

[54] **WEAR RESISTANT SINTERED ALLOY**

[75] Inventor: **Hiroshi Inoue**, Kashiwazaki, Japan

[73] Assignee: **Riken Piston Ring Industrial Co., Ltd.**, Tokyo, Japan

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75/201; 75/128 D; 75/128 P; 418/178

[51] Int. Cl.<sup>2</sup> ..... **B22F 1/00**

[58] Field of Search ..... 75/203, 204, 201, 128 D,  
75/128 P; 29/182.5; 418/178

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*Primary Examiner*—Benjamin R. Padgett

*Assistant Examiner*—B. H. Hunt

[57]

**ABSTRACT**

An iron base sintered alloy having high wear resistance produced in a feasible and effective way, provided by compounding molybdenum disulfide or the like metal sulfide having its melting point higher than the sintering temperature of the alloy.

Sulphur in the sulfide forms iron sulfide which improves wear resisting property of the alloy, while, metallic component of the sulfide diffuses throughout the base metal and serves to enhance the strength of matrix.

Test results with apex seals of rotary piston engine revealed that wear amount of seals made of the alloy according to the present invention is extremely low as compared with those made of molybdenum-copper-cast iron, graphite or sintered alloy which is sintered and thereafter sulphurized by gas sulphurizing process.

**6 Claims, 8 Drawing Figures**

**FIG. 1A**



x400x1.5

**FIG. 1B**

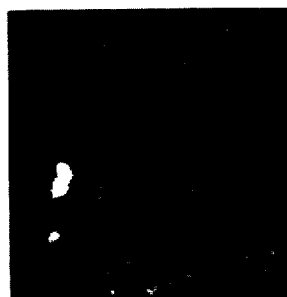


x400x1.5

**FIG. 2A**



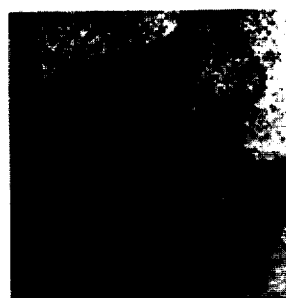
**FIG. 2B**

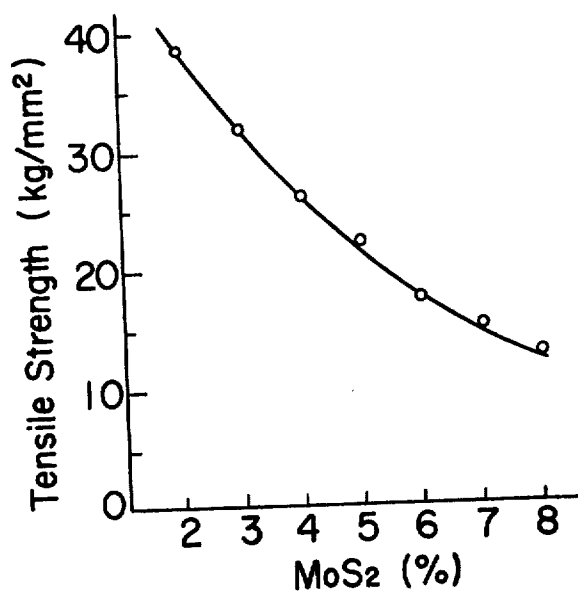
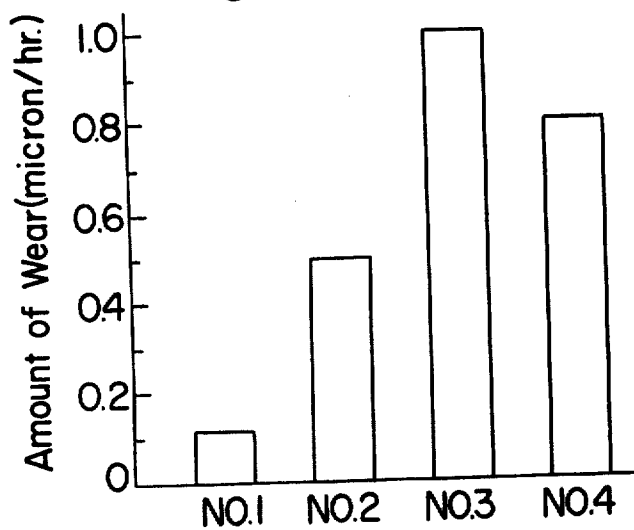


**FIG. 2C**



**FIG. 2D**



**Fig. 3****Fig. 4**

## WEAR RESISTANT SINTERED ALLOY

## BACKGROUND OF THE INVENTION

The present invention relates to wear resistant sintered alloy suitable for high speed sliding members or the like.

