March 27, 1945. F. R. HENSEL ET AL 2,372,203

SINTERED METAL ARTICLES AND PROCESS OF MAKING

Filed Sept. 6, 1943

Fig. 1

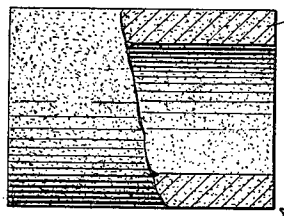
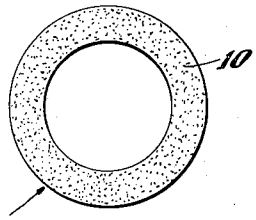



Fig. 2




SINTERED METAL POWDERS
COPPER BASE, NICKEL OR COBALT, SILICON, PHOSPHORUS

Fig. 3

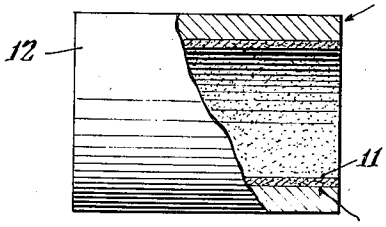
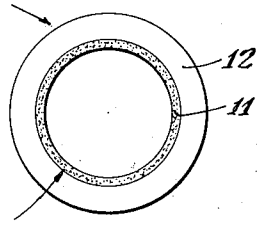



Fig. 4




SINTERED METAL POWDERS
COPPER BASE, NICKEL OR COBALT, SILICON, PHOSPHORUS

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## SINTERED METAL ARTICLE AND PROCESS OF MAKING

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Application September 6, 1943, Serial No. 501,337

10 Claims. (Cl. 75—22)

This invention relates to copper base sintered metal compositions and to articles such as bearings, made therefrom.

The present application is a continuation-in-part of our application Serial No. 333,928, filed May 8, 1940.

An object of the invention is to improve the physical properties such as the soundness, strength, hardness and wear resistance of such compositions and articles.

Other objects of the invention will be apparent from the following description and accompanying drawing taken in connection with the appended claims.

In the drawing:

Figure 1 is a longitudinal section through a bearing made from pressed metal powders according to one aspect of the present invention;

Figure 2 is an end view of said bearing;

Figure 3 is a section through a bearing of modified construction; and

Figure 4 is an end view of the bearing of Figure 3.

This invention contemplates the manufacture of metal powder articles, such as bearings from copper powder, containing nickel or cobalt with silicon and phosphorus. Such manufacture may involve the steps of pressing metal powders using suitable dies and presses, sintering the compressed articles thus produced and subsequently applying an age-hardening heat treatment. The present invention makes possible the fabrication of articles of greater strength, hardness and wear resistance than has heretofore been possible while obtaining the economies incident to the use of pressed powders as distinguished from casting of molten metal and the like.

Because of its high strength and low cost it is possible to produce a solid bearing by this invention, thereby avoiding the difficulties of prior art lined bearings such as poor bond between lining and backing, differences in thermal expansion coefficients, and the like.

By using pressed powders, it is possible to press the articles to the desired dimensions and shape in a single operation by using a suitable die and consequently extensive and time-consuming machining and grinding operations are not required or are required only to a very limited extent. While bearings have heretofore been made from pressed metal powders it has not heretofore been practicable to produce pressed powdered bearings of the high strength and hardness which results from the application of the present invention.

We have found that a body can be produced from copper powders which is of high strength and hardness by incorporating either nickel or cobalt and silicon in the powder mix to form nickel silicide or cobalt silicide, which is capable of precipitation as a dispersed phase in the sintered copper body upon application of a suitable age hardening treatment. However, the process requires very careful control of sintering and heat treating conditions, rapid heating and deoxidizing atmospheres. Otherwise a soft shell is found to form on the sintered article which sometimes makes the article useless or makes it necessary to machine away the shell.

We have now found that the addition of phosphorus to the powder mix enables the production of metal bodies under ordinary conditions of sintering and heat treatment without the formation of a soft shell. The phosphorus also has a cleansing action upon the material and improves ductility and other physical properties.

