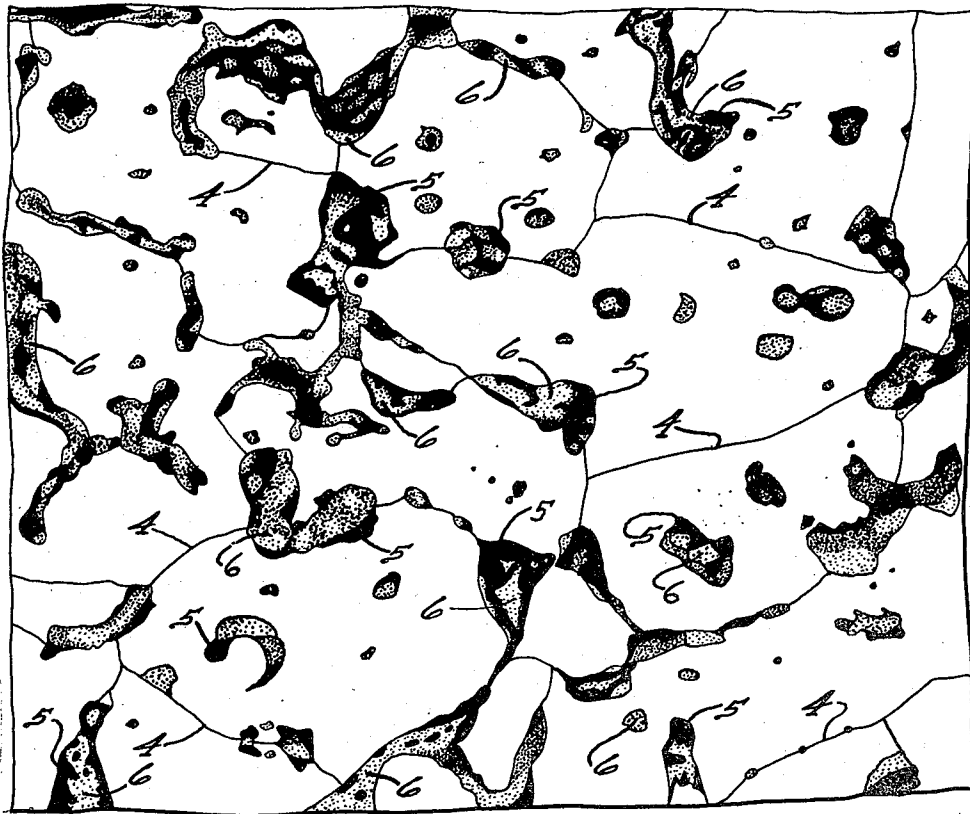
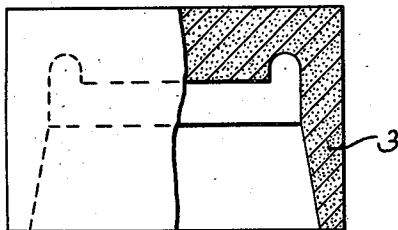


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POWDERED FERROUS METALS AND ARTICLES AND
METHODS OF MAKING THE SAME
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POWDERED FERROUS METALS AND ARTICLES AND METHODS OF MAKING THE SAME

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This invention relates to improvements in particulate ferrous metals, more generally referred to as powdered iron, for making sintered compacts and other articles or products; to products essentially comprising such particulate ferrous metals; and to methods of making said products and preparing said particulate metals for use therein.

In making porous articles or products by sintering a formed or compacted mass of powdered iron, it is normal to have some iron oxide present in the mass. However, it is also found that such iron oxide when present on the surface area of the ferrous particles is detrimental in that it substantially inhibits sintering and the obtaining of a good metallurgical bond between adjacent particles of the mass during sintering. Such has been true for example where the weight loss due to oxides as determined by MPA specification 2-48 hydrogen loss method is in excess of 2%.

