PHASE DIAGRAM FOR MAGNETITE-WUSTITE-IRON SYSTEM

$\text{Fe}^{2+}/\text{Fe}^{3+}$ PER UNIT CELL OF 32 OXYGEN ANIONS

TEMPERATURE, °F.

% $\text{H}_2$

% $\text{H}_2$
PASSIVATION OF METALS
Leo Broussard, Baton Rouge, La., assignor to Esso Research and Engineering Company, a corporation of Delaware.
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ABSTRACT OF THE DISCLOSURE

Iron obtained by the direct reduction of oxidic iron ore is passivated to prevent oxidation by forming a surface film of inverse spinel form of magnetite. The film is formed by a two-step mild oxidation process.

This invention relates to the art of passivating metals, especially powdered metals and porous, compacted forms of metals. In particular, it relates to the art of forming protective films, surfaces, layers, or coatings on such metals, particularly ferrous metals. It relates as well to the products so produced.

The art is replete with disclosures of ways and means of protecting metallic surfaces. These include various chemical surface treatments, e.g., the bluing of iron. Disclosures also bear on applications, and the use, of applied films and surface coatings, e.g., paints, lacquers, resins, waxes, and the like. Surface barriers are formed which prevent penetration by the atmosphere, moisture and various corrosive gases, fumes or impurities.

The protection of porous, compacted forms of metals, briquettes, and powdered metals offer special problems dependent upon numerous factors. A major problem is that briquettes and powders offer very large surface areas thus greatly increasing the actual exposure. Certain metals are also very highly "active" and readily chemically react when exposed to various environments. To decrease the exposure area, to lessen the activity, and to improve handling characteristics generally, powdered metals and briquettes are often admixed with various additives and binders and hence compacted. Sometimes, in addition, a surface coating is applied. Exposure of the inner portion of a so-formed mass is, at least to some extent, prevented. No mode of protection has been found entirely suitable, and particularly is this so in relation to the formation of certain forms of porous aggregates and powdered metals which are assuming an increasingly important role in today's technology.

In the field of powdered metallurgy, the techniques of producing, handling, and using finely divided metals or powders has always presented certain handling problems, and occasionally dangers, which have tended to suppress their full commercial utilization. There is, in particular, an increasing demand for methods of producing metals, especially iron, by direct reduction (reduction of ores without melting). The handling of the highly active metal powders, or the porous aggregates, from direct reduction processes, however, have presented problems which are especially acute, and militate against their widespread use. Such problems, if unsolved, would be indeed unfortunate in view of the fact that iron, the ore from which iron is obtained, which is intensified due to the diminishing supply of iron ore reserves and the desire to utilize ore deposits which are generally unsuitable for conventional iron ore reduction processes. There is, then, an urgency to find suitable and more advanced techniques for protection of exposed metal surfaces, especially high surface area active metals.

In direct ore reduction processes, e.g., direct iron ore reduction processes, iron ore, in particulate form, is thus contacted with reducing gas at elevated temperatures for sufficient time to produce a particulate metallic iron product. Iron ores, which are reduced at temperatures below the softening point of iron, generally exhibit a tendency, even after cooling, to be pyrophoric, which is a tendency for the iron to rapidly, or instantaneously, re-oxidize on exposure to air, often with violent reaction. On the other hand, reduced iron subsequently treated to lessen pyrophoricity, or iron formed by reduction at temperatures above the softening point of iron may be less violently reactive but, nonetheless, there are extremely difficult problems associated even with the handling and use of these products.

At a plant site, it is often essential that a reduced iron product, even after careful cooling, be stored, or shipped, in large quantities. There is, however, a tendency for a reduced iron product to back-oxidize, often relatively rapidly, especially where it must be stored, often for months, or shipped under relatively adverse conditions. This is so even where the iron powder is first aggregated into porous forms, as when compacted into the form of briquettes or extruded as rigid solid shapes. The tendency, however, is especially acute where it is desired to store or ship the reduction iron products as powders. Thus, e.g., even in the presence of atmospheric moisture, there is an acute tendency for the reduced iron product to back-oxidize, this to the chagrin of potential users who desire a highly metallic product. There is, however, an even more severe problem. Thus, where a reduced iron product, as briquettes or powder, has been placed in piles and stored for relatively short periods, intensely hot fires have resulted. Obviously, back-oxidation per se is bothersome enough, but spontaneous fires could be catastrophic under certain circumstances.

