

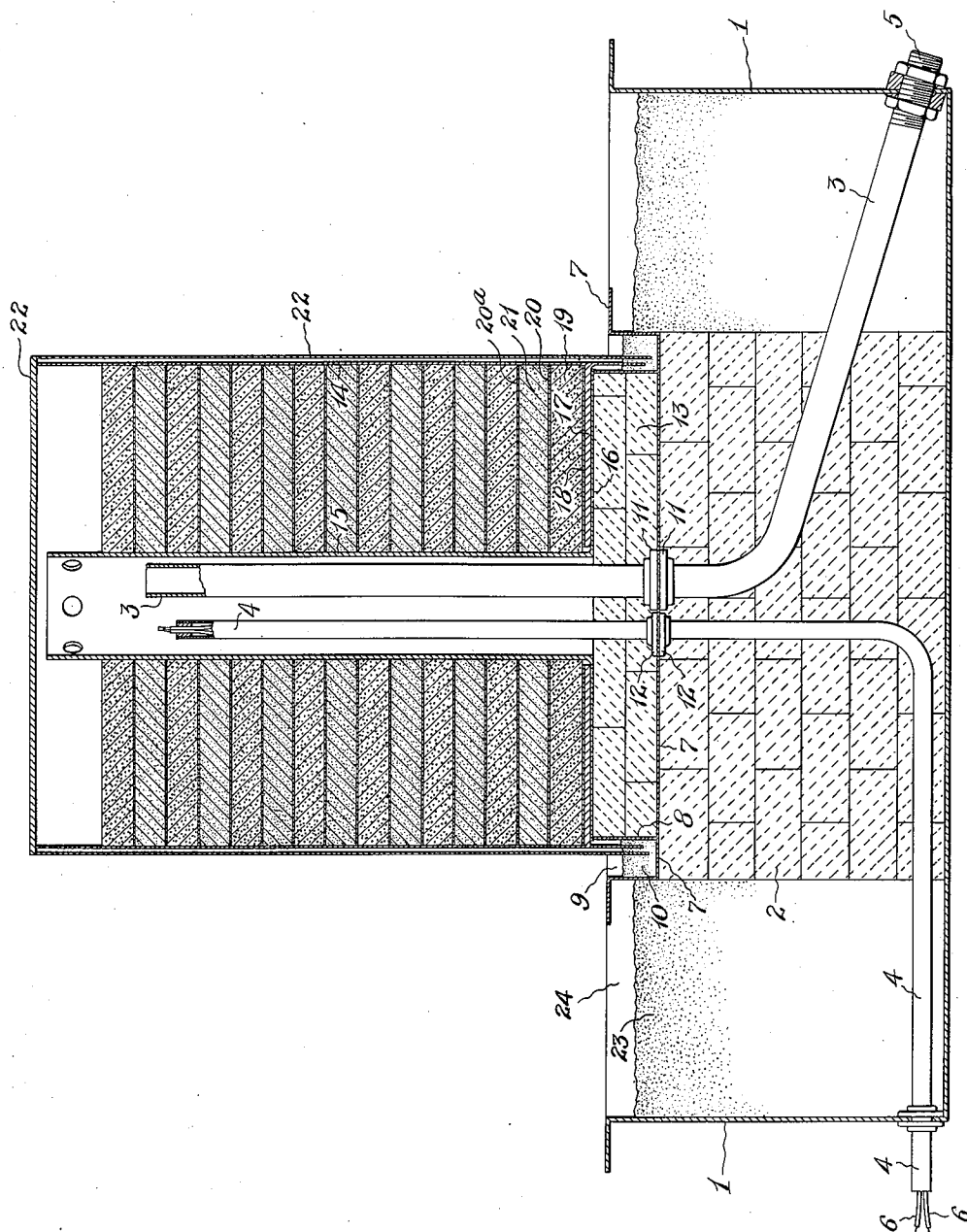
Nov. 4, 1941.

