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European Patent Office
Office européen des brevets



(11)

EP 1 253 220 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 158(3) EPC

(43) Date of publication:

30.10.2002 Bulletin 2002/44

(51) Int Cl.7: **C23C 28/00**

(21) Application number: **00985887.9**

(86) International application number:
PCT/JP00/09235

(22) Date of filing: **26.12.2000**

(87) International publication number:
WO 01/048267 (05.07.2001 Gazette 2001/27)

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**

(30) Priority: **27.12.1999 JP 37114499**

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(54) **SLIDING MEMBER**

(57) The present invention provides a sliding member, of which the surface cavities do not disappear even after progress of wear of the sliding surface, which permits maintenance of a satisfactory seizure resistance, and has better seizure resistance, wear resistance and strength properties than in a sliding member having a porous chrome plating layer formed thereon in the conventional art. The sliding member of the invention has

a laminated hard Cr plating layer comprising a plurality of hard Cr plating layers laminated on the sliding surface. Micro-cracks are formed on each hard Cr plating layer surface, and the micro-cracks of each hard Cr plating layer form micro-pores independent in the film-forming direction. On the cross-section of the laminated hard Cr plating layer, the porosity should be within a range of from 0.5 to 4.5%.

FIG. 2



20 μ m

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Description

Technical Field

5 **[0001]** The present invention relates to a sliding member comprising a lamination of a plurality of hard Cr plating layers on a sliding surface. More particularly, the invention relates to a sliding member suitably applicable to a piston ring for an internal combustion engine.

Background Art

10 **[0002]** Along with the recent tendency toward a lighter weight and a higher output of internal combustion engines, the quality requirement is increasing for sliding members such as piston rings. It is the conventional practice for these sliding members such as piston rings for internal combustion engines to apply a wear resistant surface treatment through, for example, hard Cr plating or nitriding to the sliding surface as means for improving durability. Among others, 15 the nitriding treatment, which gives an excellent wear resistance, attracts the general attention as being suitable as a surface treatment for sliding members including piston rings used under severe operating conditions, and is widely used in practice.

[0003] However, the nitriding treatment, while being excellent in resultant wear resistance, is not always sufficient for seizure resistance (scarfing resistance): there may occur an abnormal wear when used under severe operating 20 conditions. Improvement has therefore been demanded. A conventional hard chrome plating layer (hereinafter referred to as a "hard Cr plating layer" as required), having a slightly higher seizure resistance (scarfing resistance) as compared with the nitriding treatment, is not always sufficient in wear resistance. There has therefore been a demand for improvement in applications under severe operating conditions.

[0004] In these respects, porous chrome plating having fine cavities on the surface serving as lubricant oil sumps 25 formed on the conventional hard Cr plating layer was studied for improving seizure resistance and wear resistance, and the result is actually applied in some cases.

[0005] In the conventional porous chrome plating, however, cavities are present only on the surface, and cavities effective for improving sliding properties are not existent in the interior of the plating layer. When applying grinding or 30 when the sliding surface is worn out, a solid portion not containing cavities on the surface of the plating layer is exposed, leading to deterioration of seizure resistance or wear resistance.

Disclosure of Invention

35 **[0006]** The present invention was achieved in view of the aforementioned problems, and has a main object to provide a sliding member in which surface cavities do not disappear even after grinding or in progress of wear of the sliding surface, seizure resistance and wear resistance can be maintained at a satisfactory level, and seizure resistance, wear resistance and strength are higher than in the conventional sliding member having a porous chrome plating layer formed thereon.

[0007] To achieve the aforementioned object, the sliding member of the invention as recited in claim 1 has a laminated 40 hard Cr plating layer comprising a plurality of hard Cr plating layers laminated on a sliding surface, micro-cracks being formed on the surface of each hard Cr plating layer, the micro-cracks of each hard Cr plating layer forming independent micro-pores in the film forming direction; wherein porosity on a cross-section of the laminated hard Cr plating layer is within a range of from 0.5 to 4.5%.

[0008] In the invention, a plurality of hard Cr plating layers having micro-cracks formed on the surface thereof are 45 laminated, and micro-cracks in each layer form independent micro-pores in the film forming direction. When micro-cracks disappear along with progress of wear, therefore, another micro-cracks immediately appear on the surface. Even when grinding is applied or after a long use in service, therefore, there always exist micro-cracks serving as lubricant oil sumps on the surface. No problem is therefore posed in seizure resistance or wear resistance. The porosity on the cross-section of this laminated hard Cr plating layer is within a range of from 0.5 to 4.5%, resulting in a sliding 50 member satisfactory seizure resistance, wear resistance and strength.

[0009] In the sliding member of claim 1 of the invention, the porosity on the surface of the hard Cr plating layer is within a range of from 0.5 to 30%, and the number of micro-cracks on the surface is within a range of from 50 to 1,200 cracks/10 mm.

