Patented Dec. 9, 1952 2,621,137

UNITED STATES PATENT OFFICE

2,621,137

REDUCING METAL POWDERS

Harold C. Miller, New York, N. Y., assignor to Charles Hardy, Inc., New York, N. Y., a corporation of Delaware

No Drawing. Application July 13, 1948, Serial No. 38,567

14 Claims. (Cl. 148—13.1)

1

This invention relates to the heating of metal powders in a reducing atmosphere to brighten the powder, or accomplish annealing thereof, and more particularly is concerned with carrying out such a process without substantial sintering or agglomeration of the powder.

Various powdered metals, usually reduced to a particle size of −50 mesh or less, are used for producing articles of many shapes and sizes by compacting or molding the powder under pressure and then sintering the molded powder to produce fusion of the particles and form a solid product. For this purpose, as well as others, it is highly desirable to employ metal powders which are as free from the oxides of the metal as possible. If the surfaces of the powdered metal particles are oxidized to any appreciable extent, such oxide is very detrimental in producing satisfactory sintered molded compacts. In fact, oxide on the surfaces of the metal particles can even result in the production of sintered compacts which entirely lack adequate cohesion and strength.

Many metal powders, and some more than others, are easily oxidized. Grinding the powder to reduce the particle size for example, frequently results in increasing substantially the amount of oxides in the powder.

Various approaches to this problem have been tried, and limited success has been achieved in reducing the oxides in the powder after the powder is compacted under pressure and while it is being sintered. Obviously, however, this procedure is not suitable for the production of dense solid products.

Heating metal powders in a reducing atmosphere has also been tried but if a temperature is employed high enough to reduce the oxides in a relatively short time, partial sintering of the powder results, and when the powder is reground to restore the original fine subdivision, the metal powder is re-oxidized. Also, if a residue of carbon, ash or other matter is left on the powder after it is reduced, this residue can also interfere materially with obtaining the proper cohesion and strength in a molded sintered product.

One object of my invention is to provide a process of reducing or annealing metal powders by heating the powder in a reducing atmosphere under conditions which produce a reduction of the metal oxides present but do not produce any substantial sintering or agglomeration of the powdered particles which would require subsequent grinding.

Another object of the invention is to prevent substantial sintering or agglomeration of the

2

powdered particles during a reducing heat treatment by incorporating in the powder a small proportion of a volatile, high boiling point substance that is stable, does not react chemically with the powder, or leave an objectionable residue after heating.

A further object of the invention is to select the amount of the substance incorporated in the powder before heating, by taking into account its volatility and the time and temperature of heating so that the substance is distilled off throughout the heating treatment without leaving any objectionable residue in the brightened or treated powder.

Other objects and advantages of my invention will be explained or will be apparent from the following description thereof.

I have found that oxidized metal powders of various types, both ferrous and non-ferrous, can be satisfactorily annealed or brightened to produce a loose, finely divided product relatively low or free from oxides by mixing with the powder a small amount of a substance that has a relatively high boiling point but is completely volatile at the temperature of heat treatment, that is stable enough so it will not decompose at the temperature employed to form elemental carbon, and that is unreactive chemically with the metal of the powder treated. This mixture is then heated at an appropriate temperature for a suitable time in a reducing atmosphere. Apparently such a substance, if properly selected and used in the proper amount, is continuously distilled off through the powder during the reducing heat treatment, and its volatilization serves to maintain the powder in loosened form by an action that is more mechanical than chemical in character, but which prevents substantial sintering or agglomeration of the particles during the heating and by keeping the powder loose assists to some extent in reducing the oxides present.

The substance selected will naturally vary with different metal powders which are heated to different temperatures, and the amount of the substance needed will vary depending upon its volatility and the time and temperature of heating. It is most desirable to provide enough of the material so that the last of it is distilled off at approximately the end of the heating treatment. Of course, if a slight residue of the substance is left, the powder can be reheated for a few minutes, or the heating continued for a few minutes longer. On the other hand, if the heating is continued for any substantial length of time after the last of the substance is distilled off, the powder settles and packs, and is apt to become partially sintered.

The time and temperature of the reducing heat treatment are not particularly critical, although it is desirable to avoid heating the powders to a true sintering temperature, and, on the other hand, it is desirable as a practical matter to employ a high enough temperature for the particular powder treated to reduce the oxides effectively within a relatively short time, such as 30 minutes or less. For example, plain copper powders may be satisfactorily reduced by heating at a temperature of the order of 600° C. for 30 minutes or less. Somewhat higher temperatures may be used for a shorter time and somewhat lower temperatures may also be employed, as will be understood by those skilled in the art.

Bronze and brass powders can be satisfactorily reduced using the same temperatures, although with some alloys heating may have to be continued for a somewhat longer period such as 45 minutes in order to obtain complete reduction.. With other alloys of copper, such as copper-lead powders, somewhat lower temperatures of the order of 400° C. are more suitable in order to avoid any sweating out of the lead. On the other hand, with ferrous powders, such as a plain iron powder, a reducing temperature of the order of 800° C. is usually desirable, and satisfactory reduction can be accomplished with the powder at this temperature for a period of 15 minutes. These times and temperatures are given simply by way of illustration and are not intended as a limitation on my process.

