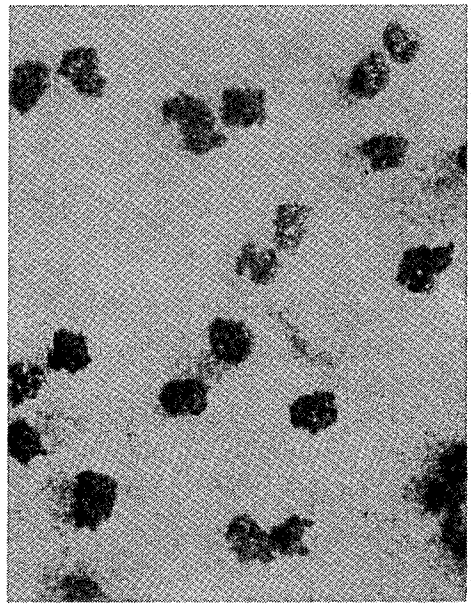
May 14, 1968 W. M. SHAFER 3,383,198
HIGH GREEN STRENGTH-LOW DENSITY COPPER
POWDER AND METHOD FOR PREPARING SAME
Filed Dec. 1, 1965



HIGH GREEN STRENGTH-
LOW DENSITY COPPER POWDER

-200 +230 U. S. STANDARD
SCREEN FRACTION

MAGNIFICATION = 100 DIAMETERS

WILLIAM M. SHAFER
INVENTOR

BY Harold M. Reese

ATTORNEY

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HIGH GREEN STRENGTH-LOW DENSITY COPPER POWDER AND METHOD FOR PREPARING SAME

William M. Shafer, Crown Point, Ind., assignor, by mesne assignments, to SCM Corporation, New York, N.Y., a corporation of New York

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ABSTRACT OF THE DISCLOSURE

Porous, low density, high green strength reduced copper powder containing trace residues of selenium, tellurium, or mixtures thereof has been discovered and is described. An improvement in the reduction process for making such copper powder which comprises the steps of forming a substantially uniform mixture of copper oxide and from about 500 to 20,000 parts per million parts of said copper oxide of at least one finely divided metal selected from the group consisting of selenium and tellurium, and reducing the mixture with a reducing gas at a temperature of at least about 900° F. has also been discovered and is described.

The present invention relates to a novel copper powder and to a process for preparing such powder.

The present invention is advantageous in that it provides copper powder having a lower apparent density than that heretofore obtainable using gaseous reduction techniques and is further advantageous in that the elemental copper powders when compacted have a higher fresh green strength than copper powders heretofore obtainable. Copper powders having such properties (e.g. low apparent density and high green strength) have long been sought in the powder metallurgy field.

The present invention provides an improvement in a conventional process for making copper powder by reducing finely divided copper oxide in a reduction zone at elevated temperature. The improvement is for making copper powder having a low apparent density and high green strength and comprises the steps of (1) forming a substantially uniform mixture of copper oxide and from about 500 to about 20,000 parts, per million parts of said copper oxide, of at least one finely divided metal selected from the group consisting of selenium and tellurium; and (2) reducing the mixture with the reducing gas in the reducing zone at a temperature of at least about 900° F.

By so proceeding, a novel finely divided porous copper powder having particles substantially all of which are finer than 200 mesh and at least 90% of which are finer than 325 mesh (e.g. substantially all of the particles pass through a No. 200 mesh U.S. standard screen and 90% or more pass through a No. 325 mesh U.S. standard screen). The copper powder then has an apparent density between about 0.4 and about 1.5 grams per cubic centimeter and a green strength of between about 2800 and about 4000 p.s.i. when pressed (e.g. compacted) at 12 t.s.i. using die wall lubricant only and A.S.T.M. test.

The accompanying drawing is a microphotograph of particles of the porous copper powder and is included to show the porous nature of the particles thereof.

By way of contrast, comparable copper powders prepared by conventional gas reduction methods consist of non-porous particles. Such powders generally have an apparent density of 2.0–2.6 grams per cubic centimeter and a green strength below 2500 p.s.i.

The term "finely divided copper oxide" as used herein is intended to mean and to include finely divided cuprous and cupric oxides or mixtures thereof. As will be evident hereinafter from the specific examples, the copper oxide which has been found to be advantageous for use in the processes of the present invention is preponderantly cuprous oxide (containing 85% or more Cu_2O) because such material is more readily and economically reduced to elemental copper than is cupric oxide.

