

MECHANISMS IN CORROSION INDUCED AUTOIGNITION OF DIRECT REDUCED IRON

Neil Birks and Abdul G. F. Alabi
Materials Science and Engineering Department
University of Pittsburgh

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INTRODUCTION

In a previous paper⁽¹⁾, presented to the 5th International Iron and Steel Congress, Washington April 6-9, 1986, the situation concerning our understanding of the mechanisms by which auto ignition of direct reduced iron arises was discussed. Direct reduced iron is produced by reduction of rich or enriched iron ore completely in the solid state. The end product has certain advantages, relating to well defined composition, low residual content and easy handling, that make it an attractive alternative to scrap for steelmaking. The production route, however, results in a product that is very porous. This in turn imparts to the product a high specific surface area that leads to rapid surface reactions and a low coefficient of thermal conductivity.

Direct reduced iron must be transported and stored in considerable amounts and it has been found that the bulk material has a tendency to undergo corrosion and oxidation reactions leading to ignition. By this it is meant that the pile of DRI begins to oxidize in a self sustaining manner that results in a 'metal' fire that is difficult to extinguish or control, except by exclusion of oxygen.

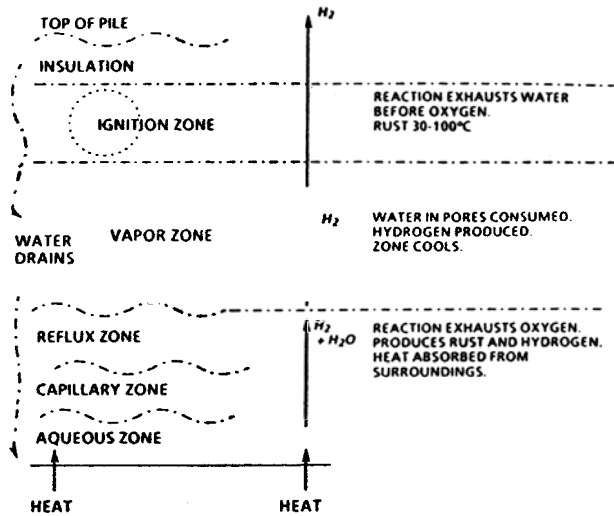
This subject has been investigated in the past⁽²⁻⁶⁾ and there is agreement that the sequence by which autoignition is achieved begins with aqueous corrosion reactions and is completed when stable high temperature oxidation reactions are established. While this seems plausible, so far there has been no mechanism established by which a series of reactions, starting at room temperature with aqueous corrosion reactions, can be shown to result in the attainment of temperatures at which high temperature oxidation reactions can become stable. Indeed, it is difficult to understand on any basis how simple aqueous corrosion processes can reach temperatures in excess of the boiling point of water saturated with salt (about 120°C).

The temperature at which high temperature oxidation of iron becomes stable or self sustaining, is that at which the rate of heat generation by chemical reaction sufficiently exceeds the rate of heat loss by all mechanisms. As will be seen later in this paper, more is involved than a simple heat balance as it has been found that the oxidation reactions themselves modify the structure of the DRI surface, substantially affecting the porosity and, thereby, the reactivity of the material.

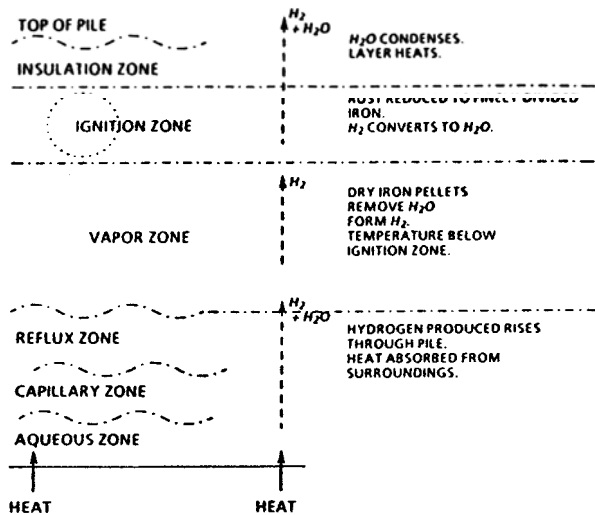
This problem has been addressed in the present work and it was proposed⁽¹⁾ that a complex interplay of corrosion reactions could lead to a mechanism by which the low temperature aqueous corrosion processes could establish conditions, at specific sites, that would foster the direct initiation of high temperature oxidation.

