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(54) **IRON-BASED SINTERED ALLOY VALVE SEAT**

(57) A valve seat of an iron-based sintered alloy having high wear resistance in a wide temperature range, which can be used in direct injection engines with improved fuel efficiency, low emission and high power, is obtained by limiting the amount of a solid lubricant dispersed in the matrix of the valve seat of an iron-based

sintered alloy, and dispersing at least two types of hard particles having different hardnesses in the matrix, thereby providing high strength and self-lubrication, as well as improved wear resistance under no lubrication in a wide temperature range.

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Description

FIELD OF THE INVENTION

5 **[0001]** The present invention relates to a valve seat for internal combustion engines, particularly to a valve seat made of an iron-based sintered alloy, which is used under the condition of low lubrication by fuel injection into cylinders.

BACKGROUND OF THE INVENTION

10 **[0002]** For environmental protection, improved fuel efficiency, lower emission and higher power are increasingly needed to internal combustion engines, and high-load combustion and high-load engine specifications require combustion chamber parts to have higher wear resistance in a wide use temperature range. Valve seats used with intake valves and exhaust valves for keeping the gas tightness of combustion chambers are exposed to combustion pressure, and receive strong shock repeatedly by the reciprocating motion of valves. In addition, because valves are not only reciprocable but also rotatable around their stems, sliding surfaces of valve seats which come into contact with valves are required to have high wear resistance. Particularly in direct injection (DI) engines in which fuel is directly injected into cylinders, valves and valve seats are sliding with each other without fuel lubrication in their sliding surfaces, so that valve seats should have higher wear resistance than required conventionally. Thus, iron-based sintered alloys having high wear resistance under no lubrication, which is improved by dispersing a large amount of solid lubricants such as calcium fluoride, etc. in the matrix to increase self-lubrication, as described in JP 2003-166025 A, have been used for valve seats.

20 **[0003]** However, valve seats of conventional iron-based sintered alloys, in which calcium fluoride as a solid lubricant is dispersed in a large amount in a matrix, have low strength, as well as insufficient wear resistance in a low temperature range, so that they are not suitable for use in a wide temperature range. Also, valve seats of conventional iron-based sintered alloys containing only ferromolybdenum as hard particles have insufficient wear resistance in a wide temperature range.

OBJECT OF THE INVENTION

30 **[0004]** In view of the above problems, an object of the present invention is to provide a valve seat of an iron-based sintered alloy having high wear resistance in a wide temperature range, which can be used in direct injection engines with improved fuel efficiency, low emission and high power.

SUMMARY OF THE INVENTION

35 **[0005]** As a result of intensive research, the inventors have found that by limiting the amount of a solid lubricant dispersed in the matrix of the valve seat of an iron-based sintered alloy, and dispersing at least two types of hard particles having different hardnesses in the matrix, the valve seat can be provided with high strength and self-lubrication, as well as remarkably improved wear resistance under no lubrication in a wide temperature range.

40 **[0006]** Thus, the present invention provides a valve seat of an iron-based sintered alloy, in which at least two types of hard particles having different hardnesses, and 0.2-0.8% by mass of a solid lubricant are dispersed.

45 **[0007]** At least two types of the hard particles having different hardnesses preferably comprise 2-8% by mass of first hard particles having an average particle size of 50-150 μm and Vickers hardness Hv of 800-1200, and 5-15% by mass of second hard particles having an average particle size of 10-150 μm and Vickers hardness Hv of 400-750. The hard particles may be Fe-Mo alloy particles, Fe-Cr-Mo-V alloy particles, and Co-Mo-Cr alloy particles. It is particularly preferable that the first hard particles are Fe-Mo-Si alloy particles comprising by mass 40-70% of Mo, and 0.1-2.0% of Si, the balance being Fe and inevitable impurities, and that the second hard particles are Fe-C-Cr-Mo-V alloy particles comprising by mass 0.2-0.5% of C, 0.5-5% of Cr, 1-5% of Mo, and 2-5% of V, the balance being Fe and inevitable impurities.