Certain iron particles for instance, low cost, low grade type iron particles for example those known commercially as mill scale or magnetite and made by reducing iron oxide in a hydrogen atmosphere, inherently contain iron oxide at their center and at the surface areas thereof. These and other iron powders, such as electrolytic iron powders, also obtain such iron oxide on their surface areas by exposure, prior to briquetting and especially during storage, to oxidizing influences such as air, which produce completely oxidized areas on the particles. A similar action occurs during the early stages of sintering. In many instances these areas extend over the greater part of the particles and exist as a heavy layer.

Where these conditions heretofore existed, it has been found essential in order to obtain a satisfactory bonded particle structure to sinter the compacted mass of such particles at substantially high temperatures, above 2000° F., and in the case of mill scale not completely reduced, to also employ higher briquetting pressures. Moreover, the resultant products have usually had a lower ultimate strength and ductility than in cases where the oxide condition is not present and their lack of uniformity in ductility and yield strength have caused rejections. Furthermore, they have left much to be desired by way of facilitating machining and coining.

Among other reasons why sintered iron products have been desirable commercially has been the cost savings possible by combining powder metallurgy and finish machining. In some applications sintered parts made from low grade iron powders do not have machining characteristics which make this combination attractive.

I have discovered that some of the surface iron oxide of the iron particles presently considered detrimental, can be advantageously employed to improve sintering, to obtain a better metallurgical bond between the particles, and to improve the physical properties of the resultant sintered product. I accomplish this by providing surface areas or films of iron sulfide on the particles which in sintering will have a scavenging effect upon the iron oxide at the surfaces of the particles by forming a liquid phase therewith, i.e. coalescing with or absorbing this iron oxide of adjacent particles to produce an iron oxysulfide (ferric-oxysulfide) composition (Fe_2OS_2) and effect clear grain boundaries and boundaries comprising iron oxysulfide between the particles.

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I have further discovered that if the ferrous particles are provided with such iron sulfide films or layers during the making thereof or at an early period after their making, it is possible to obtain optimum coverage of the particles with the iron sulfide and preferably obtain a substantial envelopment of the particle with films of iron sulfide before a complete iron oxide layer is produced on the particles by exposure to air or other oxidizing influences. This layer of iron sulfide will thereafter protect the under surface of the particles during storage from oxidizing influences and during sintering up to the temperature at which coalescence occurs.

Accordingly, the principal object of this invention is to so treat particulate ferrous metals prior to their use in the making of sintered articles to provide them with surface portions or films of iron sulfide capable of having a scavenging action on iron oxide during the sintering of compacted masses of such particles and effect a coalescence of the iron sulfide and iron oxide of adjacent particles to form particle boundaries of pure grain character and of iron oxysulfide to enhance the metallurgical bond between adjacent particles.

Another object is to carry out the treatment set forth in the preceding object at the time the particulate ferrous materials are formed, or shortly thereafter, whereby to inhibit the conversion of pure iron of the particle surfaces to iron oxide and thereby inhibit formation of excessive surface iron oxide on the particles.

Another object is to provide particulate ferrous material as described in the preceding objects which will provide in sintered articles made therefrom many favorable characteristics including uniformly high physical properties, good ductility, easy machinability, and a yield strength which facilitates sizing and coining operations and the obtaining by the latter of ultimate strengths higher than those normally expected where the particles did not contain the advantageous iron sulfide in their surface portions.

A particular object is to treat particles of low cost, low grade iron such as mill scale, in a manner to provide on them surface areas of iron sulfide whereby to inhibit the production on such particles of completely oxidized areas of the underlying pure iron by oxidizing influences subsequent to their initial formation and during storage.

Another object is to provide particulate ferrous metals of the character of the preceding objects which lend themselves to briquetting without seizure with the die and which may be sintered at relatively low temperatures at which the surface iron is most active in effecting bonding for instance 1300° to 1700° F.

A specific object of my invention is to provide individual particles of ferrous metal with surface films or layers of ferrous sulfide (FeS) capable of effecting a scavenging action on adjacent iron oxide surface portions of the particles during sintering of products made from such particles as a result of which the ferrous sulfide (FeS) surface portions coalesce and form a liquid phase with the iron oxide (Fe_2O_4) surface portions to produce ferric-oxysulfide (Fe_2OS_2) and an improved metallurgical bond characterized by substantially clear grain particle boundaries and particle boundaries comprising said ferric-oxysulfide.

