excess oxygen" it contains and reverts back to the more stable oxides, in turn releasing additional heat, and the larger amount of remaining oxygen is desorbed to the atmosphere. Their data, Fig. 2, indicate that between the seven-second and 18-second point, a net release of about five grams of oxygen is desorbed from the slag. The reversion of FeO was not complete to the most stable oxide (Fe_2O_3), and a mixture of the two most stable oxides (Fe_3O_4, and Fe_2O_3) was found.

Two-Phase Melts and Surface-Tension Effects

Upward combustion of rods is reported to accelerate after slag-droplet detachment [*2,3,13*]. The increase was attributed [*13*] to a formation of two distinct molten phases in the slag: one a thin interface of pure iron representing the melting zone of the rod, contained within the other: iron oxide containing excess oxygen. The surface tensions of these two materials are reported to differ widely (1788 dyne/cm for liquid iron and 550 dyne/cm for liquid FeO oxide). As a droplet's weight overcomes the intermolecular forces, a low-surface-tension phase might detach leaving the high-surface-tension phase behind (perhaps carrying an inert-gas halo with it) and more intimately expose the fresh metal to an abundant supply of oxygen, thereby accelerating combustion.

Local surface tension gradients are believed to the principal cause of circulation within burning slag droplets [*22*].

Burn Ratios

Analysis at Southern Research Institute proposed the use of "Burn Ratios" for the interpretation of metals flammability. They proposed that if the heat of combustion of a metal is less than the heat required to warm it and melt it, then combustion is unlikely. If the heat of combustion of a metal is less than is needed to warm it to the boiling (or sublimation) point and vaporize it, then it is unlikely to burn in the vapor state [*23,19*].

Iron reacting to form FeO transfers about 3.8 times the heat needed to melt itself. It transfers only 0.56 times the heat necessary to vaporize itself. If adiabatic combustion could be partitioned into two fractions, one melting a portion of the metal at its melting point and the remainder vaporizing the rest of the metal at its boiling point, up to 48% of an iron specimen might be vaporized (ignoring heat losses) [*17*]. In practical ordinary systems, much less (if any) of the steel might be vaporized.

Endothermic (Temperature Limiting) Transformations

During the combustion of some metals, there are upper limits on the temperature that are achievable for even adiabatic conditions. This is because endothermic transitions act to absorb energy. In some instances, metal oxides dissociate, absorb some of the heat of combustion, thereby preventing the achievement of temperature above the dissociation temperature. In the case of iron, Steinberg et al. [*13*] assert that FeO decomposes at temperatures of 3500-5000 K depending upon the system pressure and the precise reaction that occurs, thereby limiting the maximum achievable temperature, even in adiabatic systems.

Influence of Molten Slag

The role of slag has been viewed as both an inhibitor and promoter of combustion. Sato et al [*2*] and others [*3,13*] have reported that the rate of combustion accelerates just after a slag droplet falls away, suggesting that slag is an inhibitor of combustion. Zabrenski et al. [*5*] argue that the slag appears to facilitate combustion, and that when drainage of the slag was facilitated, it was more difficult to sustain combustion. Curiously, combustion in microgravity [*22*] has exhibited the greatest combustion velocities despite complete accumulation of slag in the combustion zone.

Test System

The goal of this work was to directly observe steel combustion in various ways. In each, however, the goal was to test under low-risk conditions, so that a maximum amount of close-quarter observation was possible. To accomplish this, the combustion was carried out in an open glass tube as in Fig. 3. The rod specimens were supported at the top by a frictional member and could be raised and lowered, and oxygen gas was flowed downward over the specimens at a low, unmeasured rate. A major goal of the work was to quick freeze the combustion, and so, the glass tube was open at the bottom to allow access. This required that the testing be accomplished at atmospheric pressure, and that the rods be tested in sizes that can reliably propagate combustion at atmospheric pressure.

The low test pressure in this instance is a major departure from many other test programs and its impact will need considerable study. However, the surprising results in these tests might justify their replication at higher pressures.

Ignition was accomplished with an oxy-acetylene torch in either of two ways. In the first, a portion of the specimen was allowed to project from the bottom of the glass tube where it was aggressively heated to the point of combustion. In the second, the rod was shifted downward to allow heating of the end, then the rod was pulled upward into the oxygen stream.

A substantial distance beneath the tube opening, was a vessel to catch the slag droplets. In some cases, a second vessel containing a fluid (liquid nitrogen or water) to quick-freeze the combustion was mounted on a pivot so that it could be quickly swung into place beneath the glass tube. In this way, droplets from the burning rod could be

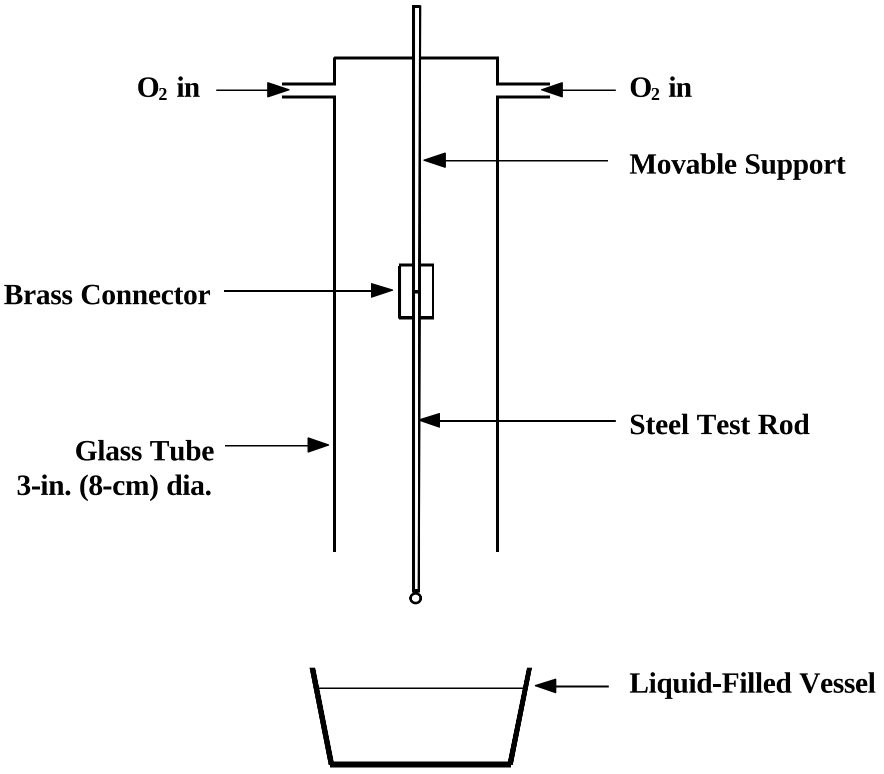

FIG. 3—*Glass open-bottom vessel.*

selected for study that came from the combustion of any desired region of the rod. In particular, droplets from the early portion of the combustion that might be igniter influenced were avoided.