50 **[0008]** The matrix, in which at least two types of the hard particles having different hardnesses and the solid lubricant are dispersed, preferably has a composition comprising by mass 0.5-2.5% of C, 0.4-2% of Si, 0.5-5% of Mo, and 1-5% of Ni, the balance being Fe and inevitable impurities. The matrix phase preferably has a tempered martensite phase and a pearlite phase.

55 **[0009]** The solid lubricant is preferably constituted by one or more powders selected from the group consisting of sulfides such as MnS and MoS_2 and nitrides such as BN, having an average particle size of 2-50 μm .

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Fig. 1 is a view schematically showing a wear rig test for evaluating the valve seat of an iron-based sintered

alloy according to the present invention.

[0011] Fig. 2(a) is a graph showing by a relative value the amounts of wear of a valve seat and a valve at a test temperature of 150°C, which was measured on each of the valve seats of Examples within the present invention and Comparative Examples by a wear rig tester.

[0012] Fig. 2(b) is a graph showing by a relative value the amounts of wear of a valve seat and a valve at a test temperature of 250°C, which was measured on each of the valve seats of Examples within the present invention and Comparative Examples by a wear rig tester.

[0013] Fig. 3 (a) is a graph showing by a relative value the total amount of wear of a valve seat and a valve at a test temperature of 150°C, which was measured on each of the valve seats of Examples within the present invention and Comparative Examples by a wear rig tester.

[0014] Fig. 3(b) is a graph showing by a relative value the total amount of wear of a valve seat and a valve at a test temperature of 250°C, which was measured on each of the valve seats of Examples within the present invention and Comparative Examples by a wear rig tester.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0015] The valve seat of an iron-based sintered alloy according to the present invention is composed of a matrix, at least two types of hard particles having different hardnesses and a solid lubricant, which are dispersed in the matrix. The solid lubricant dispersed in the matrix is 0.2-0.8% by mass.

More than 0.8% of the solid lubricant dispersed reduces powder-bonding strength in powder compression molding, resulting in a sintered body with low strength and insufficient wear resistance. On the other hand, less than 0.2% of the solid lubricant provides low machinability. The solid lubricant preferably has an average particle size of 2-50 μm . The solid lubricant uniformly dispersed in the matrix improves wear resistance, self-lubrication and machinability.

[0016] The solid lubricant is preferably one or more selected from sulfides such as MnS, MoS₂, etc., and nitrides such as BN (boron nitride), etc. It is more preferable that when two or more types of solid lubricants are used, at least one has an average particle size of 2-10 μm , and the other has an average particle size of 10-50 μm , for uniform dispersion. The fine dispersion of the solid lubricant having an average particle size of 2-10 μm improves the machinability, and the coarse dispersion of the solid lubricant having a particle size range of 10-50 μm improves the self-lubrication and the wear resistance.

[0017] With respect to the hard particles dispersed in the matrix, first hard particles are harder than second hard particles, which are harder than the matrix phase. The presence of hard particles having intermediate hardness can provide the matrix phase and the hard particles with good hardness balance, thereby suppressing attackability to a mating member while maintaining the wear resistance.

[0018] The first hard particles dispersed in an amount of 2-8% by mass preferably have an average particle size of 50-150 μm and Vickers hardness Hv of 800-1200. It is particularly preferable to use particles of an Fe-Mo-Si alloy, an intermetallic compound comprising by mass 40-70% of Mo, and 0.1-2.0% of Si, the balance being Fe and inevitable impurities. Used with the second hard particles described later, they can suppress the diffusion of alloying elements into the matrix, increasing softening resistance without modifying the matrix structure, thereby suppressing attackability to a mating member and improving the wear resistance of itself.

