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SINTERED IRON BODIES AND PROCESSES THEREFOR

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This invention relates to improvements in sintered bodies composed predominantly of copper-coated iron powders, and to processes associated therewith.

It is known that the strength of sintered bodies composed of soft iron powders can be improved considerably by incorporating copper with the iron powder prior to sintering the body. The copper has been incorporated in the past either by admixing copper powder with the iron powder, or by applying a coating of copper to the iron powder by aqueous chemical displacement or electrolytic methods. In a co-pending application of Drapeau et al., Serial No. 33,656, filed June 17, 1948, a process is disclosed for applying a coating of copper to ferrous powders by means of a thermochemical reaction between the ferrous powder and cuprous oxide, cupric oxide or mixtures of these oxides in a protective atmosphere. We have now found, however, that the atmosphere employed during the thermal treatment of soft iron powders in effecting the reaction alters the powder in some manner so that the strength of sintered bodies made from the coated iron powder depends on and varies with the nature of that atmosphere. We have found especially that by employing a reducing or inert atmosphere during the thermal coating operation, and by subsequently sintering the coated powders in a neutral or reducing atmosphere with or without the concurrent presence of small amounts of fluxes and/or metal-containing components, particularly high-strength sintered bodies may be obtained.

It accordingly is an object of this invention to provide a process for producing high-strength sintered bodies composed predominantly of iron powders, at least a major part of said iron powders having been coated with copper by a thermochemical reaction.

It is a further object to provide a process for producing high-strength sintered bodies from iron powders which have been thermally coated with copper, by sintering bodies of the coated powder in hydrogen, nitrogen, carbon monoxide and like neutral or reducing atmospheres, with or without the concurrent presence of small amounts of flux and/or metal-containing components.

These and other objects will be apparent from the following description of the invention.

As disclosed in the Drapeau et al. application identified above, iron powder may be coated with an adherent film of copper by mixing the iron powder intimately with finely-divided copper oxide and then heating the mixture for a short time at temperatures between about 1000° F. and 1500° F. in a substantially non-oxidizing, neutral

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or reducing atmosphere. The amount of copper so deposited on the iron may be varied at will by suitably proportioning the iron powder and finely-divided copper oxide, but when the copper coating is applied for the purpose of producing a coated molding powder which can be sintered into a strong body, the amount of copper ranges generally from about 4% to 30% by weight of the iron. During our investigations of the sintering properties of iron powders coated with such quantities of copper, we have found that the iron powders which have been thermally coated in the manner described in the said co-pending application of Drapeau et al., in a hydrogen, carbon monoxide, nitrogen or like reducing or inert atmospheres produced much stronger sintered bodies than otherwise-identical powders coated in an atmosphere such as carbon dioxide. The following examples illustrate this effect.

Examples 1 and 2

Eighty parts of minus 100 mesh iron powder having a hydrogen loss less than about 1.5% were mixed intimately with .2 part of stearic acid and 20 parts of minus 7 micron copper oxide powder composed of about 60% cuprous oxide and 40% cupric oxide. The stearic acid was added to improve the uniformity with which the oxide coating distributed itself over the surfaces of the iron particles, and to avoid segregation of the mixture. Half of the mixture (designated "Batch A") was then heated in a carbon dioxide atmosphere at 1200° F. for 15 minutes and afterwards was cooled in carbon dioxide to room temperature. The other half of the mixture (designated "Batch B") was heated in a hydrogen atmosphere at 1200° F. for 15 minutes and afterwards cooled in hydrogen to room temperature. Samples of both batches were then pressed at 40 tons per square inch into briquettes having the shape of rectangular bars 1¼" long by ½" wide by about ¼" thick. The bars were then sintered in hydrogen for ½ hour at 2050° F. and afterward cooled in hydrogen. The sintered bars were then tested for modulus or rupture, with the following results:

		Modulus of Rupture (lbs. per sq. in.)
Sample 1	Sintered bar made from iron powder coated with copper in carbon dioxide atmosphere (Batch A).	45,000
Sample 2	Sintered bar made from iron powder coated with copper in hydrogen atmosphere (Batch B).	70,000

Similar results were obtained when nitrogen and carbon monoxide atmospheres were tested for comparison with a carbon dioxide atmosphere, in that the nitrogen and carbon monoxide atmospheres yield higher moduli of rupture than is obtained from a carbon dioxide atmosphere.