To quench combustion on the rod itself, the burning sequence was initiated and at the appropriate time, either the cooling bath or quenching stream was swung into place, and either the burning rod was lowered into the liquid or the cooling bath or quenching stream was raised up into the open tube and engulfed the specimen. All these methods required a substantial dexterity to time correctly, but with a large number of attempts, quick frozen droplets and rods in many stages of combustion were promptly quenched. In this regard, water (with its large latent heat of vaporization) appeared to yield a much more rapid quench than liquid nitrogen.

These specimens were then manually and instrumentally examined. Some were weighed. Some were sectioned. Some were broken open. Some were examined under SEM or XRD.

Test Specimens

Test specimens about 5-in. (13-cm) were cut from rods used for welding carbon steel. This welding rod has a flash coating of copper which was abraded away prior to use. A small number of initial tests employed steel laboratory wire (Malin Co., #16, black iron) in smaller sizes to provide droplets with a high surface-area-to-volume which could be quick-frozen more rapidly in the maximum available column of liquid nitrogen.

All ignitions were accomplished with an oxy-acetylene torch manually applied to the bottom tip of the rod.

Results and Discussion

The figures and drawings in this report illustrate metallographic and photographic results of this program. Some exhibit quick-frozen droplets that were collected from burning specimens quenched in liquid nitrogen or water. Some exhibit burning rods that were quick frozen or rapidly gas quenched. Some exhibit burning rods or rods in the process of quenching.

Some specimens were sectioned and selected regions examined under SEM. Some slag was ground and analyzed by XRD. Individual features of these specimens along with other observations, discussions and surmise are presented in the individual discussions below.

What was the attached droplet structure?

The most impressive and surprising result is the apparent complex structure that the quick-frozen and rapidly quenched steel slag appeared to exhibit. The slag droplets that formed on the rods did not appear to be largely a single molten liquid mixture, as occurs with slow quenching. They appeared more likely to be distinct “bubbles” or layers of oxide slag surrounding and separate from a large molten droplet of metal (Fig. 4). Within the literature reviewed, this structure is not described nor does it appear to be anticipated. If proven valid, these results impact several existing combustion models and opinions.

This proposal of a slag “bubble” is controversial, and data which suggest this structure will be reviewed. Among the observations upon which this suggestion is based include: the relationship of the droplet size to its apparent weight during growth, the recovery of droplets quenched in water with a shell structure containing a single loose pellet of iron metal, visual observation of an apparent annulus when attempting to manually reignite specimens that extinguished while they were still at high temperature, and an apparent momentary “droplet-volume increase” that occasionally happened suddenly during attached-droplet growth or during quenching. Each of these is discussed in detail in later sections.

During combustion, it appeared that cooler material was diffusing downward from the melting zone of the rod into what would be the skin of any “bubble.” There was typically a lower brightness (towards the long-wavelength [red] end of the spectrum) exhibited in a band near the melting zone, and in many cases, there were “fingers” of long-wavelength, reduced brightness regions observed that extended down the surface of the droplet as much as half way. Many of these features are present in the droplet sequence of Fig. 1.

If this model is correct, the most significant questions raised relate to the apparent annulus and any gaseous material it might contain. Might it have been oxygen? Carbon dioxide or monoxide from the combustion of carbon in the steel? Steam from moisture in the steel? Iron vapor? Hydrogen (as has been surmised in some small-aluminum particle

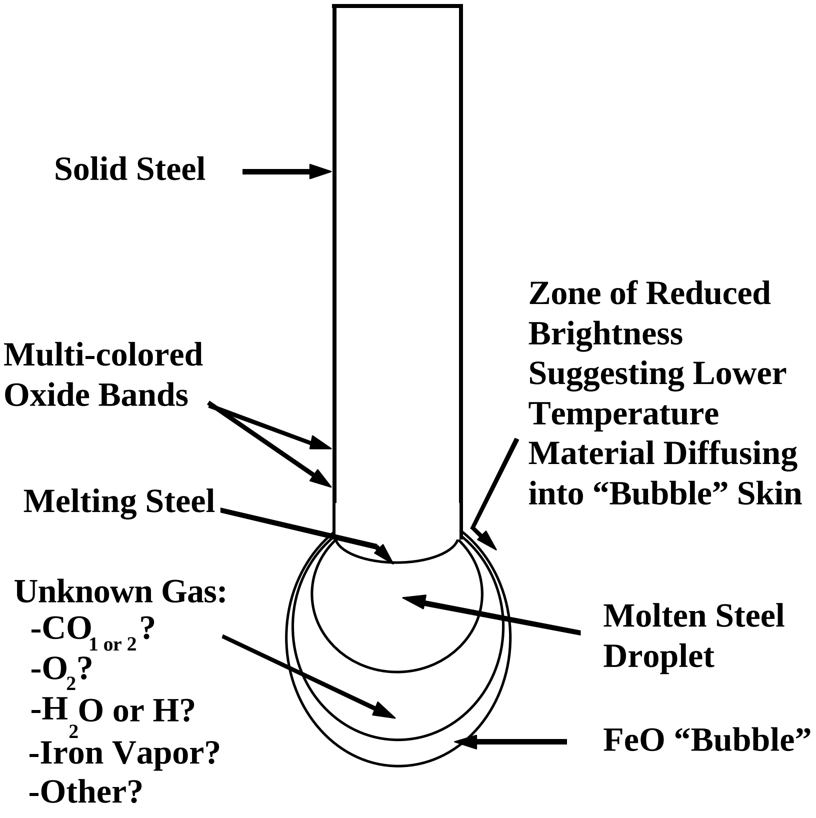

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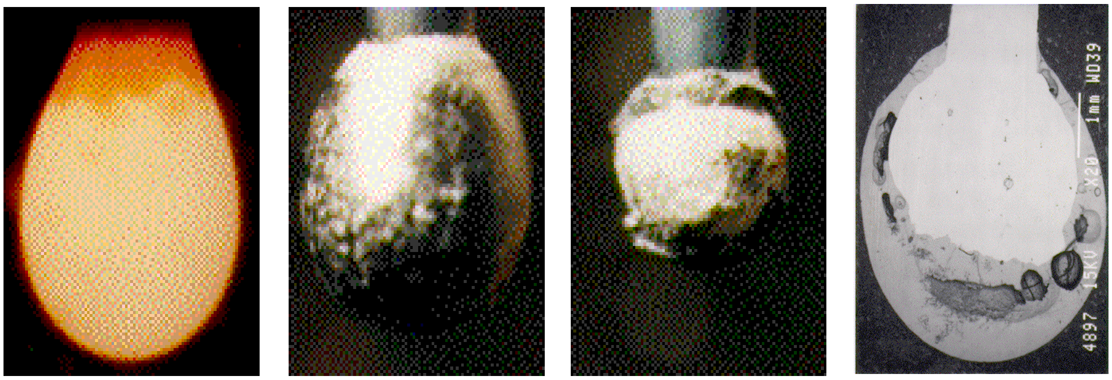
FIG. 4¾*Proposed steel combustion model (cross section). A large annulus is shown, but the size of any annulus that may be possible is unknown.*