For the members sliding at high speed and in high ambient temperature, like apex seals of rotary piston engine, which are mounted on the rotary piston and forced to slide against trochoidal inner surface of the cylinder under a circumstance where the breaking of lubricating oil film on that sliding surface is apt to occur, less hardness decrease during operation and excellent oil retaining property to hold lubricating oil film on said sliding surface are required as well as high wear resistance.

Conventionally, cast iron of pearlitic structure has been used widely as a material of such sliding members. It is considered that the self-lubricating and oil retaining properties of graphite itself contained in the cast iron, together with pearlitic structure of the matrix, make the material wear resistant. Therefore, wear resistance of such cast iron will be increased by increasing graphite content, but there is a limit for the carbon content of cast iron, and it is difficult to make the content of free graphite more than 3%.

Further, the use of graphite itself for such sliding members has been tried also, but this is unfavorable because of its rapid wear.

As is widely known, sintered alloy obtained by the powder metallurgical process is porous and has good oil retaining or holding property. Therefore, excellent wear resistant material would be obtained according to the powder metallurgical process by adding some of the elements which increase wear resisting property of the material.

As a method to improve the wear resisting property of iron base alloys, the gas sulphurizing process, in which sulphur is diffused and impregnated in the surface layer of iron or steel and thereby forms iron sulfide, has been known. However, it is difficult to apply this process to the sintered alloy at present because of such problems as corrosion of sintering furnace and generation of harmful gas, and expected results could not be obtained by this process under our experiments.

## SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a sintered alloy having high wear resistance produced in a more feasible and effective process.

Another object of the present invention is to provide a sintered alloy suitable for apex seals of rotary piston engine.

It has been found that the foregoing and related objects may be readily attained in a sintered alloy made by a process comprising the steps of preparing powder mixture by weight of 1.0-1.8% carbon, 0.5-2.0% chromium, 0.5-1.0% nickel, 2.0-8.0% metal sulfide or sulfides and rest of iron, forming said powder mixture by compressing, and sintering said formed powder mixture, wherein said metal sulfide or sulfides having melting point higher than sintering temperature of said formed powder mixture.

It has been found that sulphur in said metal sulfide or sulfides combines with iron and forms iron sulfide while

sintering which improves wear resisting property of the alloy.

Metallic component of the sulfide diffuses into the base metal and serves to enhance the strength of matrix.

It has also been found that the alloy is particularly suitable for the apex seal of rotary piston engine, and capable of forming to its shape precisely by machining.

Further objects, features and advantages of the present invention will be apparent by the following description with reference to the accompanying drawings.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1(A) and 1(B) are micrographs ( $\times 400 \times 1.5$ ) showing the structures of one example of the sintered alloys according to the present invention, in which FIG. 1(A) is as polished and FIG. 1(B) is as polished and etched by 2%  $\text{HNO}_3$  alcoholic solution.

FIGS. 2(A)-(D) are photographs taken by the electron microprobe analysis, in which,

FIG. 2(A) shows absorbed electron image,

FIG. 2(B) shows  $L_{\alpha}$ -characteristic X-ray image of molybdenum,

FIGS. 2(C) and (D) show  $K_{\alpha}$ -characteristic X-ray images of sulphur and iron, respectively.

FIG. 3 is a graph illustrating the variation of tensile strength of the alloy according to the present invention in relationship with different molybdenum disulfide contents.