Another specific object is to treat particulate ferrous metals with a sulphur bearing gas or composition whereby to effect a reaction between the latter and the pure iron or slightly oxidized iron surface portions of the particles to form in situ one or more films or layers of ferrous sulfide adapted to inhibit new or additional oxidation of such iron surfaces of the particles during storage and to serve as a scavenging and bond improving agent during sintering of a mass of such particles.

Other objects and advantages of my invention will appear from the following description and from the drawings wherein:

Figure 1 is an elevational view partly in section showing a piston embodying my invention; and

Figure 2 is a highly magnified view typifying the internal structure of the piston of Figure 1 as evident from a photomicrograph.

I have discovered that to obtain optimum distribution of the iron sulfide in the particle mass and coverage of the individual particles to resist further oxidizing effects during storage and enhance the extent of scavenging action during sintering, the ferrous particles should be treated by subjecting them at room temperature or while suitably heated to the chemical action of a sulphur bearing gaseous composition, preferably hydrogen sulfide (H_2S). Heating the particles is advantageous to increase the intensity of chemical reaction. Agitation of the particles is helpful especially when treating the particles at room temperature. On contact of the hydrogen sulfide gas with the individual particles, a reaction occurs with the pure or slightly oxidized iron surfaces of the particles to produce in situ one or more integral protective and scavenging films of ferrous sulfide described above on the individual particles.

The gaseous treatment is preferably carried out immediately after making the particles or at an early period thereafter to obtain maximum conversion of the iron surface portions to iron sulfide before new or additional iron oxide layers are formed on the particle surfaces by exposure to air or other oxidizing influences. In any event, the particles should be treated as described prior to sintering.

The ferrous metal particles or powders used in this invention may be of any suitable kind such as reduced iron ore, powdered electrolytic iron, atomized iron or particulate or powdered ferrous metal made in other suitable ways. In fact, it is found that even low grade ferrous metal, for example, mill scale iron particles or reduced magnetite particles may readily be treated in accordance with the invention and successfully made into articles having satisfactory properties. The ferrous metal particles may also contain small amounts of alloying constituents such as carbon, silicon, nickel, etc. Thus the particles may be those of reduced magnetite, low carbon steel, low carbon atomized iron, stainless iron or steel.

The particulate ferrous material may be treated by the hydrogen sulfide in any suitable piece of equipment to effect the formation of iron sulfide on the surface of the particles. Thus for example, the particles may be placed as a loose mass on a tray in a suitably heated retort-type furnace having a frontal opening into which hydrogen sulfide gas may be introduced, filtered through the mass and be exhausted through another opening at the back of the furnace. Such retort may be housed in a hood equipped with a blower to exhaust the gas from the furnace and the furnace will be provided with a suitable temperature control and recording equipment to maintain uniform temperatures. Moreover the tray may be agitated by a suitable vibrator. Satisfactory results are obtained when the powders are treated at a temperature in the range of 275° F. to 325° F. for periods ranging from 5 to 25 minutes and whereby the sulphur content of the treated particles by chemical analysis is in the range of 0.275% to 0.325%.

Thus mill scale iron powder having the following screen analysis:

	Percent
Retained on 100 mesh.....	12.8
Retained on 150 mesh.....	21
Retained on 200 mesh.....	18.1
Retained on 250 mesh.....	6.2
Retained on 325 mesh.....	13.9
Passed thru 325 mesh.....	28

and having a chemical analysis as follows:

	Percent
Carbon.....	.03
Manganese.....	.36
Phosphorous.....	.01
Sulphur.....	.01
Silicon.....	.20
Copper.....	.10
Oxygen.....	1.26
Iron.....	remainder

when treated as described in a retort furnace having a 6" diameter opening and 14" long; for a period of fifteen minutes at a temperature of 300° F. with a gas flow at the rate of 5 to 6 cu. ft. per hour to effect conversion of the iron surface portions to iron sulfide was capable of handling between 6 to 10 lbs. of material for each 15 minute period. A chemical analysis of this material after treatment showed a sulphur content of between 0.275% to 0.30%. The increase in weight of a 80 gram sample of the treated iron powder was 0.125%. Based on a mathematical computation in which it was assumed that the particles were spherical and perfectly homogeneous and were .004" in diameter, the deposit or coating produced on the particles was estimated to be approximately .00001".