combustion tests? Some other volatile combustion product? A mixture of these? And would it persist at higher pressures?

Time precluded an analytical quest to trap and identify any annular gas. However a few efforts were made to seek a better understanding of it and to gain sufficient confidence in its potential existence to warrant publishing these results.

Fig. 5 exhibits an attached droplet immediately before and after quenching in liquid nitrogen (Parts A and B, respectively). Upon rapid quenching in LIN, the droplet was found to have changed shape, but only slightly. Also present is the rod core after the slag was removed (Part C). Part D from a different specimen of smaller diameter exhibits how the slag and molten iron were suspended from the rod. After etching, the convex transition line (graphically enhanced on Part D) between solid and liquid steel was found to terminate at the intersection of the spherical molten steel droplet and the solid rod. The oxide envelope was "penetrated" by the solid rod, and therefore, the cylindrical contact surface between the oxide and solid rod serves as a heat-transfer path (a potentially important factor with regard to combustion in microgravity in which the length of this transfer path would progressively grow). Although these were rather large-diameter rods in the analysis of Benz et al. [*4*], the droplets were neither well-mixed nor largely reacted.



A
Before quench

B
After quench

C
Slag removed

D
Different specimen

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FIG. 5 ¾ *Rods quick-frozen in liquid nitrogen.*

These artifacts and several others not included here, support the model structure with regard to a spherical shape for the molten-steel core. The volumes of the droplets in parts A and B are similar, any desorbed oxygen did not greatly affect the volume, and the volume of the Fe core in part C is about 25-40% of the total. Voids in Part D may be explained by several mechanisms, including a gas-filled annulus. The molten Fe core in Part D is also about 50% of the total droplet volume.

However, the quench was not always a smooth process. Indeed, when droplets were quenched by halting the oxygen flow (Fig. 6), and oxygen remained available in the ambient atmosphere, the process often exhibited an abrupt, momentary droplet "expansion" (Fig. 6, frames 3 to 4). These events are described in more detail later.

Since there is sudden "droplet-volume increase" apparent during this quench in Fig. 6, perhaps there is also a point during the growth of a droplet at which sudden expansion occurs, and an annulus could be created. Curiously, on Fig. 1, between frames eighteen and twenty, there is an abrupt droplet volume increase by a factor of about 2.5. A similar but smaller change is present in the previous droplet cycle between frames three and four. Might these droplets have inflated suddenly to form an annulus? Might any gas-phase (or other) combustion have been possible in the annulus with temperatures capable of evaporating iron or some other constituent?

How Did the Attached Droplets Quench?

Burning droplets were quenched by several methods, and each was instructive. Results differed among rapid immersion of the rod with attached droplet into LIN or