The mechanism proposed⁽¹⁾ is hypothetical in that, although sound thermodynamically, it has thus far not been established whether or not the mechanism is viable on kinetic and morphological grounds.

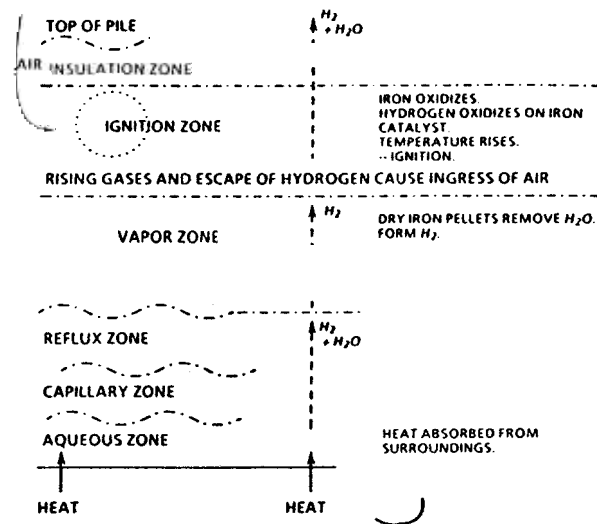
The model and sequence of events that were proposed to account for auto-ignition are shown in Figure 1. In Stage I water entering the pile of DRI from the top reacts to form rust within the upper layers under oxygenated conditions that involve exothermic reactions. The temperature of this zone thus increases during rusting. The water in this zone is eliminated by reaction and drainage. Meanwhile the zone at the bottom of the pile reacts with water under low oxygen conditions to produce hydrogen. Although these reactions are endothermic, heat exchange with the environment through the ship's hull will prevent excessive cooling. The hydrogen that is evolved rises through the pile to escape at the surface. In between the top and bottom layers described above is an intermediate layer of DRI which reacts endothermically with water percolating down in the absence of oxygen. This intermediate zone is thought to cool slightly as a result, since it is not in good thermal contact with a source of heat. In Stage II, after the water ingested from the top has been consumed or drained to the lower levels, there is a warm rusted ignition zone above a cooled rusted vapor zone and hydrogen evolved from the lower aqueous zone rises through both. The rising hydrogen gas emerges from the water saturated zones, (aqueous, capillary and reflux zones) to rise over the dry vapor zone where the water vapor reacts to form more rust and hydrogen. The gas leaving the top of the vapor zone now has a reduced water content such that its H_2/H_2O ratio corresponds to an approach to equilibrium with iron and its oxides in the vapor zone. As this gas mixture enters the warmer ignition zone the hydrogen is capable of reducing the rust to very finely divided metal, since the H_2/H_2O ratio in equilibrium with iron and its oxide is lower at higher temperatures. In



STAGE I - RUST FORMATION



STAGE II - REDUCTION



STAGE III - OXIDATION AND IGNITION

Figure 1 - Working model for the autoignition of Direct Reduced Iron

Stage III of the ignition sequence, air is ingested once more and, as the oxygen meets the warm, fine, freshly reduced iron particles, oxidation commences. Due to the extremely finely divided nature of the freshly reduced iron the reaction proceeds rapidly, and heat is evolved sufficiently rapidly to cause temperature increase locally to achieve values at which the oxidation reaction can become self sustaining. In addition to undergoing oxidation, it is expected that the finely divided iron or iron oxide can behave as a catalyst and promote the reaction between hydrogen and ingested oxygen to form water.