[0019] The second hard particles dispersed in an amount of 5-15% by mass preferably have an average particle size of 10-150 μm and Vickers hardness Hv of 400-750, harder than the matrix. Their average particle size is more preferably 20-130 μm . It is particularly preferable to use particles of an Fe-C-Cr-Mo-V alloy comprising by mass 0.2-0.5% of C, 0.5-5% of Cr, 1-5% of Mo, and 2-5% of V, the balance being Fe and inevitable impurities. With finer second hard particles dispersed in the matrix, part of alloying elements (for example, Cr and V) are dissolved in the matrix, or form carbides, to strengthen the matrix, while suppressing the diffusion of alloying elements in the first hard particles into the matrix. This makes it possible to suppress the attackability to a mating member, while improving the wear resistance of itself.

[0020] The matrix preferably has a composition comprising by mass 0.5-2.5% of C, 0.4-2% of Si, 0.5-5% of Mo, and 1-5% of Ni, the balance being Fe and inevitable impurities. C is dissolved in the matrix to strengthen it, and combined with other alloying elements to form carbides, improving the wear resistance. Si forms an oxide layer to improve the wear resistance. Mo improves the hardenability, strengthens the matrix, and lowers the oxidation start temperature of the valve seat, thereby providing the valve seat with improved wear resistance. Ni strengthens the matrix and improves the hardness, thereby improving the wear resistance. With respect to a microstructure, the matrix preferably has a mixed structure comprising tempered martensite and pearlite, so that it has proper toughness and excellent wear resistance. Of course, fine carbides are dispersed in the mixed structure.

[0021] In the production of the valve seat of an iron-based sintered alloy according to the present invention, a starting material for the matrix phase may be iron powder mixed with alloying element powders, graphite powder, etc., or prealloy powder having a predetermined composition. Iron powder and/or prealloy powder and alloying element powders constituting the matrix phase are mixed with at least two types of hard particles having different hardnesses and solid

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lubricant powder, to prepare a starting material powder. 0.5-2% of stearate, etc. may be added as a parting agent to the total amount of the powder mixture, a starting material powder comprising iron powder, prealloy powder, alloying element powders, hard particles, and solid lubricant powder. The powder mixture is compression-molded to a green compact by a press, etc., and the green compact is sintered in a temperature range of 1050-1200°C in vacuum or in a non-oxidizing (or reducing) atmosphere, and then tempered in a temperature range of 500-700°C. The sintered body after tempering may be sealed by a resin, etc.

[0022] The sintering temperature of lower than 1050°C provides insufficient diffusion bonding, failing to obtain the desired strength. On the other hand, when sintered at a temperature exceeding 1200°C, abnormal diffusion occurs between the hard particles and the matrix, resulting in deteriorated wear resistance. The non-oxidizing (or reducing) atmosphere is preferably an NH₃ gas, a mixed gas of N₂ and H₂, etc.

[0023] Examples 1-5 (E1-E5) and Comparative Examples 1-6 (C1-C6)

[0024] Pure iron powder, and/or prealloy powder comprising 2.5% of Mo, 1% of Si, and 0.02% of C, the balance being iron and inevitable impurities, each of which had a particle size distribution with a peak in 150-200 mesh, were mixed with Mo powder, Si powder, Ni powder and graphite powder in such amounts as to provide the composition of Matrix A-K shown in Table 1, and with the first hard particles L-R of Fe-Mo-Si alloys shown in Table 2, the second hard particles S-Y of Fe-C-Cr-Mo-V alloys shown in Table 3, and the solid lubricant powder shown in Table 4, at ratios (% by mass) shown in Table 4, and blended by a blender to prepare each powder mixture.