We have also found that when hydrogen, nitrogen or carbon monoxide atmospheres, or mixtures thereof are used in the thermal coating operation, the strength of the sintered bodies made from the coated iron powders may be even further improved by incorporating in the coated powder prior to sintering small amounts of alkaline fluxes and/or materials containing low-melting-point white metals. Among the alkaline fluxes which we contemplate may be mentioned the alkali metal carbonates, nitrates, and borates (in glass form) and lime. Such fluxes may be used in amounts between about .1% and 2% by weight of the coated powder. The metal-containing components which may be incorporated in the coated powder either by themselves or in combination with the alkaline fluxes include zinc, brass, tin, bronze, cadmium, zinc oxide, tin oxide and cadmium oxide. Such white-metal-containing components may be used in amounts equivalent in metal content to between about ¼% and 4% by weight of the coated powders. The following examples illustrate the effects of such additions of flux and/or metal component. In these examples, minus 40 mesh iron powder having a hydrogen loss less than about 1.5% was coated with copper by mixing the iron powder with .2% stearic acid (by weight of the copper oxide) and the indicated percentage of copper oxide (by weight of the iron powder). The copper oxide which was used was a mixture composed of about 60% cuprous oxide and 40% cupric oxide, and was of a fineness such that all particles were smaller than about 7 microns. The coating of the iron powders was effected by heating the mixture of powders for 15 minutes (except where otherwise noted) at 1200° F. in either a carbon dioxide, nitrogen or hydrogen atmosphere (as indicated below) and cooling to room temperature in the same atmosphere. The copper-coated powder was then mixed with the indicated flux and/or indicated metal component in the amount indicated, after which the molding mixture was pressed at 40 tons per square inch into a test bar of the size indicated in Examples 1 and 2. The pressed bars were then sintered in hydrogen at 2050° F. for ½ hour and finally cooled to room temperature in hydrogen. Tests for modulus of rupture were made in the same manner as the tests in Examples 1 and 2.

Ex.	Parts of Iron Powder	Coating Operations: Parts of Cu Oxide	Coating Operations: Furnace: Atmosphere	Coating Operations: Furnace: Time (Hours)	Additives	Modulus of Rupture in lbs. per sq. in.
3	70	30	H_2	¼	1% ZnO + ½% Borax	97,000
4	70	30	CO_2	½	do	39,000
5	80	20	H_2	¼	do	88,000
6	80	20	CO_2	1	do	25,000
7	90	10	H_2	¼	do	74,000
8	90	10	CO_2	¼	do	55,000
9	80	20	H_2	¼	1% Zn	77,000
10	80	20	H_2	¼	¼% Na_2CO_3	75,000
11	80	20	H_2	¼	1% Sn	85,000
12	80	20	H_2	¼	1% Cd	74,000
13	80	20	H_2	¼	½% Borax	75,000
14	80	20	H_2	¼	2% Brass+½% Borax	75,000
15	80	20	H_2	¼	None	70,000
16	95	5	N_2	¼	do	27,000
17	90	10	N_2	¼	do	61,000
18	80	20	CO	¼	do	70,000
19	80	20	[1] Atmos	¼	do	65,000
20	100	None			do	13,250

[1] Machine-produced controlled atmosphere, containing some free carbon monoxide and hydrogen, together with carbon dioxide and nitrogen.

It will be apparent from the foregoing examples that the use of a hydrogen atmosphere in the thermal coating operation is highly beneficial in producing a copper-coated powder which can be sintered into a strong body. We have found, as previously stated, that other strong reducing atmospheres which are substantially non-carburizing or slightly carburizing have a similar effect. Carbon monoxide is a substantially non-carburizing atmosphere under the conditions of time and temperature here employed, as are mixtures of hydrogen and carbon monoxide in all proportions. Atmospheres composed of carbon monoxide, hydrogen and nitrogen, such as those obtained from commercial controlled-atmosphere gas machines are also suitable.