The individual stages in the above hypothesis are currently being studied separately to assess their characteristics.

RESULTS

Evolution of Hydrogen

Previous results⁽¹⁾ had shown that, under conditions relevant to the practical case (25-90°C and 0-7 ppm oxygen in solution), using salt water the rust formed on iron as both a flocculent precipitate of goethite, FeOOH, and an adherent surface layer of magnetite, Fe₃O₄. The current experiments extended this work to examine the hydrogen evolution from DRI pellets under a similar range of conditions. To this end, an apparatus was constructed, shown in Figure 2, that allowed the temperature and oxygen content to be controlled while allowing hydrogen evolution, to be monitored. The

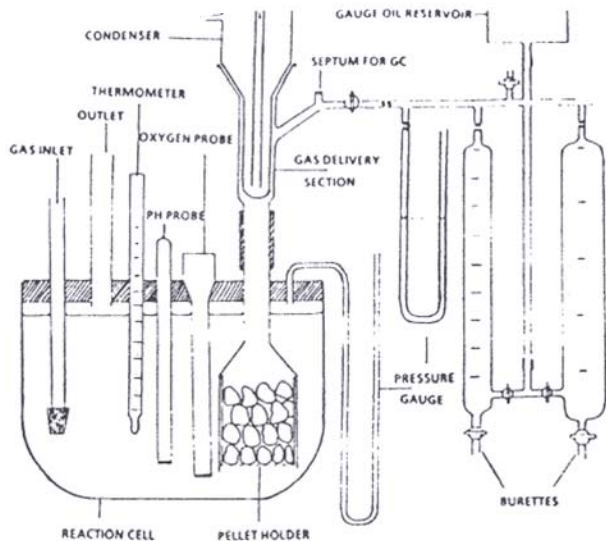


Figure 2 - Diagram of apparatus used to monitor hydrogen evolution

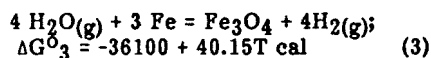
results showed quite clearly that the rate of hydrogen evolution was substantial and increased with oxygen content. In view of the competing cathodic reactions



this is contrary to expectations and is thought to be due to the formation of somewhat more porous magnetite surface layers in the presence of higher oxygen contents. The variation of hydrogen evolution with oxygen content of the salt solution is shown in Figure 3. For conditions expected to obtain in DRI cargo, it is proposed that an evolution rate of 40-400 ml kg⁻¹ day⁻¹ is representative for the type of DRI used in this study.

Reaction of Dry DRI with Water Vapor

The removal of water vapor from the rising hydrogen by the dry iron in the vapor zone occurs by the reaction



This process is important in establishing a gas composition that is capable of reducing the oxides in the warmer ignition zone.

The gas composition that would be in equilibrium with iron and its oxide can be expressed in terms of the ratio PH₂/PH₂O and is given at any temperature by

$$4 \log K_3 = 4 \log (\text{PH}_2/\text{PH}_2\text{O}) = - \frac{\Delta G_3^0}{4.575T} \quad (4)$$