[0010] According to the invention, by limiting the porosity and the number of micro-cracks within the above-mentioned 55 ranges, it is possible to obtain a laminated hard Cr plating layer satisfying the seizure resistance, wear resistance and strength requirements, as in the case of above-mentioned porosity on the cross-section. Because many micro-cracks are formed on the hard chrome plating layer, seizure resistance or wear resistance never poses problems.

[0011] In the sliding member according to claim 1 or 2 of the invention, as recited in claim 3, the thickness per layer

of the hard Cr plating layer should preferably be within a range of from 0.1 to 60 μm .

[0012] In the invention, when the thickness is smaller than 0.1 μm , it is necessary to laminate many hard Cr plating layers in order to obtain a laminated hard Cr plating layer having a necessary thickness, and this may result in a cost problem. When the thickness is over 60 μm , after disappearance of micro-cracks by wear, the thickness before appearance of micro-cracks of the next layer becomes too large, and in the meantime, problems may be encountered in seizure resistance or wear resistance.

[0013] To achieve the aforementioned object, the invention provides a sliding member having a laminated hard Cr plating layer comprising a plurality of hard Cr plating layers laminated on a sliding surface, micro-cracks being formed on the surface of each hard Cr plating layer, the micro-cracks of each hard Cr plating layer forming independent micro-pores in the film forming direction; wherein porosity of the surface of the hard Cr plating layer is within a range of from 0.5 to 5.0%, and the number of micro-cracks on the surface is within a range of from 50 to 1,200 cracks/10 mm.

[0014] In the invention, a plurality of hard Cr plating layers thus having micro-cracks on the surface thereof are laminated, and micro-cracks in each layer form independent micro-pores in the film forming direction. Even when micro-cracks disappear along with progress of wear, new micro-cracks appear on the surface immediately. When applying grinding or using for a long period of time, therefore, presence of micro-cracks serving as lubricant oil sumps always on the surface makes the sliding member free from any problem in seizure resistance or wear resistance. The porosity of the surface resulting from the micro-cracks on the surface of each hard Cr plating layer is within a range of from 0.5 to 5.0%, and the number of these micro-cracks is within a range of from 50 to 1,200 cracks/10 mm. Cracks on the surface of the hard Cr plating layer in the invention therefore largely comprise many micro-cracks. Since many micro-cracks are formed on the surface of the hard Cr plating layer, no problem is caused in seizure resistance or wear resistance, although the porosity of the surface based on the micro-cracks is within a relatively low range of from 0.5 to 5.0%. Because the porosity on the surface is on such a low level, and cracks are fine in size, strength-related properties such as peeling resistance of the hard Cr plating layer are considerably improved. The present invention have these features is particularly suitably applicable to uses in which the total thickness of the laminated hard Cr plating layer is relatively small as in piston rings of automobile.

[0015] In the sliding member of the invention according to claim 4, as recited in claim 5 of the invention, the thickness per layer of the hard Cr plating layer should preferably be within a range of from 0.1 to 60 μm .

[0016] When the thickness is smaller than 0.1 μm in the invention, it is necessary to laminate many hard Cr plating layers for the purpose of obtaining a laminated hard Cr plating layer having a necessary thickness, and this may pose a cost problem. When the thickness is larger than 60 μm , the thickness becomes excessively large during the period from disappearance of micro-cracks by wear to appearance of micro-cracks on the next layer, during which a problem may be encountered in seizure resistance or wear resistance.

Brief description of the Drawings

[0017]

Fig. 1 is a surface photo illustrating typical micro-cracks formed on the surface of each hard Cr plating layer;

Fig. 2 is a sectional photo illustrating typical lamination of hard Cr plating layers laminated on the surface of a substrate having an R_z of 3 μm ;

Fig. 3 is a sectional photo illustrating typical lamination of hard Cr plating layers laminated on the surface of a substrate having an R_z of 20 μm ; and

Fig. 4 is a schematic descriptive view illustrating an improved tester of an NPR type impact tester (a quantitative tester of plating adhesion disclosed in Japanese examined Patent Publication No. 36- 19046).

Best Mode for Carrying Out the Invention

[0018] The sliding member of the present invention will now be described in detail.

[0019] A first feature of the sliding member of the invention is that the sliding member has a laminated hard Cr plating layer comprising a lamination of a plurality of hard Cr plating layers on a sliding surface; micro-cracks are formed on the surface of each hard Cr plating layer; and the micro-cracks of each hard Cr plating layer have micro-pores independent in the film-forming direction.

[0020] As shown in Fig. 1, the sliding member of the invention comprises a lamination of the hard Cr plating layers having micro-cracks on the surfaces thereof. Therefore, for example, in the case of a sliding member having only a single hard Cr plating layer on the sliding surface, wear causes most of micro-cracks to disappear in a short period of time, thus posing a problem of a decrease in seizure resistance and wear resistance. In the invention, however, a plurality of hard Cr plating layers having such micro-cracks on the surfaces thereof are laminated so that, even when the portion of the surfaces containing micro-cracks disappears as a result of wear or working, micro-cracks (forming

micro-pores independent in the film-forming direction) appear on the next surfaces, thus permitting maintenance of satisfactory seizure resistance and wear resistance for a long period of time.