It is believed that a porous or particulate reduced iron product, when dampened or wetted, as by atmospheric moisture, rain or spray, can liberate hydrogen. It is also known that oxygen, e.g., atmospheric oxygen, can produce back-oxidation of the metal. Hydrogen can, under certain circumstances, ignite spontaneously. Two reactions are believed primarily responsible for the oxidation, and spontaneous ignition, of a reduced iron product. A first reaction, which is only slightly exothermic, involves reaction between iron and water and can be represented by the equation:

$$2Fe + 3H_2O \rightarrow Fe_2O_3 + 3H_2$$

The second reaction, which is highly exothermic, involves reaction between iron and oxygen and can be represented by the following equation:

$$4Fe + O_2 \rightarrow 2Fe_2O_3$$

It is thought that fires may be caused from circumstances wherein the geometry of the stored or piled product is such that the heat generated by the reactions cannot be sufficiently rapidly dissipated. Eventually, the temperature from the hydrogen reaction builds up to a point where the air oxidation of iron became the controlling reaction. The latter reaction, being strongly exothermic, produces ignition of the hydrogen while the liberated heat sustains and increases the rate of the oxidation reaction. Under these conditions, the reactions can continue until essentially all of the metallic iron has been rapidly converted back to iron oxides.

The disadvantages and difficulties associated with handling and shipping such metal products are therefore apparent. The art is in dire need of effective ways and means of passivating metals, especially porous, compacted forms and powders of metals, particularly ferrous metals such as those produced in direct iron ore reduction processes.

Accordingly, it is the primary objective of the present invention to supply this need. In particular, it is an object to obviate the foregoing and other disadvantages by pro-
Providing a method for forming protective films on metallic surfaces, especially on ferrous metal surfaces such as iron. More particularly, it is an object to passivate metallic surfaces, especially active metal surfaces of relatively large surface areas. A specific object is to provide a method for passivation of metals produced by direct reduction processes and, especially direct iron ore reduction processes; and, as well, to provide novel products.

These and other objects are achieved by the present invention which contemplates passivating metals by forming surface films or coatings thereon to render the so- treated metals resistant to further change upon exposure to various environments which tend to produce oxidations. In accordance therewith, a gas at sufficiently elevated temperature is contacted with the exterior surface of a metallic metal, capable of exhibiting more than one valency, to oxidize the surface of the metal to just within its lowermost valence state. The multi-valent metallic metal is then cooled, without further oxidizing treatment with the oxidizing gas, to further partially oxidize the so-formed low oxidation state surface film to an oxidation level intermediate the lowest and highest oxidation state of the metal. The product so produced is found to be quite stable and capable of becoming resistant to further oxidations which are high in inverse spinel, strongly resistant to back-oxidation. For example, metallic iron can be oxidized to form films of wustite on the base metal, and the Wustite will have an optimum arrangement of Fe²⁺ and Fe³⁺ cations at proper locations within the unit cell for conversion, or further oxidation, to the inverse spinel form of magnetite. The principles involved will be readily understood by reference to the figure.

The present invention is based on the discovery that inverse spinels, especially certain forms of inverse spinels, can be formed as films on metal surfaces of iron. The inverse spinels are far more difficult to oxidize than “normal” spinels. Though applicant does not desire to be bound by any theory of mechanism, it is believed that the present invention can be explained as a result of studies which he has undertaken.

