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IRON-COPPER PREALLOYS

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ABSTRACT OF THE DISCLOSURE

A prealloyed iron-copper powder which has high compressibility and shrinks upon sintering is prepared by melting a charge of iron and copper, atomizing the charge with water jets under pressure, further comminuting the particles if desired, and subjecting the formed powder to a heat treatment between 1400° F. and 1800° F. in a reducing atmosphere followed by a controlled cooling.

FIELD OF THE INVENTION

The present invention relates to powder metallurgy, more particularly to a process for producing iron-copper alloy powders and to the powders produced thereby.

DESCRIPTION OF THE PRIOR ART

It is known to produce alloys of copper and iron by methods of powder metallurgy. The methods hitherto employed consisted essentially in blending an iron powder and a copper powder in the required proportions, then molding the desired article or part from the blend thus prepared, and sintering the same at a temperature above the melting point of copper. This method presents serious disadvantages, notably in that the blends are often not sufficiently homogeneous and that, on storage, the powders tend to segregate. Furthermore, while the compressibility of such blends of powder is generally good, when the compressed powder blend is sintered in accordance with the usual procedures of forming articles from metal powders, it generally expands. This results in a decrease in density and an increase in porosity which are undesirable effects in the final product.

Another method of producing particles from copper-iron alloys has been to shape the desired article or part from iron powder, then to compress it to the desired density or porosity and to infiltrate the shaped article or part with liquid copper which substantially fills the pore volume. This method suffers from a similar disadvantage to the one above, i.e. the article expands on infiltration.

Yet another method has been proposed wherein reducible iron compounds, such as iron oxide, are mixed with metallic copper or a reducible copper compound and the mixture is reduced at elevated temperatures in a reducing atmosphere to form copper-infiltrated iron particles. However, the powders obtained by this method are spongy in structure and generally have low compressibility.

SUMMARY OF THE INVENTION

According to the present invention, a method is provided of making iron-copper powders wherein iron and copper are prealloyed, e.g. by melting iron with the required proportion of copper metal in a furnace, and the molten mixture is atomized and cooled to obtain a powder of suitable particle size, and the powder obtained is further subjected to a heat treatment to obtain a powder of high compressibility. The process of this invention can be carried out substantially in conventional equipment

such as exist in a modern metal powder plant. The resulting powder constitutes such an intimate mixture of iron and copper that no separation of the two elements occurs on storage or transportation.

Accordingly, the present invention provides a method of making an iron-copper alloy powder which comprises melting a charge of iron and copper in a furnace to form a liquid iron-copper mixture, subjecting the molten mixture to impingement by a jet of water thereby to obtain a solidified mixture of iron and copper in highly fragmented form, grinding the fragmented metal, if necessary, to produce a powder of desirable particle size, and heat treating said powder at an elevated temperature to obtain an iron-copper powder of high compressibility.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In one embodiment, which will be particularly described, a charge of iron and copper is melted in a furnace with the addition of a minor admixture of carbon, the molten mixture is atomized by impingement with a jet of water thereby to obtain a solidified mixture of iron-copper particles, the mixture is ground to produce a powder of desirable particle size, the powder is intimately mixed with a predetermined amount of iron oxide and heated at an elevated temperature to decarburize the powder, the powder is further ground to a desired particle size distribution, and the powder is further subjected to heat treatment at an elevated temperature to obtain an iron-copper powder of high compressibility.

In the practice of this invention, a charge of iron and copper is first prepared in predetermined proportions to obtain the desired alloy. The proportions will normally be between 1 and 25% of copper based on the total weight of the alloy. The iron will in most cases consist of scrap metal of good quality, or pig iron low in sulphur or phosphorus impurities, and the like. The charge is melted in a furnace, e.g. an electric arc furnace of known design, and, if subsequent grinding of the atomized mixture is contemplated to obtain the desired particle size distribution, it is preferable to add carbon, e.g. in the form of graphite so as to produce a melt having generally a carbon content between 0.1 and 4.5%. The carbon content renders the solid material somewhat brittle, which is a help in grinding, and is substantially removed in a subsequent decarburizing step, as hereinbelow described. Various other elements may be added as desired for the composition of the alloy and, if required, the melt may be desulphurized according to known methods.