[0021] In the invention, the thickness per layer of the hard Cr plating layer should preferably be within a range of from 0.1 to 60 μm . In the case where the entire laminated hard Cr layer should have a relatively small total thickness, as in the automotive piston ring, the thickness per layer of the hard Cr plating layer should preferably be within a range of from 0.1 to 15 μm , or more preferably, from 2 to 15 μm . In the case where the total thickness of the entire laminated hard Cr plating layer is relatively large as in a marine piston ring, the thickness per layer of the hard Cr plating layer should preferably be within a range of from 15 to 60 μm , or more preferably, from 15 to 40 μm .

[0022] When the thickness per layer of the hard Cr plating layer is smaller than the aforementioned range, it is necessary to laminate many layers when forming a laminated hard Cr plating layer having a prescribed thickness. This is not desirable because of the possibility of posing a cost problem and since a small thickness of each layer may cause a problem in strength of each layer. When the thickness is larger than the aforementioned range, on the other hand, it would take a long period of time from disappearance of most of the micro-cracks to appearance of micro-cracks on the surface of the next layer. A larger thickness is not desirable because of the possibility of posing a seizure resistance problem.

[0023] In the invention, the surface portion of the substrate should preferably be flat. The substrate surface may have fine irregularities to some extent, and after lamination of hard Cr plating layers thereon in a prescribed number, smoothed by wrapping or the like. Presence of such fine irregularities on the substrate surface causes irregularities also in all the hard Cr plating layers. This reduces the possibility of disappearance of fine cracks in a stroke upon progress of wear, and this may improve seizure resistance. As shown in Figs. 2 and 3, the hard Cr plating layer of the invention laminated by a method described later is observed, varying with plating conditions, to have fine cavities over the entire area in the thickness direction formed thereon. A solid portion free from fine cavities is therefore hard to appear. As a result, a substrate surface even with irregularities within a range of R_z (ten-point average roughness) of from 0.3 to 20 μm is suitably applicable. In a use in which the total thickness of the laminated hard Cr plating layer as a whole is relatively small as in an automotive piston ring, R_z of the substrate surface should preferably be within a range of from 0.3 to 3.0 μm . In a use in which the total length of the entire laminated hard Cr plating layer is relatively large as in a marine piston ring, R_z of the substrate surface should preferably be within a range of from 1 to 20 μm .

[0024] The number of laminated hard Cr plating layers in the sliding member of the invention is the result of division of the necessary thickness of the hard Cr plating layers by the thickness of the individual layers, to be appropriately selected in response to the circumstances of application of the sliding member. The generally applicable number of layers is within a range of from about 5 to 30 layers, or more preferably, from 8 to 20 layers. A number of laminated layers larger than the aforementioned range requires more time and labor to conduct hard Cr plating, and this may cause a cost problem. When the number of laminated layers is smaller than the range shown, on the other hand, an increase in the thickness of the individual layers is generally expected, so that seizure resistance may be deteriorated.

[0025] A second feature of the sliding member of the invention is that the porosity on a cross-section of the laminated hard Cr plating layer is within a range of from 0.5 to 4.5%.

[0026] In general, in a porous chrome plating layer used as a sliding surface, when ignoring seizure resistance and wear resistance problems, the number of cavities such as cracks present on the surface should be the smallest possible, considering properties related with strength by the porous chrome plating layer itself such as peeling resistance. Particularly, under severe service conditions as in a sliding member for marine applications, strength-related properties become more important. When seizure resistance and wear resistance problems cannot be ignored, however, there occurs a serious problem in that reduction of the number of micro-cracks of the porous chrome plating layer results in deterioration of seizure resistance and wear resistance. Therefore, the number of micro-cracks in this porous chrome plating layer is an important factor for satisfying property requirements of strength, seizure resistance and wear resistance. In the present invention, the number of micro-cracks in this hard Cr plating layer was evaluated in terms of the porosity on a cross-section of the laminated hard Cr plating layer and possibility was found to maintain satisfactory strength properties, seizure resistance and wear resistance as described above by limiting the porosity on the cross-section of the laminated hard Cr plating layer within a range of from 0.5 to 4.5%.

[0027] It is necessary, as described above, to limit the porosity on the cross-section of the laminated hard Cr plating layer of the invention within a range of from 0.5 to 4.5%. With a porosity on the cross-section of under 0.5%, seizure resistance and wear resistance are low. A porosity on the cross-section of over 4.5% leads to a decrease in strength, causing breakage and cracks.

[0028] The term the porosity on a cross-section of the laminated hard Cr plating layer as used in the invention (also referred to as the "porous degree") shall mean a value determined by first applying polishing to the cross-section by use of water-proof polishing sheets of paper in a sequence of #180, #240, #320, #600, #800, and then #1000, then applying buffing by use of alumina having a particle size of up to 1 μm for 20 seconds, finally applying buffing by use of alumina having a particle size of up to 0.1 μm for seven seconds, and analyzing the cross-section by means of an image analyzer.