The time and temperature treatment of other particulate ferrous materials may readily be determined in accordance with this example.

As an alternative piece of equipment for treating the particles, the particulate ferrous material may be fed into the top of a rotating tower suitably heated and having an outlet at the base from which to remove the powder after treatment. Hydrogen sulfide gas will be fed into the tower at the lower end through a suitable inlet and exhausted at the top through a suitable outlet therefor.

The particles of particulate ferrous material treated as described above and having the deposit of iron sulfide formed in situ may thereafter be advantageously compacted by known means and conventional briquetting pressures of about 30,000 to 60,000 p.s.i. depending upon the density desired to form desired articles of commerce such as the pistons shown in Figure 1 and the compacts sintered in a suitable furnace, for example an electrically heated furnace having means providing a controlled atmosphere therein of the exothermic type.

As previously described, I have discovered that the surface iron sulfide deposit or formation on the particles has a scavenging action during sintering of the compact causing coalescence of the iron oxide and iron sulfide to form pure grain boundaries between particles and boundaries comprising iron oxysulfide to thus produce an improved metallurgical bond between adjacent particles of the structure.

This is evident in Figure 2 for example, where the scavenging effect of the iron sulfide is apparent in the relatively clean grain boundaries illustrated at 4 and by the coalesced iron oxide and iron sulfide indicated at 5 in this figure, the areas of concentrated iron oxysulfide being indicated by the stippling at 6 in this figure.

One of the advantages of the use of iron sulfide bearing particles of iron produced as above is the substantial saving in required kilowatt power consumption of the sintering furnace and in its maintenance cost. Heretofore it was necessary for example to sinter high grade iron particles of electrolytically produced powder at a temperature of approximately 2050° F. By utilizing such iron particles as treated in accordance with the present invention compacts thereof may be successfully sintered at temperatures in the range of 1300° F. to 1700° F; best results being obtained in the range 1550° F. to 1700° F. These same low temperatures are likewise possible when employing other iron powders, even low grade mill scale iron powder.

Not only does the presence of the iron sulfide on the particles permit lower sintering temperatures and improve

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the metallurgical bond but there is also a pronounced increase in the degree of sintering that occurs at the lower sintering temperatures than would be possible without the presence of the iron sulfide. This is only possible because of the scavenger effect or coalescence described above effected by the iron sulfide on the iron oxides which inhibit sintering. In addition to the foregoing the coalescence effect of the sulfide on the oxides in absorbing the same reduces the yield strength of the product in the as sintered condition because the oxide is then no longer available to produce a precipitation hardening effect which normally exists in prior sintered iron masses in which the sulfide is not present. This reduced yield strength material with its excellent ductility makes it particularly suitable for coining and cold working by which techniques the yield strength for a given specific gravity may be greatly increased above those heretofore possible, and even doubled where such property is desirable. Moreover, the sulfide containing sintered mass of particulate ferrous material has good machineability characteristics due to the free cutting effect of the sulphur retained after the sintering operation. This is evident from the well-curved, clean-cut appearance of the chips from the sulfided material and the absence of fines.

Further increase in the ductility of the resultant sintered product of even 30% in the case of electrolytic iron powder and certain other iron powders has been found possible by the addition of 0.5% to 1.5% by weight of ferric oxide in powdered form to the gas treated iron powder particles prior to briquetting and sintering. Moreover, additions of small amounts, for instance about ¾% by weight of stearic acid to the mix prior to briquetting are desirable as a lubricant.