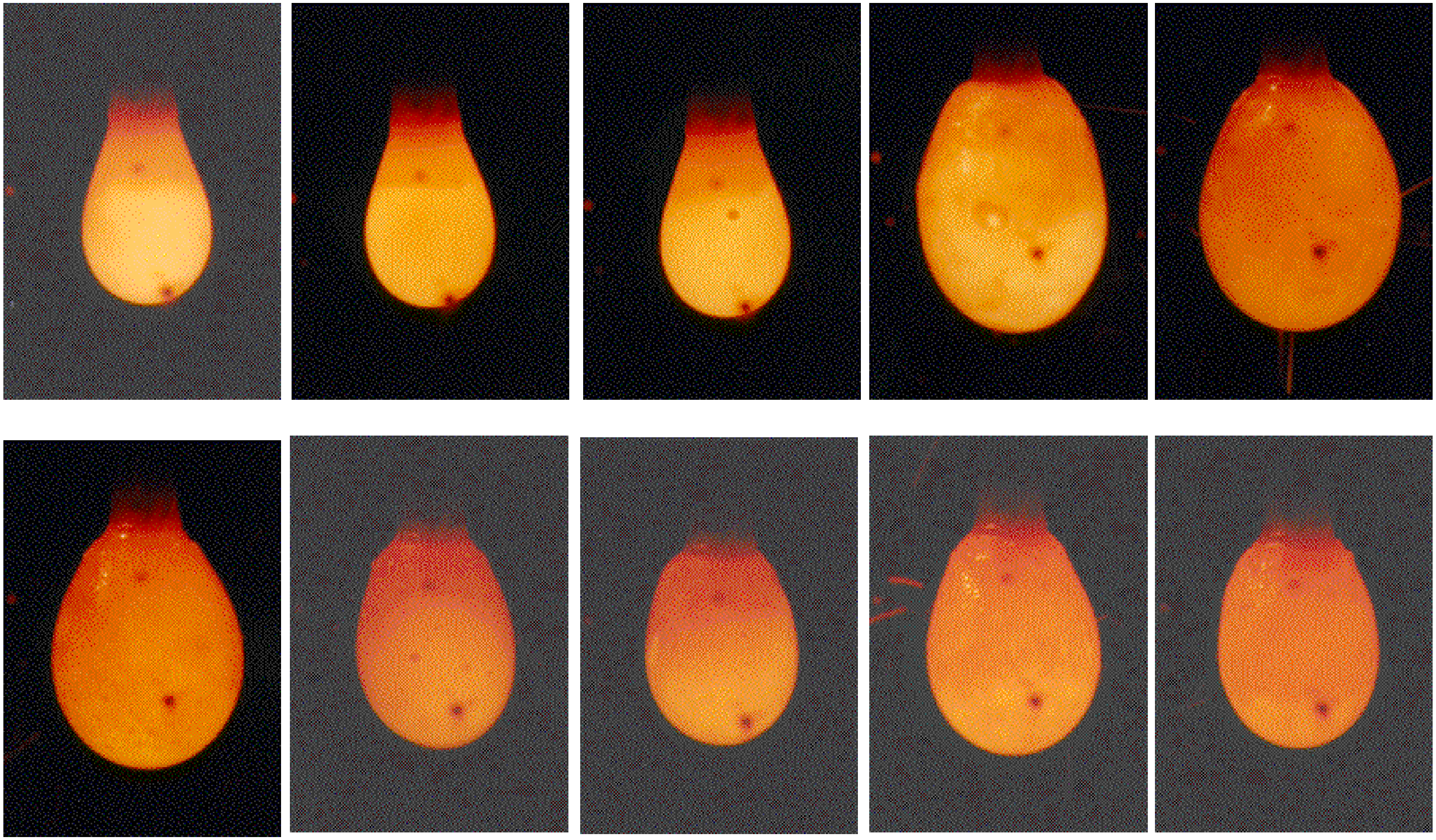

FIG. 6—*Droplet "inflation/deflation" seen following oxygen flow interruption. Views are at about 0.3 second intervals.*

water, or rapid or slow immersion of the rod into a flowing argon gas stream, or for simple cessation of the oxygen flow.

The first of the quench scenarios was for quick-freezing of the burning droplet in LIN. This has been reviewed above.

The second scenario was rapid immersion of the attached droplet into water. In this case the slag fractured and broke away, often revealing a thin-skinned oxide bubble and exposing a large spherical core with a surface resembling that of a bearing ball.

Concern over whether the rapid cooldown during quenching in liquids might prevent the reaction of any sorbed oxygen led to quenching in a gas medium to yield a slow cooldown. In this case, rapid immersion into a flowing argon gas stream again resulted in the droplet exhibiting a shell with the only significant Fe species being FeO containing a separate spherical iron core. In this case the cooldown was much slower than was the case for immersion into water or liquid nitrogen, and yet there was again no significant amounts of higher oxides formed. Nor was there visually obvious desorbing of gas.

Curiously, when immersion into gaseous argon was slow, one could observe combustion briefly intensify near the top of the droplet, and in one test, material was sprayed from the internals of the droplet near the upper shoulder.

However, the most interesting scenario was quenching that followed oxygen-flow interruption. When oxygen flow was terminated, the rod would continue to combust for a period, with the attached droplet continuing to grow but cooler (judged by a progressive decrease in brightness, a shift in color to the long-wavelength red end of the spectrum, and fewer variations in color). But then it would extinguish, perhaps as air back-diffused into the vessel or as the specimen built up a layer of diluents (Fig. 6 illustrates this sequence). In some of these events, there would be a large droplet attached at the time of actual extinction. Often, this droplet was seen to briefly and abruptly undergo a sudden volume increase (“inflation?”) then a slower volume decrease (“deflation?”) with no apparent venting from the interior.

The views in Fig. 6 exhibit this effect, are approximately 0.3 seconds apart in time, and show this abrupt “inflation” between frames three and four. In this third of a second, the apparent volume of the droplet has increased by slightly more than three-fold. During this "inflation" time, the brightness did not flare. Frames four through seven then show part of the slower “deflation” event in which the droplet size decayed towards it preinflation level and its brightness decreased. Curiously, nearly two seconds later, in frame eight, there appears to be a second smaller size increase and perhaps a slight brightness increase. Fig. 7 (taken after the rod in Fig. 6 was fully cooled) also exhibits another tendency of these types of extinctions: liquid material that often appeared to be pumped or extruded from the droplet interior and produces one or more lobes on the droplet’s exterior, disrupting the prior near-symmetrical shape.

Final, cooled, attached solid droplets from tests like this were consistent with slags reported from higher pressure work [*20,13*]. There was no large spherical core. The outer slag was brittle. They were found by XRD analysis to be largely the oxides Fe_3O_4 and FeO with traces Fe_2O_3. This apparent consistency between the slow-cooled low and high pressure results in oxygen-containing atmosphere begs for testing of rapid, inert-gas quenched slag at elevated pressures to see if they reproduce the results found here at low pressure.

FIG. 7—*Attached droplet quenched by cessation of oxygen flow, exhibiting lobes due to "extrusion" of liquid (same specimen as that of Figure 6).*

How Might the Attached Droplets Suddenly "Expand?"

Time may produce many hypotheses on this point. It is rich with possibilities. The author will review only a few hypotheses that seem to capture several of the observed features for both the expansions observed during droplet growth and during quenching in oxygen-containing atmosphere.

When a droplet detaches, there is only a small molten tip left on the rod. This molten tip temperature is very high. It is certainly higher than the melting points of steel (about 1800 K) and any of the stable oxides present. Some literature, such as Steinberg et al. [*13*], cite slag temperatures in the vicinity of 3000 K, albeit at elevated test pressures. Adiabatic combustion of iron should produce temperatures at the boiling point of iron (about 3100 K at atmospheric pressure). A paper by Kurtz et al. [*12*](pending publication as of this writing), indicates that measurements of the even the smallest attached droplets is at least 2500 K at 1.6 MPa. The analysis of Steinberg et al. [*13*], which is supported by the SEM results of this paper, offers a strong basis for concluding the only stable oxide present in this melt is FeO. However, further up the rod, an oxide film is obvious (color photos exhibit the multicolored thin-film-diffraction rainbow of oxides, but they do not reproduce adequately for inclusion as a figure). This solid oxide is quite likely to be Fe_3O_4, and/or Fe_2O_3. The closer to the molten metal zone, the thicker this oxide is likely to be.

As this droplet ascended, these oxides were fed into the molten zone, and their temperature should have risen above the decomposition point. Steinberg lists the decomposition of these oxides at 1735 K (Fe_2O_3) and 2257 K (Fe_3O_4), and at these points oxygen could be released. A portion of this might collect internally at the interface of the oxide with the molten steel and act to separate them and inflate a bubble. However, this oxygen would be expected to react quickly with either the unreacted steel and produce additional FeO or perhaps other materials such as carbon to produce a gas. Therefore, if oxygen is to persist in the annulus, some mechanism must limit its reaction rate. Two possibilities will be considered: the presence of nonreactive gases and the presence of a slow gaseous diffusion flame.

