United States Patent [19]

Niimi et al.

[11] **3,802,852**

[45] **Apr. 9, 1974**

[54] **SINTERED ALLOYS HAVING WEAR RESISTANCE AT HIGH TEMPERATURE COMPRISING A SINTERED FE-MO-C ALLOY SKELETON INFILTRATED WITH CU OR PB BASE ALLOYS OR SB**

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[22] Filed: **Jan. 11, 1972**

[21] Appl. No.: **217,029**

[52] **U.S. Cl.** **29/182.1,** 75/200

[51] **Int. Cl.** **B22f 5/00**

[58] **Field of Search** ...... 29/182.1, 156.7 A; 75/200; 123/188

[56] **References Cited**

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[57] **ABSTRACT**

The present invention relates to sintered alloys having wear resistance at high temperature, particularly suitable for fabricating valve seats of internal combustion engines. The pores of iron-base sintered skeletons are infiltrated with selected molten metals or with alloys thereof.

10 Claims, No Drawings

SINTERED ALLOYS HAVING WEAR RESISTANCE AT HIGH TEMPERATURE COMPRISING A SINTERED FE-MO-C ALLOY SKELETON INFILTRATED WITH CU OR PB BASE ALLOYS OR SB

BACKGROUND OF THE INVENTION

The present invention relates to sintered alloys having wear resistance at high temperatures.

As materials for constructing valve seats of internal combustion engines, special cast iron and heat resistant steel have been commonly used. The use of these materials provides troublefree operation when lead additive gasoline is used as fuel. This is because lead tetrachloride added in these fuels as an antiknock agent converts to lead oxide by combustion which adheres to the valves and valve seats and thereby produces a lubricating action. Through this action the valve parts are prevented from wearing away and the engines maintain a good performance. However, when leadfree gasoline of LPG (Liquefied Propane Gas) containing no lead is used, the conventional valve seat rings made of special cast iron or heat resistance steel are remarkably worn away in the absence of the aforesaid lubricating action. This causes the output of the engines to diminish, and the engines tend to work in an abnormal fashion.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to eliminate the above described disadvantages by providing sintered alloys that have excellent resistance to wear at high temperatures.

The sintered alloys of the present invention are obtained by infiltrating the pores of specific iron-base sintered alloys with selected metals that have lubricating properties or the alloys thereof. The valve seats made of these alloys are not worn away and enable the engines to operate at peak performance even when LPG containing no lead or leadfree gasoline is used as fuel. These alloys are also useful for other purposes similar to valve seats, for example, for materials in hot roller bearings and other parts which are exposed to high temperatures.

The invented sintered alloys are characterized by infiltrating the pores of iron-base sintered alloys composed of iron as the main constituent, 0.25 to 8 percent molybdenum and 0.1 to 1.0 percent carbon each by weight percentage, with molten metals having lubricating properties or with the alloys thereof. The molten metals or alloys thereof available for this purpose are: copper-base alloys added with one or two or more metals selected from chromium, tin and zinc, the percentage of weight used for infiltration being 10 to 30 percent of the total weight of the resulting alloy; copper-lead base alloys added with one or two or more metals selected from chromium, tin and zinc, the percentage of weight used for infiltration being 5 to 30 percent; lead-base alloys added with one or two or more metals selected from bismuth, antimony and cadmium, or antimony alone, the percentage of weight used for infiltration being 1 to 25 percent in this case.

DETAILED DESCRIPTION OF THE INVENTION

The sintered alloys according to the present invention have a structure in which soft metals or alloys thereof fill the pores of iron-base sintered skeletons dotted with fine and hard molybdenum in a relative hard ferrite plus pearlite matrix. These alloys exhibit excellent strength and wear resistance at high temperatures.

The effect exercised by each constituent element and the reason for defining the composition range of the alloys of the present invention is described below.

In the sintered alloys according to the present invention, carbon melts into iron in the form of a solid solution to form pearlite thereby increasing the wear resistance as well as strengthening the alloys. However, at less than 0.1 percent content such effect is inappreciable, while at more than 1.0 percent cementite is precipitated which causes increased fragility. Cementite also adversely affects the machinability of the alloys. Therefore, the range of carbon is defined as between 0.1 and 1.0 percent.

