

A Review of Oxidation on Steel Surfaces in the Context of Fire Investigations

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ABSTRACT

During the course of a fire and subsequent exposure to the environment, iron and low-carbon steels oxidize by two mechanisms: high temperature oxidation and atmospheric corrosion. Of particular interest to fire investigators are oxide properties and distribution that could be of use to better understand important characteristics of the fire such as the location the fire originated, the direction the fire traveled or even temperature versus time characteristics. This could be particularly valuable in cases where burn damage to combustible material, which is known to be an important indicator of fire origin, is so extensive that little if any material remains after the fire. However, there is little data in the literature that specifically addresses the utility of oxide properties in the context of fire investigations. In this paper, we review the literature associated with both the high-temperature oxidation and atmospheric corrosion mechanisms in the context of a fire and post-fire environment. This review illustrates that both mechanisms are very complex and coupled to an equally complex and often ill-defined combustion environment associated with fires. As a result, the contribution of oxide characteristics to fire investigations is currently limited to identifying regions at the fire scene that reached temperatures sufficient to damage the protective coatings or to form wustite (FeO), which occurs at about 570°C . While oxide thickness developed during high-temperature oxidation may be related to the fire environment, its significance in fire investigations will likely depend on numerous confounding factors, which could include complex lattice defect formation processes, a complex and variable combustion environment, the dependency on both exposure time and exposure temperature, and the mass and surface area of the steel in question. Although variations in oxide color are often observed after a fire, no clear physical link between color variations and important characteristics of the fire has yet to be demonstrated by data currently available in the literature. Instead, oxide color is dependent on oxide thickness, the type of oxides present, natural variations of color for the same oxide, and the type and concentration of combustion products or other contaminants in the lattice structure.

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INTRODUCTION

Although it is well-known that steel surfaces oxidize or corrode during and after fire exposure, there is little information in the literature that scientifically relates this oxidation to fire characteristics. Of particular interest to fire investigators are oxide properties such as type, thickness or color that could be of use to better understand important characteristics of the fire such as the location the fire originated, the direction the fire traveled or even temperature versus time characteristics. This link could be particularly valuable in cases where burn damage to combustible material, which is known to be an important indicator of fire origin, is so extensive that little if any material remains after the fire.

The properties of iron oxides present on a steel surface that has been exposed to a fire and then to atmospheric

conditions after extinguishment are coupled to two different mechanisms of oxide formation. The first is high-temperature oxidation, which generally becomes important when the temperature of a fire exceeds several hundred degrees Celsius. This mechanism does not require the presence of moisture in the air or on the surface. The second is atmospheric corrosion, which requires liquid water or high humidity, but can occur at ambient temperature. Because each of these mechanisms involves different physical processes, they are generally treated separately in the literature. In this paper, we follow the same approach and first consider the simplified case of high-temperature oxidation in a "clean" high-temperature environment consisting of only iron and pure air. We then examine how this process may be complicated by a fire environment in which combustion products interact with or are deposited



onto the surface. As with high-temperature oxidation, low-temperature atmospheric corrosion is then considered in a “clean” environment involving only iron, moisture and pure air. The manner in which this process may be complicated by previous fire exposure, including the effect of combustion products deposited onto the surface, is then described. Because the color of oxides formed after a fire are readily observable and because there are often variations in color or “patterns”, the color palettes of selected oxides are presented along with a description of factors that are known to influence oxide color. Finally, links and gaps between fire characteristics and oxide properties are reviewed in the general context of fire investigations, and conclusions based on the currently available literature are presented.