[0025] Table 1

No.	Matrix (Fe-C-Si-Mo-Ni Alloy)				
	C	Si	Mo	Ni	Fe
A	2.5	1.5	0.5	1.0	Balance
B*	1.2	2.0	2.5	2.0	Balance
C*	1.5	1.0	5.0	5.0	Balance
D	1.1	0.4	2.5	1.0	Balance
E*	1.3	1.0	2.5	3.0	Balance
F	1.3	0.5	2.5	3.0	Balance
G*	1.1	0.5	5.0	2.0	Balance
H	0.9	1.0	0.5	1.0	Balance
I	0.8	0.5	2.5	4.0	Balance
J	1.5	2.2	-	2.0	Balance
K*	2.0	1.0	2.5	-	Balance
Note: * Prealloy powder was used.					

[0026] Table 2

No.	First Hard Particles (Fe-Mo-Si Alloy)			
	Mo	Si	Fe	Average Particle Size (μm)
L	33.1	0.5	Balance	89
M	37.3	1.1	Balance	105
N	44.5	0.9	Balance	73
O	48.2	1.2	Balance	128
P	55.0	1.5	Balance	134
Q	58.1	1.6	Balance	86
R	66.7	1.8	Balance	92

[0027] Table 3

No.	Second Hard Particles (Fe-C-Cr-Mo-V Alloy)					
	C	Cr	Mo	V	Fe	Average Particle Size (μm)
S	0.2	0.5	1.0	0.9	Balance	70
T	0.4	0.6	1.6	1.1	Balance	48
U	0.5	1.0	1.9	2.1	Balance	26
V	0.3	1.2	2.1	2.4	Balance	48
W	0.4	1.8	2.2	2.5	Balance	95
X	0.3	2.4	3.1	3.8	Balance	39
Y	0.3	4.3	4.6	4.7	Balance	128

[0028] Table 4

No.	Solid Lubricant ⁽¹⁾		First Hard Particles			Second Hard Particles			Matrix		
	MnS % ⁽²⁾	BN % ⁽²⁾	Type	Hv ⁽³⁾	% ⁽²⁾	Type	Hv ⁽³⁾	% ⁽²⁾	Type	Hv ⁽³⁾	% ⁽²⁾
E1	0.2	-	N	850	2	Y	750	5	A	260	92.8
E2	-	0.2	O	910	4	W	490	10	B	355	85.8
E3	-	0.8	R	1150	8	X	590	15	C	390	76.2
E4	0.5	-	Q	1060	5	U	440	10	D	335	84.5
E5	0.5	0.3	R	1150	7	Y	750	5	E	355	87.2
C1	1.0	-	M	745	6	S	340	8	F	360	85.0
C2	-	1.0	Q	1060	1	T	380	5	G	380	93.0
C3	0.8	-	Q	1060	5	-	-	-	H	240	94.2
C4	-	2.0	-	-	-	U	440	20	I	265	78.0
C5	-	1.0	L	705	10	S	340	6	J	220	83.0
C6	1.0	2.0	P	1020	5	V	480	15	K	350	77.0

Note: (1) MnS had an average particle size of 7 μm , and BN had an average particle size of 10 μm .
 (2) Amount expressed by % by mass.
 (3) Hardness Hv.

[0029] Each powder mixture was charged into a molding die, compression-molded by a press at pressure of 6.5 t/cm², and then sintered at 1120°C in vacuum to produce a ring-shaped sintered body of 37.6 mm in outer diameter, 26 mm in inner diameter and 8 mm in thickness. Thereafter, tempering was conducted at 650°C to obtain the ring-shaped sintered bodies of Examples 1-5 (E1-E5), each comprising a matrix having a tempered martensite phase and a pearlite phase, two types of hard particles (Fe-Mo-Si alloy and Fe-C-Cr-Mo-V alloy) having different hardnesses, and solid lubricants (MnS and/or BN), which were dispersed in the matrix. With respect to Comparative Examples, using each powder mixture of Comparative Examples 1(C1), 2 (C2) and 4-6 (C4-C6), in which the total amount of solid lubricants was 1% or more, and Comparative Examples 3 and 4 (C3 and C4), in which one type of hard particles were contained, a ring-shaped sintered body of Comparative Examples 1-6 (C1-C6) was produced by the same steps as in Examples 1-5. In each sintered body, the matrix and hard particles were measured with respect to Vickers hardness at a load of 50-100 g by a micro Vickers hardness meter. The results are shown in Table 4.