$$\text{thus } \log \text{PH}_2/\text{PH}_2\text{O} = 1973/T - 2.20 \quad (5)$$

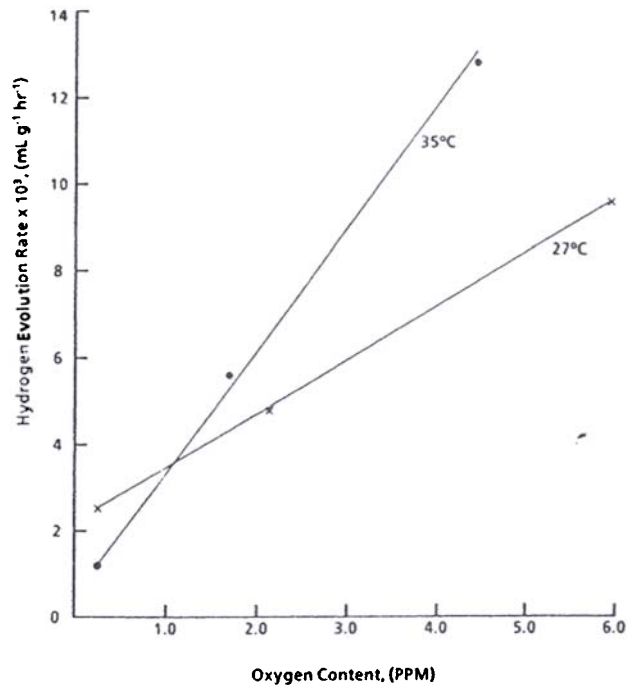


Figure 3 - Hydrogen evolution rate at various oxygen potentials at 27°C and 35°C

From equation (5) it is clear that the values of PH₂/PH₂O are lower at higher temperatures having values of 661, 5308 and 26350 at 120°C, 60°C and 25°C respectively as shown in Figure 4. Thus a stream of hydrogen equilibrated with iron at a temperature of about 40-60°C would be capable of reducing iron oxides that were at 100-120°C. The rate of the reaction between water vapor and iron at the lower temperature has not been established yet experimentally. Although the specific reaction rate is low, it occurs over a very large surface area of the DRI pellets and this aspect must be studied experimentally. Assuming that equilibrium can be approached, the difference between the equilibrium conditions at 40-60°C and 100-120°C is such that it is estimated that only about 0.1% of the hydrogen evolved is available for reduction at the ignition site. Preliminary work has shown that reaction (3) will proceed, however the rates have not been measured.

Reductions of Oxides and Hydroxides

In order to examine the reduction of oxides and hydroxides formed during rusting, pellets of DRI were rusted for various times and then dried completely. Pellets were then placed in a nichrome cage suspended from an automatic recording balance. A thermocouple was placed directly below the cage to record the temperature. Reduction was carried out using a stream of hydrogen from a cylinder. From the initial experiments it was clear that, in spite of the drying procedure, substantial evolution of water occurred at

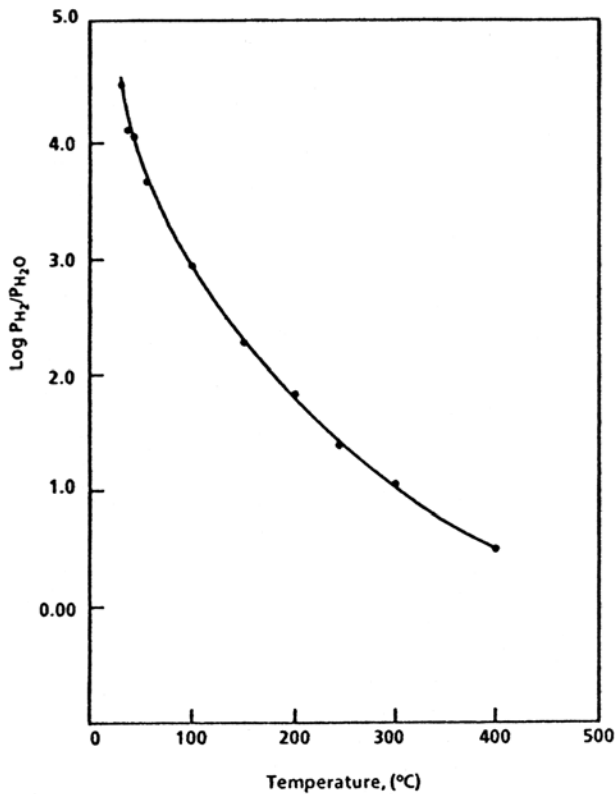


Figure 4 - Gas composition in equilibrium with iron and magnetite as function of temperature