It is known that certain metals, e.g., Group VIII metals of the periodic chart of the elements, are capable of exhibiting more than one valence state, or state wherein an element thereof can exist in several states of oxidation. Such polyvalent metals, e.g., iron, are usually considered as capable of forming stoichiometric compounds of ferrous oxide (FeO) or ferric oxide (Fe₂O₃) and ferric oxide (Fe₃O₄ or hematite). Such ideal states, however, are gross oversimplifications, for iron oxides generally are far more complex structures. This is particularly so in gas reduction systems. Hematite, the highest valence state for elemental iron, is thus a chemical compound of the normal stoichiometric type. The compound satisfies a valence of three for iron and two for oxygen. Wustite, at least in theory, might be considered an oxide compound wherein iron has a valence of two. In reality, however, ferrous oxide does not exist. It exists in theory at a temperature of about 1058 °F, and above this temperature the compound is approximated by a solution of ferric oxide rich in oxygen than in FeO. These solutions, deficient in iron as contrasted with FeO, are known as wustite, i.e., Fe₁₋ₓO. The subscript letter x in the formula FeOₓ is greater than 1.00 and ranges as high as about 1.35. Magnetite, on the other hand, has often been considered an iron oxide compound of valency intermediate that of wustite and hematite. This compound, often represented by the formulas Fe₂O₄ or Fe₃O₄, FeO, exists at temperatures ranging below about 2000 °F. It is believed, e.g., that magnetite (Fe₂O₄) can structurally exist either as normal spinel or as inverse spinel. The difference between these structures relates to the number and locations of Fe²⁺ and Fe³⁺ cations constituting the crystalline structure of magnetite. A normal magne-
cations. It is thus believed that wustite (FeO) ranges from one containing 32 Fe\(^{2+}\) cations (FeO\(_{0.60}\)) per unit cell to one containing only 8 Fe\(^{2+}\) (FeO\(_{0.32}\)) cations per unit cell. The converse is true for iron containing no Fe\(^{2+}\) cations (FeO\(_{0.60}\)) per unit cell to one containing 16 Fe\(^{2+}\) cations (FeO\(_{0.32}\)) per unit cell. Inverse spinels of magnetite are formed from wustite containing a high ratio of Fe\(^{2+}\) cations to Fe\(^{2+}\) cations. This relationship between FeO\(_x\) weight percent metallic iron, and types of Fe\(^{2+}\) and Fe\(^{3+}\) cations per unit cell can be conveniently summarized by reference to the following table:

### Table: Oxidation of Wustite

<table>
<thead>
<tr>
<th>x in Fe(_x)O</th>
<th>Weight percent Fe(^{2+})</th>
<th>Cations/unit cell</th>
<th>Ratio Fe(^{2+})/Fe(^{3+})</th>
<th>Fe(^{2+}) per unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>77.7</td>
<td>0</td>
<td>32/0</td>
<td>32/0 per unit cell</td>
</tr>
<tr>
<td>1.05</td>
<td>77.2</td>
<td>2</td>
<td>32/0</td>
<td>32/0 per unit cell</td>
</tr>
<tr>
<td>1.10</td>
<td>76.6</td>
<td>4</td>
<td>32/0</td>
<td>32/0 per unit cell</td>
</tr>
<tr>
<td>1.15</td>
<td>76.0</td>
<td>6</td>
<td>32/0</td>
<td>32/0 per unit cell</td>
</tr>
<tr>
<td>1.20</td>
<td>75.6</td>
<td>8</td>
<td>32/0</td>
<td>32/0 per unit cell</td>
</tr>
<tr>
<td>1.25</td>
<td>75.0</td>
<td>10</td>
<td>32/0</td>
<td>32/0 per unit cell</td>
</tr>
<tr>
<td>1.30</td>
<td>74.6</td>
<td>12</td>
<td>32/0</td>
<td>32/0 per unit cell</td>
</tr>
<tr>
<td>1.35</td>
<td>74.2</td>
<td>14</td>
<td>32/0</td>
<td>32/0 per unit cell</td>
</tr>
<tr>
<td>1.40</td>
<td>73.8</td>
<td>16</td>
<td>32/0</td>
<td>32/0 per unit cell</td>
</tr>
</tbody>
</table>

1 Unit cell contains 64 tetrahedral sites and 96 octahedral sites.

In passivating the surface of a metal, the first step is to oxidize under controlled conditions to form a surface film of wustite. To accomplish this, the metallic iron is heated, in a reducing atmosphere, to a temperature ranging above about 1058° F., and preferably to a temperature ranging from about 1200° F. to about 1600° F. Illustrated graphically, and by reference to the figure, therefore, it is desired to move from point A to point B, or to a position just barely within the shaded region. This will produce a wustite formation which will produce maximum quantities of the inverse spinel form of magnetite in the film. The metallic metal is therefore subjected to an oxidizing atmosphere at substantially the same temperature—viz, 1400° F.—for a time sufficient to form a surface film of wustite. Preferably, the film ranges in thickness from about 20 A. (Angstrom units) to about 10,000 A., and preferably from about 20 A. to about 100 A. The thinner films are preferable, and the thickness thereof should range only a very small fraction of the thickness of the base metal upon which the film is provided.