Molybdenum increases the resistance of metals to softening by temper and raises the impact value. Moreover, each of the precipitated and pseud-precipitated molybdenum forms an oxide at high temperature which lowers the coefficient of friction thereby contributing to increased wear resistance. However, at less than 0.25 percent of molybdenum there is little effect, while at more than 8 percent the effect does not increase as compared with the added amount. Therefore, the percentage of molybdenum is preferably fixed at less than 8 percent.

Copper used for infiltration, in part, melts into iron in the form of a solid solution thereby increasing the hardness of the alloys which in turn increases the machinability and the wear resistance. On the other hand, the remaining part of copper exists in the pores of the sintered skeletons thereby increasing the heat conductibility which in turn reduces the heat load of the alloys. At the same time, at high temperature, copper forms a thin film of its oxide on the surface which produces a lubricating effect thereby remarkably improving the wear resistance of the alloys.

Chromium added to copper, in part, melts into copper in the form of a solid solution thereby strengthening the copper and also preventing it from melting and adhering to materials in contact with it. In a practical application the addition of chromium decreases the wearing away of the copper by melting adhesion. On the other hand, the remaining part of the chromium finely disperses into copper and forms a thin film of its oxide at high temperature which lowers the coefficient of friction thereby increasing wear resistance.

Tin added to copper melts into copper in the form of a solid solution thereby strengthening the copper and increasing the wear resistance. Zinc has an effect similar to that of tin, but zinc tends to be oxidized selectively at high temperature. Zinc oxide thus formed offers a lubricating effect thereby remarkably increasing the wear resistance of the alloys.

Each additive element of chromium, tin and zinc exhibits the individual influences noted above even when two or more of these elements are simultaneously added to copper. When the amount for infiltration of these alloys is less than 10 percent, there is little effect. However, when the amount is more than 30 percent, the density of the sintered skeletons and the strength of the resulting alloys are significantly lowered. Therefore, the preferable range is 10 to 30 percent.

Referring to infiltration with copper-lead base alloys added with one or two or more metals selected from chromium, tin and zinc, the lead of these alloys forms a film on the surface of the alloys which turns into lead oxide at high temperature to produce a lubricating effect and thereby remarkably increase the wear resistance and machinability of the resulting alloys. At the same time, in addition to the effect described above, copper has an effect of improving the wettability of lead towards the iron matrix thereby making the film of lead more uniform. By adding chromium, tin and zinc to the above copper-lead alloys of an excellent lubricating property, the aforesaid effect of each element joins in that of the copper-lead alloys thereby producing excellent wear resistance. In the case of the copperlead base alloys, more than 5 percent of the amount for infiltration produces an excellent wear resistance. But, an addition of more than 30 percent lowers the density of the iron-base sintered skeletons thereby decreasing the mechanical strength. Thus, the preferable range is less than 30 percent.

As described above, lead has excellent lubricating properties. Since bismuth and antimony each has the same effect as lead, infiltration with lead alloys added with such metals provides the iron-base sintered skeletons of the present invention with greatly increased wear resistance at high temperature. In this case, the difference in melting point between lead, bismuth and antimony is used to advantage. The melting point of lead is 327°C.; bismuth 271°C.; and antimony 630°C. When the resulting sintered alloys are applied to a practical use involving relatively low temperature, infiltration should be made using a lead alloy added with a larger amount of bismuth. When the resulting sintered alloys are practically used at relatively high temperature, infiltration should be made using a lead alloy added with a larger amount of antimony or using antimony alone. Therefore, optional use of the most suitable metals or alloys thereof for infiltration is advantageously made with reference to the temperature of use in the practical application of the sintered alloys.

Cadmium is useful in restraining lead from expansion when melting whereby the lead is more captured.

The elements, lead, bismuth, antimony and cadmium tend to offer little effect for infiltration at less than 1 percent. On the other hand, at more than 25 percent addition for infiltration, the mechanical strength becomes insufficient since these elements have no effect of strengthening the iron-base sintered skeletons in the form of a solid solution which copper does. Therefore, the range of 1 to 25 percent is desirable.