temperatures of 100, 150 and 200°C before reduction could proceed. Reduction occurred very slowly at 100° and 150° due to the small difference in values of the P_{H_2O} in equilibrium with the iron at this temperature and that present in the inlet gas (≈ 1 ppm). The rate of reduction under these conditions is likely to be controlled by the hydrogen flow rate, which was low. Nevertheless, reduction was observed at all temperatures studied as evidenced by small weight changes and the presence of H_2O is the exit gas detected using a gas chromatograph. Even when the hydrogen flow rate was increased from 200 ml min^{-1} to 400 ml min^{-1} the rate of reduction remained low. Using the thermodynamic limit between which the H_2/H_2O ratio of the gas can change during this reduction, the theoretical maximum reduction per mol of hydrogen passed can be calculated. Assuming that the cylinder hydrogen contains typically 1 ppm of water vapor and given that the H_2/H_2O ratio in equilibrium with Fe and Fe_3O_4 is 10^3 at 100°C it is clear that only 0.1% is available for reduction at 100°C and this figure falls to 0.01% at 50°C. Clearly the efficiency of use of hydrogen for these reactions is low.

Since the results indicated that reduction of the rust product could proceed, albeit slowly at these temperatures, it was decided to carry out reduction more rapidly at 400°C in order to develop a structure of very finely

dispersed reduced iron on the surface of the pellets. This temperature was chosen in order to allow sufficient reduction to occur to allow the subsequent oxidation test to be carried out over a reasonable time period. It is acknowledged of course that the morphology of the reduced product may be influenced and coarsened by reduction at the higher temperature.

Several such runs were carried out and the pellets extracted for SEM examination showing a fine acicular arrangement of freshly reduced iron on the surface of the pellets as shown in Figure 5. Much more work is required to characterize the reduction kinetics and the morphology of the reduced product. For the present purpose it was sufficient to establish that reduction could occur under these conditions. The next step was to examine how the existence of such reduced material on the surface of the pellets would affect their subsequent oxidation behavior.

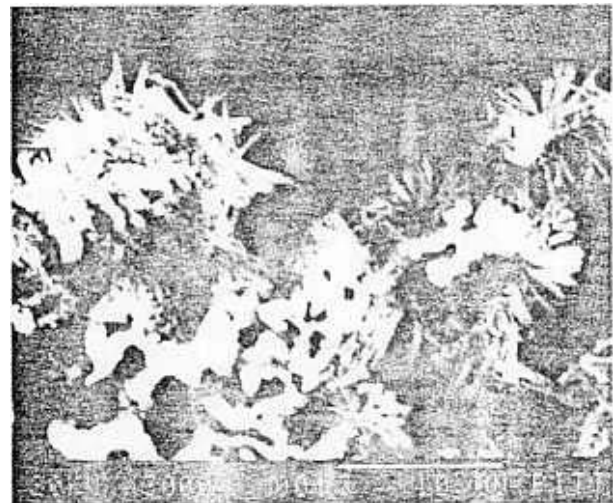
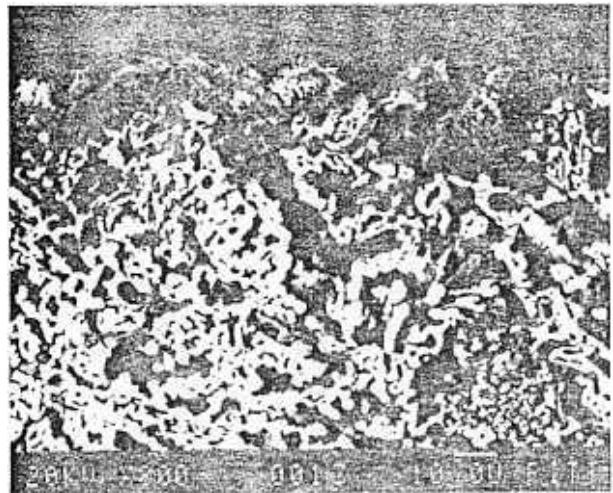


