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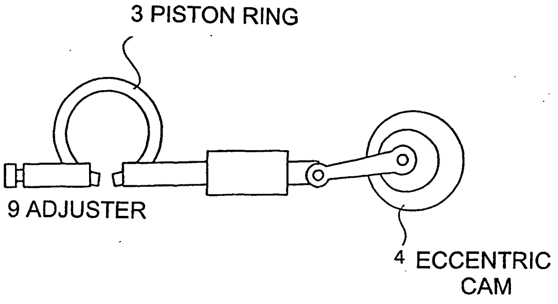
(54) PISTON RING EXCELLENT IN RESISTANCE TO SCUFFING, CRACKING AND FATIGUE AND METHOD FOR PRODUCING THE SAME, AND COMBINATION OF PISTON RING AND CYLINDER BLOCK

(57) A piston ring having improved scuffing resistance, cracking resistance and fatigue resistance, consists of a high-chromium martensitic stainless steel and a sliding nitriding layer formed on the surface of said steel. The stainless steel consists of C: 0.3 to 1.0%; Cr: 14.0 to 21.0%, N: 0.05 to 0.50%, at least one of Mo, V, W and Nb: 0.03 to 3.0% in total, Si: 0.1 to 1.0%, Mn 0.1 to 1.0%, P: 0.05% or less, S: 0.05% or less, the balance being Fe and unavoidable impurities. The sliding nitriding layer comprises on its surface hard particles mainly consisting of nitrides in a range of from 0.2 to 2.0μm of average particle size, 7μm or less of the longest diameter, and from 5 to 30% in area ratio.

Fig. 5



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Description

BACKGROUND OF INVENTION

Technical Field

[0001] The present invention relates to a piston ring used in an internal combustion engine, particularly, a piston ring consisting of high chromium martensitic stainless steel with nitriding, having improved scuffing resistance (seizure resistance), cracking resistance (failure resistance) and fatigue resistance. The present invention is also related to a production method of the piston ring.

Background Technique

[0002] Along with recent demands for low fuel consumption, weight reduction and high performance of internal combustion engines, the piston rings are thinned to reduce weight and to follow the high rotation of the engine. Material properties of the piston rings, such as wear resistance, scuffing resistance and fatigue resistance, and the like must be improved to enable thinning of a piston ring. The conventional cast-iron piston rings have, therefore, been replaced with steel piston rings particularly from a view point of the fatigue resistance and heat resistance. However, since the scuffing resistance of the steel piston-ring is inferior to that of the cast-iron piston-ring, any surface-treatment is usually applied to the sliding surface of steel piston ring. Steels for piston ring are roughly classified into carbon steel, silicon-chromium steel, and martensitic stainless steel. These classifications correspond to different kinds of surface treatments applied to the respective steels. Mainly, the chromium plating is applied to carbon steels and silicon chromium steels. Gas nitriding is applied to martensitic stainless steels. The chromium plating was the most frequent surface treatment of the steel piston ring previously, but has been mostly replaced at present with the nitriding, because the scuffing resistance of the chromium plating under high load is poor, and, further, the waste-liquid of the plating must be treated so as not to incur any environmental problem.

[0003] High chromium martensitic stainless steel mainly used at present for the piston ring with nitriding is JIS SUS440B equivalent composition of C: 0.80-0.95%; Cr: 17.0-18.0%; Si: 0.25-0.50%; Mn: 0.25-0.40%; Mo: 0.70-1.25%; V: 0.07-0.15%; and Fe in balance. When the steel having this composition is subjected to nitriding, nitrogen atoms intrude and diffuse from the surface into the steel and form a nitriding layer. The nitrides in the nitriding layer are mainly compounds of Cr, V and Mo, which may contain the solute Fe. Chromium, which is the main component of this steel, is dissolved in the iron matrix, and is also present in the form of Cr carbides.

[0004] Since the affinity of Cr for nitrogen is higher than that for carbon, when nitrogen diffuses from the surface by the nitriding, the reaction between the nitrogen and Cr carbides occurs to form the Cr nitrides. Since the Cr content of SUS 440B equivalent material is as high as 17.0-18.0%, hard Cr nitrides are dispersed in the nitriding layer in an appropriate area %. The nitriding layer is, therefore, relatively hard and improves the wear resistance and scuffing resistance.

