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[54] **SINTERED ALLOY HAVING WEAR RESISTANCE AT HIGH TEMPERATURE**

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

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[57] **ABSTRACT**

The present invention relates to iron-base sintered alloys having excellent wear resistance at high temperatures, and more particularly to alloys adapted for fabricating valve seat rings of internal combustion engines. The alloys of the present invention are characterized by infiltrating selected metals having lubricating properties or the alloys thereof into the pores of iron-chromium-carbon base sintered alloys having significant mechanical strength and heat resistance.

12 Claims, No Drawings

SINTERED ALLOY HAVING WEAR RESISTANCE AT HIGH TEMPERATURE

BACKGROUND OF THE INVENTION

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

Materials such as special cast iron and heat resistant steel have commonly been used for constructing valve seat rings of internal combustion engines. The use of these materials does not adversely affect the engines when leaded gasoline is used as fuel because lead tetrachloride added to the fuel as an antiknock agent forms lead oxide at combustion which adheres to the surface of valve seat rings. The lubricating action offered by lead oxide is quite useful in preventing the valve seat rings from wearing away, thus maintaining full performance of the engine. However, when engines are fueled by LPG (Liquefied Propane Gas) containing no lead or lead-free gasoline, the lubricating action by lead oxide is lost and the valve seat rings made of the above materials are remarkably worn away during engine operation. This results in decreased engine output and abnormal engine operation.

In order to overcome the above-mentioned disadvantages, the sintered alloys of the present invention exhibit superior wear resistance at high temperatures. As a result, the valve seat rings made of the present alloy do not wear away even when LPG or lead-free gasoline is used as fuel. The engines are therefore maintained at normal working conditions. Also, the alloys of the present invention are suitable for use in fabricating bearings for hot rollers and other parts that are exposed to or reach high temperatures during use thereof.

SUMMARY OF THE INVENTION

Accordingly, the primary object of the present invention is to provide alloys having excellent wear resistance at elevated temperatures.

In accordance with the present invention sintered alloys having excellent wear resistance at high temperatures are obtaine by infiltrating selected metals having lubricating action or the alloys thereof into the pores of iron-chromium-carbon base sintered skeletons which, by weight percentage, are composed of 0.2 to 1.0 percent carbon, 0.2 to 15 percent chromium and the remainder iron. The selected metals or alloys thereof for this purpose include: copper (or copper-base alloys added with one or two or more metals selected from tin, zinc and chromium) which is used for infiltration by 10 to 30 percent of the total alloy weight; copper-lead alloys (or copper-lead base alloys added with one or two or more metals selected from tin, zinc and chromium) which is used for infiltration by 5 to 30 percent; and lead or antimony (or lead-base alloys added with one or two or more metals selected from antimony, bismuth and cadmium) which is used for infiltration by 1 to 25 percent.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to sintered alloys having excellent wear resistance at high temperatures. These alloys are characterized by infiltrating selected metals having lubricating properties or the alloys thereof into the pores of iron-chromium-carbon sintered skeletons having high mechanical strength and heat resistance.

The effect of each constituent element and the reason for defining the content of each element is explained below. First, the description refers to each element added to the sintered skeletons.

Carbon forms pearlite in combination with iron which increases the strength and the wear resistance of the alloys. However, at less than 2 percent content there is only insufficient strength and wear resistance, while addition of more than 1.0 percent of carbon results in precipitating cementite which makes the alloys fragile and difficult, if not impossible, to machine properly. Since both cases are undesirable, the carbon content is between 0.2 and 1.0 percent.

Chromium melts into iron in the form of a solid solution and makes iron tough by forming composite carbides such as $(Fe_3C)_{18}Cr_4C$, $(Fe_3C)_9Cr_4C$ and $Fe_3C.Cr_4C$. These carbides are coexistent with Fe_3C, and quite useful in increasing the hardness of the steels and their wear resistance. Furthermore, chromium remains stable at high temperatures. It diminishes the deterioration of the materials caused by a rise in temperature and increases their heat resistance. However, at less than 0.2 percent content there is little if any effect, while at more than 15 percent very little effect results when compared with the amount added. The machinability of the resulting alloys is also poor. Both cases should be avoided. Thus, the chromium content is between 0.2 and 15 percent.

The description explains each element to be added for the purpose of infiltration.