Figure 5 - Micrograph of DRI rusted and subsequently reduced, showing the very finely divided acicular nature of the pure iron produced by the reduction

Reoxidation of DRI Pellets

The reoxidation of DRI is being studied using an automatic recording thermobalance. The pellets (about 12) are held in a nichrome cage in the hot zone of a furnace and oxidation is carried out in air. The experiments address both the rate of reoxidation and the accompanying temperature rise. It is difficult to study both of these parameters simultaneously and a compromise is used whereby, during experiments in which the weight change is measured, the temperature is followed by holding a thermocouple about 1mm below the bottom of the nichrome basket. This reflects the temperature change of the specimens in the nichrome cage, as has been demonstrated in separate experiments involving a second thermocouple buried in the sample as shown in Figure 6. During these runs it was not possible to obtain useful weight change data. It was found that the lower thermocouple experienced temperatures about 100°C below those of the center of the specimen.

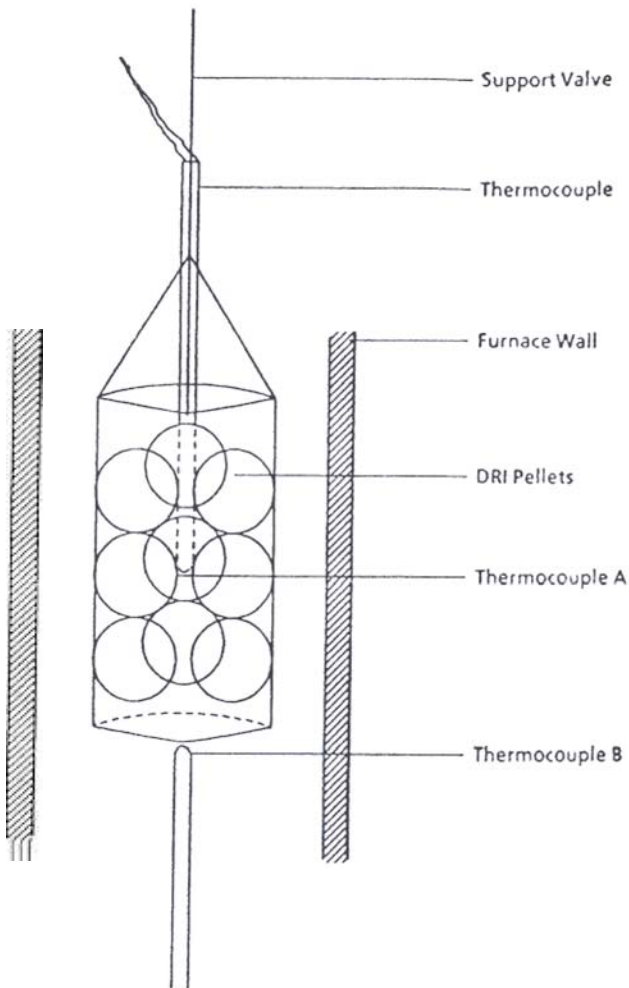


Figure 6 - Diagram showing relative positions of internal (A) and external (B) thermocouples in relation to reacting DRI sample

Similar experiments were carried out using fresh DRI as delivered from the producer, and also using DRI pellets that had previously been rusted and reduced. In the latter case the pellets were rusted for a few hours and thoroughly dried, they were then loaded into the nichrome cage and reduced at 400°C with hydrogen in the furnace using the thermobalance to monitor the reduction. After reduction of the rust is completed the hydrogen in the system is displaced with nitrogen, the temperature is lowered to the oxidation starting temperature, air is admitted and the oxidation reaction is monitored. Oxidation was started at 200°C in the initial experiments in order to obtain some details of the morphology of the reaction is reasonable experimental times.