S. K. WELLMAN ET AL

2,261,196

PROCESS FOR MAKING METAL POWDER

Filed July 9, 1940



INVENTORS:

SAMUEL K. WELLMAN

CHARLES H. TOWER

BY

G. E. Christensen

ATTORNEY

UNITED STATES PATENT OFFICE

2,261,196

PROCESS FOR MAKING METAL POWDER

Samuel K. Wellman, Cleveland Heights, and
Charles H. Tower, Cleveland, Ohio, assignors
to The S. K. Wellman Company, Cleveland,
Ohio, a corporation of Ohio

Application July 9, 1940, Serial No. 344,558

10 Claims. (Cl. 75-122)

This invention relates to a process for the production of metal powders by carbonaceous reduction of a mixture of oxidic compounds of lead and oxidic compounds of one or more of the metals, iron, cobalt, nickel and manganese. It relates especially to metal powders the individual particles of which consist of an aggregate of lead and one or more of the foregoing high-melting-point metals, and to the process for producing such powders.

It is an object of the invention to provide a process by which oxidic metal compounds may be reduced by means of carbon in such manner as to form a loosely-sintered cake of reduced metal which may be readily separated from the unconsumed reducing agent and which may be readily disintegrated into fine particles of powder.

It is another object to provide a process by which mixtures of oxidic compounds of lead and oxidic compounds of the high-melting-point metals, iron, cobalt, nickel and manganese may be reduced conjointly to produce finely divided metal powders, the particles of which have the lead intimately dispersed throughout the pores and over the exposed surface of the individual particles of reduced high-melting-point metal.

It is a further object to provide metal powders the individual particles of which consist of aggregates of lead and high-melting-point metals, the aggregate particles being especially suitable for use in powder metallurgical processes.

In the manufacture of sintered powder-metal articles and particularly in the manufacture of sintered copper friction articles such as clutch facings and brake linings, it is customary to add small amounts of iron powder and lead powder to the copper powder for the purpose of producing desired frictional characteristics, rates of wear, strength, etc. Heretofore, it has been customary to make these additions by incorporating the proper proportions of the separate finely divided powders, but in manufacturing friction articles of the classes described above, we have found that it is desirable to provide a single metal powder the individual particles of which contain the iron and lead in relatively fixed proportions and which have the lead dispersed with moderate uniformity over the surface of the iron and preferably throughout the body of the iron. We have also found that powder particles of such character should be porous and spongy so that they will mat with the other powders when briquetted. As will be understood, such powders are difficult to make by a process which attempts to cast the desired composition in the molten state

for the reason that the molten metals are immiscible in each other in the liquid and solid states and hence do not alloy together. They accordingly must be treated by special and intricate procedures which are designed to trap the molten lead mechanically within the solidifying iron before it has an opportunity to settle out. Even when such procedures are resorted to, however, the resulting iron-lead casting may not be reduced to a powdered condition without breaking the mechanical structure which holds the iron and lead particles together. The same difficulties attend the production of nickel-lead, cobalt-lead and manganese-lead powders since these metals are mutually immiscible in the same manner as iron and lead.

Other methods for making aggregates of the character described have also been tried, such as by sintering lead powder with powders of one or more of the high-melting-point metals, or by mixing finely pulverized iron, cobalt, nickel or manganese in sponge form into molten lead, but none of these methods results in a product which may be reduced to a powdered condition without causing separation of the lead from the high-melting-point metal.

We have found, however, that if oxidic compounds of lead, such as the oxide, nitrate, sulfate, carbonate or singulo-silicate of lead, are intimately mixed with similar oxidic compounds of one or more of the high-melting-point metals, iron, cobalt, nickel and manganese, the mixture may be reduced by means of carbon at a temperature below the melting point of the high-melting-point metals with the formation of powder having the desired characteristics. We have also found that the resulting powder may be finely divided without causing appreciable separation of the lead from the high-melting-point metal.