[0029] This definition is adopted because it is experimentally revealed that the value of porosity measured on the cross-section of the laminated hard Cr plating layer varies with the sample polishing conditions and time, and the necessity arises to set constant polishing conditions. The porosity on the cross-section of the laminated hard Cr plating layer in the invention means a porosity after polishing as described in the above-mentioned definition in all cases.

[0030] In the invention, furthermore, the porosity on the surface of the laminated hard Cr plating layer should preferably be within a range of from 0.5 to 30%, and the number of micro-cracks on this surface should preferably be within a range of from 50 to 1,200 cracks/10 mm.

[0031] A porosity on the surface of under 0.5% leads to poorer seizure resistance or wear resistance, and a porosity on the surface of over 30% causes a decrease in strength and production of breakage and cracks. In this case, in a use in which the total thickness of the entire laminated hard Cr plating layer is relatively small as in an automotive piston ring, the porosity should preferably be within a range of from 0.5 to 5.0%, or more preferably, from 2.0 to 4.5%. In a use in which the total thickness of the entire laminated hard Cr plating layer is relatively large as in a marine piston ring, the porosity should preferably be within a range of from 5 to 30%, or more preferably, from 10 to 20%. By limiting the number of micro-cracks on the surface within the above-mentioned range, many micro-cracks are formed on the hard chrome plating layer. No seizure resistance or wear resistance problem is therefore encountered.

[0032] In the above case where the surface porosity is within a range of from 0.5 to 30% and the number of micro-cracks is within a range of from 50 to 1,200 cracks/10 mm, the formed micro-cracks have a width within a range of from 0.42 to 2.5 μm . In the case with a surface porosity of from 0.5 to 5.0% and a number of micro-cracks of from 50 to 1,200 cracks/10 mm, the width is from 0.42 to 1.0 μm . A surface porosity of from 5.0 to 30% and a number of micro-cracks of from 50 to 1,200 cracks/10 mm result in a width within a range of from 1.0 to 2.5 μm .

[0033] In the sliding member of the invention, particularly, in the sliding member in uses in which the total thickness of the entire laminated hard Cr plating layer is relatively small as in an automotive piston ring, as described above, it is possible to achieve the object of the invention by specifying the surface porosity (also referred as the surface area ratio) based on micro-cracks on the surface and the number of micro-cracks without the need to clearly specify the porosity on the cross-section. More specifically, as recited in claim 4 of the invention, it is possible to achieve the object by limiting the surface porosity based on micro-cracks formed on the surface of each hard Cr plating layer within a range of from 0.5 to 5.0%, and the number of the micro-cracks within a range of from 1,200 cracks/10 mm.

[0034] As in the aforementioned second feature, when the problems of seizure resistance and wear resistance are disregarded in a porous chrome plating layer used generally as a sliding surface, the number of cavities such as cracks present on the surface should preferably be the smallest possible in terms of strength-related properties of the porous chrome plating layer itself including peeling resistance. Since seizure resistance and wear resistance are important properties, however, cavities are provided so that cracks are formed, for example, through an inverse current treatment on the surface of the hard Cr plating layer, and a prescribed porosity (surface area ratio) is achieved even when allowing a decrease in strength in the plating layer itself such as peeling resistance to some extent.

[0035] In an aspect of the invention, as recited in claim 4, new findings were obtained that, by causing micro-cracks to serve as such surface cavities, no problem was posed in seizure resistance or wear resistance even with a porosity based on a smaller number of cavities than in an usual case. This aspect of the invention has a marked feature in that it is intended to improve strength of the plating layer itself such as peeling resistance without causing a decrease in seizure resistance or wear resistance.

[0036] These micro-cracks are such that, as described above, in the case where the porosity of the surface based on surface micro-cracks of each hard Cr plating layer is within a range of from 0.5 to 5.0%, the number of micro-cracks is within a range of from 50 to 1,200 cracks/10 mm, or more preferably, that in the case where the porosity is within a range of from 2.0 to 4.5%, the number of micro-cracks is within a range of from 150 to 800 cracks/10 mm. In the case with a surface porosity within a range of from 0.5 to 5.0% and a number of micro-cracks within a range of from 50 to 1,200 cracks/10 mm, the width of the formed cracks is within a range of from 0.42 to 1.0 μm .

[0037] The sliding member of the invention described above is manufactured by repeating a hard Cr plating step and an etching step including an inverse current treatment prescribed times by use of a Cr plating bath on a substrate, and laminating hard Cr plating layers. By forming hard Cr plating layers one on top of the others as described above, an excellent adhesion between plating layers can be obtained. A hard Cr plating layer having a porosity on the cross-section or the surface as shown in the invention is obtained by adjusting conditions for the plating step and conditions for the etching step including the inverse current treatment.

[0038] The present invention is not limited to the aforementioned embodiments. These embodiments are only examples, and any sliding members having substantially the same configuration and providing the same advantages as in the technical idea recited in the claims of the invention are included in the technical scope of the invention.