Typical results of weight change and sample temperature (using the lower thermocouple) are shown in Figure 7, which shows data for both fresh DRI pellets and pellets that were initially rusted and reduced as described. Oxidation was carried out in air flowing at 200 ml/min. Figure 7 also includes the results of a similar run using an air flow of 300 ml min⁻¹ and shows several significant features.

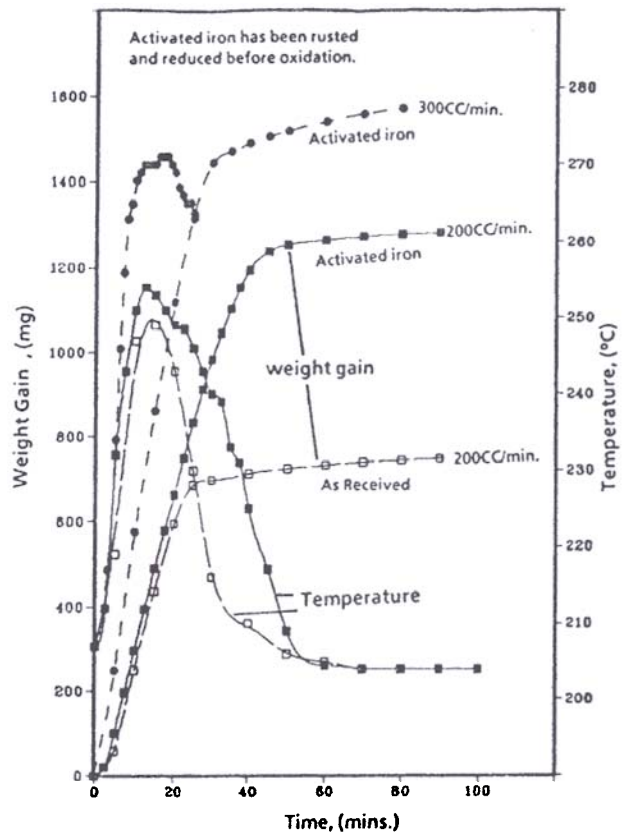


Figure 7a - Weight change and temperatures resulting from the oxidation in air of activated and as received DRI pellets starting at 200°C

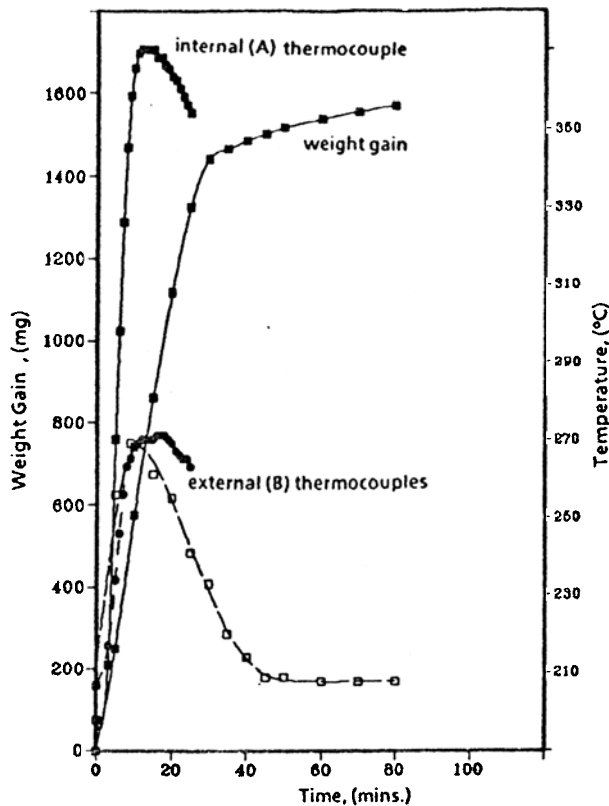


Figure 7b - Comparison of temperatures measured within the reacting pellet sample and just outside as the sample is oxidized

A plot of weight gain and temperature just outside the sample is superimposed for a second experiment to demonstrate reproductibility of temperature excursion measured at this position

The weight gain is rapid initially but suddenly becomes very slow. This has been shown to be due to the outer layers of the pellets becoming completely oxidized and the pores becoming completely blocked. The specimens passivate within 20-60 min. of starting the reaction. The passivation can be seen in Figure 8.