The molten metal is removed from the furnace, e.g. by means of a ladle, at a temperature sufficiently high to maintain the charge in a molten state, and is transferred to a shotting area. This consists essentially of a tundish, i.e. a vessel having a refractory lining and a refractory bottom in which holes are provided for the passage of the molten metal. The stream of molten metal passing through the holes in the bottom of the tundish is impinged with a fluid, usually water, in the form of a jet or a series of jets under pressure. The jets are usually provided to intersect in space substantially along a line or lines of intersection, through which, or in the immediate vicinity of which, the stream of metal is passing. As a result of the impact of the water jets, the metal is broken up into small particles which drop into a receptacle suitaly located to receive them. The receptacle is filled, e.g. with water, to ensure adequate cooling of the atomized particles. The degree of atomization or comminution of

the metal depends on the temperature of the water and the velocity of the jet, and to obtain a fine particle at this stage it is necessary to use water jets under substantial pressure.

The material produced in the shotting operation may be subjected to grinding, e.g. in a ball mill, to obtain the desired particle size distribution as defined by screen analysis. The particle size obtained at this stage will determine the particle size of the finished powder and hence also the type of finished powder resulting from the operation. If a decarburizing step is employed, the powder thus ground to the desired size is then intimately mixed with mill scale (iron oxide) which has been ground in a separate ball mill to a particle size of the same order as, or even smaller than, the size of the ground shot. The mixing is done in suitable blenders and the proportions of the ground shot and the mill scale will be in a ratio calculated to bring about substantially stoichiometric proportions of oxygen and carbon in the mix, so as to effect a substantially complete combination of one with the other. The mixture is then subjected to heating, e.g. in a continuous strip belt furnace heated electrically with suitable elements, the temperature used at this stage being of the order of 1700° F. to 2300° F. The amount of powder passing through the furnace, the speed of the passage, the time it is maintained at the elevated temperature, and the amount and type of reducing atmosphere, are all interrelated and suitably adjusted to obtain substantially complete decarburization and deoxidation of the powder. The atmosphere in the furnace is the one produced by the chemical combination of the oxygen and carbon in the constituents of the mix, and consists essentially of a major proportion of carbon monoxide, a smaller proportion of carbon dioxide, with traces of nitrogen and oxygen. This atmosphere may be supplemented, if desired, with manufactured reducing atmospheres such as endothermic gas, dissociated ammonia, hydrogen, etc.

The material sinters partly in the furnace and issues from the cooling section of the furnace as a brittle porous cake. The cake is crushed and ground in conventional equipment and screened to produce a powder of the specified screen analysis.

The decarburized powder is preferably further subjected to a heat treatment, as mentioned hereinabove, which is often referred to as annealing. This is a heat treatment which can be carried out, e.g. in a continuous belt furnace, at a temperature between 1400 and 1700° F., in a slightly reducing atmosphere, for instance, one of dissociated ammonia (i.e. essentially of nitrogen and hydrogen gases). The effect of this treatment is primarily to increase the compressibility of the powder and to decrease the hardness of the powder particles. The increase in compressibility is substantial and often will make the difference between a usable and unusable powder. It is believed that the improvement in compressibility is due to the precipitation of copper from the iron-copper solid solution, solutions of copper and iron tending to be hard and difficult to compress. It has been found that to obtain relatively soft compressible powders the annealing temperature should be either below the temperature of transformation of γ iron to α iron containing 1.5% or more copper, i.e. about 1535° F., or if higher annealing temperature is used, a slow cooling rate is necessary for the powders to have the desired compressibility.

The cooling can normally vary within a wide range, from about 10° F./min., which corresponds approximately to the cooling rate of the powder left within the furnace without supply of fresh heat, to about 100° F./min., which corresponds to the rate of cooling of the powder removed from the furnace and left to cool in the open air at ambient temperature. The reference to slow or rapid cooling rates will thus be understood with reference to the aforementioned range of cooling rates.