[0030] Each ring-shaped sintered body was machined to a valve seat, whose wear resistance was evaluated by a wear rig tester shown in Fig. 1. The valve seat 4 was fit into a valve seat holder 2 made of the same material as for a cylinder head in the tester, to conduct a wear test by vertically reciprocating a valve 3 by the rotation of a cam 7, with the valve 3 and the valve seat 4 heated by a burner 1. Using thermocouples 5, 6 embedded in the valve seat 4, the power of the burner 1 was controlled such that a contact surface of the valve seat was kept at a predetermined temperature.

Repeatedly hit by the valve 3, the valve seat 4 was worn, and their amounts of wear were expressed by the degrees of recession of the contact surfaces of the valve seat and the valve, which were calculated from their sizes measured before and after the test. The valve used had a size corresponding to the valve seat, and was made of an SUH alloy (JIS G 4311). The test conditions were as follows:

Temperatures	150°C and 250°C,
Rotation speed of cam	2500 rpm, and
Test time	5 hours.

The test results are shown in Table 5, Fig. 2(a) (at a test temperature of 150°C), and Fig. 2(b) (at a test temperature of 250°C).

[0031] Table 5

No.	Amount of Wear ⁽¹⁾ Tested					
	at 150°C			at 250°C		
	Valve Seat	Valve	Total	Valve Seat	Valve	Total
Example 1 (E1)	0.7	0.2	0.5	0.6	0.3	0.5
Example 2 (E2)	0.5	0.4	0.5	0.5	0.4	0.4
Example 3 (E3)	0.2	0.8	0.4	0.3	0.5	0.4
Example 4 (E4)	0.3	0.5	0.4	0.4	0.3	0.4
Example 5 (E5)	0.3	0.7	0.4	0.4	0.5	0.4
Com. Ex. 1 (C1)	1.0	0.2	0.7	0.9	0.5	0.8
Com. Ex. 2 (C2)	0.9	0.8	0.9	1.0	0.8	1.0
Com. Ex. 3 (C3)	1	1	1	1	1	1
Com. Ex. 4 (C4)	2.0	1.3	1.7	1.7	1.2	1.6
Com. Ex. 5 (C5)	1.1	0.8	1.0	1.1	1.1	1.1
Com. Ex. 6 (C6)	1.0	1.0	1.0	0.9	0.9	0.9
Note: (1) The amount of wear is expressed by a ratio to that of Comparative Example 3, which is assumed as 1.						

[0032] The amount of wear of each valve seat is expressed by a relative value, assuming that the amount of wear is 1 in Comparative Example 3 (C3), in which only hard particles of an Fe-Mo-Si alloy were dispersed. Any valve seats and their mating members (valves) in Examples 1-5 (E1-E5) within the present invention were smaller in the amount of wear than in Comparative Example 3 (C3) at test temperatures of 150°C and 250°C, indicating that they had excellent wear resistance and relatively mild attackability to mating members in both low and high temperature ranges. Also, the total amount of wear of the valve seat and the valve in Examples 1-5 (E1-E5) within the present invention was half or less than in Comparative Example 3 at 150°C and 250°C, indicating that they had remarkably improved wear resistance in a wide range from low temperatures to high temperatures. On the other hand, some of Comparative Examples 1 (C1), 2 (C2) and 4-6 (C4-C6), in which the total amount of the solid lubricants was 1% or more, and Comparative Examples 3 and 4 (C3 and C4), in which only one type of hard particles was used, exhibited improved wear resistance at a test temperature of 150°C or 250°C, but remarkable improvement of wear resistance was not achieved in a wide range from low temperatures to high temperatures. Examples within the present invention were smaller in the amounts of wear of the valve seat and the mating member than Comparative Examples in a wide range from low temperatures to high temperatures, indicating improved wear resistance and lower attackability to mating members.

