

UNITED STATES PATENT OFFICE

2,181,123

TREATMENT OF METALLIC POWDERS

Joseph E. Drapeau, Jr., Calumet City, Ill., and
Louis G. Klinker, Hammond, Ind., assignors
to The Glidden Company, Cleveland, Ohio, a
corporation of Ohio

No Drawing. Application February 11, 1937,
Serial No. 125,304

9 Claims. (Cl. 148—11.5)

This invention relates to metallic powders, and has particular reference to a new and novel treatment designed to permit powdered metal, in particular powdered copper and its alloys, to be more readily compressed. In particular, it relates to the improvement of compressibility of powdered metal by first subjecting the powder to mechanical deformation which sets up internal stresses in the individual powder particles, followed by heating to remove the internal strains, the heating being at a temperature above the recrystallization point of the particular metal.

Powdered metal has been used for a good many years in the decorative industries, to simulate metallic leaf. This type of powder is made by milling or stamping thin sheets of metal, with a lubricant, and the resultant flake product, with its lubricant coating, has then been suspended in a menstruum for application.

More recently a demand has sprung up for metallic powders of nodule like shapes, free of such lubricating coatings, for manufacture into molded metal objects. The metallic powder is mixed with other metal powders to make a desired alloy, and the entire mass molded under high pressure to the desired shape. The molded mass is then sintered by heating, in order to sinter the mass and obtain the desirable mechanical strength. The older type of lubricated leaf powder is practically useless for this work.

This field of powdered metals has but recently been opened up. Because of the difference in action between metal in the powder form, and in large homogeneous masses, an entirely new technique has had to be developed. Any treatment of powdered metal must be of such type as not to interfere with the powdery nature of the material; and this factor has led to considerable difficulties in many instances.

Particularly in the manufacture of bearings and other molded objects made from powdered metals and non-metallics, extreme care in manufacture of the metal powder must be exercised, if a desirable finished molded object is to be obtained. One particularly essential characteristic is the manner in which the powder acts on molding. Ordinarily, on the application of pressure, a molded object is obtained which is then to be sintered; it is highly desirable that the molded object should not shrink on sintering, as such shrinkage is always uneven, and the resultant object will be out of shape. The characteristic desired is a fixed or constant slight expansion, in order to permit of finishing to shape by machining.

It has been discovered that the desirable expansion on sintering can be obtained by using a highly compressible metal powder. With copper, the principal metal powder in use, a simple standard test has been adopted by some users, which

comprises mixing 20 grams of powder and $\frac{1}{2}\%$ graphite and placing the powder in a mold of 0.20 square inch cross sectional area. The mixture is subjected to a hydraulic pressure of 20,000 pounds per square inch. The height of the molded cylinder should not be over 1.070 inches, as experience has indicated that shrinkage is obtained on sintering a less compressed mass. Lengths from 1.000 to 1.070 inches are considered good.

Copper powder with sufficient compressibility has been produced by electrolytic deposition of spongy copper, using cathodic current densities of 50 to 150 amperes per square inch, in the presence of certain colloidal agents. The spongy mass is washed as free as possible of electrolyte, and dried under non-oxidizing conditions. The outstanding disadvantages of this type of powder are high cost, and a marked tendency to reoxidize when exposed to atmospheric conditions. The traces of electrolyte salts, which remain even after prolonged washing, apparently serve as catalytic agents, promoting oxidation of the copper powder to the oxide.

Another method of making copper powder has been to stamp it out of thin sheets of copper metal, using a lubricant. The resultant powder, when examined under the microscope, is in the form of flat sheets, coated with lubricant. While excellent color and leafing are obtained in paint vehicles, the lubricant results in poor mechanical strength and electrical conductivity. The excellent color is due to the alloying of small percentages of zinc or aluminum with copper. This type of powder, because of its lubricant coating, is useless in the mechanical industries, and is largely confined to the paint industry.

It has also been proposed to obtain copper powder by reducing cupric or cuprous oxide powder, in a furnace, by the use of various reducing gases. The process may be carried out on the furnace hearth, or in trays. The mass that is removed from the furnace in the form of sintered lumps or cakes, is then broken up by milling. The resultant powder has an apparent gravity ranging from just above 2.5 up to 3.0 and higher; under the microscope, it gives the appearance of solid nodules. It has fair electrical conductivity, and may be used in bearings with fair results, but the compressibility is poor, the cylinders obtained on the standard compression test being often as high as 1.150 inches.

In the co-pending Drapeau application, Serial Number 3,499, filed January 25, 1935, there is described a method of producing a porous copper powder of low apparent density, porous structure and good mechanical properties, which is at the same time resistant to atmospheric corrosion, by the reduction of copper oxide powder with a gaseous reducing agent at temperatures of the

order of 350 to 700° F., while subjecting the mass to constant agitation. This powder gives exceptionally good results in the mechanical fields; but where high compressibility is desirable, it cannot be used, the standard molding having a length of from 1.090 to 1.120 inches.