The nickel or cobalt and silicon are added in the proportions in which they are capable of age hardening the copper. The phosphorus present may also contribute to age hardening due to the formation of nickel or cobalt phosphide.

A powder mixture containing:

| | | |
|---|---|---|
| Nickel, cobalt, or both | per cent by weight | 0.5 to 5 |
| Silicon | per cent | 0.1 to 1 |
| Phosphorus | do | 0.05 to 1 |
| Copper | | Balance |

is used.

In some cases up to 10% of a diluent metal, such as zinc or tin may be added to the mixture.

It is preferred that the nickel or cobalt and silicon be present in a ratio between 4:1 and 6:1. Where the higher proportions of phosphorus are used the silicon may be lower as part of the phosphorus will form intermetallic compounds with the nickel or cobalt.

Some of the phosphorus may be lost during sintering and heat treatment so that the final composition may contain 0.01 to 1% phosphorus.

In the manufacture of bearings or other bodies of the composition the powdered elements are thoroughly mixed in the desired proportions and then pressed into a suitable shape using appropriate dies in a hydraulic or automatic press.

Inasmuch as pure silicon readily oxidizes it is preferable to form a nickel or cobalt silicide, such as $Ni_2Si$ or $Co_2Si$ which may be comminuted to a fine powder and included in the powder mixture instead of pure nickel or cobalt and silicon pow-

der. Such a compound also is more amenable to diffusion alloying than are the uncombined elements. Some excess nickel or cobalt may also be added, within the proportions given, as well as the compounds.

For bearings the density to which the powder mixture is pressed will depend upon the type of bearing intended to be made. Bearings can be made of varying porosity according to the service they are to perform;

(1) One type uses a dense material which after heat treatment approaches the theoretical density of the composition and which is used as a bearing without impregnation with a lubricant, relying on a surface film of oil or other lubricant or on surface impregnation only. The final density of this bearing is between 8 and 8.5 grams per cc. This material has a high tensile strength after heat treatment and a fatigue strength in excess of 15,000 pounds per square inch.

The fatigue strength is determined by subjecting sample bars to repeated stress reversal cycles under various loads. The fatigue strength is the maximum loading stress at which the material will withstand an indefinitely large number of stress reversals. In practice, if the test piece withstands 50 million reversal cycles under a given loading it is considered as capable of withstanding it indefinitely.

Hardness can be obtained between 70 and 85 Rockwell B. The material is strong enough to be used as a solid bearing member which does not require integral bonding to a steel reinforcing backing. In some cases the solid bearing can be pressed into a steel sleeve. In the case of connecting rod bearings for internal combustion engines the connecting rod may be lined directly with the sintered bushing.

It is also possible to press the powders into a steel sleeve and sinter them together and to the steel in one operation. It is preferable that a steel be used which responds to the same heat treatment. Such steels include carbon steels, chromium-vanadium steels, and manganese-molybdenum steels.

After pressing the bearing blanks they are sintered at an elevated temperature. The sintering time will be inversely proportional to the sintering temperature. At a higher temperature a shorter sintering time may be used. Moreover, when pre-alloyed silicide powders are used the sintering time may be somewhat shorter than where the elements are mixed as powders since in the latter case sintering time must be allowed for proper diffusion of the elements into each other. It is preferable in this case to utilize metals which have a high diffusion rate and which are not unduly susceptible to oxidation.

The pre-alloying method has the advantage of requiring less sintering time and there is less danger of undue oxidation of the elements. Thus where the elements are difficult to sinter and especially where they cannot be sintered with entire satisfaction even in an atmosphere of commercial hydrogen the pre-alloying method should be used.

It is sometimes possible, however, to obtain sufficient protection by utilizing a protective flux during the sintering operation. For example, certain hydrides, such as calcium hydride, give off nascent hydrogen which is an extremely powerful reducing agent.