One might anticipate a nonreactive gas to be present. In the case of steel combustion, there is a carbon constituent (0.15-0.8%) that should produce carbon-monoxide and/or carbon-dioxide in the annulus. Other minor constituents in the steel might have a similar effect if their oxides are volatile. Because of the extremely high temperature, which decreases the densities of gases, and the several-hundred-fold volume change that occurs upon vaporization, the amount of material in the oxide film or in the alloy needed to inflate such an annulus is very small, and therefore, the nonreactive gas might even be steam from tramp moisture in the metal or hydrogen, either resident or from the reaction of the oxygen in such steam. This mechanism would suggest that steel alloy flammability could be influenced greatly by the presence of minor constituents. There is some support for this. For example, NASA data indicate that the combustion threshold of alloy 440C decreased (became more flammable) significantly when the metal was decarburized.

Indeed, the author's associates: Michael D. Lanyi and Zbigniew Zurecki have both provided rather compelling arguments that any annulus would be very likely to contain carbon monoxide which would be a powerful reducing agent. If this were the case, any further combustion of the iron might have to result from its contact zone with the slag bubble near the point of attachment to the rod. Further, the volume of any annulus gas would be related to the amount of carbon in the carbon steel. Pure iron specimens might have no annulus at all. Time and ability precluded an exploration of this complex prospect here, and another paper to explore this case will be encouraged.

However, less compelling prospects will also be cited. Perhaps the annulus could contain iron vapor (with or without other components) sufficient to enable a gaseous diffusion flame or vaporous migration of metal to the slag bubble. This is a very controversial hypothesis, because many publications have asserted the inability of iron to burn as a vapor based largely on its low boiling-point burn ratio. An hypothesis based on partitioned combustion will be offered.

Any bubble temperature is clearly high, previously noted to be at least 2500 K and in later stages of droplet development potentially approaching or exceeding the adiabatic combustion temperature of iron (reported to be about 3100 K). At the upper level of this range there is an appreciable vapor pressure of iron present at atmospheric pressure. Remember, the model features a molten pure iron droplet contained within a slag bubble. The temperature of this pure iron droplet would also be in the range of 1800 to 3000 K. Whereas the boiling-point burn ratio for room temperature iron relative to an FeO product is just 0.56, at 3000 K this ratio would be more nearly 0.78. Further, when FeO forms from molten Fe, there is much more heat of combustion available than required to produce an FeO molecule at its dissociation temperature, well above the boiling point of iron (the dissociation of FeO would be the temperature-limiting endothermic process). Radiation energy from the slag bubble, focused on the molten metal core combined with the available heat of combustion of the hot iron may thermodynamically allow for later stage evaporation of a fraction of the iron core.

Since the composite droplet of Fig. 1 is not well mixed, its temperature is not thermodynamically limited to the boiling point of iron, and the oxide region is free to assume higher temperatures. The temperature of the inner surface of the bubble might build until the boiling point of the iron is approached and then the annulus grows in proportion to the temperature. Indeed, among the mechanisms that may be operating in the second droplet sequence of Fig. 1, the rapid droplet growth between frames 19 and 20 may signal the achievement of this temperature. There is other experimental support for this prospect also. During quenching of both attached and detached droplets in water, the oxide bubble was often fractured away and the formerly molten iron core was often exposed to yield a remarkably shiny, smooth surface with no indication of oxide (often having the appearance of a ball from a ball bearing). This might be more consistent with a vaporizing surface than for a reaction surface, and may suggest that the oxide may not contact the high-temperature metal.

And so an admittedly remote prospect exists that vapors of iron may mix with nonreactive gases and then burn with oxygen condensing into molten FeO that deposits on the inside of the bubble surface, or that might migrate to the inside surface of the FeO bubble and reacting there or mixing with the slag or dissolved oxygen there.

Another datum supports this later portrait. It is the previously cited tendency of large attached droplets to abruptly inflate during the quench process when ambient oxygen flow is halted. Consider the circumstances. The rate of oxide growth on the hot zone of the rod is decreasing, perhaps ceased. A molten droplet of iron is hanging from the rod presumably surrounded by a molten bubble of FeO oxide, the annulus of which would be containing a gas, perhaps a mixture of iron vapor and a nonreactive gas. The rate of heat loss from the droplet would be substantial, and it would be on a cooldown curve.

However, FeO is a reactive material in oxygen-containing gases at and below the decomposition temperature range of Fe_3O_4. Above this decomposition temperature range, it is nonreactive. In the fashion of Monroe et al. [*23,19*], one could define a new burn ratio at the decomposition point, BR_{DP}, given as the ratio of the enthalpy of reaction divided by the enthalpy (latent and sensible heats) necessary to bring the material through the Fe_3O_4 decomposition temperature range. However, in this case, the FeO is initially above the Fe_3O_4 decomposition temperature.

As the average FeO temperature decays toward the Fe_3O_4 decomposition temperature, more stable oxides of iron may begin to form. This oxide formation would release heat, because FeO is flammable, having a heat of combustion in oxygen (to form Fe_3O_4) of about 0.33 kcal/g (24 kcal/mol). The heat released would have a tendency to maintain and even increase the temperature of the cooling/reacting oxide. One would anticipate the liquid to exhibit substantial temperature gradients as well as the normal distribution of molecular velocities. Therefore, any newly formed stable oxide will be regulated near its decomposition temperature range for a period and may have a tendency to reversibly decompose and react, again and again, as molecules move through the normal range of velocities present at this temperature. In other words, as the temperature passes through the decomposition range there may be a substantial amount of both reaction and decomposition occurring according to the overall net reversible reaction:

$$3FeO + 0.5O_2 \quad \longleftrightarrow \quad Fe_3O_4 \tag{1}$$

Whenever the reaction goes in the decomposition direction, oxygen might be released, some to the ambient if the Fe_3O_4 molecule were on the outside surface of the bubble, some into the annulus if the Fe_3O_4 molecule were on the inside surface of the bubble. In other words, the frequently reversing oxidation/decomposition might pump oxygen into the annulus, where it might promote further reaction of the molten steel core. This may explain why the cooldown produces a momentary inflation without obvious temperature rise followed by the extrusion of molten oxide from the interior of the droplet. Indeed, droplets quenched in oxygen have been found to be principally FeO and Fe_3O_4 oxides.

Except for the absence of Fe_2O_3 a similar but more complex analysis could be made for the point at which the temperature of the cooling slag (whether FeO, Fe_3O_4, or a mixture) decays to the decomposition temperature range for Fe_2O_3. However, this mechanism might not be excluded during quenching at higher pressures.

The above analyses are admittedly tenuous but should fuel thought within the ASTM Committee G-4 collegium. It would certainly be interesting to monitor droplet temperature during combustion and quench to see whether there is a correlation between the temperatures during inflation/deflation (for example those present at frames 19 to 20 of fig. 1 and at frames 3 to 4 of Fig. 6).