We have tried to increase the compressibility of these powders by changing the conditions of reduction. With increases of temperature for the reduction, the compressibility increases slightly up to 700° F., and very slightly beyond. For example, a 325 mesh cuprous oxide, reduced at 550° F., gave a compression length of 1.120 inches. An increase in temperature to 600° F. gave a powder which compressed to 1.115 inches; a 700° F. reduction gave 1.110 inches; while a jump to 1350° F. gave 1.100 inches, and the powder had lost the desirable properties of porosity in the individual particles, and had increased in apparent density. The actual change from the very poorest to the very best was less than 5%, indicating how slightly the temperature of reduction affects this temperature.

We have also tried to change the compressibility of the powders by changing the particle size, with practically no effect. For powder reduced at 700° F., 325 mesh material gave a compression length of 1.100 inches, 150 mesh material gave the same figure, 100 to 150 mesh material gave 1.090, 100 to 40 mesh gave 1.100, and 40-20 mesh gave 1.095, indicating an optimum value at about 125 mesh powder.

We have discovered, however, that this copper powder and other copper, copper alloy and other metal powders of poor compressibility, can be improved in this regard, by first subjecting the metal to mechanical deformation which sets up internal stresses in the powder, followed by heating in a non-oxidizing atmosphere to eliminate these stresses, at temperatures above the recrystallization point of the metal.

The mechanical deformation to which the powder is subjected must be of such a nature as not to destroy the nodule powder structure, so that rolling at high pressure cannot be resorted to. We find that best results are obtainable by the use of impact mills such as the ordinary hammer mill. Ball mills which act partially by impact and partially by attrition, may likewise be used but tend to flake out the individual particles, although they do set up internal stresses; while attrition mills are practically useless for setting up these mechanical stresses in the particles from an economic viewpoint.

The mechanically treated powder is next heated in the absence of air, to eliminate the stresses in the powder particles set up by the mechanical deformation. The elimination of the stresses proceeds more rapidly as the temperature approaches the melting point of the metal; but it is necessary that the treating temperature be kept sufficiently below the melting point of the metal so that substantial sintering does not occur. The temperature should not, however, be permitted to drop below the recrystallization point of the metal. For copper powder, heating at 1600° F. is a safe upper point, while below 1000° F., the heating has but little effect; with an alloy of 90% copper and 10% tin, the upper limit for temperature is about 1500° F., reaction being inconsequential below 900° F.; while pure alpha iron powder should preferably be treated up to a maximum temperature of about 1650° F., with a minimum of about 900° F.

With most metals, the recrystallization tem-

perature is sufficiently below the melting point that temperatures considerably above this lower limit are required for efficient operation.

The time of treatment varies with the temperature, being less at the higher temperatures. With any powder, the heating required depends on the stresses set up in the powder treated, and the degree of compressibility desired. While increased compressibility is desirable up to and just beyond the point where the molded objects to be made will expand slightly rather than shrink, it is apparent that a uniform desirable compressibility is far more important than a maximum; and the mechanical action and heating should be controlled with this thought in mind.

After the heat treatment, the powder is cooled and broken up with the minimum amount of effort, preferably in an attrition mill. Further mechanical straining of the powder should be avoided, in order to prevent a loss of compressibility. This is why substantial sintering should be avoided, as the mechanical treatment necessary after sintering tends to destroy the effect of the heating.

As a specific example of our invention, we took 24,000 pounds of 150 mesh copper oxide, which was prepared by reducing copper oxide at 700° F. with reducing gas. This copper has an apparent density of 2.45 grams per c. c., and a compressibility of 1.100 inches, using a .20 square inch cross section area die, 20 grams of powder and 0.1 gram of graphite, subjecting it to 20,000 pounds per square inch pressure. This was uniformly fed into an impact pulverizer at a rate of 500 pounds per hour, using heavy hammers, and run through the mill, taking 48 hours for the complete mill test. The powder was then placed in trays and heated in an atmosphere of artificial gas, (mainly H₂ and CO), for 45 minutes at 1300° F. The resultant powder was cooled, broken up, and screened to 150 mesh. It had an apparent density of 2.90, a compressibility of 0.990.