I also prefer to carry out the reducing heat treatment with the powder spread out in a relatively thin layer in shallow trays or boats, or distributed on a belt moving through a furnace. Layers from a fraction of an inch to three inches or more in depth may be treated successfully according to my invention.

The reduction of the metal oxides may be obtained by maintaining in the furnace an atmosphere of suitable reducing gas, preferably one that contains a high proportion of hydrogen. Pure hydrogen is preferable, although such gas as disassociated ammonia gas or cracked illuminating gas may also be employed. It is also desirable, of course, to maintain the reducing atmosphere around the powder while it is cooling from the highest temperature.

The substance added to the metal powder may be either a solid or a liquid, and I have found that high boiling point hydrocarbons or mixtures of such hydrocarbons are particularly satisfactory for this purpose. Other high boiling point organic compounds than hydrocarbons may be employed, if they have the proper volatility, do not react with the metal, and do not decompose under the conditions of heating to leave a deposit of carbon or other objectionable material in the final product. For example, I have found that various mineral oils are suitable for purposes of my invention, and waxes such as paraffin, can also be used. Polybutene has also been found satisfactory. Either single compounds or mixtures of compounds may be employed. On the other hand, turpentine and other vegetable oils carbonize at a relatively low temperature and are not suitable. Compounds that decompose during heating to form completely volatile constituents without leaving any ash or other deposits may be used.

The proportion of the substance employed will vary depending upon various factors such as the volatility of the substance used, the temperature and time of heating to be employed, and to some extent on the depth of the layer of powder subjected to treatment. As a general proposition, I have found that from about 0.3% to 2% is satisfactory for most purposes, although my invention is not limited to this particular range.

The process may be applied to metal powders in various conditions and may even be applied to powders fresh from the electrolytic bath which are still wet with water and electrolyte. In this case, however, it is usually desirable to employ a slightly higher proportion of the substance to be added since part of it is carried off by generation of steam as the wet powder is heated up.

The substance added to the powder may be simply stirred into the powder by any suitable form of light mechanical mixing. Thorough incorporation or a high degree of distribution of the material through the powder is not essential, and in fact if a powder is to be reduced in a layer of about ¼″ in depth or less, the volatile substance may be simply added to the surface of the powder before it is heated.

Highly oxidized powders may also be treated successfully by the process of my invention, although it is usually desirable in the case of a very highly oxidized powder to subject it successively to two separate reducing treatments with appropriate addition of volatile substances before each treatment. This is desirable because of the length of time required for good reduction at a single heating, and because the volatile substance may be distilled off completely some time before the end point is reached if the heating period is too long.

The following examples are given as illustrative of the process of my invention and show clearly the ease with which reduction can be accomplished by this procedure without producing sintering or agglomeration of the powder such as to require regrinding.

Example I.—An oxidized copper powder having a screen analysis of −80 mesh with over 40% of the powder −325 mesh was mixed with 0.5% by weight of "3 in 1" oil, spread out in a tray in a layer 0.25 inch deep and heated in a hydrogen atmosphere at 600° C. for 30 minutes. Upon cooling, the powder had a bright copper color, was practically free from oxides and still analyzed −80 mesh with 39.6% −325 mesh.

A sample of the same powder heated without the oil addition but with all of the other conditions the same, was agglomerated to such an extent that considerable attrition was necessary to break it up into a fine powder.

Example II.—The same powder was mixed with #10 W motor oil and heated in a layer 1.25 inches deep at 600° C. for 5 minutes. It was found that under these conditions an addition of 0.3% by weight of the oil produced a product that could be easily broken up by shaking on a screen, and that an addition of 0.5% produced a final product which was completely free and loose after heating.

Example III.—A sample of the same powder was heated under the conditions of Example I but mixed with 0.4% by weight of polybutene instead of the oil. The results were equally good.

Example IV.—The procedure of Example II was carried out by substituting paraffin chips for the oil and it was found that 1% by weight of the paraffin was needed to produce as good results as were obtained with 0.3% of the motor oil.

Example V.—An 80–10–10 bronze powder having a screen analysis similar to the copper powder in the foregoing examples was mixed with 0.5% by weight of "3 in 1" oil and heated in a layer 1.25 inches deep in a hydrogen atmosphere at 600° C. for 15 minutes. At the end of this treatment, the powder was shaken on a screen and found to be satisfactory for immediate use. A sample of the same powder heated under the same conditions but without the oil addition agglomerated or sintered into a hard mass that required regrinding.

Example VI.—A copper coated lead powder fresh from the chemical deposition bath was mixed with 0.5% by weight of "3 in 1" oil and heated in a 0.25 inch layer in a hydrogen atmosphere at a temperature of 400° C. for 30 minutes. Because of the very high oxygen content of the original powder (around 6%) this process was repeated a second time. At the end of this second treatment, the powder was a bright copper color and in a completely, satisfactory loose finely divided state.