The strength of sintered bodies made in accordance with the foregoing principles can be further improved by repressing and resintering the body. The repressing and resintering of bodies made from powders which have been coated with copper in a carbon dioxide atmosphere is particularly beneficial, since by this expedient such powders can be manufactured into sintered bodies which are strong as bodies made from powders which have been coated in a hydrogen, nitrogen, or carbon monoxide atmosphere. Thus whatever impairing effects a carbon dioxide atmosphere has on copper-coated iron powders, these effects may be offset by pressing the powders at moderate pressures, sintering the body in the customary atmospheres, then repressing the sintered body at a higher pressure and resintering the repressed body. For example, an iron powder which had been coated with about 18% of copper in a carbon dioxide atmosphere, when pressed at 20 tons per square inch and sintered at 2050° F. for ½ hour in hydrogen, developed a modulus of rupture of 28,300 p. s. i. When a corresponding sintered bar was repressed at 40 tons p. s. i. and resintered at 2050° F. for ½ hour, it developed a modulus of rupture of 105,000 p. s. i. The strengths of sintered bodies made from iron powders which have been coated with copper in a hydrogen atmosphere may also be increased appreciably by repressing and resintering, although such repressing and resintering

is seldom needed with such powders, since moduli of rupture of close to 100,000 lbs. or higher may be obtained from the first pressing and sintering thereof, as shown by Example 3.

We have found that copper-coated iron powders on which the copper coating was applied by chemical precipitation of copper from aqueous copper salt solutions do not respond materially to the additions of flux and/or metal-component prior to sintering, in producing increased strength in the sintered body. Likewise, electrolytic copper coatings on iron powders do not respond to the flux and/or metal-component additions.

We have also found that strong sintered bodies composed largely of iron powders may be made from mixtures of uncoated iron powders with the thermochemically coated iron powders, the latter being more than about 50% of the total mixture and carrying sufficient copper as a coating to provide between about 4% and 30% of copper by weight of the total iron powder in the mixture.

In this specification, the term "iron powder" refers to the briquettable powders composed almost entirely of iron and containing so little carbon that they are readily briquettable as contrasted with the hard powders containing larger amounts of carbon or alloying elements which are unbriquettable at pressures below about 60 tons per square inch. The briquetting and sintering of such hard ferrous powders coated with copper is described and claimed in the copending application of Drapeau et al., Serial No. 33,652, filed June 17, 1948.

In summary, our invention broadly involves the steps of (*a*) providing a sinterable mass composed substantially completely of iron powders, at least a major part of the iron powders being thermochemically coated with copper, said iron powder mass being mixed or not, as desired, with from about 0.1% to 2% by weight of the coated powders of a fluxing material as described herein, and/or from about ¼% to 4% by weight of the coated powders of a white-metal-containing material as described herein; and (*b*) sintering the so-provided sinterable mass with or without an intermediate or concurrent briquetting operation. In providing the coated powders of the sinterable mass, the thermochemical coating reaction is carried out by reacting the iron powder in intimate admixture with cuprous oxide or cupric oxide or mixtures thereof, to provide a copper coating weighing between about 4% and 30% of the weight of the iron powder. The reaction is effected in a neutral atmosphere or in a hydrogen or other reducing atmosphere which may be carburizing or non-carburizing with respect to the iron powder, and the reaction temperature is between about 1000° F. and 1500° F., but is preferably between about 1100° F. and 1300° F. The thermochemical reaction mass is heated at the indicated temperatures for a sufficient length of time to deposit the required weight of coating. This time may vary between about 3 minutes and 60 minutes but the actual amount of time required, whether within this range or more or less, may be determined readily by trial. The admixture of copper-coated iron powder with uncoated iron powder or with the flux and/or white-metal-containing material may be effected by mixing any combination of the latter materials with the copper-coated powder, or alternatively the fluxes and/or white-metal components may be mixed with the thermochemical reaction mass of iron powder and copper oxide, any uncoated iron powders desired in the mass being added after the thermochemical coating has been formed. In making the admixture by either procedure, the fluxes and white-metal-containing materials which are used should preferably be very finely divided so that the resulting admixture will be very intimate. For example, pigment grade of zinc oxide is very suitable since its fineness promotes its thorough dispersion throughout the reaction mass. The use of about 0.1% to 1%, preferably about .2% of stearic acid or mineral oil by weight of the copper oxide not only aids the uniform dispersion of the copper oxide but similarly aids the dispersion of the fluxes and/or white metal oxides when these latter materials are incorporated in the thermochemical reaction mixture.

