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POWDER METALLURGY PROCESS FOR PRODUCING STEEL PARTS

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This invention deals with powder metallurgy; specifically it presents an efficient method of eliminating deleterious oxygen from iron powder compacts, especially in the presence of alloying elements.

The chief object of the invention is the making of iron and steel compacts having superior physical properties such as strength and ductility, from iron powder containing amounts of sorbed material which has heretofore caused inferior physical properties.

A further object is to make such compacts in which valuable alloying constituents may be contained, such as manganese, but free from oxide inclusions which have heretofore been troublesome.

Further objects are to avoid expensive pretreatments of oxygen-containing powders, and yet prevent oxidation of alloying metals which have a high affinity for oxygen, during the sintering processes. When oxidized such alloying metals do not diffuse into the iron and they not only thus lose their effectiveness but they actually become deleterious by being present as inclusions.

It is well known that iron powders may contain appreciable amounts of sorbed material such as water and oxygen, that is material which is adsorbed or absorbed or chemically combined with the powder. Such sorbed material may impair the physical properties of compacts made with such powder. This is especially the case when the process involves two or more pressing operations with two or more heat-treatments.

I have found that the presence of such sorbed material causes difficulty in consistently obtaining uniformly high physical properties in the articles made from powdered starting material of apparently the same composition and apparently identically processed.

When the starting material comprises iron powder containing sorbed material to the extent of 0.6–0.8%, (even though it includes no substantial amount of alloying agents having high affinity for oxygen at the sintering temperature) and such material is processed by prior methods involving two pressings and two sinterings, the articles produced are not consistently uniform in their physical properties. Generally the physical properties are inferior as compared with results which are occasionally obtained. This variation is not explained by variation in density because the densities of the articles are all approximately the same, nor does the microscope distinguish any apparent difference between those articles having the best physical properties and those which are inferior.

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When manganese or other alloying metal having a high affinity for oxygen is an ingredient of the starting material one aspect of this inconsistency shows in the fact that there are sometimes oxide inclusions in the final product.

Final products showing such inclusions are definitely inferior in their physical characteristics, as illustrated by the following comparisons:

Two groups of steel compacts were made from apparently identical starting material which consisted of electrolytic iron powder, 0.55% of a manganese-silicon eutectic (90% manganese and 10% silicon) and 1% of stearic acid lubricant. The final densities of the two groups were substantially the same. In one group there were numerous oxide inclusions in the final product while in the other the oxide inclusions were few. The average physical properties of the first group were, tensile strength 122,000 p. s. i., elongation 15%, and reduction of area 23%. The other group, which contained comparatively few oxide inclusions, had average physical properties of tensile strength 130,000 p. s. i., elongation of 20%, and reduction of area of 36%.

Two other compacts made from starting material of apparently identical composition and apparently processed in the same manner were tested for impact strength. One compact had numerous oxide inclusions while the other had relatively few. The compact having relatively few inclusions had an impact strength of 29 ft. lbs. while the one having numerous inclusions had comparatively an impact strength of only 14.6 ft. lbs.

One way of obtaining final products having relatively uniform high physical properties and thus avoiding the above mentioned difficulties is to remove the sorbed water and sorbed gases and to reduce any iron oxide contained in the iron powder used as a starting material or component thereof, until the oxygen content of such iron powder, as determined by a vacuum fusion test, is reduced to substantially 0.2% or less. Instead of a vacuum fusion test another test that may be made to show whether the iron powder is sufficiently low in sorbed material is to heat the iron powder in dry hydrogen for 2 hours at 1800° F. and determine the loss in weight of the powder, during such heat treatment. Such loss in weight should not be substantially more than 0.2%.

It is found that removal of the sorbed material to the desired degree may be effected by heat-treating the powder at elevated temperatures, such as 1350° F., in an atmosphere, such as hy-

drogen, for relatively long periods of time, such as 3 hours, and thereafter re-pulverizing the sintered cake formed in such heat-treating step. However, that may be a too costly operation.

Instead of processing the iron powder as above to remove sorbed material I have found that articles can be obtained having consistently high physical properties and which are consistently free from oxide inclusions by mixing carbon with iron powder having a high sorbed material content, to form a starting material or component thereof, compressing such starting material to form a cake and thereafter sintering the cake in such a way as to remove a substantial amount of the carbon.