HIGH-TEMPERATURE OXIDATION OF IRON AND LOW-CARBON STEEL

Due to their low cost, wide availability and physical properties, iron and low-carbon steels are some of the most widely used metals and, as a result, some of the most common metals at fire scenes. While low-carbon steels (0.05-0.2% carbon) have improved mechanical properties compared to iron, they are still relatively vulnerable to corrosion. As a result, both iron and low-carbon steels are often protected by various types of coatings such as paint, conversion coatings, electrophoretic coatings (electrocoat), organic coatings and powder coatings. During fire exposure, these protective coatings can be consumed or otherwise breached and, as a result, the underlying iron or steel is exposed to oxygen and high temperature, resulting in oxidation. In this section, the basic processes associated with high-temperature oxidation of iron and low-carbon steel in “clean” air are described. Then, the more complex case of oxidation in the presence of combustion gases is addressed.

While the reaction of iron and oxygen to form various types of iron oxides is thermodynamically favored, the reaction rates are relatively low at ambient temperature in a dry environment. However, when exposed to temperatures greater than several hundred degrees Celsius, the rates of oxidation increase and appreciable amounts of oxidation products can be formed. Due to the chemical structure of iron and oxygen, numerous types of iron oxides are typically formed and present simultaneously on the substrate, generally in layers. At temperatures below about 570°C, two oxides generally exist on the surface of the iron substrate: magnetite (Fe_3O_4) adjacent to the iron substrate and hematite (Fe_2O_3) forming the outer layer. As temperature increases above about 570°C, a third oxide form, wustite (FeO), becomes stable, and a three-layer model of oxide formation is generally assumed. In this case, wustite (FeO) is adjacent to the iron substrate, magnetite (Fe_3O_4) is the center layer, and hematite (Fe_2O_3) is the outer layer, as shown in Figure 1 [1]. At a temperature of 1000°C, typical of a fully involved structure or vehicle fire, the approximate thickness ratio of those three layers is 95:4:1 for wustite (FeO), magnetite

(Fe_3O_4), and hematite (Fe_2O_3), respectively [2]. Upon cooling to temperatures below about 570°C, the wustite (FeO) layer begins to decompose into iron and magnetite (Fe_3O_4).

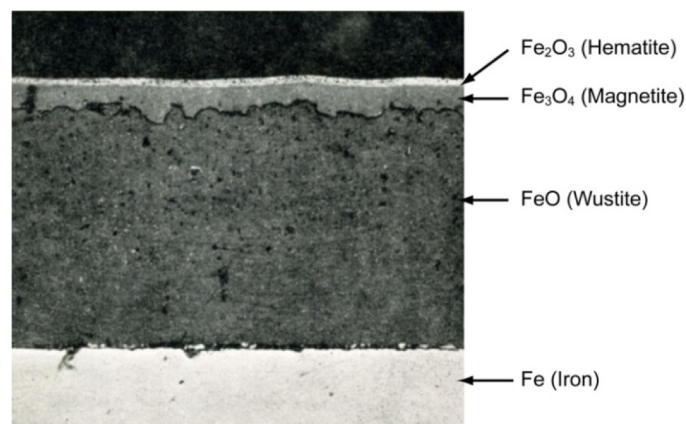


Figure 1. Cross-section of oxide layers formed on iron in air at 625 °C after 24 hours [1]. Reproduced with permission.

The rate of oxidation and associated oxide thickness is coupled to diffusion of mass and charge through the oxide layers and to reaction kinetics. A schematic of the three-layer oxidation model illustrating the important reaction zones and diffusion processes is shown in Figure 2. Iron and electrons diffuse outward from the substrate to the various reaction zones via iron vacancies and electron holes, respectively. Oxygen reacts with iron at the outer surface to form hematite and also diffuses via vacancies through the hematite layer to react with iron to form new hematite at the hematite-magnetite interface and its vicinity. Magnetite is formed via reactions with hematite, while wustite is formed from reactions involving magnetite. Internal oxidation is also possible where oxygen or other corrosive species diffuse deeper into the oxide layers or base material.