Various processes have been proposed and are known for reducing iron oxide and the like by means of carbon at subfusion temperatures. In most of these procedures, however, the carbonaceous reducing agent is thoroughly mixed with the oxide. Such processes have the disadvantage that the reduced metal is contaminated with the excess reducing agent. Now since it is an object of this invention to produce a moderately pure product, recourse is had to a process in which the carbonaceous reducing agent is segregated or kept apart from the oxidic compounds of the charge. In accordance with our process, a charge is provided in which a suitable oxidic compound of lead is uniformly mixed with a suitable oxidic compound of one or more of the metals

iron, cobalt, nickel or manganese, the proportion of the lead in the mixture being preferably less than 50%. A charge of this type is introduced into a suitable reaction chamber preferably in such manner as to form a layer of uniform thickness therein. A carbonaceous reducing agent such as finely ground coal, coke, charcoal or other form of carbon is introduced into the chamber but is kept spaced from the oxidic material. For example, the reducing agent may be spread on top of the oxidic layer, being separated therefrom by means of a sheet of paper. The chamber should be heated externally and should be constructed in such manner as to permit the escape of gases liberated during the reduction but to prevent the ingress of air from outside. The chamber and its contained charge is heated to a temperature which is high enough to reduce the oxidic compounds of the charge but not high enough to melt the reduced high-melting-point metal, and is held at this temperature for a sufficient length of time to cause substantially complete reduction of the oxidic compounds. The chamber and charge are then permitted to cool, provision being made to protect the charge against reoxidation during cooling. After the charge has cooled substantially to room temperature, it is removed from the chamber and may be treated further. When the process has been properly conducted at an appropriate temperature and for an appropriate length of time as hereinafter indicated, the original layer of oxidic material will be found to have been reduced to the metallic state and to have formed a loosely-sintered cake or mass which may be removed bodily from any unconsumed reducing agent which remains. After any loose or adhering reducing agent has been blown from the surface of the sintered cake by means of an air blast, or otherwise removed, the cake may be pulverized in any suitable manner such as by merely tumbling in a revolving drum. The powder so obtained may be used by itself, with or without subsequent grinding in making sintered articles, or it may be mixed in any desired proportions with other metal powders and the resulting mixture made into sintered articles.

It will be understood that the process as described above is capable of producing a metal powder which is clean and uncontaminated with carbonaceous reducing agent. By means of this process, powders of desired purity may be produced by the simple expedient of providing suitably pure oxidic materials. It will be apparent, of course, that if impure oxidic materials are provided, the resulting powder will be contaminated with the impurities which are not vaporized and expelled from the chamber. These impurities will exist either in their original state or in a reduced state depending on whether or not they are affected by the reduction process. For example, if silicates are used, the resulting powder will contain silica. Likewise, if the oxidic compounds which are used contain such materials as alumina, magnesia, or the like, these materials will be found in the resulting powders. In general, the oxides or carbonates are to be preferred since they may be obtained commercially in a suitably pure condition. Whichever oxidic compounds are used should generally be finely ground where a finely divided powder is desired ultimately, since in general, if the oxidic compound is finely divided, a large percentage of the resulting powder will also be finely divided. The particle size of the reducing agent is less important and we have

found that a lump material is, in many cases, as suitable as finely ground material. As was pointed out, the reducing agent may consist of coal, coke, charcoal, or any other form of carbon.

5 Preferably, charcoal should be used since it has been found that this material aids in expelling, during the early part of the heating step, the oxidizing gases which are trapped within the reaction chamber. We also believe that the charcoal is more effective than the other forms of carbon in establishing the reducing atmosphere which is essential to the reduction, this atmosphere established at a lower temperature when charcoal is used than is the case with the other

15 forms of carbon.

This invention will be understood more fully through the following example explained in connection with the accompanying drawing. It will be understood that the process may be conducted 20 in a continuous manner but for purposes of illustration, a batch or intermittent process will now be described. The single figure of the drawing shows a supporting base and a reaction chamber which are suitable for performing the reduction, the base and container being especially adapted for use with any convenient bell-type heating furnace.