After the pressed metal body has been sintered it is given an age-hardening treatment to effect precipitation of the intermetallic compound or compounds as a dispersed phase in the copper or copper alloy matrix. This age-hardening treatment may preferably comprise quenching the sintered body from a temperature above 700 degrees C. and subsequently aging the body at an elevated temperature within the range of 350 degrees C. to 700 degrees C. for an extended period of time, such as from one-half hour to several hours. The resulting aged body has much higher strength, hardness and wear resistance than a body of similar composition which has not been age-hardened.

It is sometimes desirable to introduce a repressing step after the sintering step to increase the density of the body.

As a specific example a mixture of the following composition is prepared:

| | Per cent by weight |
|---|---|
| Nickel | 2.5 |
| Silicon | 0.7 |
| Phosphorus | 0.3 |
| Copper | balance. |

The nickel and silicon may be pre-alloyed or the elemental powders used. The mixed powders are ball milled for 18 hours and pressed at 35 tons per square inch into bearing blanks, such as rings, cylinders or half-cylinders in a lubricated die.

The pressed blanks are sintered in hydrogen at 1015° to 1025° C. for about one hour.

They may then be repressed at 50 tons per square inch in the original die.

A heat treatment is then given them by quenching from 800° C. in water and then aging for 5 hours at 450° C. in hydrogen. In one case bearings made as described had a density between 8.4 and 8.5 gms. cc., a hardness of 74 to 79 Rockwell B, a tensile strength of about 50,000 pounds per square inch and a fatigue limit of 17,500 p. s. i.

The high tensile strength obtained with these bearings is highly advantageous in heavy duty applications where extreme pressures and high speeds are encountered. Sintered bearings of the prior art ordinarily have extremely low tensile properties and the tensile strength seldom exceeds 25,000 pounds per square inch. Such bearings are apt to fail due to cracking during heavy duty operation. The bearings of the present invention have another advantage in having relatively high thermal conductivity. This material reduces the concentration of heat developed at localized bearing areas which has heretofore been one important cause of bearing failure due to the resulting expansion at the heated areas resulting in galling, scoring or freezing of the bearing.

Bearing tests made by an independent research agency on the bearings of the composition and properties described in a General Motors bearing test machine which simulates automotive connecting rod service showed remarkable results for so hard and strong a material. With 50% overloading, so that the test conditions were midway between the loads for automotive and aircraft service the bearings ran without showing distress of any kind in a 50 hour test and were in excellent condition at the end. There was no galling, scoring or freezing. The co-operating shaft showed no excessive wear. These results are truly remarkable for so hard a material, first because it could be run at such high speeds and loads, and second because the shaft showed no excessive wear.

(2) Another type of bearing is pressed at a lower pressure to produce a final density after

heat treatment of 7.5 to 8 gms./cc. This bearing has a discontinuous network of voids. It has a lower fatigue strength, namely around 10,000 p. s. i. and a hardness of 30 to 50 Rockwell B.

After completion this bearing may be surface impregnated with lead, thallium or other lubricant metals or with oils or waxes. Bearing tests on this type of material similar to those described above gave similar uneventful good performance. Oil was used as a lubricant.

(3) A third type of bearing is pressed at a still lower pressure to give a still more porous product, the final density of which is between 5 and 7.5 grams per cc., the fatigue strength of which is below 10,000 p. s. i. and the hardness of which is below 35 Rockwell B before impregnation. This bearing is most suitable for impregnation with lead, thallium or other lubricant metal which penetrates through the porous body, or with oils or waxes. It is generally necessary to bond this material to a reinforcing backing unless the service conditions are light.

We have attempted to produce bearings of the compositions described herein by casting the metals in the form desired. In this case where a soft lower melting metal is incorporated, as is often required for bearings, it has been impossible to produce castings which compare favorably with the sintered product herein described. Where lead is used, for example, the cast members were found to be extremely weak and unsound with low tensile strength and having numerous flaws and dirt inclusions. It is also genally recognized that silicon is detrimental to the making of copper-lead alloy bearings by casting. The present invention eliminates these difficulties.