As described hitherto, the sintered alloys according to the present invention are characterized by infiltrating iron-molybdenum-carbon sintered alloys having an excellent strength and wear resistance at high temperature, with molten metals having superior lubricating properties or the alloys thereof. Specifically, the molten metals include a copper-base alloy or a copper-lead base alloy added with one or two or more metals selected from chromium, tin and zinc; or a lead-base alloy added with one or two or more metals of bismuth, antimony and cadmium; or antimony alone. Thus, the sintered alloys of the present invention are composite materials obtained by combining two types of materials of high strength and excellent lubricating properties. As a result of this combination, these sintered alloys are provided with greatly increased wear resistance at high temperature. Because of their properties, these alloys are most suitable for materials in valve seats of internal combustion engines in which leadfree gasoline or LPG is used as fuel, and for materials in bearings for hot rollers or other construction parts which reach or are exposed to high temperatures.

The present invention is described with reference to its method of production as follows:

EXAMPLE 1

Reducing iron powder of minus 100 mesh, fine electrolytic molybdenum powder of 3 to 6μ in particle size and graphite powder are mixed to give a composition by weight percentage (the percentages set forth herein are all by weight) of 94.5 percent iron, 5 percent molybdenum and 0.5 percent carbon. After the mixture is formed under a forming pressure of 5 t/cm^2 to a density of 6.7 g/cm^3, the formed mass is subjected to a sintering process at 1150°C. for 1.5 hours in a reducing gas atmosphere. The sintered skeleton (the skeleton to be infiltrated) is thereby obtained. Thereafter, the pores of the sintered skeleton are infiltrated with a copper 95 percent — chromium 5 percent alloy at 1150°C. for 1.5 hours in a reducing gas atmosphere. A sintered alloy according to the present invention is obtained.

EXAMPLE 2

Using the sintered skeleton obtained in Example 1, the pores of the skeleton are infiltrated with a copper 65 percent — zinc 30 percent — tin 5 percent alloy at 1130°C. for 1.5 hours in a reducing gas atmosphere. Thus, a sintered alloy of the present invention is obtained.

EXAMPLE 3

Using the sintered skeleton obtained in Example 1, the pores of the skeleton are infiltrated with a copper 60 percent — zinc 30 percent — tin 5 percent — chromium 5 percent alloy at 1130°C. for 1.5 hours in a reducing gas atmosphere. A sintered alloy of the present invention is obtained.

EXAMPLE 4

Using the sintered skeleton obtained in Example 1, the pores of the skeleton are infiltrated with a copper 60 percent — lead 30 percent — tin 10 percent alloy at 1050°C. for one hour in a reducing gas atmosphere to obtain an alloy of the present invention.

EXAMPLE 5

Using the sintered skeleton obtained in Example 1, the pores of the skeleton are infiltrated with a copper 62 percent — lead 25 percent — tin 10 percent — chromium 3 percent alloy at 1050°C. for one hour in a reducing gas atmosphere. A sintered alloy of the present invention is obtained.

EXAMPLE 6

Using the sintered skeleton obtained in Example 1, the pores of the skeleton are infiltrated with a copper 50 percent — lead 25 percent — zinc 20 percent — tin 5 percent alloy at 1050°C. for one hour in a reducing gas atmosphere. A sintered alloy of the present invention is obtained.

EXAMPLE 7

Reducing iron powder of minus 100 mesh, fine electrolytic molybdenum powder of 3 to 6μ in particle size and graphite powder are mixed to provide a composition of 94.5 percent iron, 5 percent molybdenum and 0.5 percent carbon. Then, the mixture is formed under a forming pressure of 6 t/cm^2 to a density of 7.1 g/cm^3. After the formed mass is subjected to a sintering process at 1150°C. for 1.5 hours in a reducing gas atmosphere, a sintered skeleton is obtained. The pores of the sintered skeleton are infiltrated with a lead 80 percent — bismuth 20 percent alloy at 1000°C. for 45 minutes in a reducing gas atmosphere. A sintered alloy of the present invention is obtained.

EXAMPLE 8

Using the sintered skeleton obtained in Example 7, the pores of the skeleton are infiltrated with an antimony 60 percent — lead 40 percent alloy at 1030°C. for 1.5 hours in a reducing gas atmosphere. A sintered alloy of the present invention is obtained.

EXAMPLE 9

Using the sintered skeleton obtained in Example 7, the pores of the skeleton are infiltrated with antimony at 1050°C. for 1.5 hours in a reducing gas atmosphere. A sintered alloy of the present invention is obtained.