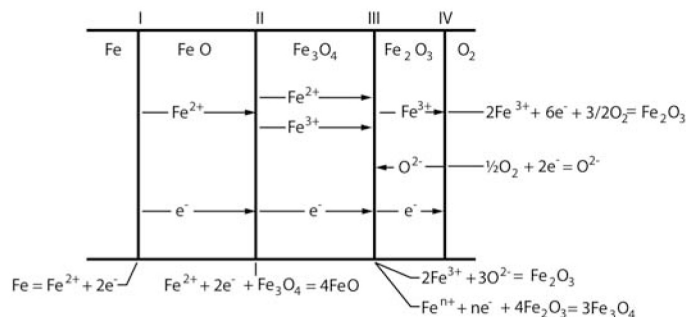


Figure 2. Overview of the three-layer, high-temperature, iron oxidation model.

When the oxide layer is very thin, diffusion of ions and charge through the oxide layers is fast, the rate limiting step is the chemical kinetics at the oxide interfaces, and the

relationship between oxide thickness and time is linear. However, the oxide layer quickly becomes sufficiently thick that diffusion is the rate limiting step [3, 4], and it is generally accepted that the relationship between the oxide thickness and time is parabolic. At constant temperature, the relationship between oxide thickness and time is

$$x^2 = k'_p t \quad (1)$$

The rate constant k'_p is the rate of diffusion and follows the well-known Arrhenius behavior below, where k_p is a constant, Q is the activation energy, R is the gas constant and T is temperature.

$$k'_p = k_p e^{-Q/RT} \quad (2)$$

Combining the above relationships, it is apparent that oxide thickness depends on both temperature and time, such that any given oxide thickness can be achieved by a large number of time and temperature combinations. Furthermore, it is apparent that oxide thickness is more strongly influenced by temperature in the exponential term than by time.

$$x = \sqrt{(k_p e^{-Q/RT})t} \quad (3)$$

The diffusion rates of iron and oxygen through the various oxide layers vary considerably, as shown in Figure 3. The slowest diffusion rates occur within the hematite layer, while the diffusion of iron ions in wustite and magnetite are more than an order of magnitude faster. It is also apparent in this figure that diffusion is strongly coupled to temperature. As temperature increases, the diffusion rates all rapidly increase. Because diffusion rates dictate the overall reaction rate, oxide properties that affect diffusion also affect the rate of oxidation. The broad scatter in measured diffusion rates in magnetite and hematite in the literature is testament to the fact that diffusion is strongly influenced by impurity contents and structures of the materials examined [5]. This is particularly true in the hematite layer, as these diffusion rates are often the slowest and control the overall reaction rate [3]. For example, Caplan et al. [6] found that a smaller grain size in the hematite layer enhanced diffusion along grain boundaries, resulting in higher oxidation rates.

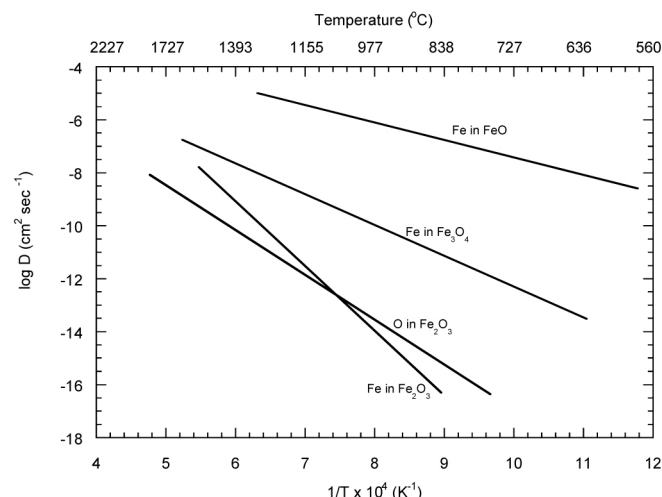


Figure 3. Arrhenius plot for iron and oxygen self-diffusion constants in iron oxides [5].

