United States Patent Office 2,754,195
Patented July 10, 1956

2,754,195

PROCESS FOR MAKING COPPER-IRON POWDER

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No Drawing. Original application December 29, 1953, Serial No. 401,063. Divided and this application May 9, 1955, Serial No. 507,159

3 Claims. (Cl. 75—.5)

This invention relates to a process for making articles consisting essentially of copper and iron, having a high tensile strength and high density and more particularly to a process for making copper-iron powder from which such articles may be fabricated by powder metallurgy methods.

This case is related to a copending application of Marion Ernest Graham and William A. Reed entitled "Process for Making Copper-Iron Powder," Serial No. 401,064, filed December 29, 1953. This copending application discloses a method for making copper-iron powder by the reduction of iron oxide in the presence of certain reducible copper compounds or metallic copper and particularly in the presence of gaseous hydrogen chloride which must be supplied from an external source. The line of division between the invention of that application and the present invention resides in the fact that the present invention relates to the reduction of certain iron and/or copper compounds by hydrogen. The supplying of gaseous hydrogen chloride from a separate source during reduction is not a necessary feature of the present invention. Said copending application relates to the production of copper-iron powder by a reduction step effective on iron oxide plus a source of copper by hydrogen wherein HCl gas must be supplied from an external source during the reduction.

The present case is also a division of our prior and copending application Serial No. 401,063, filed December 29, 1953, for "Process for Making Copper-Iron Powder." The line of division between the present case and its parent application Serial No. 401,063 is that the present case is limited to the treatment of a starting mixture including metallic copper with one or more of the chlorides of iron; whereas the parent application, Serial No. 401,-063, is limited to the treatment of a starting material including metallic iron powder of either of two particular kinds in admixture with an oxide and/or a chloride of copper.

High strength and high density articles consisting essentially of copper and iron have found numerous industrial applications, notably in the manufacture of turbine blades and other parts subjected to wear and requiring quite high strength. In the past, such parts have been produced by such methods as infiltration of molten copper into iron parts previously prepared by powder metallurgy methods and the coining of parts made from mixtures of copper and iron powders. While such methods may be effective in producing articles having a high tensile strength, they are objectionable in that they involve substantially more complexity and expense of operation than do powder metallurgy processes.

It is an object of this invention, therefore, to provide a process for making articles of high tensile strength consisting essentially of copper and iron that utilizes the relatively simple methods of powder metallurgy.

It is a further object of the invention to provide a process for making copper-iron powder, which is capable of being formed into articles having a high tensile

strength and high density by pressing and sintering and without the necessity of infiltration, coining or similar operations.

Other objects of the invention will be in part apparent and in part pointed out by the subsequent description.

The process of the present invention may be carried out by reducing iron chloride with metallic copper in finely divided form as copper powder, these materials being in intimate admixture prior to the process thereof in accordance with the present invention. The reduction is effected with hydrogen or a gas containing hydrogen. It has been found that in order to produce a copper-iron product having the desired physical properties in accordance with the present invention, an actual chemical reduction of the iron chloride must take place while it is in intimate contact with the copper powder as aforesaid. In some cases it may be desirable to produce a metal powder having some predetermined carbon content. To this end it may be necsssary to add a small amount of carbon (e. g. about 1%) to the starting mixture.

After the ingredients of the starting material, selected in accordance with the principle outlined above, have been mixed together in the proportions that will result in the desired ratio of iron to copper in the reduced product, the starting material is introduced into a reaction zone and there contacted with a reducing gas containing hydrogen. The solid starting material and the reducing gas are both maintained at an elevated temperature in the range of about 1000° F. to about 1800° F. and contact between them is continued until the reduction of the hydrogen-reducible iron compound has been substantially completed. The resultant material is then cooled and, in the event that it be in a massive or semi-sintered condition, is comminuted to powder. This copper-iron powder may then be pressed to a self-sustaining mass of predetermined size and shape, which is subsequently sintered in a suitable non-oxidizing atmosphere usually at a temperature of about 2000° F. The physical properties of the resulting article will be in part dependent upon the ratio of iron to copper contained therein, the pressure at which it was molded, the sintering temperature and other factors, but in all cases the product of the present invention will have a higher tensile strength than conventional copper-iron parts of the same chemical composition which have been pressed and sintered under similar conditions respectively. In some instances, the tensile strength of articles made in accordance with the process of the present invention will exceed 100,000 pounds per square inch.