FIG. 4 is a graph illustrating the amount of wear of apex seal made of the alloy according to the present invention in comparison with those made of molybdenum-copper-cast iron, graphite and sulphurized sintered alloy respectively, after the actual engine test.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

Following kinds of powder were prepared as the raw materials of the alloy;

iron: under 100 mesh deoxidized mill scale powder,  
carbon: 98% purity natural graphite powder of 10 microns in average size,  
nickel: carbonyl nickel powder,  
chromium: under 100 mesh ferrochromium containing 60% chromium by weight,  
sulfide: molybdenum disulfide ( $\text{MoS}_2$ ) powder of 10 microns in average size.

These powders were compounded and mixed thoroughly so as to contain 1.5% carbon, 1.8% chromium, 0.7% nickel, 4% molybdenum disulfide and rest of iron, each by weight.

The mixture was compressed under 4 ton/cm<sup>2</sup> pressure to form  $75 \times 10 \times 6$  mm size specimens with density of 6.6 gram/cm<sup>3</sup>.

The formed specimens were then sintered at 1,120°C for 30 minutes in a prepared atmosphere of RX gas of 24% CO, 31%  $\text{H}_2$  and 45%  $\text{N}_2$  in average composition and 0°C dew point. The RX gas here means reducing gas mixture obtained by modifying hydrocarbon gases.

Thereafter, the specimens were cooled to 500°C over 40 minutes, and then cooled in furnace to room temperature.

Density of the sintered specimens was 6.0 gram/cm<sup>3</sup>.

Microstructures of the specimen are shown in FIG. 1.

FIG. 1(A) is a micrograph of specimen as polished, and FIG. 1(B) is a micrograph of the same specimen etched by 2%  $\text{HNO}_3$  alcoholic solution, wherein black

portions indicate pores, grey portions indicate sulfides, white portions located at the grain boundaries indicate free cementites and matrix is pearlite.

FIGS. 2 show photographs taken by the electron microprobe analysis, wherein FIG. 2(A) indicates absorbed electron image showing the region including sulfide, FIG. 2(B) indicates  $L\alpha$  characteristic X-ray image of molybdenum, FIG. 2(C) indicates  $K\alpha$  characteristic X-ray image of sulphur and FIG. 2(D) indicates  $K\alpha$  characteristic X-ray image of iron.

From these photographs, it will be seen that the sulfide formed is iron sulfide and molybdenum does not remain in the sulfide, but diffuses uniformly into the matrix.

FIG. 3 is a graph indicating tensile strength of the sintered alloy made by the process mentioned above, but changing the amount of molybdenum disulfide addition.

The tensile strength decreases with an increase of amount of molybdenum disulfide, but it will retain about 13 kg/mm<sup>2</sup> at 8% molybdenum disulfide addition, which strength would be enough for the practical use.

Samples obtained by the above mentioned process were machined to the shape of apex seal for rotary piston engine and mounted on a rotary piston and assembled in the center housing having a chromium plated trochoidal inner surface, and subjected to 300 hours actual engine test.

No. 1 in FIG. 4 shows the wear amount of the tested apex seals.

Seals made of different materials were also tested for comparison.

No. 2 and No. 3 show the wear amount of seals each made of molybdenum-copper-cast iron and graphite respectively, both were tested for 100 hours.

No. 4 shows the wear amount of apex seals made by the similar process as No. 1, except that in this case molybdenum was added in the form of ferromolybdenum containing 60% molybdenum and the sintered alloy was thereafter gas sulphurized. Running test in this case was performed for 300 hours.

Test results show that the apex seals according to the present invention is extremely excellent in wear resistance as compared with those of the other three materials. Wear of the cylinder wall after the test was practically negligible small except the case of No. 2 in which wavelike wears of about 8 micron depth were observed on the wall surface.

Referring now to each component of the alloy, carbon is a basic element which imparts wear resistance and mechanical strength to the alloy. It makes the matrix pearlitic, further precipitates free cementite to make the alloy endurable against hard sliding mating parts.

Carbon content of less than 1% will not be sufficient for such purposes, but the content of more than 1.8% would rather deteriorate the mechanical properties because of the precipitation of excessive cementite.

Chromium increases mechanical strength and wear resistance of the alloy, but it is not preferable to contain chromium more than 2%, because the alloy becomes too hard due to increase of chromium carbide content.

Nickel improves the alloy structure and increases mechanical strength and wear resistance. However, it requires considerably high temperature to diffuse

nickel into the matrix uniformly. Therefore, it is preferable to limit nickel content to less than 1% for the present sintering temperature.