Examples

[0039] The present invention will be described in detail by means of examples and comparative examples.

(Example 1)

[0040] A silicofluoride bath (CrO_3 : 250 g/L, H_2SO_4 : 1.5 g/L. and NaSiF_6 : 5 g/L) held constantly at 60 °C was used as a chrome plating bath. First, the substrate surface was subjected to an inverse current treatment as an activation treatment at a current density of 60 A/dm² for 30 seconds (inverse current treatment 1). Then, a positive current treatment was applied at a current density of 60 A/dm² for 17 minutes (positive current treatment 1). Then, an inverse current treatment was carried out at a current density of 60 A/dm² for 60 seconds (inverse current treatment 2). The positive current treatment 1 and the inverse current treatment 2 were repeated 17 times so as to achieve a predetermined plating thickness, thereby forming a laminated hard Cr plating layer used in the sliding member of the invention.

[0041] The resultant laminated hard Cr plating layer had a thickness per layer of about 10 µm and a total thickness of about 170 µm as a laminated hard Cr plating layer. The surface porosity based on micro-cracks on the surface was about 3.0%, and the number of micro-cracks was about 600 cracks/10 mm. Measurement of the sectional porosity in this state showed a porosity of about 3.0%.

(Example 2)

[0042] A silicofluoride bath (CrO_3 : 250 g/L, H_2SO_4 : 1.5 g/L, and NaSiF_6 : 1 g/L) held constantly at 65 °C was used as a chrome plating bath. First, the substrate surface was subjected to an inverse current treatment as an activation treatment at a current density of 60 A/dm² for 30 seconds (inverse current treatment 1). Then, a positive current treatment was applied at a current density of 60 A/dm² for 18 minutes (positive current treatment 1). Then, an inverse current treatment was conducted at a current density of 60 A/dm² for 60 seconds (inverse current treatment 2). The positive current treatment 1 and the inverse current treatment 2 were repeated 17 times so as to achieve a predetermined plating thickness, thereby forming a laminated hard Cr plating layer used in the sliding member of the invention.

[0043] The resultant laminated hard Cr plating layer had a thickness per layer of about 10 µm and a total thickness of about 170 µm as a laminated hard Cr plating layer. The surface porosity based on micro-cracks on the surface was about 0.5%, and the number of micro-cracks was about 50 cracks/10 mm. Measurement of the sectional porosity in this state showed a porosity of about 0.5%.

(Example 3)

[0044] A silicofluoride bath (CrO_3 : 250 g/L, H_2SO_4 : 1.5g/L. and NaSiF_6 : 8 g/L) held constantly at 50 °C was used as a chrome plating bath. First, the substrate surface was subjected to an inverse current treatment as an activation treatment at a current density of 60 A/dm² for 30 seconds (inverse current treatment 1). Then, a positive current treatment was applied at a current density of 60 A/dm² for 16 minutes (positive current treatment 1). Then, an inverse current treatment was carried out at a current density of 60 A/dm² for 60 seconds (inverse current treatment 2). The positive current treatment 1 and the inverse current treatment 2 were repeated 17 times so as to achieve a predetermined plating thickness, thereby forming a laminated hard Cr plating layer used in the sliding member of the invention.

[0045] The resultant laminated hard Cr plating layer had a thickness per layer of about 10 µm and a total thickness of about 170 µm as a laminated hard Cr plating layer. The surface porosity based on micro-cracks on the surface was about 4.5%, and the number of micro-cracks was about 1,200 cracks/10 mm. Measurement of the sectional porosity in this state showed a porosity of about 4.5%.

(Example 4)

[0046] A plating bath (CrO_3 : 256.7 g/L, trivalent chromium: 3.47 g/L, H_2SO_4 : 3.00 g/L, and iron: 9.20 g/L) held at a temperature within a range of from 56 to 58 °C was used as a chrome plating bath. First, the substrate surface was subjected to a positive current treatment at a current density of 30 A/dm² for 110 minutes (positive current treatment 1). Then, an inverse current treatment was carried out at a current density of 30 A/dm² for three minutes (inverse current treatment 1). Then, a positive current treatment was conducted at a current density of 30 A/dm² for 80 minutes (positive current treatment 2). In addition, an inverse current treatment was applied at a current density of 30 A/dm² for three minutes (inverse current treatment 1). The positive current treatment 2 and the inverse current treatment 1 were repeated 11 times, thereby forming a sliding member having a hard Cr plating layer laminated on a sliding surface.

[0047] In the resultant laminated hard Cr plating layer, a first layer, had a thickness of about 50 µm, and a second and subsequent layers had a thickness of about 30 µm per layer. The thus obtained laminated hard Cr plating layer had a thickness of about 410 µm. The sectional porosity was measured by polishing a cross-section of this laminated hard Cr plating layer by the aforementioned method, a porosity was 2.1%. The surface porosity measured as above gave a porosity of about 15%.