Curiously, this mechanism would be a mixed-phase combustion scenario about which there has been speculation (Werley et al [*17*]), in which a metal such as iron with a burn ratio at the boiling point (BR_{bp}) of less than unity partitions its heat of combustion into two fractions, one of which promotes combustion in the liquid phase (perhaps at the shoulder of the rod/bubble interface) then in a slightly different location (perhaps, within the annulus of the bubble) produces a higher-temperature environment in which a portion of the heat is used to vaporize a portion of the rod and yield fractional combustion in the gaseous state. Time prohibited exploration of this hypothesis.

What Was the Detached Droplet Structure?

Although this work was done at a lower system pressure than that reported by Hirano et al. [*20*], the volumes of just-detached droplets were reasonably consistent with Hirano's trends. Fig. 8 exhibits the approximate droplet size found in this work as determined from photographs of just-detached droplets and contrasts it to data from Hirano. This consistency may suggest that any presence of a bubble may not be exclusively due to the low ambient pressure, for if Hirano's specimens were exhibiting bubbles, then those bubbles were larger at higher system pressures. This may also suggest that, at higher external pressures, any compression of the annulus and bubble size is not great. The further surmise might be that much of the gas in the oxide balloon is not ideal—its vapor pressure may increase with external pressure (perhaps as a result of increased combustion temperature at the higher external pressure). Since combustion temperatures increase with

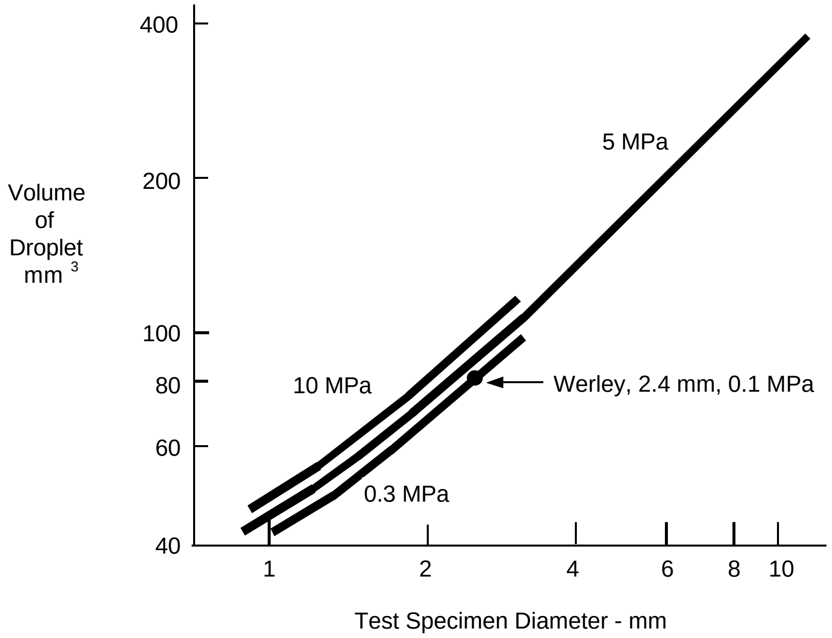

FIG. 8—*Variation of the droplet volume with the rod diameter at various pressures according to Hirano* [*20*]. *The figure also depicts the volume of just-detached droplets for 0.94-in. (2.4-mm) rod results from this work.*

external pressure, this may suggest that any contained gas includes a high-temperature volatile material, such as iron. However, other scenarios are also plausible.

Fig. 9 exhibits a detached droplet quick-frozen in a 30-in. (76-cm) column of liquid nitrogen. This droplet was formed from the combustion of #16 steel wire to reduce its size and allow for a more rapid solidification. These frozen droplets were nearly spherical, exhibiting only a slightly flat region apparently from impact or resting on the vessel bottom while still soft. This sectioned droplet exhibits several entrained Fe spheres contained within a cracked spherical FeO matrix. The presence of entrained pure metal in these droplets provides a strong argument that the detachment is not exclusively low-surface-tension oxide draining from high-surface-tension molten metal as has been proposed [*13*]. Rather, it appears the droplet detachment may be determined by surface tension effects of the contained metal core.

What Was the Droplet Mass?

Two approaches were used to quantify droplet mass. One was to weigh four consecutive droplets that were quenched in liquid nitrogen. These results might be compromised by the mass of any excess oxygen that desorbed during cooldown. However, the average mass of these droplets was approximately 0.44-g. On average, each droplet resulted from the loss of 0.38g of rod.

The second tactic involved suspending the burning rod on a scale, and measuring its weight immediately before and after a droplet detached. In this case, the weight change of the rod upon droplet detachment was in the range 0.35-0.4 g. However, in this case the

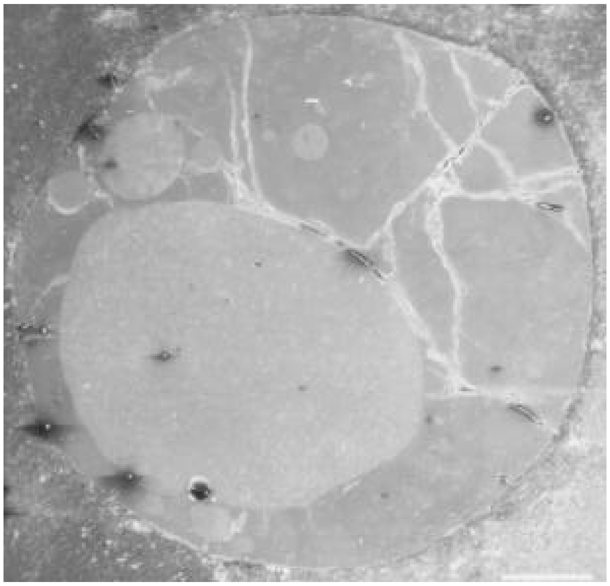

FIG. 9—*Detached droplet from #16 wire quick frozen in liquid nitrogen.*

settling time of the scale after detachment of the droplet may have allowed some of the new oxide to grow on the rod before giving a readout. Therefore, the lower results during the weighing are plausible, and certainly, they do not suggest large amounts of sorbed oxygen in the droplets. Both methods gave reasonably good accord and do not support the presence of massive “excess oxygen” in the droplets, at least at atmospheric-pressure conditions.

What Was the Slag Composition?

Fig. 9 exhibits a sectioned detached droplet that was quick-frozen in liquid nitrogen. This droplet was formed from the combustion of #16 steel wire in order to form a droplet with a high surface-to-volume ratio that would solidify within the 30-in. (76-cm) column of liquid nitrogen that was available. Grinding of these droplets and XRD analysis indicates that the matrix phase is principally FeO oxide. The entrained phases are principally Fe. If a “bubble" structure was present, it has disappeared, although some droplets of this type exhibited voids that may have been vestiges.