As for the metal sulfide, which is considered as a carrier of the sulphur into the alloy, sulfide or sulfides of such metals as aluminium, chromium, cobalt, tungsten, copper, lead and molybdenum may be recommended for the use in consideration of its melting point, affinity of each metal to sulphur comparing to that of iron, and the effect of each metal on the mechanical properties of the alloy.

If melting point of a metal sulfide is lower than the sintering temperature, sulphur may come out of the alloy and cause not only decrease of sulphur content but contamination of the sintering atmospheric gases, so that it is necessary that the melting point of metal sulfide is higher than the sintering temperature of usual iron base sintered alloy which is approximately 1050° - 1150°C.

It is preferable to limit the quantity of metal sulfide to be added to less than 8% from the reason mainly of the adverse effect on mechanical strength of the alloy as shown in FIG. 3, but in case of less than 0.5%, it has little effect on wear resisting property, and it is recommended to add more than 2% to retain remarkable effect even when mechanical parts are used under severe conditions.

As aforementioned, the alloy of the present invention is porous and has good oil retaining property. Moreover, a higher proportion of iron sulfide of high wear resisting property is easily formed within the base metal which itself is wear resistant, without any problems of such as harmful gas generation. Further, metallic component of the metal sulfide diffuses into the base metal and serves to enhance the strength of matrix.

Therefore, according to the present invention, the alloy of high wear resistance and good oil retaining property and still retaining enough mechanical strength may be obtained in a feasible and effective way.

The alloy is not only suitable in use for the ordinary sliding mechanical parts, but is also particularly usable for the members used under severe conditions, like the apex seal of rotary piston engine, in which the breaking of lubricating oil film may occur due to very high speed sliding at high ambient temperature.

Further, like molybdenum disulfide, many of the metal sulfides used in the present invention have excellent selflubricating property, so that the products of high compressed density may be obtained with such sulfides even under less compressive load and with less additional lubricant at the step of forming, and this may also enable the use of existing equipments. The sulfide may also improve the machinability of sintered alloy which heretofore has been considered as inferior.

What is claimed is:

1. A method of preparing a wear-resistant iron-base alloy comprising the steps of:

preparing a powder mixture comprising 1.0-1.8% carbon, 0.5-2.0% chromium, 0.5-1.0% nickel, 2.0-8.0% of one or more metal sulfides selected from a group consisting of aluminum sulfide, cobalt sulfide, tungsten sulfide, copper sulfide, lead sulfide, and molybdenum sulfide, and the balance iron;

compressing said powder mixture into a form; sintering said form at a temperature below the melting point of said one or more metal sulfides;

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maintaining said form at temperatures up to said sintering temperature to distribute the sulfur of said one or more metal sulfide substantially in the microstructure of said alloy as iron sulfides, and the metal of said one or more metal sulfides substantially uniformly within the matrix of said alloy; and cooling said form to room temperature.

2. The method as claimed in claim 1, wherein said one or more metal sulfides comprises molybdenum disulfide.

3. The method as claimed in claim 2, wherein said step of sintering comprises heating said form at 1,120°C for 30 minutes in a reducing gas atmosphere.

4. A wear resistant sintered alloy prepared from a mixture of powders comprising:

1.0–1.8% carbon, 0.5–2.0% chromium, 0.5–1.0% nickel, 2.0–8.0% of one or more metal sulfides selected from a group consisting of aluminum sulfide,

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cobalt sulfide, tungsten sulfide, copper sulfide, lead sulfide, and molybdenum sulfide, and the balance iron;

said alloy having a sintered microstructure comprising a pearlite matrix, free cementite located at grain boundaries, and pores, and wherein

the sulfur of said one or more metal sulfide is distributed substantially in said microstructure as iron sulfide inclusions, and the metal of said one or more metal sulfides is distributed substantially uniformly within said matrix.

5. The sintered alloy as claimed in claim 4, wherein said one or more metal sulfides comprises molybdenum disulfide.

6. An apex seal for a rotary piston engine made from the wear resistant sintered alloy as claimed in claim 4.

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