(Comparative Example 1)

[0048] A silicofluoride bath (CrO_3 : 250 g/L, H_2SO_4 : 2.5 g/L, and NaSiF_6 : 8 g/L) kept at a constant temperature of 55 °C was used as a chrome plating bath. First, a substrate was electrolytically polished, with the substrate as an anode and an opposite electrode comprising a tin-lead alloy as a cathode, by applying a selective uniform current corresponding to 60 A/dm² from a current controlling power source for a minute to electrolytically eluting the substrate surface. Then, the anode and the cathode were rapidly reversed, and a selective uniform current of 60 A/dm² was applied from the current controlling power source until precipitation of a hard Cr plating layer having a prescribed thickness.

[0049] A conventional single-layer chrome plating layer continuously formed was obtained.

(Comparative Example 2)

[0050] A silicofluoride bath (CrO_3 : 250 g/L, H_2SO_4 : 2.5 g/L, and NaSiF_6 : 8 g/L) kept at a constant temperature of 55 °C was used as a chrome plating bath. First, a substrate was electrolytically polished, with the substrate as an anode and an opposite electrode comprising a tin-lead alloy as a cathode, by applying a selective uniform current corresponding to 60 A/dm² from a current controlling power source for a minute to electrolytically eluting the substrate surface. Then, the anode and the cathode were rapidly reversed, and a selective uniform current corresponding to 60 A/dm² was applied from the current controlling power source for 17 minutes to cause precipitation of a single hard Cr plating layer having a prescribed thickness. Then, the cathode and the anode were rapidly reversed again, and a selective uniform current corresponding to 60 A/dm² was applied from the current controlling power source for a minute to electrolytically elute the surface of the precipitated hard Cr plating layer. Then, the above-mentioned precipitation step and electrolytic elution step were continuously repeated until precipitation of a Cr plating layer having a prescribed thickness, and the process was completed by a precipitation step.

[0051] Thus, there was obtained a conventional chrome plating layer having a multi-layer structure in which hard Cr plating layers were formed into a thickness per layer of 10 µm, and micro-cracks were independently formed without continuation between two adjacent layers.

(Comparative Example 3)

[0052] A plating bath prepared by adding ceramic particles (size within a range of from 0.05 to 1.0 µm; degree of suspension: 100 g/L) to a silicofluoride bath (CrO_3 : 250 g/L, H_2SO_4 : 2.5 g/L, and NaSiF_6 : 8 g/L) kept at a constant temperature of 55 °C was used. Plating was performed while stirring the bath by aeration. First, a substrate was electrolytically polished by applying a selective uniform current of 60 A/dm² by a current controlling power source for a minute with the substrate as an anode and an opposite electrode comprising a tin-lead alloy as a cathode and electrolytically eluting the substrate surface. Then, the anode and the cathode were rapidly reversed, and a selective uniform current corresponding to 60 A/dm² was applied from the current controlling power source for 17 minutes to cause precipitation of a single hard Cr plating layer having a prescribed thickness. Then, the cathode and the anode were rapidly reversed again, and a selective uniform current corresponding to 60 A/dm² was applied from the current controlling power source for a minute, and the surface of a precipitated hard Cr plating layer was electrolytically eluted. Then, the above-mentioned precipitation step and electrolytic eluting step were continuously repeated until precipitation of a Cr plating layer having a prescribed thickness, finally ending the process by the precipitation step.

[0053] In each of the Cr plating layers composing the Cr plating film having the multi-layer structure, a conventional Cr plating film retaining ceramic particles (size: 0.05 to 1.0 µm) in pores of chrome plating micro-cracks was obtained.

(Test method and test conditions)

[0054] The thus obtained Cr plating layers, serving as examples 1 to 4 and comparative examples 1 to 3 were subjected to a wear test, a scarfing test and a peeling resistance test. Test conditions were as follows:

1. Wear test

Tester and method: An Amsler type wear tester was used. The wear test was carried out by immersing substantially a half of the rotary piece into oil, bringing a fixing piece into contact therewith, and applying a load onto it.

Counterpart material: FC25 (HRB 98)

Lubricant: Turbine oil (#100)

Oil temperature: 80 °C

Circumferential speed: 1 m/sec (478 rpm)

Load: 80 kg

Time: 7 hr

Measurement of amount of wear: The amount of wear (μm) was measured in terms of a step profile by use of a roughness meter.

2. Scarfing test

Tester and method: An Amsler type wear tester was used. The test was carried out by coating an oil in a certain amount onto the rotary piece, and then, applying a load up to occurrence of scarf.

Counterpart material: FC25 (HRB 98)

Lubricant: No.2 Spindle oil

Oil temperature: Letting it run its natural cause

Circumferential speed: 1 m/sec (478 rpm)

Load and time: Load was increased continuously and straightly at a rate of 5 kg/min up to occurrence of scarf.

The load at which a signal indicating seizure by scarf was evaluated as scarfing load.