EFFECT OF THE INVENTION

[0033] The valve seat of an iron-based sintered alloy according to the present invention, which comprises 0.2-0.8% by mass of a solid lubricant and at least two types of hard particles having different hardnesses dispersed in the matrix, has high strength as well as self-lubrication, thereby exhibiting extremely improved wear resistance under no lubrication in a wide temperature range. Two types of hard particles contribute to improving wear resistance at high and low

temperatures, because part of elements constituting one type of hard particles are dissolved in the matrix or form compounds with elements in the matrix to strengthen the matrix, while suppressing elements constituting the other type of hard particles from being dissolved in the matrix, thereby increasing softening resistance. Thus, the valve seat used in DI-type engines in which fuel is directly injected into cylinders exhibits excellent wear resistance, under little lubrication and in a wide range from low temperatures of about 150-350°C to high temperatures. The valve seat of an iron-based sintered alloy according to the present invention is more preferable as an intake valve seat.

Claims

1. A valve seat of an iron-based sintered alloy, in which at least two types of hard particles having different hardnesses, and 0.2-0.8% by mass of a solid lubricant are dispersed.
2. The valve seat of an iron-based sintered alloy according to claim 1, wherein at least two types of said hard particles having different hardnesses comprise 2-8% by mass of first hard particles having an average particle size of 50-150 μm and Vickers hardness Hv of 800-1200, and 5-15% by mass of second hard particles having an average particle size of 10-150 μm and Vickers hardness Hv of 400-750.
3. The valve seat of an iron-based sintered alloy according to claim 1 or 2, wherein said first hard particles are made of an Fe-Mo-Si alloy comprising by mass 40-70% of Mo, and 0.1-2.0% of Si, the balance being Fe and inevitable impurities, and said second hard particles are made of an Fe-C-Cr-Mo-V alloy comprising by mass 0.2-0.5% of C, 0.5-5% of Cr, 1-5% of Mo, and 2-5% of V, the balance being Fe and inevitable impurities.
4. The valve seat of an iron-based sintered alloy according to any one of claims 1-3, wherein a matrix, in which at least two types of said hard particles having different hardnesses and said solid lubricant are dispersed, has a composition comprising by mass 0.5-2.5% of C, 0.4-2% of Si, 0.5-5% of Mo, and 1-5% of Ni, the balance being Fe and inevitable impurities.
5. The valve seat of an iron-based sintered alloy according to claim 4, wherein said matrix has a tempered martensite phase and a pearlite phase.
6. The valve seat of an iron-based sintered alloy according to any one of claims 1-5, wherein said solid lubricant is one or more selected from the group consisting of sulfides and nitrides, having an average particle size of 2-50 μm .