During the sintering process carbon may be removed partly by combination with oxygen, in whatever form the oxygen exists in the pressed cake, and partly by combination with a medium of the sintering atmosphere, for example hydrogen, the gases thus formed escaping from the cake. In this way the oxygen escapes from the cake, in preference to combining with or remaining combined with the iron or alloying agent. It is thus removed instead of remaining in the cake as an oxide inclusion.

Where carbon has heretofore been included in the starting material for powder metallurgy processes, it usually has been for the purpose of providing the entire carbon content of the desired final steel composition. Although this carbon may effectively remove substantially all of the oxygen, if the compact is heated, the large amount of carbon remaining is undesirable for processes which involve two or more pressing operations with intervening sinterings because this carbon, when dissolved in the iron during the first sintering operation, makes the material too resistant to subsequent pressing or forming operations, thus resulting in a porous product. In this invention I remove a substantial amount or even all of the carbon by the initial sintering step so that the pressed and sintered cake is soft and can be repressed to high density in a second pressing operation. Carbon can then be introduced into the cake by any desired method, such as sintering the cake in a carburizing atmosphere, to produce a steel compact having much higher strength and ductility than would otherwise be possible.

In pressing the material I prefer to employ for my initial pressing operation a pressure of less than 40 tons per square inch and for my second pressing operation a pressure of less than 100 tons per square inch, preferably between 60 and 90 tons per square inch. In most cases I would like the minimum pressure used in the first pressing operation to be substantially 15 tons per square inch. After my first pressing operation I prefer that the cake have a density of 6.3–6.8 and that after the 2nd pressing operation the density be substantially 7.5–7.6 or over.

In my first sintering operation after the first pressing, I prefer to use an atmosphere of dry hydrogen or cracked anhydrous ammonia and to employ a temperature of at least substantially 1800° F.

I prefer not to exceed 2050° F. when free carbon is an ingredient of the starting material because at temperatures only slightly above this (approximately 2100° F.) melting occurs at the zones of contact between the iron and the free carbon in the compact due to the localized formation at such contact zones of the iron-carbon eutectic alloy. The existence of this eutectic alloy is only temporary, being present only while free carbon is still present. Normally, substantially all this carbon will be dissolved in the iron at the sintering temperature in about 10 minutes or less. The presence of a liquid phase during sintering is undesirable because it causes excessive shrinkage and distortion.

I may use as starting material or as a component thereof iron powder which, aside from sorbed material, contains no more than substantially 0.2% of other impurities. Said sorbed material may be present to the extent of 1%. The carbon component of the starting material should not exceed 0.6% and the carbon remaining after the first sintering operation should not exceed 0.4%, and I prefer that these two amounts should not exceed substantially 0.3% and 0.1% respectively. As previously stated when a substantial amount of carbon is required in the final product I prefer to introduce it after the second pressing operation.

While I have referred chiefly to manganese as the alloying element, the invention is also applicable to other elements having a stronger affinity for oxygen than has iron. These include such elements as aluminum, chromium, vanadium, titanium, silicon, tungsten, molybdenum, etc.

As an example of the practice of my invention I may take an electrolytic iron powder containing 0.6% to 0.8% oxygen, and mix it with 0.5% to 0.9% manganese metal powder or preferably sufficient low-carbon ferromanganese powder to be equivalent in manganese content, and with 0.3% powdered graphite and about 1% of a lubricant such as stearic acid. I press this mixture at about 15–40 tons per square inch to form a coherent compact and sinter the compact in dry hydrogen at 2000° F. until the remaining carbon does not exceed substantially 0.1%. This requires, in the case of pieces ¼" thick, approximately three hours. I then repress or coin the piece, using at least 75 tons per square inch, to final dimensions. The density of the compact will now be approximately 7.65. In the above example, if instead of starting with 0.3% graphite, I start with more than 0.3% graphite, say 0.6% graphite and in the first sintering operation reduce the carbon to approximately 0.4% instead of 0.1% or less, I can still reach densities of 7.65 and over by employing a coining pressure of less than 100 tons per square inch if no metallic alloying ingredients are present. With 0.9% manganese added densities of 7.5 and over can be obtained at coining pressures of less than 100 tons per square inch.