Next, the alloys of the present invention as obtained in Examples 1 through 9 are tested for their properties and quantities of wear at high temperature. The results are shown in the following table. In tha table, quantities of wear are indicated by the worn away quantities in millimeters in the direction of the height of the specimens measured after the testing has been continued for 100 hours by a so-called "sliding high-cycle impact tester" wherein 2500 shocks a minute are given to the angular specimens under a surface pressure of 30 kg/cm^2 by means of a jig made of heat resistant steel, while the angular specimens fixed to cast iron are rotated 10 times a minute at an elevated temperature of 500° to 550°C.

What is claimed is:

1. A wear resistant metal comprising a sintered skeleton consisting essentially of iron having 0.25 to 8 percent by weight molybdenum and 0.1 to 1.0 percent by weight carbon, and an infiltrant selected from the group consisting of 10 to 30 percent by weight copper-base alloy, 5 to 30 percent by weight copper-lead base alloy, 1 to 25 percent by weight lead-base alloy, and 1 to 25 percent by weight antimony.

2. A valve seat for an internal combustion engine fabricated of the wear resistant metal of claim **1.**

3. The wear resistant metal of claim **1** in which the copper-base alloy infiltrant includes at least one metal selected from the group consisting of chromium, tin and zinc.

4. A valve seat for an internal combustion engine fabricated of the wear resistant metal of claim **3.**

5. The wear resistant metal of claim **1** in which the copper-lead base alloy infiltrant includes at least one metal selected from the group consisting of chromium, tin and zinc.

6. A valve seat for an internal combustion engine fabricated of the wear resistant metal of claim **5.**

7. The wear resistant metal of claim **1** in which the lead-base alloy infiltrant includes at least one metal selected from the group consisting of bismuth, antimony and cadmium.

8. A valve seat for an internal combustion engine fabricated of the wear resistant metal of claim **7.**

9. A wear resistant metal comprising a sintered skeleton consisting essentially of iron having 0.25 to 8 percent by weight molybdenum and 0.1 to 1.0 percent by weight carbon, and an infiltrant consisting of 5 to 30 percent by weight copper-lead base alloy.

10. A valve seat for an internal combustion engine fabricated of the wear resistant metal of claim **9.**

* * * * *

TABLE

	Composition (percent by weight)	Tensile strength (kg./mm.²)	Hardness (Hv 0.2)	Quantity of wear (mm.)
Sintered alloys of the present invention, example:				
1	(Fe-5Mo-0.5C)-14(Cu-5Cr) infiltrated	65	323–350	0.41
2	(Fe-5Mo-0.5C)-14(Cu-30Zn-5Sn) infiltrated	60	308–341	0.40
3	(Fe-5Mo-0.5C)-14(Cu-30Zn-5Sn-5Cr) infiltrated	65	330–355	0.37
4	(Fe-5Mo-0.5C)-14(Cu-30Pb-10Sn) infiltrated	60	263–305	0.32
5	(Fe-5Mo-0.5C)-14(Cu-25Pb-10Sn-3Cr) infiltrated	60	274–302	0.28
6	(Fe-5Mo-0.5C)-14(Cu-25Pb-20Zn-5Sn) infiltrated	55	241–297	0.31
7	(Fe-5Mo-0.5C)-9(Pb-20Bi) infiltrated	50	224–263	0.35
8	(Fe-5Mo-0.5C)-9(Sb-40Pb) infiltrated	55	238–279	0.35
9	(Fe-5Mo-0.5C)-9Sb infiltrated	55	246–277	0.33
Comparison example:				
Special cast iron	Fe-3.5C-2.5Si-1Mn-0.5P-0.5Cr-0.5Mo-0.1V	40	250–300	7.42
Heat resistant steel	Fe-0.4C-2Si-15Cr-15Ni-2W-0.5Mn	90	290–310	6.88

PO-1050
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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,802,852 Dated April 9, 1974

Inventor(s) Itaru Niimi et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

On the Front Page, insert

-- Foreign Application Priority Data

July 14, 1971 Japan .... 46-052288, --

Signed and sealed this 10th day of Spetember 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

[redacted]

PO-1050
(5/69)

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