To indicate the effect of mechanical action, the heavy hammers were replaced by the light hammers and medium hammers provided with these mills, with the following results:

Hammers	Time	Temperature	Apparent density	Compressibility
	Minutes	° F.		
Light.....	45	1500	2.67	1.085
Medium.....	45	1500	2.78	1.047

The same powder mechanically treated with the heavy hammers, was heated at varying times and temperatures, with the following results:

Time	Temperature	Apparent density	Compressibility
	° F.		
10 min.....	1200	2.60	1.080
30 min.....	1200	2.68	1.060
60 min.....	1200	2.75	1.048
10 min.....	1400	2.65	1.070
30 min.....	1400	2.75	1.050
60 min.....	1400	2.82	1.035
10 min.....	1600	2.65	1.080
30 min.....	1600	2.75	1.020
60 min.....	1600	2.95	0.950
90 min.....	1600	3.00	0.948

Bronze powder produced through the sintering together of freshly reduced copper powder and freshly atomized tin powder which is broken down into 150 mesh powder shows a compressibility of 1.135 and apparent density of 2.62. When

is same bronze powder is given a heavy mechanical deformation in an impact mill followed by a heat treatment at 1400° F. for 10 hours, and the lightly sintered mass is disintegrated in an attrition mill, it shows a compressibility of 1.010 and an apparent density of 2.90. However, a bronze powder which has not been thus deformed shows practically no change in compressibility thru such extended heat treatment.

Iron powder of 150 mesh and 2.23 apparent density made thru the reduction of pure iron oxide with reformed local city gas at 1300° to 1500° F. has an average compressibility length of 459. The compressibility of this iron powder may be decidedly changed thru a heavy mechanical deformation in an impact mill, which induces deformation of the individual particles of iron powder, followed by a heat treatment in neutral atmosphere at 1500° F. to 1600° F. for 60 minutes. The final compressibility is 1.100. Iron powder reduced and heat treated without mechanical deformation does not show any appreciable improvement in compressibility.

Other metal powders may of course be treated in a manner similar to that shown in the examples, to improve the compressibility thereof.

We claim:

1. The treatment for improving the degree of compressibility of a given powdered metal when compressed into solid shapes which comprises subjecting the powder to mechanical deformation to set up internal stresses in the powder particles, and thereafter heating the powder in a non-oxidizing atmosphere at a temperature and for a time sufficient to substantially reduce the internal stresses, but sufficiently below the melting point to prevent substantial sintering, all without substantial change in the powdery nature of the initial powder.

2. The treatment for improving the degree of compressibility of a given powdered metal when compressed into solid shapes which comprises subjecting the powder to mechanical deformation to set up internal stresses in the powder particles, and thereafter heating the powder in a non-oxidizing atmosphere at a temperature above the recrystallization point of the metal, but sufficiently below its melting point to prevent substantial sintering, for a time sufficient to substantially reduce the internal stresses set up by the mechanical deformation, all without substantial change in the powdery nature of the initial powder.

3. The treatment for improving the degree of compressibility of powdered copper when compressed into solid shapes which comprises subjecting the powder to mechanical deformation to set up internal stresses in the powder particles and thereafter heating the powder in a non-oxidizing atmosphere at a temperature and for a time sufficient to substantially reduce the internal stresses, but sufficiently below the melting point to prevent substantial sintering.

4. The treatment for improving the degree of

compressibility of powdered copper when compressed into solid shapes, which comprises subjecting the powder to mechanical deformation to set up internal stresses in the powder particles, thereafter heating the powder in a non-oxidizing atmosphere at 1000° F. to 1600° F. for a time sufficient to substantially reduce the internal stresses.

5. The treatment for improving the degree of compressibility of a mixture of copper and tin powders when compressed into solid shapes which comprises subjecting it to mechanical deformation to set up internal stresses in the powder particles, and thereafter heating the powder in a non-oxidizing atmosphere at 900 to 1500° F. for a time sufficient to substantially reduce the internal stresses.

6. The treatment for improving the degree of compressibility of alpha iron powder when compressed into solid shapes which comprises subjecting it to mechanical deformation to set up internal stresses in the powder particles, and thereafter heating the powder in a non-oxidizing atmosphere at 900 to 1650° F. for a time sufficient to substantially reduce the internal stresses.

7. The treatment for improving the degree of compressibility of a given powdered metal when compressed into solid shapes which comprises inducing internal stresses in the powder particles substantially wholly by impact, and thereafter heating the powder in a non-oxidizing atmosphere at a temperature and for a time sufficient to substantially reduce the induced internal stresses, but sufficiently below the melting point of the metal to prevent substantial sintering, all without substantial change in the powdery nature of the initial powder.

8. The treatment for improving the degree of compressibility of a nodule copper powder when compressed into solid shapes which comprises subjecting the powder to mechanical deformation to set up internal stresses in the powder without substantial destruction of the nodule powder structure, and thereafter heating the powder in a non-oxidizing atmosphere at a temperature and for a time sufficient to substantially reduce the induced internal stresses, but sufficiently below the melting point of the copper to prevent substantial sintering.

9. The treatment for improving the degree of compressibility of a powdered metal containing a metal selected from the class consisting of copper and iron, which comprises subjecting the powder to mechanical deformation to set up internal stresses in the powder particles, and thereafter heating the powder in a non-oxidizing atmosphere at a temperature and for a time sufficient to substantially reduce the induced internal stresses, but sufficiently below the melting point of the metal to prevent substantial sintering.

JOSEPH E. DRAPEAU, Jr.
LOUIS G. KLINKER.