In the formation of the wustite film, it is important to use an oxidizing gas of just sufficient oxidation potential and at suitable conditions to allow just sufficient exposure to form a film of desired thickness and to move just barely inside the wustite region to produce the maximum number of Fe\(^{2+}\) cations at octahedral sites. In this manner, a film will be obtained which will produce a maximum concentration of the inverse spinel form of magnetite upon conversion of the wustite to magnetite. The greater the amount of the inverse spinel structure within the film, the greater will be the resistance to back-oxidation when the wustite is converted to magnetite. Preferably, in formation of wustite, the ratio of Fe\(^{2+}\) cations to Fe\(^{3+}\) cations should range no less than 20/8 and, more preferably, no less than 26/4 to obtain highest yields of inverse spinel within the protecting film. Stated in another way, x in the formula FeO\(_x\) for wustite should range no greater than about 1.15 and preferably no greater than about 1.08 to obtain highest yields of the inverse spinel form of magnetite in the film.

After formation of the desired wustite film, then, the wustite is converted to magnetite. This is represented graphically by moving from point B to point C. To accomplish this, the coated metallic metal is rapidly quenched or cooled, preferably in the same oxidizing gas used to produce wustite, to convert the film of wustite to magnetite. Since conditions were selected whereby the wustite which was converted contained a large number of Fe\(^{2+}\) cations in octahedral sites, the resulting magnetite, due to a shift, will contain a large number of the Fe\(^{2+}\) cations in octahedral sites and will thus produce an inverse spinel form of the magnetite. After such passivation, the protected metal can be further processed, as desired.

Particulate reduced iron products from direct iron ore reduction processes have been found particularly susceptible to treatment in accordance with this invention. In such processes, oxidic iron ores, i.e., ores containing or consisting essentially of iron oxides, are generally gradually progressively reduced with various reducing gases generally with hydrogen or carbon monoxide, or mixtures of these and other gases. In a particularly preferred form of practicing the present invention, the product from a fluidized iron ore reduction process is utilized. In such process, the iron oxides are initially staged in a series of beds, stages or zones, and directly contacted and fluidized by ascending gases, and reduce. The ore is generally reduced in an initial bed, or beds, from, e.g., ferric oxide to ferrous oxide and, finally in another bed, or beds, from ferrous oxide to a product ranging from about 80 to about 95 percent, and higher, magnetization, depend upon the anticipated use. The beds of the series are operated at the same or at different elevated temperatures.

The reduced iron product from such processes can be withdrawn and, depending upon the temperature of withdrawal, heated or cooled in a reducing, or substantially inert, atmosphere to the desired elevated temperature of the above-defined passivation method. The method is particularly applicable to treatment for passivation of reduced iron powder.

Products withdrawn from such direct iron ore reduction processes at metallizations ranging from about 80 to about 95 weight percent shall preferably be treated at temperatures ranging from about 1100° F. to about 1500° F., and preferably at temperatures ranging from about 1200° F. to about 1400° F. for sufficient periods of time, ranging generally from about 30 minutes to about 20 minutes, and preferably from about 1 minute to about 5 minutes, to produce wustite films of the desired quality and thickness. Pursuant to such conditions, reducing gases of hydrogen or carbon monoxide, or mixture thereof, are found satisfactory if steam be injected therein to provide the desired oxidation potential for conversion of the metallic iron to the desired wustite form.

This invention, its attributes and advantages, will the even better understood by reference to the following illustrative examples, demonstrations and data.

In the demonstrations and examples of Experiments I and II immediately following, raw specular hematite ore is charged to the top or initial stage of a reactor containing a series of four fluidized beds and progressively reduced, upon descent from one bed to the next of the series, by treatment with an ascending gaseous mixture of hydrogen and carbon monoxide at temperatures ranging from an initial 900° F. to 1500° F. in the final fluidized bed. The particulate reduced iron product is withdrawn from the final stage of the reactor and treated as subsequently described.

### Example I

Portions of the reduced iron powder are withdrawn from the reactor.

A first portion of the high metallization product is then placed in an auxiliary vessel, fluidized and subjected, at 1400° F., to treatment for thirty minutes with a mixture of 50 percent hydrogen-fifty percent steam to produce wustite capable of forming an inverse spinel form of magnetite.