Droplets from 0.094-in (2.4-mm) rods quick-frozen in water exhibited an oblate, single-lobed shape after falling through a 30-in. (76-cm) column, at which time they were still glowing red. However, they soon came to rest on the bottom and went through an “inflation” perhaps similar to that observed for extinction in oxygen. These quenched droplets exhibited several hollow lobes (top row of Fig. 10) and one lobe of each contained a single loose pellet (bottom row of Fig. 10) of relatively pure iron with one region resembling a bearing ball. The shell of one of these droplets was ground and analyzed by XRD and found to be principally FeO. These submerged inflations demonstrate the ability of FeO to form bubble structures.

FIG. 10—*Slag droplets quick frozen in a 30-in. (76-cm) column of water. The top row exhibits the multi-lobed shells. The bottom row exhibits the loose oblate pellets in typical shells (one pellet per shell): a portion of each pellet surface was typically shiny and smooth.*

A peer reviewer has argued that the similarity of detached slag inflations under water and attached slag in oxygen disprove the previously cited prospect of oxygen transport through the FeO. However, it is appropriate to note that such inflations were not observed for droplets quenched in liquid nitrogen and that water is a source of oxygen, containing appreciable amounts of dissolved oxygen and which is one-third oxygen, itself.

As noted before, when slag that had been slowly quenched in oxygen-containing gas was analyzed, it contained a blend of Fe_3O_4, and FeO oxides similar to that observed by other workers [*20,13*] raising a crucial question as to whether slag from high pressure tests burns to stable oxides during cooldown using environmental oxygen rather than contained oxygen.

Did the Slag Release Oxygen?

Clearly, this work did not find evidence of significant amounts of oxygen beyond that needed to form FeO at the atmospheric pressure test conditions. Indeed, the most surprising observation was that of an apparent slag “bubble” encapsulating the rod tip with an annular gap between them. Since the inner droplet surface was basically iron, it is unlikely the annular gap contained a high oxygen concentration as that should have promoted a rapid growth of oxide on the interior surface. Perhaps instead, the slag bubble and perhaps the annular space gas provides barriers to combustion that help account for cyclic decay in burn rate as the droplet grows.

Was There Excess Oxygen in the Slag?

This results of this work argue against the concept of large quantities of excess oxygen in carbon steel combustion at atmospheric pressure. Other work inferred oxygen presence and one effort at much higher pressure appeared to find substantial amounts [*13*].

Might these present data argue against excess oxygen presence at higher pressures?

The author has been skeptical that the molten material (whether oxide, metal or a mixture) in a high temperature droplet could contain a massive amount of free oxygen. At the extreme temperatures present, it is reasonable that any oxide would undergo partial dissociation and an equilibrium would be established between the oxides and oxygen. However, this equilibrium (that is also exhibited in gaseous fuel combustion) is not a sink of oxidant that sustains further fuel reaction. Indeed, additional metal "fuel" would tend to drive the reaction to completion, depleting the inventory.

The magnitude of the excess oxygen suggested by Fig. 2 from previous work is awesome. As previously noted, at the seven-second point, the minimum oxygen concentration in the oxide/metal/oxygen droplet would be at least 83-89 mol-%.

When droplets of oxide/metal/oxygen were quick-frozen in liquid nitrogen, there was no spongy character to the interior, although there were voids. The massive release of a gas was not visually observed. Similarly, droplets quenched in inert media, gas or liquid, had a two-phase nature—large regions of rather pure Fe and regions of rather pure FeO. And the droplets weight before and after quenching were similar. This suggests there was no after-burning in any contained oxygen that might have been present. Attached droplets that were rapidly quenched in gaseous argon also exhibited Fe only as FeO and Fe. This suggests that no major amount of burning in excess oxygen occurred and perhaps that there was very little sorbed inventory present. This might suggest that in the work that produced Fig. 1, the slag may have continued to react during cooldown, consuming oxygen not from within itself but from the ambient-gas environment, as apparently happened in the present tests when slags were similarly quenched slowly in oxygen-containing gas.

It is difficult to account for the apparent reductions in gaseous oxygen inventory that were calculated in this other study [*13*], but one might speculate that the attempt to dynamically measure the oxygen inventory is daunting. During combustion, there are extreme temperature gradients, and any inventory calculation must know the temperature distribution throughout the entire test vessel. The experimentalists' use of four thermocouples may not have provided sufficient data to precisely effect this calculation. For example, they report that the initial oxygen temperature was about 10°C, that during the combustion, the oxygen reached a maximum average temperature of 61-70°C, and that after the rod was gone and the slag had presumably desorbed its excess oxygen, the oxygen was 48-60°C. The maximum temperature throughout the test was only 10-15°C greater than the final. Could incident radiation have impinged the thermocouples and produced a surface temperature elevation above the gas temperature, yielding an error on the high side by this 10°C amount?

At Air Products, simple bare thermocouples have been used to measure burning velocities. The thermocouples were situated in long stagnant tubes of small bore where the ambient gas temperature was not likely to swing, and they "looked" at differing regions of the test rod. As the combustion passed through the "observed" site, radiation through even these small “windows” produced a temperature swing of several Centigrade degrees [a personal estimate of the experimentalist, John Zabrenski]. It would be interesting to see what would happen in the apparatus that produced Fig. 2 if the test vessel were filled with argon and a thermite pill were to be ignited on the bottom with a heat release comparable to the heat of combustion of the steel specimens that were previously used. Would incident radiation lead to the suggestion of a reduced gas inventory in this circumstance in which an inventory reduction is not a physical prospect? If so, it would argue any presence of excess oxygen was less than calculated.

Of course, much smaller amounts of oxygen than calculated in former work may still be present and may be important, but at present, the observations in this work do not support the general concept of “excess oxygen” in the slag. Perhaps future study will attribute this differing result to the lower pressure or possibly different alloy chemistry.

Further Work

The results in this paper are surprising and certainly not conclusive. By focusing on fairly simple observation methods at atmospheric pressure, apparent conflicts with present models have been found and an apparently new model for the combustion of metals has been suggested. Considerable confirmatory work would be needed to validate this new view, and the ASTM Committee G-4 collegium would be an excellent forum for further effort. However, these results may also point out a problem with the tests of small diameter rods and the application of these data to larger components that might not form “bubbles”nor experience droplet detachment in their combustion schemes, especially if the larger-size results were to indicate greater flammability.