The term "finely divided metal" as used herein is intended to mean and to refer to finely divided elemental selenium, tellurium or mixtures thereof.

The term "green strength" as used herein is intended to mean and to refer to the modulus of rupture (in p.s.i.) of a 15 gram sample of fresh copper powder freshly compacted in a press employing a standard mold at 12 t.s.i. with a die wall lubricant. It is an A.S.T.M. standard test method in powder metallurgy.

The porous copper powders produced by the processes of this invention generally contain residue consisting of a trace amount of tellurium, selenium, or mixtures thereof. The amount of such residue is usually between about 50 and about 300 parts per million parts of copper powder and generally depends upon the amount of metal mixed with the copper oxide powder prior to its reduction. The higher quantities of metal residue in the copper powder generally corresponds to the higher quantities of metal initially used in the mixture. When selenium is present in the copper oxide mixture, the residue in the copper powder is selenium; when tellurium is present in the oxide, the residue in the copper powder as tellurium, and when selenium and tellurium are both present in the copper oxide, the copper powder will contain selenium and tellurium residues.

The exact nature of the selenium and/or tellurium residue in the porous copper powder is not known with certainty, but it is believed, in view of the reducing conditions to which the copper oxide is subjected, to be in the form of elemental metal.

Whether or not such residues operate in producing the properties of low density-high green strength in the porous copper powder is also not known with certainty. Usually, however, the presence of residue impurities in metal powders tends to reduce the green strength of the metal powders and surprisingly the porous copper powders of this invention have a higher green strength than that heretofore obtainable despite the metal residue content.

The substantially uniform mixture of finely divided copper oxide and finely divided metal employed in the process of this invention can be readily formed, usually by conventional mechanical methods such as tumbling, ball milling or mixing the ingredients in a mechanical mixer. Because of the small quantities of finely divided metal employed (e.g. from about 500 to about 20,000 parts per million parts of copper oxide), it is usually desirable to first form a pre-mix composition containing from about 5 to about 20 weight percent of the finely divided metal with the balance consisting of finely divided copper oxide. This pre-mix, which is formed by conventional mixing techniques, is then mixed with additional finely divided copper oxide in an amount sufficient to provide and obtain a substantially uniform mixture containing the desired quantity of finely divided metal.

If the above described mixture contains less than about 500 parts per million of finely divided metal, the copper powder obtained usually will have an undesirably high apparent density and a low green strength. Although more than about 20,000 parts per million of finely divided metal can sometimes be employed, the use of greater

quantities is economically disadvantageous and copper powder produced from such mixtures sometimes will have a green strength below 2800 p.s.i. when pressed at 12 t.s.i. Generally, mixtures containing from about 1000 to about 3000 parts of finely divided metal per million parts of finely divided copper oxide are preferred since copper powders having properties (e.g. low density-high green strength) falling within the afore-defined ranges are almost always obtained when such mixtures are employed.

Finely divided copper oxide particles are employed because the process of this invention involves contacting the solid copper oxide particles in the above defined mixture with reducing gases at elevated temperatures. Such particles are in the micron size range and advantageously have an average particle size from 5 to 15 microns as measured by Fisher sub sieve sizer. If the copper oxide particles have an average particle size below about 5 microns, the copper powders produced therefrom may sometimes have a low green strength (e.g. below 2500 p.s.i.), on the other hand, if the copper oxide particles have an average particle size above about 15 microns, reduction time will be unduly prolonged and the resultant copper powder may sometimes contain small amounts of unreduced copper oxide which can also adversely affect the green strength of the copper powder. Finely divided copper oxide which has been found to be particularly advantageous for use in the process of this invention is obtained by mixing from about 40 to about 60 weight percent of copper oxide whose particles have an average particle size of from about 2 to 5 microns as measured by Fisher sub sieve sizer with from about 60 to about 40 weight percent of copper oxide powder whose particles have an average particle size of from about 10–15 microns as measured above. Such finely divided copper oxides have an average particle size of from 5–15 microns. When mixed with the finely divided metals (hereinbefore defined), the mixture can be readily reduced to form the copper powders of this invention.