The manner in which an oxide grows influences its lattice structure which, in turn, influences diffusion and the associated oxidation rates. These growth processes are complex and can introduce defects such as cracks, pores, blisters, and detachment from the substrate. Pores, for example, can be formed by growth stresses that cause detachment of the oxide from the iron substrate. Because cations cannot diffuse through a pore, the overall rate of ion diffusion and associated oxidation rate are decreased [2]. Pores can also be created by grains overgrowing other grains, as illustrated in Figure 4 [7]. In this study, iron was exposed to 4O₂-N₂ (80% O₂) at a temperature of 1200°C for time durations ranging from 30 seconds to 1 hour, bounding some fire durations. The scale was initially a smooth, fine grained, continuous layer of primarily wustite (Figure 4a). After further oxidation, some grains overgrew others, leaving small pores trapped at the crystal junctions (Figure 4b). In a later stage of oxidation, the wustite crystals became capped with magnetite (Figure 4c). The magnetite layer bridged the wustite crystals, thereby trapping larger pores. After 10 minutes, stable layers had been established with major and minor pores (Figure 4d). Note that the hematite layer, if present, is too thin to be observed. The samples shown in Figures 4a-d were quenched in water, resulting in high thermal stresses that fractured the oxide layers. The sample in Figure 4e was cooled in a furnace such that thermal stresses produced fewer cracks. The effects that these types of cracks may have on subsequent atmospheric corrosion will be addressed in the next section.

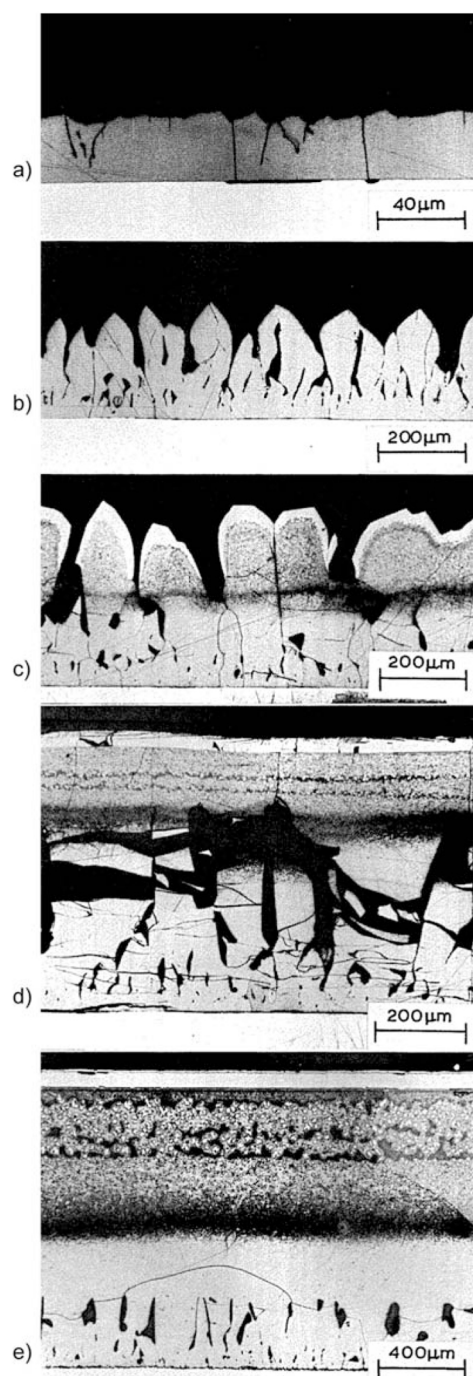


Figure 4. Cross-section of oxide layers on pure iron formed at 1200°C and exposure times of a) 30 s, b) 3.75 min, c) 6 min, d) 10 min and e) 1 hr with samples a-d quenched in water and e cooled in a furnace [7].