Although my invention has been illustrated in conjunction with a piston 3, it will be understood that the same is not limited to the making of such articles but can be employed in the making of other articles and in the making of various stock material from which articles are fabricated. Moreover, while the invention has been described utilizing hydrogen sulfide gas as the agent for treating the ferrous particles it will be understood that some of the desirable effects of the invention although to a markedly lesser extent and with less uniformity may be obtained by directly adding to the powdered mass and thoroughly mixing therewith, prior to briquetting, from 0.5 to 5% by weight of powdered metallic sulfides. Examples of suitable additives are cupric sulfide, cuprous sulfide, iron sulfide (FeS and FeS₂), manganese sulfide, nickel sulfide, cuprous sulfide and nickel sulfide eutectic, cuprous sulfide and sodium sulfide eutectic, cuprous sulfide plus metallic copper, nickel sulfide plus metallic copper, iron sulfide plus iron oxide and nickel sulfide plus iron oxide.

I claim:

1. As a product of manufacture a mass of individual powdered metal particles for use in making sintered compacts, said particles comprising ferrous metal bodies having integral chemically bonded surface films of ferrous sulfide and said particles having a sulfur content between 0.275% to 0.375% by weight.

2. As a product of manufacture a mass of powdered metal particles for use in making sintered compacts, said particles comprising ferrous metal bodies having integral surfacings of ferrous sulfide comprising the reaction product of said ferrous bodies and sulfur bearing composition and said particles each having a sulfur content between 0.275% to 0.375% by weight.

3. As a product of manufacture a mass of powdered metal particles for use in making sintered compacts, said particles comprising ferrous metal bodies having integral surface portions of iron oxide and further integral surface portions of ferrous sulfide, said particles each having a sulfur content in the range of about 0.275% to 0.375% by weight.

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4. As an article of manufacture a metal body comprising the sintered product of a substantially homogeneous mass consisting essentially of ferrous metal particles carrying an integral chemically bonded surfacing of ferrous sulfide, said particles of said product being metallurgically bonded to each other and said bond being characterized by substantially clear grain particle boundaries and by particle boundaries comprising iron oxysulfide.

5. In a process of preparing particulate ferrous metals for use in the making of sintered products the improvement which consists in heating said particles to a temperature in the order of about 275° F. to 325° F., passing hydrogen sulfide gas through a loose mass of said particles and effecting contact of said gas with the surfaces of said particles whereby to form by chemical reaction of said gas on the ferrous surfaces of said particles an integral layer of iron sulfide and produce treated particles having a sulfur content in the range of 0.275% to 0.325% by weight.

6. The method of making articles from particulate ferrous metals having completely oxidized surface portions comprising iron oxide and having other surface portions comprising substantially pure and slightly oxidized iron, comprising providing a loose collection of said particles, passing hydrogen sulfide gas through said mass of particles to effect contact thereof with said substantially pure and slightly oxidized portions of the surfacing of said particles whereby to produce by chemical action thereon integral films of iron sulfide, compacting a mass of said treated particles into a predetermined form and heat treating said compact to effect a metallurgical bond at adjacent surfaces of said particles, the iron sulfide films of said particles serving during said heat treatment to effect a coalescence of the completely oxidized portions of said particle surfacing therewith into iron oxysulfide and the formation of clear grain boundaries.

7. The method of making articles from particulate ferrous metals having completely oxidized surface portions comprising iron oxide and having other surface portions comprising substantially pure and slightly oxidized iron, comprising heating a loose collection of said particles, passing hydrogen sulfide gas through said mass of particles to effect contact thereof with said substantially pure and slightly oxidized portions of the surfacing of said particles whereby to produce by chemical action thereon integral films of iron sulfide, compacting a mass of said treated particles into a predetermined form and heat treating said compact at a temperature between about 1300° F. to 1700° F., to effect a metallurgical bond at adjacent surfaces of said particles, the iron sulfide films of said particles serving during said heat treatment to effect a coalescence of the completely oxidized portions of said particle surfacing therewith into iron oxysulfide and the formation of clear grain boundaries.