The particle size of the particles of the finely divided metal is such that all or substantially all of the particles will pass through a No. 325 mesh U.S. standard screen. If metals having a coarser particle size are employed, high density-low green strength copper powder will usually be produced. Although the reasons for the criticality with respect to coarse particles is not known with certainty, it is believed that coarse particles do not have sufficient surface area to effect the desired conversion of copper oxide to a copper powder having the properties desired. Finely divided selenium, tellurium, or mixtures thereof whose particles pass through a 325 mesh screen may be advantageously employed.

As previously noted, the substantially uniform mixture of finely divided copper oxide and finely divided metal is reduced with reducing gas in a reducing zone at a temperature of at least about 900° F. If zone temperatures below 900° F. are employed, the copper powder obtained will not have the desired low density and high green strength properties hereinbefore defined. The low temperature criticality is surprising since prior art attempts to produce low density-high green strength copper powder have employed reduction temperatures in the range of from 500–700° F. to produce copper powders having only slightly lowered apparent density and slightly higher green strength.

Although zone temperatures of 1500° F. or higher may be employed in the above process, it has been found generally preferable to maintain the reduction zone at a temperature between about 900° F. and 1200° F. Zone temperatures of 1000° F. to 1100° F. are particularly preferred for reasons of economy and to obtain maximum uniformity within the copper powder produced. As will be evident hereinafter from the specific examples, the temperature of the reducing zone is achieved by conventional gas fired or electrical heating means.

The reducing gas employed can be any reducing gas conventionally used for the reduction of finely divided metal oxides such as, for example, gaseous carbon monoxide, hydrogen, dissociated ammonia, steam reformed natural gas, and the like, and mixtures thereof.

As will be seen below, the quantity of reducing gas employed will depend upon reducing capacity of the gas and the amount of copper oxide mixture which it is desired to reduce. Generally, the amount of reducing gas employed will be from about 10 to about 20 standard cubic feet of gas per pound of copper powder produced.

The finely divided copper oxide-metal mixture may be reduced in conventional reducing zones (such as a reduction furnace) using well known batch or continuous procedures wherein the mixture is contacted with a reducing gas stream within the temperature ranges hereinbefore defined. The contact of the gas with the mixture may be effected with the powdered mixture being fluidized by the gas which is introduced into the reaction zone as a flowing stream. Alternatively and preferably, the reduction is performed on a bed, preferably a thin bed, of the mixture. Reduction may be suitably accomplished by placing a thin layer (e.g. a layer of about ⅛" to ⅝" thick) of the copper oxide mixture on a movable metal belt and contacting the layer with a stream of reducing gas in the reduction zone by moving the belt through the zone. (A layer of ⅝" or less in depth is important in achieving total reduction of the oxide.) The flow of reducing gas through the zone may be concurrent cross current or counter-current to the movement of the thin bed of the mixture through the zone. However, more efficient contact of the reducing gas and the mixture in the zone is obtained when the bed of the mixture is moving in counter-current contact with the flow of the reducing gas stream. Although beds thinner than ⅛" can be employed, there is no advantage gained and the use of the reducing gas is inefficient in such circumstances.

The rate of gas flow through the gas stream is directly proportional to the amount of finely divided copper oxide-metal mixture to be reduced and has been found to be at least 10 standard cubic feet per hour per pound of reduced copper powder product produced at temperatures within the afore-defined ranges and when the contact time in the reaction zone is at least about 20 minutes using a finely divided copper oxide-metal mixture which is preponderantly cuprous oxide. The rate at which the reducing gas flows through the reduction zone must be increased by a factor greater than 2 if the mixture is preponderantly cupric oxide. Using preferred mixtures (e.g. mixtures which are preponderantly cuprous oxide) and an efficient reducing gas such as hydrogen or steam reformed natural gas, the gas flow through the reduction zone will be at the rate of from about 100 to about 120 cubic feet per hour per pound of copper powder produced when the contact time of the powder with the gas stream is from about 20 to about 25 minutes. By so proceeding, it is possible to obtain substantially complete reduction of the copper oxide. The moving belt passes the thin layer of mixture through the reduction zone and the mixture emerges from the zone as a thin layered, frangible agglomerated mass consisting substantially of elemental porous copper containing a trace amount of selenium, tellurium, or mixtures thereof depending upon the elemental metal originally mixed with the powdered copper oxide. The mass is de-agglomerated by comminution to particles having the afore-defined particle size and apparent density.