In the figure is shown a base structure consisting of an iron shell 1 partly filled with a central column 2 of insulating or refractory material and having a gas outlet tube 3 and thermocouple tube 4 embedded therein and extending outwardly near the base to beyond the shell 1 and extending upwardly above the column for purposes 35 which will be understood from the following description. The exposed end 5 of tube 3 may be threaded as desired for making suitable pipe connections. A thermocouple junction extends beyond the upper end of tube 4, and the thermocouple leads 6, 6 pass through tube 4 and extend from its lower end to any suitable temperature indicating device not shown. The base structure is adapted to support a reduction container, and, for this purpose, is surmounted with 45 a metallic cup-shaped container 7. A metal ring 8 is secured, as by welding, to the container so as to be spaced inwardly from the walls of the latter. An annular chamber 9 is thereby formed, this chamber being partially filled with any suitable pulverulent sealing material 10, such as sand or powdered Sil-O-Cel. The tubes 3 and 4 pass through the bottom wall of the container, being secured to it by means of suitable fittings 11, 11 and 12, 12. After the tubes have been positioned 55 in the container, the space enclosed by ring 8 is filled in with suitable refractory material 13, such as fire-clay, Sil-O-Cel, or the like.

The reduction container consists of an outer shell 14 and an inner tube 15. The tube 15 has an external flange 16 welded to its lower end. The outer shell 14 is open at both ends but has an internal flange 17 welded to its inner surface a short distance up from its bottom end. The shell and inner tube are placed together concentrically with the internal flange 17 resting on top of the external flange 16. An annular plate 18 rests on top of flange 17. In use, the assembly, constituting the reduction container, is placed so that flange 16 rests on the refractory material 13, the assembly being centered thereon so that tube 15 surrounds gas outlet tube 3 and thermocouple tube 4. The bottom end of shell 14 should extend into the sealing material 10 contained in the annular chamber 9 of the 75 container 7.

Assuming that the reduction container is capable of treating about 100 pounds of mixed oxides, and assuming that a pure iron-lead powder containing about 12% lead is to be made by the conjoint reduction of iron and lead oxides, approximately 88 pounds of pure magnetite, a mineral which may be obtained commercially and which contains 72% iron and 28% oxygen, is preferably ground so as to pass through a 40-mesh sieve. The ground magnetite is then mixed with slightly more than the stoichiometric weight of a suitable form of lead oxide, such as about 12 pounds of litharge, which preferably should have been ground to pass through a 100-mesh sieve. A slight excess of lead oxide is provided to allow for losses due to vaporization of the reduced lead. Mixing may be done by stirring the two powders together, or by stirring and subsequently regrounding the mixture in a ball-mill. In any event, the litharge and magnetite should be mixed in such manner as to provide a mixture which is as nearly uniform as possible. If it were desired to include a small amount of silica in the resulting powder, a lead silicate could be substituted for part of the oxide.

About 25 pounds of charcoal, a weight corresponding to an excess of about 25% over stoichiometric proportions, is provided, and merely for convenience in handling, is ground to moderate fineness. A portion of the charcoal weighing approximately 5 pounds is first spread into a uniform layer 19 upon base plate 18. A disc of paper 20, having a diameter equal to the inner diameter of shell 14 and having a central hole in it corresponding in size to the outer diameter of tube 15, is slipped down around the tube so as to cover the charcoal layer. A portion of the oxide charge is then spread upon the paper disc so as to form a layer 21 of uniform thickness. Another paper disc 20a is then slipped down around the tube to cover this last layer. Another charcoal layer weighing about one-fourth of the weight of the metal oxide layer 21 is then spread upon the second paper disc. This alternate arrangement is continued until the desired weight of mixed oxides and the corresponding weight of charcoal have been inserted. Preferably the top layer should be of charcoal, but it is relatively immaterial whether it consists of oxide or charcoal. The layers of oxide and charcoal should not fill the container completely since it is desirable to provide an expansion chamber of appreciable size at the top of the container.