3. Peeling resistance test

Tester: An improved tester (see Fig. 4) of NPR type impact tester (Japanese Unexamined Patent Publication No. 36-19046: Quantitative Tester of Plating Adhesion) was used.

Method: An impact energy of 43.1 mJ (44 kg/mm) per run was applied to the film surface, and the peeling resistance was evaluated in terms of the number of runs up to occurrence of peeling.

Presence of peeling: Presence of peeling was observed and evaluated by enlarging the surface to 15 magnifications.

(Test result)

[0055] The wear resistance was evaluated by assuming the amount of wear for the test piece of Example 1 to be 1.00, by means of the amount of wear for the other test pieces (Examples 2 to 4 and Comparative Examples 1 to 3) as a wear index relative to the test piece of Example 1. The test result is shown in Table 1. In Table 1, a smaller wear index than 1.00 suggests a smaller amount of wear.

[0056] The seizure resistance was evaluated by assuming the amount of seizure causing load for the test piece in Example 1 to be 1.00, by means of the amount of seizure causing load for the other test pieces (Examples 2 to 4 and Comparative Examples 1 to 3) as a seizure resistance index relative to the test piece of Example 1. The result is shown in Table 1. In Table 1, a larger seizure resistance index than 1.00 corresponds to a larger seizure causing load, suggesting a more excellent seizure resistance.

[0057] The peeling resistance was evaluated by assuming the number of occurrences of peeling for the test piece of Example 1 to be 1.00, and comparing the same to the number of occurrences of peeling for the other test pieces (Examples 2 to 4 and Comparative Examples 1 to 3) as the peeling resistance index relative to the test piece of Example 1. The result is shown in Table 1. In Table 1, a peeling resistance index smaller than 1.00 suggests that peeling occurred in a number of runs smaller than that for the test pieces of Example 1, revealing a poorer peeling resistance.

[0058] As is evident from Table 1, according to a comprehensive evaluation of the three above-mentioned kinds of test results, the test pieces of Examples 1 to 4 are confirmed to be superior to the test pieces of Comparative Examples 1 to 3. These properties were determined as a result of the comprehensive evaluation because, on a commercial equipment, a single poor property may lead to a defective result even when the other two properties are excellent. Determination was therefore made through comprehensive evaluation of the lowest property.

Table 1

	Sectional porosity	Surface porosity	Number of cracks/10 mm	Wear index	
Example 1	3.0 %	3.0 %	ab.600 cracks	1.00	○
Example 2	0.5 %	0.5 %	ab.50 cracks	0.97	◎
Example 3	4.5 %	4.5 %	ab.1200 cracks	0.99	○
Example 4	2.1 %	15 %	ab.800 cracks	1.00	○
Comparative Example 1	Single-layer film	-----	-----	1.11	X
Comparative	Multi-layer film	40 %	ab.1000 cracks	0.96	◎

Example 2	10.0 %				
Comparative Example 3	Multi-layer film sealing ceramics (volume ratio:6.0%)	20 %	ab.1200 cracks	1.53	X

	Seizure resistance index		Peeling resistance index		Comprehensive evaluation
Example 1	1.00	○	1.00	○	Reference ○
Example 2	0.95	○	1.20	◎	○
Example 3	1.05	◎	0.98	○	○
Example 4	1.00	○	1.00	○	○
Comparative Example 1	0.83	X	0.95	△	X
Comparative Example 2	1.08	◎	0.90	X	X
Comparative Example 3	1.16	◎	0.85	X	X

Note) ◎: Excellent, ○: Equivalent, △: Fair, X: Inferior

Industrial Applicability

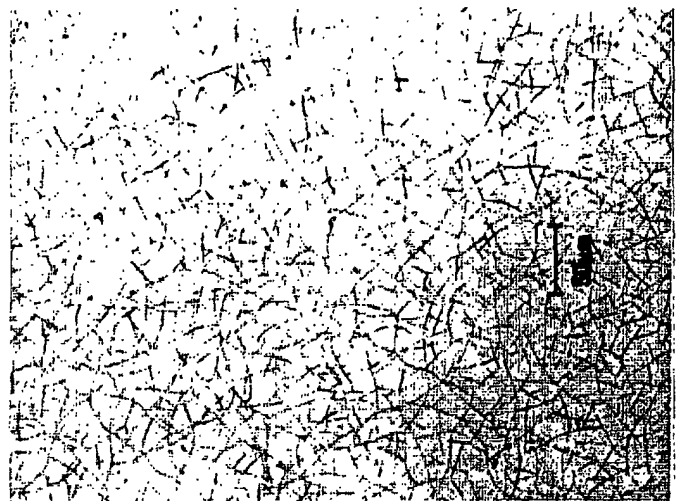
[0059] As described above, the sliding member of the present invention has the following features: the sliding member has a laminated hard Cr plating layer comprising a plurality of hard Cr plating layers on the sliding surface thereof; micro-cracks are formed on the surface of each hard Cr plating layer; and the micro-cracks of each hard Cr plating layer form fine pores independent in the film-forming direction. The sliding member of the invention is characterized in that the porosity on a cross-section of the laminated hard Cr plating layer is within a range of from 0.5 to 4.5%. It is thus possible to obtain a sliding member excellent in strength properties, seizure resistance and wear resistance. The sliding member thus obtained is suitably applicable to automotive piston rings and marine piston rings exposed to severe service conditions such as a high-output engine and an engine used at high temperatures and a high load.