The following specific examples are intended to illustrate the invention, but not to limit the scope thereof, parts and percentages being by weight unless otherwise specified.

Example 1

Sixty-five hundred pounds of a powder consisting substantially of cuprous oxide particles having a particle size distribution between 10 and 15 microns were intimately

blended with 6500 pounds of "copper oxide dust," a finely divided cuprous oxide powder having an average particle size of 3 microns, to provide a uniform mixture which upon analysis was shown to have the following composition:

Ingredient:	Percent
Cu_2O	86.90
CuO	8.90
Free Cu	4.10
Hydrogen loss	11.64

Screen analysis

Screen (mesh):	
On 100	Trace
On 150	0.20
On 200	.10
On 250	12.80
On 325	17.10
Through 325	69.80

A pre-mix containing 90% powdered copper oxide and 10% powdered selenium was prepared by intimately blending 180 pounds of the above described copper oxide mixture and 20 pounds of powdered elemental selenium which had a particle size such that all of its particles passed through a No. 325 mesh standard screen.

One hundred twenty pounds of the pre-mix was then added to and mixed with 5,880 pounds of the initially prepared copper oxide mixture in a shell blender to provide 6000 pounds of a substantially uniform mixture of finely divided copper oxide containing 0.2% of powdered selenium. This mixture was layered on a 40 inch wide metal endless belt. The layer had a depth which varied between 3/16" to 1/4". The belt was passed through a furnace 20 feet long in hot section which was maintained at a temperature between 1000° and 1100° F. in hot section. The belt speed as it passed through the furnace was one foot per minute.

Simultaneously, there was charged into the furnace a stream of reducing gas (which had been heated to between 1000° F. and 1100° F.) consisting of steam reformed natural gas. The flow of the stream was countercurrent to the movement of the belt containing the thin layer of copper oxide mixture. The heated gas was sparged into the reduction furnace at a rate sufficient to provide a flow of 4000 standard cubic feet per hour through the 20 foot heated zone of the furnace. The copper oxide powder as it passed through the 20 foot reduction zone was reduced to copper by the time it had passed through the zone. As the copper emerged from the zone, it was in the form of a friable agglomerated layer which had increased in depth to 3/4" to 1". The layer was cooled, de-agglomerated and classified (using screens) to a particle size such that all the particles passed through a 100 mesh U.S. standard screen, 10% were retained on a 325 mesh screen, 90% passing through the latter screen.

The rate of production of the copper powder was between 270 and 280 pounds per hour and the yield was 5300 pounds of copper powder. The reduction of the total 6000 pounds lot of copper oxide required slightly more than 19 hours.

Analysis of the copper powder by the hydrogen loss method indicated a hydrogen loss of 0.66% demonstrating that it consisted substantially of elemental copper.

The copper powder had a green strength of 3,790 p.s.i. and an apparent density of 1.22 grams per cubic centimeter.

A copper powder prepared under substantially identical conditions, but which did not contain selenium or tellurium had a green strength of 2,230 p.s.i. and an apparent density of 2.2 grams per cubic centimeter. The copper powder contained a trace amount (e.g. 120 parts per million) of selenium.

Example 2

The procedure of Example 1 was repeated, except that the copper oxide powder mixture contained 0.2% selenium and 0.2% tellurium instead of the copper powder mixture employed in that example.

The copper powder obtained had a green strength of 3,125 p.s.i., an apparent density of 1.3 grams per cubic centimeter, and contained trace quantities of selenium and tellurium. Analysis of hydrogen loss (e.g. copper purity) of the copper was 0.44% demonstrating that the powder was substantially pure copper.

Example 3

The procedure of Example 1 was repeated except that the copper powder mixture contained 0.2% of tellurium instead of the 0.2% of selenium employed in that example.

The copper powder obtained had a green strength of 3,300 p.s.i. and an apparent density of 1.2 grams per cubic centimeter. Hydrogen loss was 0.48 indicating that the copper powder consisted substantially of pure copper. The copper powder contained 150 parts per million of tellurium.

Example 4

Ten pounds of each of the following copper oxide-metal powder mixtures were prepared using the amounts and ingredients listed below. The copper oxide employed contained 86.0% Cu_2O, 22% CuO_2, 2% free Cu, and had an average particle size of 12 microns and a particle size distribution between 10 and 15 microns. The metal powders were all finer than 325 mesh.