When copper is added a portion melts into iron in the form of a solid solution and is effective in strengthening the alloys. The remaining portion fills the pores of the sintered skeletons and brings about increased heat conductibility which in turn lowers the heat load by the alloys. At the same time, copper forms a thin film of its oxide on the surface and increases the wear resistance of the alloys through the lubricating action of this oxide film. However, at less than 10 percent copper the effect of infiltration is very small, while at more than 30 percent the strength of the sintered skeletons deteriorates. Accordingly, the preferred copper content is between the above two percentages.

Lead used for infiltration turns into lead oxide during actual use of the alloys. The lead oxide adheres in a thin layer on the surface of the alloys, and thereby produces a lubricating action which increases the wear resistance of the alloys. The secondary effect of lead is to remarkably increase the machinability of the alloys. However, at less than 1 percent the effect is very slight and a uniform distribution of lead is unobtainable. At more than 25 percent of the amount for infiltration the strength of the alloys drops. Therefore, the preferred range of lead is 1 to 25 percent.

The affect of antimony is similar to lead. Since the melting point of antimony is higher than that of lead (melting point of antimony is 630° C., lead 327° C.), antimony is suitable for alloys used at higher temperatures when compared with the alloys infiltrated with lead. As in the case of lead infiltration, at less than 1 percent antimony the effect is slight, while at more than 25 percent the strength of the alloys drops. Therefore, the preferred range of antimony is 1 to 25 percent.

As shown in Example 2, a 70 percent copper — 30 percent lead alloy (Kelmet) is used for infiltration. In this case, in addition to the above-mentioned individual effect of copper and lead, copper improves the wettability of lead towards iron and gives lead a promoted lubricating action which increases the wear resistance. However, at less than 5 percent the effect by infiltration is slight, while at more than 30 percent the strength of the sintered skeletons drops. The preferred range of the above alloy types is 5 to 30 percent.

As shown in Example 4, a copper-lead base alloy added with tin is used for infiltration. The tin has the effect of partly melting into copper in the form of a solid solution and increasing the strength and the wear resistance of copper. Tin also has the effect of dispersing lead in a fine and uniform state in copper and further increasing the wear resistance of the alloys.

Zinc added to copper reacts similar to tin. Moreover, zinc forms a film of its oxide at high temperature during practical use of the alloys and lowers the coefficient of friction which increases the wear resistance.

In Example 3 infiltration with a copper-chromium alloy is explained. A portion of the chromium melts into copper in the form of a solid solution and strengthens the copper, while the remaining portion forms a film of its oxide on the surface at high temperature and gives the alloy a reduced coefficient of friction which increases the wear resistance of the alloys even more.

Infiltration with a 90 percent lead – 10 percent bismuth alloy is explained in Example 6. The bismuth reduces the melting tendency of lead, and increases the lubricating action by lead in cases where lower temperature and load are employed with valve seats or bearings.

Cadmium is effective in restraining lead from its expansion at melting whereby lead may be more captured.

As described hitherto, the sintered alloys according to the present invention are provided with greatly increased wear resistance at high temperatures by infiltrating metals or alloys thereof having significant lubricating properties into the pores of iron-chromium-carbon base alloys having superior strength and wear resistance at high temperature. The metals or alloys thereof used for infiltration are: copper, lead; antimony; copper-base alloys added with one or two or more metals selected from tin, zinc, lead and chromium; lead-base alloys added with one or two or more metals selected from antimony, bismuth and cadmium.

It should be noted that according to the conventional method of producing iron-carbon base sintered alloys, lead is premixed with iron powder and graphite powder as a means of adding lead. In such mixing methods, it is difficult to achieve uniform distribution of lead or other elements or alloys thereof, and the lead is scattered in the air during the sintering process whereby lead is less captured. On the other hand, the infiltration according to the present invention has the advantage of obtaining a uniform distribution and a satisfactory capture of lead and other substances. Therefore, alloys of uniform quality are obtained in mass production.

The present invention is described below with reference to its various embodiments.

EXAMPLE 1

Reducing iron powder of minus 100 mesh, iron-chromium alloy powder of minus 100 mesh and graphite powder are mixed to provide a composition of 99.4 percent iron, 5 percent chromium and 0.6 percent carbon, each by weight percentage. After this 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 sintered at 1,300° C. for one hour and a half in a reducing gas atmosphere to obtain a sintered skeleton. The sintered skeleton is then infiltrated at 1,130° C. for one hour and a half in a reducing gas atmosphere using a material composed of 90 percent copper, 5 percent iron and 5 percent manganese. A sintered alloy of the present invention is obtained.

EXAMPLE 2

Using the sintered skeleton of Example 1, the pores of the skeleton are infiltrated with a 70 percent copper — 30 percent lead alloy (Kelmet) at 1,050° C. for one hour in a reducing gas atmosphere. A sintered alloy of the present invention is obtained.