The powders so produced can be used for the making of various articles and parts by the usual method of powder metallurgy, i.e. by molding to a desired shape, compacting under conventional pressures, and sintering at an elevated temperature, preferably at a temperature above the melting point of copper. The powders obtained by the process of this invention generally exhibit, to a high degree, the properties required in such powders; however, the properties will vary according to the many variables of the composition or of the process. The copper content of the powder would be one such variable. The presence of copper, primarily dissolved copper, affects the hardness of the metal. Thus the hardness of the powder particles will increase with the copper content to a maximum corresponding to the solubility limit of copper in iron, this limit being about 8% in the case of relatively pure iron treated at conventional sintering temperatures, e.g. 2050° F. carbon-containing alloys made according to the present process, reach maximum hardness at about 5% of copper and the hardness values obtained are higher than those of the premixed powders of the prior art. Other variables which will affect the properties of the powder include the temperature of decarburizing and annealing. Higher temperatures and longer times of decarburizing yield harder decarburized powders for a given cooling rate. More important, as already stated, are the temperatures and times of annealing and the rate of cooling the powder from the annealing temperature; these, when properly selected, lead to the formation of a powder of excellent compressibility. Greater compressibility means that with a given compacting pressure higher densities can be obtained, and since strength is a function of the sintered density of the powdered material, the advantages of these powders will be apparent.

Furthermore, powders of the present process, like other prealloyed powders, but quite unlike premixes, shrink when sintered after compacting. The degree of shrinkage depends on the particle size and is generally greater the smaller the particle size. Particle size, as previously stated, depends on the fineness of the particle obtained during atomization by means of a water jet, or, if a grinding step is employed following the shotting, the fineness obtained as a result of said grinding. The property of shrinking on sintering can be taken advantage of to obtain sintered powders of very high density, and since strength of the final product depends on the sintered density, greater strength can be obtained from prealloyed powders of the present invention. Addition of carbon, in the form of graphite, before compacting further increases the strength of the prealloyed powders.

Examples will now be provided to further illustrate the invention. However, it is not intended that the invention be restricted by any of the examples disclosed herein.

EXAMPLE I

A charge was made up as follows and melted in an electric arc furnace.

	Percent
Pig iron	89.5
Scrap copper	9.5
Petroleum coke	1.0

The molten charge was removed from the furnace, then disintegrated by pouring it through impinging water jets. The shot thus produced was collected, dried, and ball-milled until about 50% by weight of the particles passed through a 200 mesh screen. This material was mixed with finely ground mill-scale in the proportion 4.9 to 1. The mixture was passed through a belt furnace at 2000° F. The sintered cake issuing from this furnace was crushed to ½ inch and then ground in an attrition mill until substantially all passed through an 84 mesh screen. This material was again heated in a continuous belt furnace at 1600° F. in an atmosphere of dissociated ammonia. The product was crushed to ½ inch and ground in an attrition mill until substantially all the powder passed

through an 84 mesh screen. The powder had the following properties:

CHEMICAL ANALYSIS

	Percent
Copper	8.12
Carbon	0.00
Sulphur	0.01
Silicon	0.23
Manganese	0.09
Phosphorus	0.01
Hydrogen loss	0.33
Acid insolubles	0.05
Iron	Balance

SIEVE ANALYSIS

	Percent
−80 |+100	3.9
−100 +150	16.0
−150 |+200	29.0
−200 +230	18.9
−230 |+325	14.7
−325	17.3

The powder was mixed with ¾% zinc stearate lubricant and pressed to transverse rupture bars. These were sintered in an endothermic gas atmosphere at 2050° F. for 30 minutes. Their properties were as follows:

Compacting pressure, T.S.I.	Green density, gm./cc.	Sintered density, gm./cc.	Dimensional change, percent	Hardness R_B	Modulus of rupture, p.s.i.
16	5.89	5.89	−0.23	41	56,000
24	6.31	6.32	−0.18	63	79,000
36	6.77	6.75	−0.12	75	110,000
50	7.07	7.05	−0.05	84	145,000

EXAMPLE II

Powders were prepared according to the procedure of Example I, except that varying amounts of copper were added to the arc furnace charge. The resulting powders were compacted at 36 T.S.I. with ¾% zinc stearate lubricant and sintered as in Example I. The properties of the powders were as follows:

Copper content, percent	Green density, gm./cc.	Sintered density, gm./cc.	Dimensional change, percent	Hardness R_B	Modulus of rupture, p.s.i.
2.4	6.74	6.74	−0.20	48	79,000
5.4	6.79	6.80	−0.28	72	103,000
12.8	6.81	6.87	−0.43	79	122,000

EXAMPLE III

A powder was prepared as in Example I, except that the shot was ball-milled until 96% passed through a 200 mesh screen. The copper content of the finished powder was 5.6%. Shown below is a comparison of the powder with a powder of approximately equal copper content but ground to a size such that about 50% passed through a 200 mesh screen (as in Examples I and II). Compaction was at 50 T.S.I. and sintering was as in Example I.