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The discussion of high-temperature oxidation of iron and low-carbon steel has heretofore been limited to a “clean” environment, consisting only of air. However, it is well known through an extensive body of research that combustion products play a complex and important role in high-temperature oxidation [2, 8, 9, 10]. Much of this

research has focused on the performance of steel alloys in industrial applications due to their improved performance in the severe conditions that high-temperature combustion gases present. As a result, there is a much smaller subset of data in the literature concerning the performance of iron and low-carbon steels in high-temperature combustion gas environments, particularly for the relatively short exposure times of some fires. However, available data in the literature concerning iron and low-carbon steels for relatively long exposure periods has shown that both major and minor species of combustion products can influence oxidation rates by altering diffusion rates in the lattice structure, changing the likelihood or effect of lattice defect formation, reacting with base material, or by facilitating oxide spalling. For example, the presence of major combustion species H_2O and CO_2 , to a greater extent than in the atmosphere, has been found to noticeably increase the observed reaction rate of steels. It has been proposed that these gases set up redox systems of H_2 - H_2O and CO - CO_2 to transfer oxygen across pores in the oxide structure [2]. Minor combustion species such as HCl , SO_2 and SO_3 , formed by combustion of fuels containing chlorine or sulfur, can also play an important role in high-temperature oxidation [9, 10]. Research associated with corrosion mechanisms in waste-to-energy boilers and incinerators, which produce combustion gas composition similar to that measured during fires [9, 11, 12, 13, 14, 15, 16] has shown that the major mode of corrosion is due to the formation of chlorides such as $PbCl_2$ and $ZnCl_2$, which are formed when chlorine-containing fuels are burned in the presence of electronics or batteries that contain heavy metals [9]. When heated to their melting points, these molten salts are good fluxing agents, effectively removing oxide scales from the metal surface. In the absence of a thick oxide layer, the freshly exposed iron or low-carbon steel is then rapidly oxidized.

The already complex two-element system could be significantly more complex by introduction of alloying additions to the iron. In addition, surface pretreatments in preparation of painting or other means of surface protection, and presence of various impurities that could contaminate the surface at any given point during manufacture or service life, further complicate oxide growth.

ATMOSPHERIC CORROSION OF STEEL SURFACES

After the fire is extinguished and the temperature decreases, the diffusion processes associated with high-temperature oxidation become very slow and, with the presence of water or high humidity, electrochemically-based atmospheric corrosion becomes the dominant mechanism of additional oxide formation or growth. In the case of a clean, un-oxidized iron surface, the first stage of atmospheric corrosion is the formation of a thin (1-4 nm) oxide/hydroxide film over the steel surface. This stage generally occurs on a

time scale of milliseconds to seconds. Given the presence of liquid water or a relative humidity greater than about 60-80% at room temperature [17, 18], a sufficient water layer is present on the surface for electrochemical reactions to take place. In near neutral aqueous environments, the second stage of the process is then the conversion of the oxide/hydroxide film into one of two types of green participate: "green-rust I" $[\text{Fe}^{\text{II}}_2\text{Fe}^{\text{III}}\text{O}_x(\text{OH})_y]$ and "green-rust II" $[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{O}_x(\text{OH})_y]$ [17]. This process generally occurs on the order of 2-3 hours. These green rust compounds are transitory in nature and, in the third stage, evolve into more stable iron oxides and hydroxides with prolonged exposure. This stage has been observed to occur after two weeks or less of exposure in the ambient atmosphere. Although more than a dozen different oxides and hydroxides of iron occur in natural rust layers on iron and steel surfaces, FeOOH , in several crystal forms, is the predominant stable species [17]. According to Cornell and Schwertmann [18], the predominant stable species consist primarily of lepidocrocite ($\delta\text{-FeOOH}$) and goethite ($\alpha\text{-FeOOH}$) with trace amounts and magnetite (Fe_3O_4). Leygraf and Graedel [17] suggest an inner region of dense, amorphous FeOOH and some crystalline magnetite (Fe_3O_4), and an outer, loose, crystalline assemblage of goethite ($\alpha\text{-FeOOH}$), lepidocrocite ($\delta\text{-FeOOH}$), and maghemite ($\gamma\text{-Fe}_2\text{O}_3$).