Fig. 1

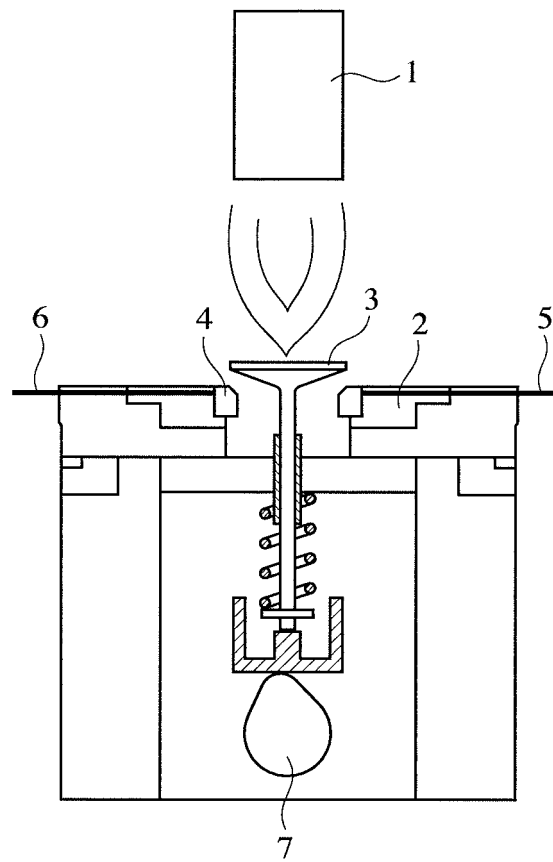


Fig. 2(a)

Test Temperature: 150°C

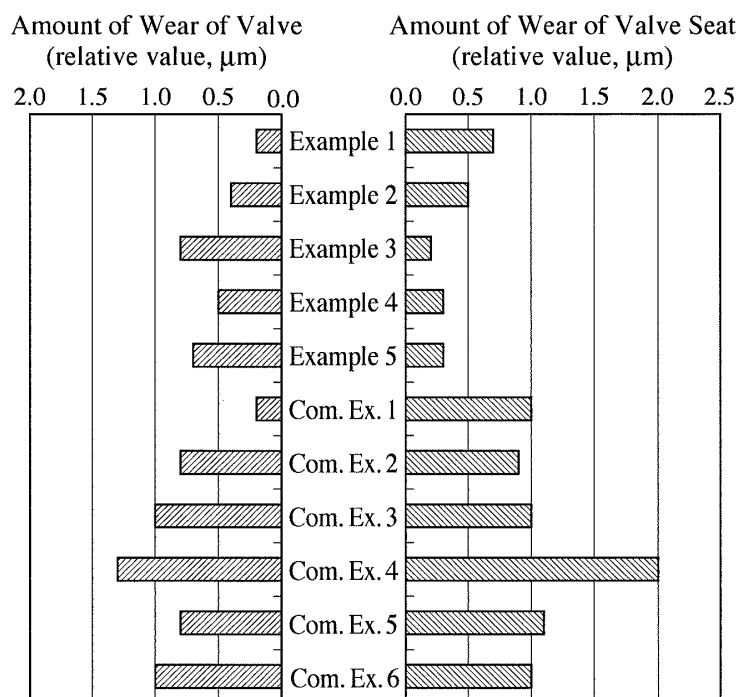


Fig. 2(b)

Test Temperature: 250°C

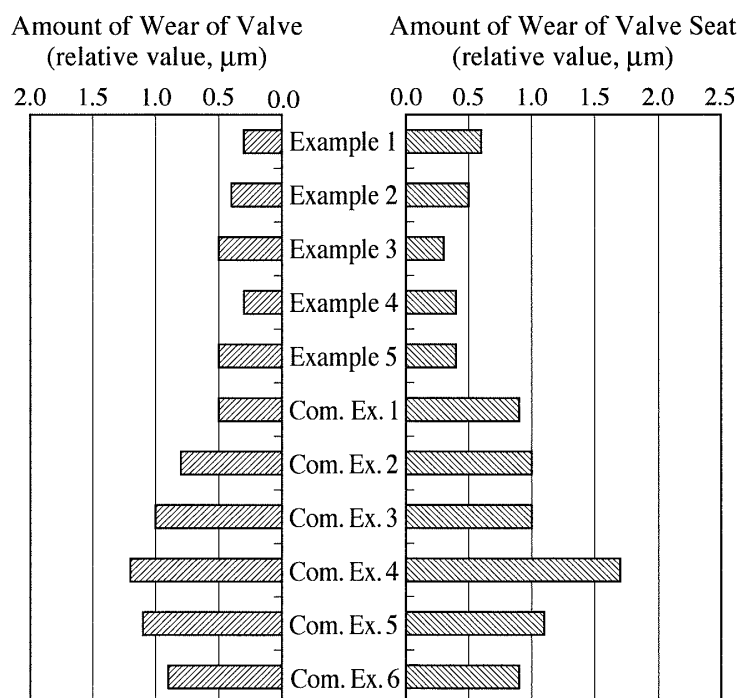


Fig. 3(a)