The sintering of the aforesaid provided "sinterable mass" is effected in a hydrogen, carbon monoxide or mixtures thereof at temperatures somewhat below, at or above the melting point of copper, and preferably at temperatures between about 2000° F. and 2200° F. Commercially useful strengths can be obtained by sintering at temperatures as low as about 1800° F. The duration of the sintering operation within the indicated range of temperatures depends on various factors such as the selected temperature, the size of the body being sintered, its density (whether briquetted or unbriquetted), the capacity of the sintering furnace, the rate of heating, etc. The optimum duration of heating can readily be determined by one skilled in the art. However, a soaking period of about ½ hour is generally required after the body has attained the desired temperature, even for small bodies heated in about 3 to 4 minutes to temperatures of 2200° F. The invention contemplates the cooling of the sintered body under non-oxidizing conditions, such as by cooling in the same atmosphere as used in the sintering furnace. However, any suitably non-oxidizing cooling treatment may be used whether it be a gaseous reducing or inert atmosphere, an oil cooling bath or otherwise.

Many modifications may be made in the practice of the invention as disclosed herein, and will be apparent to those skilled in the art. We contemplate as part of our invention all such modifications as fall within the scope of the following claims.

Having disclosed our invention, what we claim is:

1. The method of making sintered iron bodies of improved strength from thermochemically-coated iron powders, said method comprising the steps of: providing a sinterable mass consisting essentially of an intimate mixture of (*a*) iron powders, at least a major part of which powders carries a copper coating amounting to between about 4% and 30% of the total weight of the iron powders, said coating having been applied to the said major part of the iron powders by a thermochemical reaction between said iron powder and finely-divided copper oxide at temperatures between about 1000° F. and 1500° F. in a non-oxidizing atmosphere, and (*b*) between about 0.1% and 2% by weight of the copper-coated iron powder of at least one powdered fluxing material selected from the group consisting of the alkali metal carbonates, the alkali metal nitrates, the alkali metal borates in glass form, and lime; sintering said sinterable mass in a

reducing atmosphere at temperatures between about 1800° F. and 2200° F.; and cooling said sintered mass under non-oxidizing conditions.

2. The method of making sintered iron bodies of improved strength from thermochemically-coated iron powders, said method comprising the steps of: providing a sinterable mass consisting essentially of an intimate mixture of (*a*) iron powders which carry a copper coating amounting to between about 4% and 30% by weight of the iron powders, said coating having been applied to the said iron powders by a thermochemical reaction between said iron powder and finely-divided copper oxide at temperatures between about 1000° F. and 1500° F. in a non-oxidizing atmosphere, and (*b*) between about 0.1% and 2% by weight of the copper-coated iron powder of at least one powdered fluxing material selected from the group consisting of the alkali metal carbonates, the alkali metal nitrates, the alkali metal borates in glass form, and lime; briquetting said sinterable mass; sintering said briquetted mass in a reducing atmosphere at temperatures between about 1800° F. and 2200° F.; and cooling said sintered mass under non-oxidizing conditions.

3. The method as claimed in claim 2 wherein the fluxing material is powdered borax glass in an amount of about ½%.

4. The method as claimed in claim 2 wherein a reducing atmosphere is employed in said thermochemical reaction.

5. A sintered product as produced by the method claimed in claim 2.

6. The method as claimed in claim 2 wherein said sinterable mass also includes between about ¼% and 4% of metallic tin equivalent in finely-divided form, by weight of the copper-coated iron powder.

7. The method as claimed in claim 2 wherein said sinterable mass also includes between about ¼% and 4% of metallic zinc equivalent in finely-divided form, by weight of the copper-coated iron powder.

8. The method as claimed in claim 2 wherein said sinterable mass also includes between about ¼% and 4% of metallic cadmium equivalent in finely-divided form, by weight of the copper-coated iron powder.

9. The method of making sintered iron bodies of improved strength from thermochemically-coated iron powders, said method comprising the steps of: providing a sinterable mass consisting essentially of an intimate admixture of (*a*) iron powders, at least a major part of which powders carries a copper coating amounting to between about 4% and 30% of the total weight of the iron powders, said coating having been applied to the said major part of the iron powders by a thermochemical reaction between said iron powder and finely-divided copper oxide at temperatures between about 1000° F. and 1500° F. in a non-oxidizing atmosphere, and (*b*) between about ¼% and 4% in metallic tin equivalent in finely-divided form, by weight of the copper-coated iron powder; sintering said sinterable mass in a reducing atmosphere at temperatures between about 1800° F. and 2200° F.; and cooling said sintered mass in a non-oxidizing atmosphere.

10. A sintered product as produced by the method claimed in claim 9.

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