[0060] The entire disclosure of Japanese Patent Application No. 11-371144 filed on December 27, 1999, including the specification, claims, drawings and summary is incorporated herein by reference its entirety.

Claims

1. A sliding member having a laminated hard Cr plating layer comprising a plurality of hard Cr plating layers laminated on a sliding surface, micro-cracks being formed on the surface of each hard Cr plating layer, the micro- cracks of each hard Cr plating layer forming independent micro-pores in the film forming direction; wherein porosity on a cross-section of said laminated hard Cr plating layer is within a range of from 0.5 to 4.5%.
2. A sliding member according to claim 1, wherein porosity on the surface of said hard Cr plating layer is within a range of from 0.5 to 30%, and the number of micro- cracks on said surface is within a range of from 50 to 1,200 cracks/10 mm.
3. A sliding member according to claim 1 or 2, wherein the thickness per layer of said hard Cr plating layer is within a range of from 0.1 to 60 μm .
4. A sliding member having a laminated hard Cr plating layer comprising a plurality of hard Cr plating layers laminated on a sliding surface, micro-cracks being formed on the surface of each hard Cr plating layer, the micro- cracks of each hard Cr plating layer forming independent micro-pores in the film forming direction; wherein porosity on the surface of said hard Cr plating layer is within a range of from 0.5 to 5.0%, and the number of micro-cracks on said surface is within a range of from 50 to 1,200 cracks/10 mm.
5. A sliding member according to claim 4, wherein the thickness per layer of said hard Cr plating layer is within a range of from 0.1 to 60 μm .

FIG. 1



50 μ m

FIG. 2



20 μ m

FIG. 3

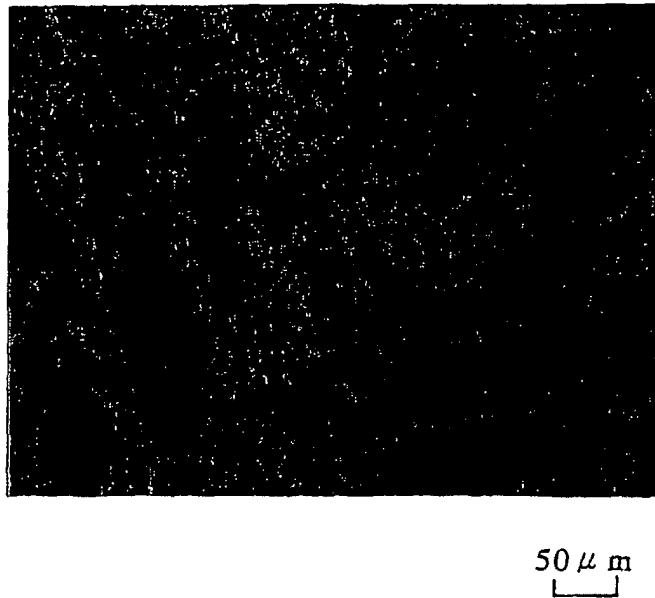
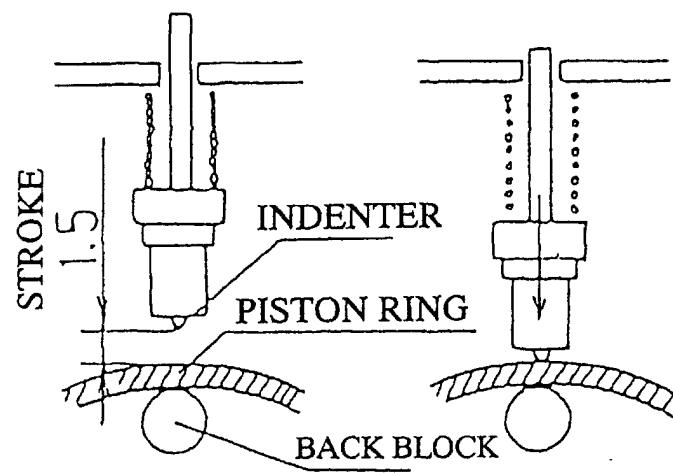


FIG. 4



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/09235

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl.⁷ C23C 28/00

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)

Int.Cl.⁷ C23C 28/00

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

Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2000

Kokai Jitsuyo Shinan Koho 1971-2000 Jitsuyo Shinan Toroku Koho 1996-2000

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.
A	JP, 3-36300, A (Uemura Kogyo Co., Ltd.), 15 February, 1991 (15.02.91) (Family: none)	1-5

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

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
23 March, 2001 (23.03.01)Date of mailing of the international search report
03 April, 2001 (03.04.01)Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.