The treated portion of product is then quenched to 1000° F. in a mixture of gas of the same composition used for formation of the wustite film. The product is maintained at this temperature for an additional thirty minutes and then cooled to ambient temperature in a blanketing layer of inert nitrogen. Mossbauer spectrometry shows...
that the so-formed magnetite film contains 85 percent inverse spinel (and 15 percent normal spinel).

To determine the degree of passivity of the so-treated product, analyses are performed to measure the amount of oxygen consumed and hydrogen generated. The measurements are calculated on the basis of standard cubic feet of oxygen consumed or hydrogen generated per hour per ton of reduced iron product. Analyses are also performed on an untreated portion of the product and comparisons of the results are made. In accordance therewith, it is found that relatively little oxygen is consumed or hydrogen liberated by the passivated metal. This, however, is in sharp contrast with similar tests conducted on the unpasivated product.

In fact, even after the passivated powder is fed into the nip of a double roll press and formed, at about 900° F., into pillow-shaped briquettes (3% x 1½ x ¾ inches in size) having a density of 5 lb. the briquettes show very low activity.

EXAMPLE II

In fact, when piles of the passivated and unpasivated briquettes are formed and subjected to storage conditions in the presence of moisture, the following results are obtained:

Two pyramidal-shaped piles, eight feet high and fourteen feet in diameter at the base, are formed and covered with black polyethylene sheets. One pile is formed with passivated briquettes, and the other with unpasivated briquettes. The temperatures within the piles are observed by placing thermocouples in the piles at heights of 3 feet and 5 feet above the ground and toward the outer edge of the pile. As the temperature record shows, as set forth in the following table, there is little indication of a sudden temperature rise, at least initially.

<table>
<thead>
<tr>
<th>Time in hours after pile formation</th>
<th>Lower thermocouple</th>
<th>Upper thermocouple</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>120</td>
<td>174</td>
</tr>
<tr>
<td>0</td>
<td>120</td>
<td>144</td>
</tr>
<tr>
<td>12½</td>
<td>134</td>
<td>169</td>
</tr>
<tr>
<td>21¾</td>
<td>146</td>
<td>164</td>
</tr>
<tr>
<td>30¾</td>
<td>140</td>
<td>180</td>
</tr>
</tbody>
</table>

After about 45 hours it is noticed in the untreated pile that the polyethylene toward the top of the pile, at a point away from the wind, begins to burn. Two hours later, temperatures of 600°-700° F. are recorded on both thermocouples. However, briquettes at the outer bottom edge of the pile are quite cold, close to freezing, and the outer briquettes of the upper part of the pile are only warm to the touch. A blue flame is observed at the point where the plastic first burned. The fire is quickly extinguished by spreading the pile. Extremely high temperatures are observed in the center of the pile. The briquettes are glowing red in this area, about 1200°-

F. The temperature is intense in the center of the pile and diminishes toward the edge of the pile.

In contrast, however, there is no indication of further temperature rise, or of burning, in the pile of treated briquettes.

The tremendous advantages achieved by the passivation technique are indeed apparent.

EXAMPLE III

Reduced iron powder of 98.7 percent metallization is formed by reduction of a specular hematite at 1400° F. with hydrogen, and thence formed into two portions. One portion is passivated in accordance with the procedure of Example I and the other is left untreated. Analysis shows the following for the two particular products:

<table>
<thead>
<tr>
<th>Oxygen consumption (cubic ft./hour/ton of product)</th>
<th>Hydrogen generation (cubic ft./hour/ton of product)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treated product, inverse spinel film..................</td>
<td>0.85</td>
</tr>
<tr>
<td>Un-treated product......................................</td>
<td>7.6</td>
</tr>
</tbody>
</table>

These results are indeed significant, and the advantages are apparent.

It will be understood that the specific method described, and the products produced, can be modified to some extent without departing the spirit and scope of the present invention.

Having described the invention, what is claimed is:

1. An article of manufacture comprising metallic reduced iron ore from a direct iron ore reduction process, said reduced iron ore being covered by a film of inverse spinel form of magnetite containing about 8 Fe²⁺ of the Fe cations in octahedral sites within the unit cell of magnetite.

2. The article of claim 1 wherein said film has a thickness ranging about 20 Å to about 10,000 Å.

3. The article of claim 1 wherein said metallic reduced iron ore is in powdered form.

4. The article of claim 1 wherein said metallic reduced iron ore is in the form of briquettes pressed from reduced iron ore powder.

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RALPH S. KENDALL, Primary Examiner

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