It is a feature of my invention that I have discovered that I need not use as much carbon as is required for chemical combination with all of the sorbed oxygen in the powder. For example, if I use an iron powder containing 0.6–0.8% of oxygen, I find that if I add 0.3% carbon the oxygen will be completely eliminated with the consumption of only 0.2% carbon, with 0.1% carbon remaining in the iron. Since it would require 0.45 to 0.6% carbon to combine with the 0.6–0.8% oxygen if the reaction were simply a burning of carbon and oxygen to carbon monoxide, I accomplish my deoxidation of the powder with the consumption of only approximately ½ to ⅓ of the expected amount of carbon. This is an important feature of my invention because the inclusion of amounts of carbon such as 0.45 to 0.6% in the starting powder causes the powder compacts to be weak and frangible prior to the sintering operation.

After the coining or second pressing opera-

tion, several alternative procedures are possible. As examples, I will describe two:

(1) If it is desired to produce a product which may be suitable for subsequent machining operations I heat-treat the compact about 1 hr. at a temperature between 1000° F. and 1200° F. in a non-oxidizing atmosphere such as dry hydrogen. This produces a structure of good machinability which is well adapted to conventional machining operations. Thereafter the article may be subjected to any of the well-known surface treatments, such as case-hardening, plating, nitriding, Parkerizing, etc.

(2) If it is desired to produce a steel product I may heat treat the repressed article in a carburizing medium, preferably in a two-stage method such as disclosed and claimed in the co-pending application of Lyman F. Whitney, Serial No. 666,034, filed on even date herewith. As therein more fully disclosed that method comprises using a rich carburizing medium and then changing the medium to reduce its carburizing effect, thereby to equalize the distribution of carbon in the article. The degree of richness of the initial medium may be varied to suit different conditions but it is always greater than the equilibrium concentration, that is the concentration of carbon in the medium at which the medium would be in substantial equilibrium with the finished article. The change in richness may be made abruptly, as by replacing a rich atmosphere by a lean atmosphere, or it may be made gradually, as by drawing off rich atmosphere and feeding in lean atmosphere. The change may be carried to or below the equilibrium point. Indeed the richness may be reduced to zero, as by replacing the carburizing atmosphere with an inert atmosphere. If the richness is carried below the equilibrium point it may be brought back to this point either gradually or abruptly. In equalizing the distribution of carbon in the article by changing the medium, the equalization may be carried as far as desired and throughout all or only part of the article. For example, in many cases it is necessary to carry the equalization only to the point where the distribution is partly equalized and only throughout a limited depth adjacent the surface of the article. Preferably the equalization of carbon in the article is effected by heat-treating the article at approximately 1700° F. in an atmosphere of hydrogen containing 0.30% of methane for a period of time which is determined by the dimensions of the piece. The piece will have very nearly the characteristics of ordinary steel of similar carbon content and may be further hardened by conventional quenching procedures. While I have referred to 1700° F. as my preferred carburizing temperature I do not limit myself to this temperature as the temperature employed for these two operations may range from 1600° F. to 2050° F. which is just below the melting point of the iron-carbon eutectic.

As a specific example of the utilization of my invention I have produced pieces of square cross section ¼" x ¼" and 2" long having final uniform carbon content of 0.8%. Annealed electrolytic iron powder, —100 mesh, containing approximately 0.7% oxygen was mixed with 1% stearic acid lubricant, 0.63% —400 mesh low-carbon ferromanganese powder, and 0.3% graphite. The mixture was given an initial pressing at 27 tons per square inch, followed by a pre-sintering heat treatment in hydrogen at about 900° F. for about one hour to eliminate the stearic acid, and by a sintering for 3 hours at 2000° F. in dry hydrogen. The compact was then given a final pressing at 90 tons per square inch. The compact was then carburized for 10 hours at 1700° F. in dry hydrogen containing 1.0% propane. It was then equalized for 22 hours at 1700° F. in hydrogen containing 0.30% methane. After cooling from this heat treatment the piece was re-heated to 1500° F., oil quenched, and drawn at 1100° F. Its physical properties were then found to be: tensile strength 131,400 lbs. per square inch, elongation 18.7%, reduction of area 36%, and Rockwell B hardness 99.