Summarizing the present invention, copper-iron powder suitable for use in powder metallurgy for forming articles having high tensile strength and high density is produced by introducing into a reaction zone a starting material, the essential active ingredients of which consist of: metallic copper powder and a chloride of iron which may be either ferric or ferrous chloride or a mixture of the two and which is hydrogen-reducible; and then contacting said starting material with a reducing gas containing hydrogen as an essential active reducing ingredient under such conditions of temperature and for such a time as to reduce the hydrogen-reducible compound to metallic iron.

Since it is an object of the present invention to produce a copper-iron powder, the ingredients of the starting material are preferably provided in finely-divided form. This further facilitates thorough mixing of the ingredients of the starting material, which is necessary to insure the production of a chemically uniform and homogeneous material.

The ingredients used for the starting material must include at least one copper-containing ingredient and at

least one iron-containing ingredient. The copper-containing ingredient in accordance with the present invention is metallic copper, which is in finely divided or powder form. This metallic copper may be derived from any source whatsoever, provided it is present in a form sufficiently finely divided so that it may be thoroughly mixed with the iron-containing ingredient. In practice, it has been found that copper powder having an average particle size of about ten microns is satisfactory, but the copper need not be this finely divided to be useful in the process. All that is required is that the metallic copper used shall have a particle size sufficiently small to insure the production of a substantially homogeneous mixture as the starting material. The same consideration is controlling with regard to the particle size of the iron chloride ingredient of the starting material.

The iron-containing ingredient of the starting material may be either ferric or ferrous chloride or a mixture of the two. It is believed that when ferric chloride, for example, is reacted with a suitable reducing agent, such as hydrogen, it is initially converted to ferrous chloride as an intermediate stage in the reduction of the iron to its metallic form or to an oxidation state of zero. Whether this theory be accurate or not, it has been found that both the ferric and ferrous forms of iron chloride are equally effective and as such are the equivalents of one another for the purposes of the present invention. They are both intended to be included in the term "iron chloride" as that term is used throughout the present case.

It is further understood that the term "iron chloride" is meant to include those compounds which decompose easily under the influence of heat to form such chloride including, for example, the hydrated forms of iron chloride which are known. Because of the low evaporization point of ferric chloride (700° F.), it is somewhat inconvenient to reduce this compound while mixed with copper since the ferric chloride may vaporize and pass out of contact with the copper before reduction takes place. For this reason it is usually preferred to use ferrous chloride where iron chloride is required. However, both the ferric and ferrous chlorides are considered equivalents of each other for the purposes of the present invention.

It is essential to the production of high strength articles, which is an object of this invention, that the ingredients of the starting material be selected in such a way that at least one of them (a hydrogen-reducible iron chloride) is reduced in the presence of the other (metallic copper). Thus, metallic copper and metallic iron (even iron made in the presence of HCl or by reducing iron chloride) and when no hydrogen-reducible material is present, the whole then treated in hydrogen, did not produce the desired material. Subsequent examples will illustrate that copper-iron powder made in this way is definitely inferior as to its tensile strength to copper-iron powder made in accordance with the teachings of the invention. The fact that a chemical reduction reaction takes place while the ingredients are mixed together appears to be necessary for the production of the novel copper-iron powder of the present invention, which is capable of producing sintered bodies of unusually high tensile strength. The reason for this novel requirement of the present invention is not fully understood.

After the ingredients of the starting material have been selected in accordance with the principles outlined above, they are proportioned so as to result in a reduced powder having the desired ratio of copper to iron and are thoroughly mixed. In order that thorough mixing take place, it is desirable that the starting ingredients be supplied in the form of powder, and preferably, as finely divided as is convenient. In practice it has been found that excellent mixing is obtained by the use of —100 mesh starting materials.

The mixed ingredients may then be placed in a suitable container, such as a metal boat or pan, and introduced into a reaction zone, wherein the hydrogen-reducible iron compound constituent of the starting material is reduced. In order to insure maximum yield based on the amount of raw material used, it is necessary that the chemical reaction be carried to substantial completion. By this it is meant that the iron of the hydrogen-reducible iron compound be reduced to an oxidation state of zero. This phrase, as used in this description and the appended claims, is meant to embrace both the production of either a physical mixture of elemental metallic powders or the production of some alloy of copper and iron alone or which may be mixed with a simple mixture of copper and iron. In any case the metallic constituents are present in an oxidation state of zero as opposed to the positive oxidation state in which the iron chloride ingredient was introduced in the starting material.