After the charge has been inserted in the manner just described, the container is closed by means of a closely-fitting cup-shaped mantel 22 which is slipped down over shell 14. The mantel should be substantially the same length as the shell so that its lower end will penetrate into the sealing layer 10. In this way, the container is substantially closed to the escape of gases therefrom except through tube 3. By reason of this construction, it will be understood that as long as gases pass outwardly through the tube 3, the influx of air from outside will be prevented. After the mantel 22 has been placed over the container, any suitable bell-type heating furnace may be lowered around the assembly and brought to rest upon suitable supports which permit the lower end of the furnace to penetrate into a bed of sealing material 23, such as powdered Sil-O-Cel, filling the annular cavity 24 between column 2 and the walls of

shell 1. The heating furnace may be then connected to a suitable electric circuit and the heating cycle begun. Shortly after the heating unit has been connected, it will be found that gases escape from tube 3. At first these gases will be found to be of an oxidizing character, but after a short while, they will have changed sufficiently to become combustible. At that time, the gases issuing from the end of the tube may be ignited to form a pilot flame. To a skilled operator, the character and condition of the flame serves as an indication of the manner in which the reduction is proceeding.

It has been found that in effecting complete reduction of the oxides and at the same time sintering the reduced metal into a self-sustaining cake, the charge may be heated to as high a temperature as 2000° F., but we have found it preferable to operate below about 1800° F. Of course, the minimum temperature to which the charge must be heated is the temperature at which the reduction of iron oxide takes place. We have found, however, that if the temperature is lower than about 1500° F., the time required to complete the reduction is too long for economical operation. The preferred temperature range accordingly lies between 1500° F. and 1800° F. With a charge containing about 100 pounds of mixed oxide, we have found that complete reduction and proper sintering may be effected by holding the charge within this range of temperatures for a period of about 2 hours after the charge has been heated thereto.

When reduction is complete, the heating unit is disconnected from the electric circuit and hoisted away from the base and container so that the charge may cool faster. Exit tube 3 should be connected at this time to a source of reducing gas, such as natural or artificial illuminating gas, so that as cooling occurs, the reducing gas will be drawn into the container. After the charge has cooled to about room temperature, mantel 22 may be removed and the charge emptied onto a screen, for example, where the cakes of metal may be separated from the charcoal. The metal cakes may then be freed of adhering charcoal by blowing them with an air blast. The cakes obtained in this way are very clean and are practically uncontaminated with charcoal.

The metal cakes which are so obtained consist of fine particles or grains of iron loosely bonded together. As previously indicated, the cakes may be readily broken down into their component particles of an iron-lead aggregation. In grinding the cakes we have found that the aggregation is of such nature that there is little or no separation of the lead from the iron. This fact, together with the other observations and with the fact that lead is but slightly soluble in iron, leads us to the belief that the two metals are retained together as a physical or mechanical mixture rather than as an alloy. It will be appreciated that many difficulties are involved in determining the exact nature of the aggregation. Our experience in treating and handling the material, however, leads us to believe that a large part of the lead is entrained in the pores of the sponge iron or is otherwise united in close physical union with the extensive surface of the porous iron particles.

An iron-lead powder having the above mentioned characteristics may be pressed and sintered by the usual methods so as to form strong dense articles from which there is little, if any,

liquation of the lead during the sintering step. Furthermore, as has been pointed out previously, iron-lead powder having the above mentioned characteristics is particularly desirable for mixing with copper powder in the manufacture of porous bronze friction or anti-friction articles such as bearings, clutch facings, brake linings, etc.