EXAMPLE 3

Using the sintered skeleton of Example 1, the pores of the skeleton are infiltrated with a 95 percent copper – 5 percent chromium alloy at 1,130° C. for one hour in a reducing gas atmosphere. A sintered alloy of the present invention is obtained.

EXAMPLE 4

Using the sintered skeleton of Example 1, the pores of the skeleton are infiltrated with a 60 percent copper — 30 percent lead — 10 percent tin alloy at 1,050° C. for one hour in a reducing gas atmosphere. A sintered alloy of the present invention is obtained.

EXAMPLE 5

Reducing iron powder of minus 100 mesh, iron-chromium alloy powder of minus 100 mesh and graphite powder are mixed to provide a composition of 93.2 percent iron, 6 percent chromium and 0.8 percent carbon, each by weight percent. The mixture is formed under a forming pressure of 6 t/cm^2 to a density of 7.1 g/cm^3. Thereafter, the formed mass is sintered at 1,300° C. for one hour and a half in a reducing gas atmosphere, and a sintered skeleton is obtained. The pores of the sintered skeleton are infiltrated with lead at 1,000° C. for 45 minutes in a reducing gas atmosphere. A sintered alloy of the present invention is obtained.

EXAMPLE 6

Using the sintered skeleton of Example 5, the pores of the skeleton are infiltrated with a 90 percent lead — 10 percent bismuth alloy at 1,000° C. for 45 minutes in a reducing gas atmosphere. A sintered alloy of the present invention is obtained.

EXAMPLE 7

Using the sintered skeleton of Example 5, the pores of the skeleton are infiltrated with antimony at 1,100° C. for one hour and a half 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 7 are tested for their properties and quantities of wear at high temperature. The results are shown in the following table. In the 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. The angular specimens fixed to cast iron are rotated 10 times a minute at an elevated temperature of 500 to 550°C.

TABLE

		Composition (% by weight)	Tensile strength (Kg/mm^2)	Hardness (Hv.0.2)	Quantity of wear (mm)
Alloys of the Present Invention					
	Example 1	(Fe-5Cr-0.6C)-14 Cu infiltrated	72	327–354	0.51
	Example 2	(Fe-5Cr-0.6C)-14(70Cu-30Pb) infiltrated	70	315–342	0.32
	Example 3	(Fe-5Cr-0.6C)-14(95Cu-5Cr) infiltrated	72	327–366	0.44
	Example 4	(Fe-5Cr-0.6C)-14(60Cu-30Pb-10Sn) infiltrated	67	310–353	0.32
	Example 5	(Fe-6Cr-0.8C)-9Pb infiltrated	58	250–322	0.40
	Example 6	(Fe-6Cr-0.8C)-9(90Pb-10Bi) infiltrated	60	262–321	0.37
	Example 7	(Fe-6Cr-0.8C)-9Sb infiltrated	62	276–329	0.38
Comparison Examples	Special Cast Iron	(Fe-3.5C-2.5Si-1Mn-0.5P-0.5Cr-0.5Mo-0.1V)	40	250–300	
6.88	Heat Resisting Steel	(Fe-0.4C-2Si-15Cr-15Ni-2W-0.5Mn)	90	290–310	7.42 290–310

What is claimed is:

1. A wear resistant metal comprising a sintered skeleton consisting essentially of iron having 0.2 to 15 percent by weight chromium and 0.2 to 1.0 percent by weight carbon, and an infiltrant selected from the group consisting of 10 to 30 percent by weight copper, 10 to 30 percent by weight copper-base alloy, 1 to 25 percent by weight lead, 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 tin, zinc and chromium.

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 lead-base alloy infiltrant includes at least one metal selected from the group consisting of bismuth, antimony and cadmium.

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

7. A wear resistant metal comprising a sintered skeleton consisting essentially of iron having 0.2 to 15 percent by weight chromium and 0.2 to 1.0 percent by weight carbon, and an infiltrant consisting of 5 to 30 percent by weight copper-lead base alloy.

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

9. The wear resistant metal of claim 7 in which the copper-lead base alloy infiltrant comprises 5 to 30 percent by weight copper-lead alloy.

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

11. The wear resistant metal of claim 7 in which the copper-lead base alloy infiltrant includes at least one metal selected from the group consisting of tin, zinc and chromium.

12. A valve seat for an internal combustion engine fabricated of the wear resistant metal of claim 11.

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