The nickel or cobalt aids in protecting the copper from corrosive attack from the acid content in or produced from the lubricating oils present at the bearing surfaces. They materially increase the resistance to attack from such acids.

It is sometimes preferred to apply a slow quenching procedure rather than the rapid quenching in water or oil. One procedure is to sinter the bearing at approximately 1000 degrees C. and immediately after sintering to place the bearing in a water cooled chamber where it will cool to room temperature in about ten minutes. Tensile strengths in excess of 50,000 pounds per square inch can be obtained. Leaded bronze bearings of the prior art have only half this strength.

Where the higher thermal conductivity is desired in the bearing it is preferred to use a copper base substantially free from alloying ingredients which form solid solution with the copper since these tend to decrease the thermal conductivity. It is possible, however, to add elements to copper which do not substantially reduce the thermal conductivity but which add corrosion resistance to the alloy and improve its qualities as bearing. For example, cadmium added in proportions ranging from .05 to about 5% of the total composition is helpful.

The age-hardened copper powder composition has an ideal microscopic structure for bearing purposes. The hardened intermetallic compounds are present as microscopic particles distributed throughout the copper base which is itself soft in comparison thereto. The intermetallic compounds being in extremely fine form and embedded in a softer base have no tendency to score the surface of the co-operating bearing.

In some cases it may be desired to add a material having lubricating properties to the powder mixture prior to pressing and sintering. For example, a small amount of graphite may be added to the mixture. It is also possible to add the low melting point metals and alloys such as lead, zinc, cadmium, tin, thallium and babbitt at this stage.

In most cases, however, where lubricant metals are used, it is preferred to impregnate the sintered and age-hardened bearing, which ordinarily has a porous structure, with the lubricant after the age-hardening step has been applied. For example, the bearing can be impregnated with one of the lower melting point and softer metals mentioned by immersing the bearing in a bath of the molten soft metal for a sufficient period of time. This impregnation may also in some cases be combined with the age-hardening step by maintaining the bath at the desired temperature for age-hardening purposes and keeping the bearing immersed for a sufficient period of time.

Referring to the drawing, Figures 1 and 2 illustrate a cylindrical bearing 10 made from pressed copper powders, the bearing being sintered and age-hardened as described herein. Figures 3 and 4 illustrate a modified form of bearing wherein the bearing surface 11 is formed of the pressed, sintered and age-hardened metal powders, the powders being pressed against a backing support 12 of a strong alloy such as iron or steel or the like, and sintered thereto.

While the present invention, as to its objects and advantages, has been described herein as carried out in specific embodiments thereof, it is not desired to be limited thereby but it is intended to cover the invention broadly within the spirit and scope of the appended claims.

What is claimed is:

1. A sintered metal composition formed from 0.5 to 5% of metal selected from the group consisting of nickel and cobalt, 0.1 to 1% silicon, 0.05 to 1% phosphorus, and the balance substantially all copper, said metal composition containing a silicide of said nickel or cobalt present as a dispersed phase therein imparting strength and hardness thereto.

2. A sintered metal composition composed of 0.5 to 5% of metal selected from the group consisting of nickel and cobalt, 0.1 to 1% silicon, 0.01 to 1% phosphorus, and the balance substantially all copper, said metal composition containing a silicide of said nickel or cobalt present as a dispersed phase therein imparting strength and hardness thereto.

3. A bearing formed of a compact body of copper powder sintered together and containing a precipitation hardening ingredient selected from the group consisting of nickel silicide and cobalt silicide as a dispersed phase therein imparting thereto greater hardness and strength than leaded bronze, said bearing nevertheless having freedom from galling, scoring and freezing under automotive engine service conditions and freedom from a tendency to wear the co-operating shaft excessively, said bearing being composed of 0.5 to 5% nickel, 0.1 to 1% silicon, 0.01 to 1% phosphorus, and the balance substantially all copper.