It will be understood that the process just described exemplifies also the procedure which may be followed in reducing lead oxide conjointly with an oxidic compound of nickel, cobalt or manganese. Those skilled in the art will, of course, recognize that the preferred temperature range given above for iron is not necessarily the preferred temperature range for these other metals. In the case of cobalt, a reduction temperature in excess of 1800° F. is preferred except when iron is present. In the latter case, a small amount of iron oxide or other oxidic compound of iron aids in reducing the temperature at which the reduction proceeds at a commercial rate, temperatures of 1700° to 1800° F. being suitable. In the case of nickel or manganese, temperatures of 1800° to 1900° F. are suitable when no iron is present, but as in the case of cobalt, when iron is present, a slightly lower temperature may be used. It has been found that temperatures below 2100° F. are suitable for reducing any of the above high-melting-point metals, and that the process may be carried out at temperatures as low as 1500° F. When more than one high-melting-point metal is present in the reduction mixture, due regard should be given to the fact that the resulting powder may consist of an alloy of those metals and that the alloy may have a melting point below the melting point of each of the individual high-melting-point metals which compose it. When this feature is given consideration, a suitable temperature may be selected which will avoid melting the high-melting-point alloy powder. Incipient melting should be avoided in all cases since it impairs the sponginess of the powder or may even destroy it. Furthermore, it impairs the formation of powder particles having the aggregate characteristics which are desired.

Modifications of the process will occur to those skilled in the art since many variations are possible in the matter of temperatures, rates of heating, compositions, etc. It should accordingly be recognized that the scope of the invention is to be determined from the following claims rather than from the illustrative example described above.

Having now explained the invention, what we claim is:

1. The method of making metal powder consisting of grains of high-melting-point metal interspersed with lead particles, said method comprising the steps of: providing a finely divided reduction mixture consisting substantially of a minor quantity of at least one oxidic compound of lead mixed with a major quantity of at least

one oxidic compound of at least one of the high-melting-point metals selected from the group consisting of iron, cobalt, nickel and manganese; heating said reduction mixture to an elevated temperature in a reduction chamber in the presence of at least a stoichiometric quantity of solid carbonaceous reducing agent which is disposed adjacent said oxidic material but segregated effectively therefrom to prevent contamination of the oxidic material therewith, said elevated temperature being sufficiently high to cause said carbonaceous reducing agent to reduce the oxidic compounds of the charge, but not high enough to melt the reduced high-melting-point metals; continuing said heating at said elevated temperature for a period of time sufficient to sinter the reduced metal into a coherent loosely-bonded mass which subsequently may be removed substantially bodily from said reduction chamber; thereafter cooling the reduced mass while maintaining it under conditions which substantially prevent its reoxidation; separating the cooled mass from any remaining carbonaceous reducing agent; and disintegrating the loosely-bonded mass into its component particles of lead-retaining high-melting-point metal.

2. The method as claimed in claim 1 wherein the elevated temperature at which said reduction is effected lies between about 1500° F. and about 2100° F.

3. The method as claimed in claim 1 wherein said reduction mixture consists of iron oxide and lead oxide.

4. The method as claimed in claim 1 wherein said reduction mixture consists of about 88% iron oxide and about 12% lead oxide.

5. The method as claimed in claim 1 wherein said reduction mixture consists of about 88% high purity magnetite and about 12% litharge.

6. The method as claimed in claim 1 wherein said reduction mixture consists of nickel oxide and lead oxide.

7. The method as claimed in claim 1 wherein said reduction mixture consists of manganese oxide and lead oxide.

8. The method as claimed in claim 1 wherein said reduction mixture consists of about 88% magnetite and about 12% litharge and wherein the elevated temperature at which said reduction is effected lies between about 1500° F. and about 1800° F.

9. The method as claimed in claim 1 wherein said reduction mixture and reducing agent are initially separated by means of a sheet of paper.

10. The method as claimed in claim 1 wherein said reduction mixture and solid carbonaceous reducing agent form a plurality of superimposed layers composed alternately of reduction mixture and of reducing agent, and wherein adjacent layers are effectively separated from contact with each other initially by means of a sheet of paper.

SAMUEL K. WELLMAN.
CHARLES H. TOWER.