Percent [1]	Copper content, percent	Green density, gm./cc.	Sintered density, gm./cc.	Dimensional change, percent	Hardness R_B	Modulus of rupture, p.s.i.
51	5.4	7.07	7.10	−0.20	79	127,000
96	5.6	6.87	6.96	−0.47	70	129,000

[1] Ground through 200 mesh after shotting.

Equivalent strength at a lower density, for the more finely ground material, indicates higher strength at the same density for powder made from more finely ground shot.

EXAMPLE IV

Powders were prepared as in Example I, except that the ground decarburized powder was annealed at various temperatures as shown, in a tube furnace for 30 minutes in a hydrogen gas atmosphere. The rate of cooling from the annealing temperature was 100° F./min. Compacts were pressed at 36 T.S.I. with ¾% zinc stearate lubricant. Sintering was as in Example I.

Annealing temperature, ° F.	Green density, gm./cc.	Sintered density, gm./cc.	Dimensional change, percent	Hardness R_B	Modulus of rupture, p.s.i.
1,200	6.38	6.41	−0.31	66	89,000
1,400	6.66	6.71	−0.36	73	122,000
1,600	6.17	6.22	−0.32	62	84,000
1,700	6.03	6.09	−0.27	57	73,000

More compressible powders are produced at annealing temperatures below the α-γ transformation temperature of 1535° F. than above if the cooling rate is relatively rapid.

EXAMPLE V

A powder was prepared according to the procedure of Example I, except that the material contained 5.4% copper and was annealed in two different fashions: "A" as in Example I, and "B" for the same time at the same temperature but in a tube furnace with a relatively rapid cool from the annealing temperature.

Anneal type	Approximate cooling rate, ° F./min.	Green density,[1] gm./cc.	Particle hardness, VHN [2]
A	20	6.79	141
B	100	6.26	207

[1] At 36 T.S.I. with ¾% zinc stearate.
[2] Vickers hardness number.

A substantially higher compressibility or green density is obtained with the powder which was cooled from the annealing temperature at a relatively slow rate.

EXAMPLE VI

A powder was prepared according to the procedure of Example I, except that the material contained 5.4% copper and was annealed at a temperature of 1680° F., but in otherwise identical conditions, and was cooled from the annealing temperature at three different rates, designated here as "C," "D" and "E."

Anneal type	Approximate cooling rate, ° F./min.	Green density,[1] gm./cc.
C	10	6.36
D	75	6.04
E	100	5.52

[1] At 30 T.S.I. with no lubricant.

A substantially higher compressibility thus is obtained in the powder when the rate of cooling from a high annealing temperature is slower compared with a rate of cooling which is higher within the available range.

I claim:

1. A process for preparing a prealloyed iron-copper powder which shrinks upon sintering comprising melting a charge consisting essentially or iron, 1–25% copper and .1–4.5% carbon in a furnace, atomizing said molten charge by impingement of a jet of water under pressure against a stream of said molten charge thereby to form a mass of solid iron-copper articles, subjecting said mass of particles to a heat treatment at a temperature between

1400° F. and 1800° F. in a reducing atmosphere and cooling said mass of particles to normal temperature at a rate controlled to provide a prealloyed iron-copper powder having a green density greater than 6 gms./cc. at a compacting pressure of 30 T.S.I.

2. The process of claim 1 wherein said mass of solid iron-copper particles is subjected to a decarburizing step prior to said heat treatment, said decarburizing step consisting of mixing said iron-copper particles with powdered iron oxide and heating said particles with said iron oxide at a decarburizing temperature.

3. The process of claim 2 wherein said iron-copper particles are subjected to grinding prior to said decarburizing step thereby to comminute said particles to a predetermined particle size distribution.

4. The process of claim 1 wherein the heat treatment is carried out at a temperature below about 1535° F.

5. The process of claim 2 wherein the heat treatment is carried out at a temperature above 1535° F. and the cooling is carried out at a rate not greater than 75° F./min.

6. The process of claim 2 wherein the heat treatment is carried out at a temperature below about 1535° F.

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U.S. Cl. X.R.

75—156, 211, 213

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,752,712 Dated August 14, 1973

Inventor(s) Robert T. Holcomb

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the heading to the printed specification, after line 5 insert -- Claim Priority, Application Canada, 086556, June 25, 1970 --.

Signed and sealed this 26th day of February 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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