In the above corrosion process, iron is initially oxidized to Fe^{II} , and then intermediate corrosion products that include both Fe^{II} and Fe^{III} . Finally, these intermediate products evolve into more stable forms that include only Fe^{III} . A summary of the oxidation products and their valence states that are formed from high-temperature oxidation and low-temperature atmospheric corrosion is shown in Table 1 [17, 18, 19].

Atmospheric corrosion of iron involved in a fire may be further complicated by the preexisting oxides formed by high-temperature oxidation. When relatively free of defects, these oxide layers may serve to protect the underlying iron, at least for a period of time. However, areas that contain defects such as blisters, cracks, detachment and spalling zones may experience enhanced atmospheric corrosion, as they can provide a means of contact between the iron substrate, oxygen and moisture. As shown in Figure 4, rapid cooling due to quenching can fracture the oxide layers and introduce significant cracks. Such cracks could also serve as small pockets or crevices where corrosives, such as acidic compounds, could get trapped, resulting in significant localized corrosion. In addition, geometrical discontinuities or surface treatment-induced damage could also produce crevice corrosion, resulting in areas of more pronounced corrosion damage.

ENHANCED ATMOSPHERIC CORROSION DUE TO CORROSIVE SMOKE

Atmospheric corrosion of iron and low-carbon steel is further complicated by the presence of combustion products such as HCl , SO_2 , SO_3 , NO , NO_2 , and NH_3 . Even trace amounts of these combustion gases in the atmosphere, on the order of parts per billion (ppb), can influence the rate of corrosion over long periods of time [17]. In fact, accelerated atmospheric corrosion testing with these gases is typically conducted at concentrations on the order of 100 ppb [17], which is much lower than the concentration of these gases that have been measured in fires [11, 12, 13, 14, 15, 16].

The types of corrosive gases produced during a fire are dependent on the chemical composition of the fuel source. When halogenated hydrocarbons burn, the halogen can combine with hydrogen to form hydrogen halides. In the case of chlorine-containing fuels such as polyvinylchloride (PVC), HCl can be formed, whereas fluorine-containing fuels can form HF . Similarly, when nitrogen-containing compounds like nylon are burned, NO_x compounds (NO , NO_2) and NH_3 (ammonia) can be produced [14]. Sulfur-containing fuels such as vehicle tires, 1.5% by weight sulfur [20, 21], can produce SO_2 and SO_3 . Some fuels are particularly effective at producing corrosive gases. When polyvinylchloride (PVC) is burned, for example, 50-58% of the weight loss is converted into HCl [12, 22, 23].

It is well known in the literature that, once a fire is extinguished, the atmospheric corrosion of iron can be accelerated due to the deposition of corrosive combustion gas species on these surfaces. These effects have been documented in accidental fires [22, 24] and in numerous studies [13, 15, 22, 23, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37]. Several test standards have been developed, as described by Tewarson [38], and evaluated to quantify and compare the corrosiveness of different types of smoke [26, 31, 39, 40, 41].

Once formed, corrosive combustion gases are transported by the local airflow. If adsorbed by other particles, such as soot or water vapor, the extent to which the particle tracks the airflow is dependent on the particle size. Heavy particles will tend to settle, while smaller, lighter particles will more closely track the local airflow and are more likely to remain airborne. Because soot particles change in size as a function of time, as more and more particles coalesce together, the extent to which the particles track the local airflow depends on their growth process. As a result, the location and deposition concentration of corrosive combustion products on surfaces depends on both the transient rate of production of the corrosive gas species as well as the rate of production of scavenging agents such as soot and water vapor. It is further influenced by the rate at which these scavenging agents change in size, which influences the likelihood that they will be deposited onto a surface or remain airborne. Furthermore,