4. A bearing formed of a compact body of copper powder sintered together and containing a precipitation hardening ingredient selected from the group consisting of nickel silicide and cobalt silicide as a dispersed phase therein imparting thereto greater hardness and strength than leaded bronze, said bearing nevertheless having freedom from galling, scoring and freezing under automotive engine service conditions and freedom from a tendency to wear the co-operating shaft

excessively, said bearing being composed of 0.5 to 5% nickel, 0.1 to 1% silicon, 0.01 to 1% phosphorus and the balance substantially all copper, and having a density between 8 and 8.5 grams per cc. and a fatigue strength in excess of 15,000 pounds per square inch.

5. A bearing formed of a compact body of copper powder sintered together and containing a precipitation hardening ingredient selected from the group consisting of nickel silicide and cobalt silicide as a dispersed phase therein imparting thereto greater hardness and strength than leaded bronze, said bearing nevertheless having freedom from galling, scoring and freezing under automotive engine service conditions and freedom from a tendency to wear the co-operating shaft excessively, said bearing being composed of 0.5 to 5% nickel, 0.1 to 1% silicon, 0.01 to 1% phosphorus and the balance substantially all copper, and having a density between 7.5 and 8 grams per cc. and a porosity characterized by a discontinuous network of voids.

6. A bearing formed of a compact body of copper powder sintered together and containing a precipitation hardening ingredient selected from the group consisting of nickel silicide and cobalt silicide as a dispersed phase therein imparting thereto greater hardness and strength than leaded bronze, said bearing nevertheless having freedom from galling, scoring and freezing under automotive engine service conditions and freedom from a tendency to wear the co-operating shaft excessively, said bearing being composed of 0.5 to 5% nickel, 0.1 to 1% silicon, 0.01 to 1% phosphorus, and the balance substantially all copper, and having a density, exclusive of any impregnant, of 5 to 7.5 grams per cc. and characterized by a continuous network of voids.

7. A bearing formed of a compact body of copper powder sintered together and containing a precipitation hardening ingredient selected from the group consisting of nickel silicide and cobalt silicide as a dispersed phase therein imparting thereto greater hardness and strength than leaded bronze, said bearing nevertheless having freedom from galling, scoring and freezing under automotive engine service conditions and freedom from a tendency to wear the co-operating shaft excessively, said bearing being composed of 0.5 to 5% nickel, 0.1 to 1% silicon, 0.01 to 1% phosphorus and the balance substantially all copper, and having a density, exclusive of impregnant, of 5 to 7.5 grams per cc. and characterized by a continuous network of voids and a lubricant impregnating said voids.

8. A bearing formed of a compact body of copper powder sintered together and containing a precipitation hardening ingredient selected from the group consisting of nickel silicide and cobalt silicide as a dispersed phase therein imparting thereto greater hardness and strength than leaded bronze, said bearing nevertheless having freedom from galling, scoring and freezing under automotive engine service conditions and freedom from a tendency to wear the co-operating shaft excessively, said bearing being composed of 0.5 to 5% nickel, 0.1 to 1% silicon, 0.01 to 1% phosphorus and the balance substantially all copper, and having a density, exclusive of impregnant, of 5 to 7.5 grams per cc. and characterized by a continuous network of voids and a lubricant metal selected from the group consisting of lead and thallium impregnating said voids.

9. The method of making a sintered copper powder body age hardened with nickel or cobalt silicide without forming a soft shell thereon, which comprises mixing with copper base metal powders sufficient nickel or cobalt and silicon to effect age hardening thereof by heat treatment and adding phosphorus to said mixture, pressing, sintering and age hardening said mixture.

10. The method of making a sintered copper powder body age hardened with nickel or cobalt silicide without forming a soft shell thereon, which comprises mixing with copper base metal powders sufficient nickel or cobalt and silicon to effect age hardening thereof by heat treatment and adding 0.05 to 1% phosphorus to said mixture, pressing, sintering and age hardening said mixture.

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