Example VII.—Iron powder was successfully reduced to a bright gray powder by mixing it with 1% of #10W motor oil and heating it in hydrogen in a layer 1.25 inches deep at 800° C. for 15 minutes. The same powder heated under the same conditions without the oil sintered or agglomerated into a hard mass that had to be ground to reform it into a powder.

It will be apparent to those skilled in the art from the foregoing explanation and examples that my process can be carried out economically and simply with standard equipment to produce powders free from or extremely low in oxygen content and yet retaining completely their powdered form.

The procedure may be carried out in batches or continuously and the volatile substance may be added in any convenient manner to obtain at least a fair degree of distribution. If the substance added is a solid or a viscous liquid, it may be diluted or dissolved in a volatile solvent before it is added.

The terms and expressions which I have employed are used as terms of description and not of limitation, and I have no intention, in the use of such terms and expressions, of excluding any equivalents of the features shown and described or portions thereof, but recognize that various modifications are possible within the scope of the invention claimed.

I claim:

1. A process of annealing or brightening oxidized metal powder without substantial sintering thereof which comprises mixing with the powder a small proportion of a high boiling point, completely volatile, chemically stable substance, and heating the mixture in a reducing atmosphere to reduce metal oxides in the powder, the proportion of said substance being selected in accordance with the time and temperature of heating so that the substance is distilled off throughout the reducing treatment without leaving any appreciable residue in the brightened powder.

2. A process of annealing or brightening oxidized metal powder without substantial sintering thereof which comprises mixing with the powder a small proportion of a high boiling point, completely volatile, stable hydrocarbon, and heating the mixture in the form of a relatively thin layer in a reducing atmosphere to reduce the metal oxides in the powder, the proportion of said hydrocarbon used being selected in accordance with the time and temperature of heating so that the hydrocarbon is substantially completely distilled off throughout the reducing treatment.

3. In a process of heating a metal powder in a reducing atmosphere to brighten or anneal the powder and reduce metal oxides therein, the step of adding to the powder a high boiling point substance capable of complete volatilization at the temperature to which the powder is heated in an amount which is sufficient to supply products of volatilization in the powder throughout substantially the entire period of heating.

4. A process of brightening oxidized metal powder composed principally of copper which comprises adding to the powder a small proportion of a mineral oil that volatilizes without leaving a residue, and heating the powder and oil in an atmosphere containing hydrogen as a major constituent at a reducing temperature for said powder within the range of about 350° to 650° C. for a sufficient time to reduce oxides in the powder, the proportion of said oil added being sufficient to supply products of volatilization in the powder throughout substantially the entire period of heating.

5. A process of brightening oxidized metal powder composed principally of copper which comprises adding to the powder a small proportion of polybutene, and heating the mixture in an atmosphere containing hydrogen as a major constituent at a reducing temperature for said powder within the range of about 350° to 650° C. for a sufficient time to reduce oxides in the powder, the proportion of said polybutene added being sufficient to supply products of volatilization in the powder throughout substantially the entire period of heating.

6. A process of brightening oxidized metal powder composed principally of copper which comprises adding to the powder a small proportion of paraffin, and heating the mixture in an atmosphere containing hydrogen as a major constituent at a reducing temperature for said powder within the range of about 350° to 650° C. for a sufficient time to reduce oxides in the powder, the proportion of said paraffin added being sufficient to supply products of volatilization in the powder throughout substantially the entire period of heating.

7. A process of heating a metal powder composed principally of iron in a reducing atmosphere composed principally of hydrogen which comprises adding to the powder a small proportion of a high boiling point volatile hydrocarbon, and heating the mixture at a temperature of about 700° to 850° C. for a sufficient time to reduce oxides in the powder, the proportion of said hydrocarbon added being sufficient to supply products of volatilization in the powder throughout substantially the entire period of heating.

8. A process as defined in claim 4 in which the proportion of mineral oil is from about 0.3% to 1.0% of the weight of the original powder.

9. A process as defined in claim 5 in which the proportion of polybutene is from about 0.4% to 1.5% of the weight of the original powder.

10. A process as defined in claim 6 in which the proportion of paraffin added is from about 0.6% to 2.0% of the weight of the powder.

11. A process as defined in claim 7 in which the proportion of hydrocarbon added is from about 0.8% to 2.0% of the weight of the powder.

12. A process of brightening oxidized copper powder without substantial sintering thereof which comprises mixing a small amount of a completely volatile hydrocarbon oil with said powder, spreading the powder out in a relatively thin layer, and heating the layer in a reduc-

ing atmosphere for a few minutes at a temperature of about 600° C.

13. A process as defined in claim 12 in which the powder is bronze powder.

14. A process of brightening oxidized copper-lead powder without substantial sintering thereof which comprises mixing a small amount of a completely volatile hydrocarbon oil with said powder, spreading the powder out in a relatively thin layer, and heating the layer in a reducing atmosphere for a few minutes at a temperature of about 400° C.

HAROLD C. MILLER.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,905,809	Cowan	Apr. 25, 1933

FOREIGN PATENTS

Number	Country	Date
152,956	Switzerland	Feb. 29, 1932