	Reduction Time (Min.)	Metal	Metal in Copper Oxide Powder, Percent
Composition No.:			
1	20	None	None
2	20	Te	0.05
3	20	Te	0.10
4	20	Te	0.20
5	20	Te	0.40
6	20	Te	0.60
7	20	Te	0.80
8	20	Te	1.00
9	30	Se	0.20
10	30	Se	0.30
11	30	Se	0.40
12	30	Te	0.20
13	30	Te	0.30
14	30	Te	0.40

The compositions were placed in metal trays at a bed depth of 1/2". The trays were placed on the metal belt and fed through the reduction furnace described in Example 1. The reduction conditions were identical except that the temperature of the furnace was maintained at 1500° F. for the first eight compositions and at 900° F. for compositions 9–14. Hydrogen gas was fed through the reduction zone at a rate of 4000 standard cubic feet per hour. After reduction to copper, the resultant agglomerates were de-agglomerated to the particle size of the copper particles of Example 1. Copper powders having the properties listed below were obtained:

	Apparent Density, Gms./cc.	Green Strength, p.s.i.	Hydrogen Loss, Percent
Copper Powder from Composition No.:			
1	1.84	2,190	0.13
2	1.59	2,850	0.19
3	1.40	2,908	0.20
4	1.47	2,800	0.24
5	0.90	3,650	0.39
6	0.92	3,750	0.50
7	0.86	4,033	0.49
8	0.85	4,015	0.54
9*	1.17	3,300	0.45
10*	1.01	2,900	1.03
11*	1.14	2,840	2.16
12*	1.00	3,800	0.28
13*	1.06	3,200	0.65
14*	1.02	3,013	0.52

*Reduced at 900° F. with 30 minute reduction time.

The above table demonstrates the increase in green strength and the lowering of apparent density of the compositions of this invention. The copper powder obtained from Composition 1 has the properties of copper powders obtained by prior art reduction techniques.

The table also shows that as the apparent density of the copper powder decreases, the hydrogen loss tends to increase. Such increase is due to the reaction of the increased surface with atmospheric oxygen due to the porosity of the copper particles after the reduction process. Such increased hydrogen loss in the copper powder can be prevented by placing the copper powder under an inert atmosphere such as nitrogen as soon as it is produced.

All of the above compositions except Composition No. 1 contain trace amounts (e.g. from 50 to 300 parts per million of residues of tellurium and/or selenium) the higher residues corresponding to the higher quantities of metal employed.

The copper powders of this invention are useful in areas where powdered copper compacted articles are manufactured and are especially useful in those areas in which apparent low density-high green strength copper powders are required.

What is claimed is:

1. Finely-divided porous copper powder containing between about 50 and about 300 parts per million parts of said powder of a residue selected from the group consisting of selenium, tellurium and mixtures thereof and having particles substantially all of which are finer than 200 mesh and at least about 90% of which are finer than 325 mesh; said powder having an apparent density between about 0.4 and 1.5 grams per cubic centimeter and a green strength of between about 2800 and about 4000 p.s.i. when pressed at 12 t.s.i.

2. The copper powder of claim 1 wherein said residue is selenium residue.

3. The copper powder of claim 1 wherein said residue is tellurium residue.

4. A process for making copper powder by reducing finely divided copper oxide with reducing gas in a reduction zone maintained at elevated temperature, the improvement for making copper powder having a low apparent density and high green strength which comprises the steps of (1) forming a substantially uniform mixture of said copper oxide and from about 500 to about 20,000 parts, per million parts of said copper oxide, of at least one finely divided metal selected from the group consisting of selenium and tellurium; and (2) reducing said mixture with said reducing gas in said zone at a temperature of at least about 900° F.

5. The process of claim 4 wherein said copper oxide is preponderantly cuprous oxide.

6. The process of claim 5 wherein said reduction is performed on a thin bed of said mixture.

7. The process of claim 6 wherein said bed is maintained moving in counter-current contact with a flow of said reducing gas in said reduction zone.

8. The process of claim 7 wherein the reducing gas flow is maintained at a rate of at least about 100 standard cubic feet per hour, per pound of reduced copper powder produced and the contact time in said reducing zone is at least about 20 minutes.

References Cited

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HYLAND BIZOT, *Primary Examiner.*

DAVID L. RECK, *Examiner.*

W. W. STALLARD, *Assistant Examiner.*