Test Temperature: 150°C

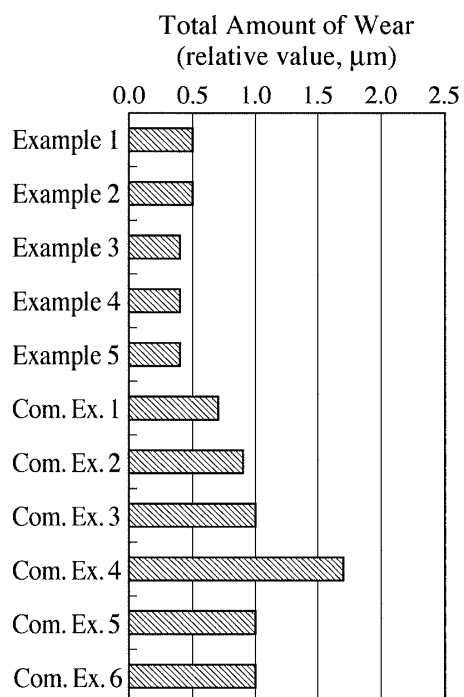
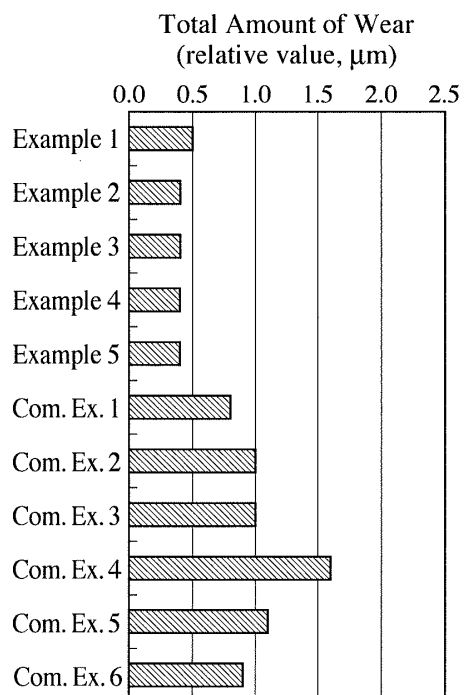


Fig. 3(b)

Test Temperature: 250°C



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/051191

A. CLASSIFICATION OF SUBJECT MATTER

F01L3/02(2006.01)i, B22F1/00(2006.01)i, B22F5/00(2006.01)i, C22C27/04(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

F01L3/02, B22F1/00, B22F5/00, C22C27/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2012
Kokai Jitsuyo Shinan Koho	1971-2012	Toroku Jitsuyo Shinan Koho	1994-2012

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 2002-129296 A (Nippon Piston Ring Co., Ltd.), 09 May 2002 (09.05.2002), paragraphs [0013] to [0030]; tables 1 to 2 & US 2002/0084004 A1 & GB 2370281 A	1-2 3-6
X Y	JP 2006-299404 A (Nippon Piston Ring Co., Ltd.), 02 November 2006 (02.11.2006), paragraphs [0014] to [0023]; tables 1 to 2 & KR 10-2006-0103155 A & KR 10-2008-0003763 A & KR 10-2008-0058316 A & CN 1837397 A	1 3-6

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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Date of the actual completion of the international search
22 February, 2012 (22.02.12)Date of mailing of the international search report
06 March, 2012 (06.03.12)Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2006-193831 A (Nippon Piston Ring Co., Ltd.), 27 July 2006 (27.07.2006), paragraphs [0015] to [0031]; tables 1 to 2 (Family: none)	1
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REFERENCES CITED IN THE DESCRIPTION

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- JP 2003166025 A [0002]