Other gases may be substituted for hydrogen if desired. Gases which I can successfully use include cracked anhydrous ammonia, the conventional partially combusted types of heat-treating atmospheres, completely burned atmospheres of the type consisting of CO, N_2, and H_2 in various proportions, and inert gases such as nitrogen. Where methane or other hydrocarbon is required to be used with any of the above gases during the equalizing cycle, the proportion of methane or other hydrocarbon may be so chosen and maintained as to be in equilibrium with the carbon of the final desired steel composition.

Carbon may be introduced into the piece in ways other than those described above. For example, instead of gaseous carburizing atmospheres, I may use a pack, or I may use liquid carburizing salt baths. For an equalizing medium, I may substitute inert liquids such as lead or inert salt baths. When the compact is of high density, for example 7.65–7.70, the pores in the compact are not interconnecting and the liquids do not penetrate to the interior of the compact.

While I have referred to the use of a mixture of pure iron powder and one or more of my preferred alloying agents as a preferred starting material or as one component thereof, I could equally well use an iron powder in which one or more such alloying agents is dissolved, but containing aside from oxygen and other sorbed gases other impurities to the extent of not over 0.2%.

It should be understood that the present disclosure is for the purpose of illustration only and that this invention includes all modifications and equivalents which fall within the scope of the appended claims.

I claim:

1. A method of making a soft iron compact substantially free of oxide inclusions comprising the steps of loosely mixing powdered iron containing non-ferrous solid impurities in an amount not exceeding 0.2% and sorbed materials including oxygen not exceeding 1%, with free carbon, pressing the mixture at less than approximately 40 tons per square inch to form a coherent compact, sintering said compact in a non-oxidizing atmosphere at the temperature at which the carbon and said sorbed oxygen will combine in such proportion as to remove substantially all of the sorbed oxygen from the compact and to leave an excess of carbon in an amount not exceeding 0.4%, all percentages being by weight, and cooling said compact in a protective atmosphere to a temperature inhibiting oxidation of the substantially pure iron of the compact.

2. A method of making a soft iron compact substantially free of oxide inclusions comprising the steps of loosely mixing substantially pure powdered iron containing non-ferrous solid impurities in an amount not exceeding 0.2% and sorbed material including oxygen not exceeding 1%, with manganese in an amount not exceeding

0.9% and free carbon, pressing the mixture at less than approximately 40 tons per square inch to form a coherent compact, sintering said compact in a non-oxidizing atmosphere and at a temperature of not less than approximately 1800° F. and below its melting point at which the carbon and said sorbed oxygen will combine in such proportion as to remove from the compact substantially all of the sorbed oxygen, to cause the manganese to diffuse into the iron and to leave an excess of carbon in an amount not exceeding 0.4%, all percentages being by weight, and cooling said compact in a protective atmosphere to a temperature inhibiting oxidation of the compact.

3. A method of making metal articles having a high final density, comprising the steps of loosely mixing substantially pure powdered iron containing non-ferrous solid impurities in an amount not exceeding 0.2% and sorbed materials including oxygen not exceeding 1%, with free carbon, pressing the mixture at a pressure of less than approximately 40 tons per square inch to form a coherent compact, sintering said compact in a non-oxidizing atmosphere at the temperature at which said sorbed oxygen and carbon will combine in such proportion as to remove from the compact substantially all of the sorbed oxygen and leave carbon in an amount not exceeding 0.4%, all percentages being by weight, cooling the compact in a protective atmosphere to a temperature inhibiting oxidation of the iron and hence to provide a soft iron compact of intermediate density, and repressing said soft oxygen-free iron compact at a pressure of at least approximately sixty tons per square inch.

4. A method of making a steel article having a density above 7.5 and which is substantially free of oxide inclusions, comprising the steps of loosely mixing powdered iron containing non-ferrous solid impurities in an amount not exceeding 0.2% and sorbed materials including oxygen not exceeding 1%, with manganese up to 0.9% and free carbon up to 0.6%, compacting the mixture under a pressure of between 15 to 40 tons per square inch to form a coherent compact, sintering the compact in a reducing atmosphere at 1800° to 2050° F. at which the carbon and said sorbed oxygen will combine in such proportion as to form an integrated structure which is substantially free of sorbed oxygen and contains carbon in an amount not exceeding 0.4%, cooling the compact in a protective atmosphere to inhibit oxidation, and then repressing the soft oxygen-free compact at between 60 to 90 tons per square inch.

GEORGE WARREN WEBB.

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