The conditions of reduction are not critical to the success of the process, except that they must be sufficient as to both time and temperature as to insure substantially complete reaction between the hydrogen-reducible iron chloride and the hydrogen-containing gas. In practice it has been found that temperatures of the order of 1200° F. are adequate for completing this reduction in about two hours. Lower temperatures, for example about 1000° F. are fully operative, but require a longer time. Unduly high temperatures may cause the production of a hard sintered product, which will be difficult to grind. This condition is to be avoided, since one of the objects of the present invention is the production of pulverulent material, which may be used in powder metallurgy processes. It has been found that temperatures up to about 1800° F. will result in the production of material which is quite frangible and thus may be comminuted to powder without undue trouble or expense.

After the reduction has been completed, the reduced powder is cooled in a non-oxidizing atmosphere to about 200° F. or less. The resultant mass is then comminuted to powder, which is then used in various powder metallurgy processes, according to standard practice.

The process of the present invention is further illustrated by the following examples, which are not intended as narrowly limiting upon the scope of the present invention.

Example I

Anhydrous ferrous chloride and metallic copper in flake form were blended in a dry state in such proportions that a completely reduced product would contain about 85% iron and 15% copper by weight. The mixture was spread on a tray to a depth of about ¼ inch and the tray placed in an electrically heated muffle furnace. Dry hydrogen was passed through the furnace over the surface of the mixture at the rate of 6000 cubic centimeters per minute. The temperature of the contents of the furnace was raised to 1200° F. over a period of about one hour. These conditions of hydrogen flow and temperature were maintained for three additional hours. The sealed inner tube of the furnace was then removed from the heating muffle and the contents allowed to cool to a temperature below 200° F. The completely reduced copper-iron product, which had formed into a semi-sintered, but easily frangible, cake was then ground to a particle size of about —100 mesh. The powder was found by analysis to contain 16.3% metallic copper and 83.7% metallic iron. This powder was mixed with 1% zinc stearate as a lubricant, pressed at 50,000 p. s. i. to form a standard test bar, which was sintered in hydrogen at 2000° F. for one hour. The resulting piece had a tensile strength of 77,500 p. s. i. A test bar prepared under identical conditions of pressing and sintering from a mixture of flake copper and commercial iron powder (made by the reduction of iron oxide) in the proportion 85% iron and 15% copper and tested under parallel conditions had a tensile strength of only 34,300 p. s. i. A subsequent coining or similar reworking operation would be necessary to raise the strength of this latter piece to

an acceptable value, such reworking being avoided in accordance with the present invention.

As compared with the above, when a reduced metallic iron made by the hydrogen reduction of ferrous chloride is mixed with metallic copper, both metals when mixed being in finely divided form, and mixed in the proportions of 15% copper and 85% iron, then pressed and sintered according to the standard procedure above set forth, a piece having a tensile strength of only 48,200 p. s. i. was obtained. This clearly indicates that an actual chemical reduction must take place while the ingredients of the starting material are in contact with one another in order that the novel and desirable results of the present invention shall be attained.

While there have been disclosed herein several specific processes and certain variants thereof, other alternatives and equivalents will occur to those skilled in the art from the foregoing disclosure. We do not wish to be limited, therefore, except by the scope of the appended claim, which is to be construed validly, as broadly as the state of the prior art permits.

What is claimed is:

1. The process of making copper-iron powder suitable for use in powder metallurgy for forming articles having high tensile strength and high density, comprising the steps of introducing into a reaction zone a starting material, the ingredients of which consist essentially of iron in the form of at least one of the chlorides of iron and finely divided metallic copper, and contacting said starting material in said reaction zone and at an elevated temperature with a reducing gas containing hydrogen as its essential active reducing ingredient for a time and under conditions sufficient to reduce the iron of said iron chloride to an oxidation state of zero.

2. The process according to claim 1, in which the chloride of iron present is reduced in the range of about 1000° F. to about 1200° F.

3. The process according to claim 1, in which the chloride of iron initially present is ferrous chloride, and in which said elevated temperature at which the ferrous chloride is reduced is about 1200° F.

No references cited.