Perhaps the most desirable additional work would be to extend the same observation techniques to carbon-steel combustion at elevated pressure, however, this experiment would be enormously challenging. The higher temperatures and longer freezing times, the boil-off of quench liquids at high pressure, the greater frequency of droplet formation, would all be daunting to deal with. A secondary effort might be to examine several other alloys at low pressure, however, many do not propagate combustion in the same atmospheric pressure circumstance and may require elevated pressures to succeed.

Perhaps a more easily accomplished effort would be to expose this hypothesis to the critical commentary of other researchers (which this publication does) and in addition, to reconsider the existing body of work at higher pressures that presumes the attached droplets are multiphase liquids with sorbed oxygen. Does this alternative view enable a meaningful reinterpretation of the existing data? In particular, an error analysis on oxygen mass computation techniques and a previously proposed test to explore tramp radiation as an error source in a gas that might not sorb would be relatively simple followup.

Finally, if this model gains acceptance, its use to analyze the curiously high speed combustion reported for iron in microgravity may be worthwhile. In microgravity, the wall thickness of the oxide bubble would be expected to be more uniform. Therefore, the cylindrical sleeve of oxide that contacts the solid rod above the melt line would be several-fold longer and this could be an important heat transfer source. One can envision an accumulating oxide that might extend far above the boundary at which the iron becomes molten. This would progressively facilitate melting and in combination with the rate of growth of oxide thickness might appear to produce the observed rapid regression rates. But, perhaps the rods are only melting faster to yield a relatively larger spherical metal core.

A final cautionary note: In any future work, experimentalists should be careful of the need to protect workers from the prospects of phase-transition explosions or unexpected reactions that might occur when molten materials are abruptly introduced into liquids.

Peer Review Results

This is a controversial paper. It was presented in 1995 and originally planned for publication in ASTM *Special Technical Publication (STP) 1319* [*24*] in 1997. It had been hastily prepared based on only a brief available period for experimentation. There has been no significant effort since 1995 to update the manuscript relative to any more recent publications or experimentation. The new model has not been proven and, and like any infant theory, may not survive careful scrutiny, but the case for its consideration warrants its publication. Nonetheless, the author is willing to again caution the reader that the hypothesis and analysis must be treated as tentative until it is convincingly proved or disproved.

It was subjected to peer reviews beyond the norm, including more-than-the-standard number of reviews within the ASTM system. The nature and scale of the resulting controversy from two of the peer reviews precluded its inclusion in *STP 1319*. Many comments and requests were simply not reconcilable. Peer response was divided into two groups.

Seven of nine peer reviewers (including two of three peer reviews solicited by ASTM) supported the publication of the paper, and several felt that a much stronger case can be made to defend the validity of its proposal using data from other organizations that have been unknown to the author and uncited to date in the ASTM G-4 collegium. However, one of the three ASTM-solicited peer reviewers strongly disagreed with the content, and this led to one of that reviewer's associates submitting an unsolicited fourth peer review to ASTM that was similarly opposed.

The opposition peer review was from experimentalists who are active on the area of carbon steel combustion and with impeccable credentials. The manuscript was changed to incorporate several comments cited by these two peer reviewers [typographical and other editorial errors, rough edges resulting from haste, clumsy sentence constructions that appear to have produced misunderstandings of the intent, reporting of data with more precision, etc.]. However, the author believes the peer reviewers seriously misread the manuscript in many instances. Reconciliation of their massive opposition is not possible in any reasonable fashion in an already lengthy manuscript. They are welcome to publish rebuttals. Among the controversial issues that were not persuasive to the author included:

- Some [but not all] of the observed and proposed features of the new combustion model can be explained by or represented by existing theories voiding any need to propose the new model.

- The potential presence of an annulus was firmly disputed and the validity of an excess oxygen presence was firmly asserted.

- The context of literature data presented was disputed, and the presentation of speculation as to areas warranting study and analysis was opposed. Indeed, these two peer reviewers felt the inclusion of speculation in this paper, despite its clear designation as speculation, was particularly inappropriate.

- Extremely strong opposition was voiced to the suggestion that iron vapor should be considered as a potential constituent in any annulus.

- Calls were made for additional experimentation and analysis that the author cannot accommodate.

The supportive peer review which included specialists in steel combustion, also of impeccable credentials, found the potential existence of an annulus far more than plausible, perhaps even likely. Some offered data, analysis, and literature sources to support the paper. An immediate strong suggestion was that the candidate gas for the annulus was most likely to be carbon monoxide. One supporter offered several literature sources that would support the carbon monoxide assertion. The author's background and available time precluded a rewrite to address the case for a carbon-monoxide-filled annulus or even to explore the information proffered. Potential authors are being encouraged to develop a paper to elaborate on this prospect.

Summary

Carbon steel combustion has been studied briefly in different ways than have apparently been used in the past. When tests at atmospheric pressure were conducted similarly to past testing at various pressures (involving relatively slow quenching of specimens and slag) fairly similar results were obtained. When specimens and slags were quick-frozen and rapidly quenched, the results were dramatically different.

A different perspective resulted than that contained in the literature. These data suggest carbon steel in the subject test procedures may burn in a complex way with a gas-filled annular separation between a relatively thin oxide bubble and a relatively large liquid-metal droplet. The only stable Fe inferred in these slag specimens during combustion was FeO without major amounts of higher oxides. Indicators of oxygen beyond that associated with FeO slags were sought but not found. Therefore, this work contradicts an hypothesis of "excess oxygen" in atmospheric-pressure steel slags and suggests similar testing (quick-freezing and/or rapid quenching) is needed at higher pressures. Detached droplets in this work contained large quantities of unreacted metal. Differences in alloys and test pressures may explain the conflict between these results and some of the literature data that were collected at higher pressure. However, the theses in this work bear evaluation and dialog among other experimentalists, and potential error-hypothesis in this and prior work (such as radiation-induced temperature rises) need to be tested and ruled either in or out.

Existing carbon steel usage is founded in historical experience, but if this apparently new fundamental view is validated in time, it could result in inherently different mathematical combustion models that could affect the way carbon steel is evaluated for use in new oxygen applications.

Acknowledgments

This paper was conceived with Joseph W. Slusser as a coauthor, but time constraints and other demands forced his withdrawal. Nonetheless, he provided invaluable counsel; input to the paper including the identification, provision and interpretation of the SEM and XRD data; and most importantly, a crucial vetting of the manuscript under dire time constraints prior to its presentation.

Photographic efforts that are presented (and many others that are not) benefited from the skill and contributions of Robert E. Knorr.

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