8. The method of making articles from particulate ferrous metals comprising subjecting said particles to the action of a hydrogen sulfide atmosphere until an integral film of iron sulfide has been formed on the particles by chemical reaction of said gas and the iron surfacing of said particles, adding between about ½% to 1½% by weight of powdered ferric iron oxide to said mass of particles and mixing therewith, compacting a mass of said mixed particles into predetermined form, and heat treating the compressed particle mass at a temperature between 1300° F. to 1700° F. to metallurgically bond together adjacent surfaces of said particles, the said iron sulfide of said particles acting in response to said heat treatment to effect a coalescence of the iron oxide present at the surfaces of said particles therewith.

9. In a process of preparing particulate ferrous metals for use in the making of sintered products, the improvement which consists in heating said particles to a temperature below about 325° F., and treating a loose mass of said particles with a sulphur containing composition

to effect contact of the latter with the surfaces of said particles whereby to form an integral layer of iron sulfide on the ferrous surfaces of the particles by chemical reaction of said composition with said surfaces said particles having a sulfur content after treatment of between about 0.275% to 0.325% by weight.

10. The method of making articles from particulate ferrous metals having completely oxidized surface portions comprising iron oxide and having other surface portions comprising substantially pure and slightly oxidized iron, comprising providing a loose collection of said particles, passing hydrogen sulfide gas through said mass of particles to effect contact thereof with said substantially pure and slightly oxidized portions of the surfacing of said particles whereby to produce by chemical action thereon integral films of iron sulfide, compacting a mass of said treated particles into a predetermined form and heat treating said compact at a temperature between about 1300° to 1700° to effect a metallurgical bond at adjacent surfaces of said particles, the iron sulfide films of said particles serving during said heat treatment to effect a coalescence of the completely oxidized portions of said particle surfacing therewith into iron oxysulfide and the formation of clear grain boundaries.

11. The process of making articles from particulate ferrous metals comprising mixing ferrous particles having completely oxidized surface portions comprising iron oxide with 0.5% to 5% by weight of powdered metallic sulfides, compacting a mass of said mixed particles into a predetermined form, and heat treating the compressed particle mass at a temperature between about 1300° F. to 1700° F. to metallurgically bond together adjacent surfaces of said particles with the sulfides acting in response to said heat treatment to effect a coalescence of the iron oxide present at the surfaces of said ferrous particles therewith.

12. The method of making articles from particulate ferrous metals comprising treating the iron particles to

produce by chemical action thereon integral films of iron sulfide, mixing with said particles 0.5% to 1.5% by weight of ferric oxide, compacting a mass of said mixed particles into a predetermined form and heat treating said compact at a temperature between about 1300° F. to 1700° F. to effect a metallurgical bond at adjacent surfaces of said particles, the iron sulfide films of said particles serving during said heat treatment to effect a coalescence thereof with said ferric oxide into iron oxysulfide for improving the bond between the particles and the formation of clear grain boundaries.

13. In a process of preparing particulate ferrous metals for use in the making of sintered products the improvement which consists in heating the particles at a temperature of about 300° F. for a period of about fifteen minutes while treating the particles with hydrogen sulfide whereby to effect conversion of the iron surface portions to iron sulfide, the said particles having a sulfur content after treatment of between 0.275% to 0.30% by weight.

14. The method of making articles from particulate ferrous metals comprising compacting a mass of particles having completely oxidized surface portions comprising iron oxide and having other surface portions comprising integral films of iron sulfide into a predetermined form and heat treating said compact at a temperature between 1300° F. to 1700° F. to effect a metallurgical bond at adjacent surfaces of said particles, the iron sulfide films of said particles serving during said heat treatment to effect a coalescence of the completely oxidized portions of said particle surfacing therewith into iron oxysulfide and the formation of clear grain boundaries.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,942,334

June 28, 1960

Roy E. Blue

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 66, before "sulfur" insert -- a --;
column 6, line 4, strike out "chemically bonded".

Signed and sealed this 31st day of January 1961.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents

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