The initial rate of weight gain is also seen to be similar in the cases where the air flow was 200 ml/min and higher when the air flow was 300 ml/min. The temperature peaked at about the maximum reaction rate, reached similar values for the two cases where the air flow rate was 200 ml/min and was significantly higher when the flow rate was 300 ml/min.

These observations are consistent with the oxidation of the surface being responsible for all of the heat effects. In fact metallographic observation, as shown in Figure 8, confirms that only a rim of about 100µm is affected by reoxidation.

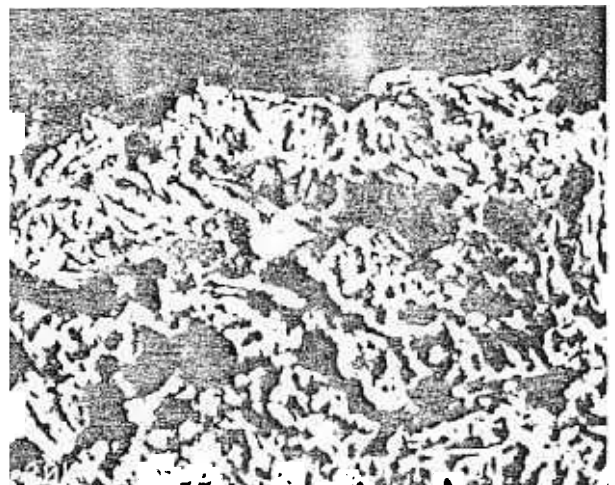
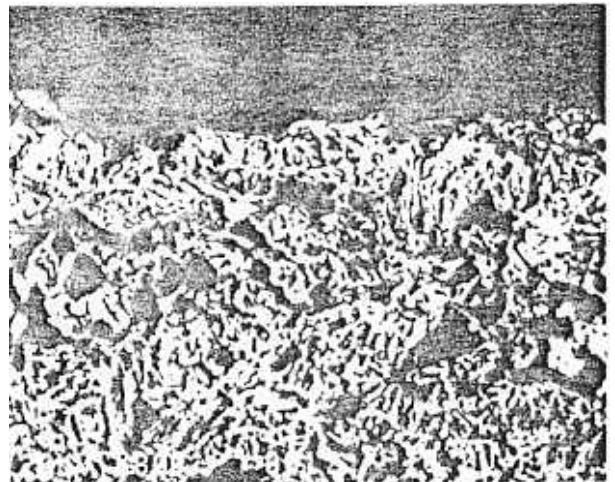


Figure 8 - Micrographs showing complete blocking of pores at the periphery of the DRI pellet that imposes passivation on the oxidation reaction

This observation is very important in terms of modelling this phenomenon as it is now possible to postulate that, in order to achieve successful ignition of DRI, the initial reaction must cause the surface temperature to reach values in the region of 600°C where the oxide wustite (FeO) is stable before complete passivation occurs due to pore closure. This is necessary because the rate at which iron oxidizes to form wustite, FeO, is much more rapid than the reaction to form magnetite, Fe₃O₄, and would be necessary to provide ignition after pore closure has occurred. This aspect is now being studied.

The possibilities that catalytic oxidation of hydrogen may form water vapor at the ignition site and that ignition may be achieved in several oxidation-reduction cycles that will incrementally increase the temperature of the ignition site on each cycle are currently

under consideration. This of course would greatly improve the efficiency of the reduction steps as well as the rates of the subsequent oxidation steps.

ACKNOWLEDGEMENTS

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