[0005] Recently published Japanese Unexamined Patent Publication No. 11(1999)-80907 proposes martensitic stainless steel with nitriding, having improved scuffing resistance, which contains Si: 0.25% or less, Mn: 0.30% or less; one or more of Mo, W, V and Nb: 0.3-2.5% or Cu: 4.0% or less; Ni: 2.0% or less, and Al: 1.5% or less.

[0006] Japanese Unexamined Patent Publication 11(1999)-106874 discloses that when the quantity of M_7C_3 carbide in the microstructure is suppressed to 4.0% or less in area %, not only scuffing resistance but also workability of the piston ring steel material are improved.

[0007] Although the wear resistance and scuffing resistance have been improved by the proposals as described above, when these piston rings are used in recent internal combustion engines operated under high revolution, and high power conditions, scuffing is liable to occur.

[0008] Heretofore, liners are forced into the cylinder block of Diesel engines. These engines are changed to a monolithic block cast-iron of narrow bore distance without liners so as to attain weight reduction and cost saving. The combustion pressure tends to be increased from the viewpoints of waste gas purification and power increase. In the microstructure of the cast iron mono-block, from relatively large cooling rate difference in casting of the mono-block, graphite dispersion is not uniform and soft ferrite phase as the cause of scuffing is unevenly distributed.

[0009] When the cylinder surface having the microstructure mentioned above is combined with the martensitic stainless-steel piston ring with nitriding, scuffing is liable to occur in the initial operation period for the following reasons.

[0010] When the cylinder surface is finished by honing, the abrasives of a grinding wheel cause clogging due to ferrite phase, and the surface of the cylinder is liable to be roughened after the honing. The graphite is covered by the ferrite flowed plastically. As a result, lubrication and oil-reserving effects of the graphite are lowered since the area % of the graphite decreases. In the case of high combustion pressure, the back pressure applied to the piston ring becomes high. Scuffing frequently results from cracks on the outer peripheral surface of a piston ring, elongating in a direction perpendicular to the sliding direction. When the nitriding layer is inspected, cracks are detected along the lamellar compounds. The compounds are relatively coarse and are present along grain boundaries of the iron matrix, and is referred to as the gull phase in the field of the Japanese piston ring industry. The compound lamella distribute parallel to the surface of the piston ring.

[0011] In order to solve the problems of the piston rings, the formation of TiN, CrN and the like is carried out by means of ion plating. The ion plating can improve the wear resistance and the scuffing resistance but the production cost is high. The reputation of ion plating by the users at present is not favorable in the light of the cost performance.

[0012] It is, therefore, an object of the present invention to provide a high chromium martensitic stainless steel piston ring with nitriding and its production method, which ring is cost-effective and, which incurs neither wear, scuffing, cracking nor fatigue fracture even when used in a Diesel engine operated at high revolution and high combustion pressure, particularly, a cast-iron monolithic block Diesel engine, which is expected to be increasingly used in the future because of weight reduction.

SAMMARY OF INVENTION

[0013] According to explanation of "Automotive Piston Ring" edited by Editing Committee of Automotive Piston Ring, Sankaido Publisher, page 188, 1997, when load is concentrated on the convexities (especially of soft phases) of microscopic unevenesses on a sliding surface, the temperature rises there due to friction heat, and abnormal softening and melting occurs. This phenomenon results in scuffing of the piston ring.

[0014] In the high chromium martensitic stainless steel with nitriding, the microstructure of the nitriding layer generally shows mainly hard nitrides dispersed in the tempered martensite matrix. The mechanism of scuffing is strongly dependent upon the microscopic unevenness on the sliding surface. In the nitriding layer, hard particles disperse in the relatively soft matrix. The microscopic unevenness is, therefore, defined by the size and dispersion state of the hard particles. When the cross section of the surface layer having such structure is observed, the following is apparent. The convex hard particles are brought into contact with an opposite sliding surface, while the relatively soft matrix is relatively concave. The lubricating oil retained in the concave portions is subjected to pressure during sliding. Frequency of the entire direct contact of the steel with nitriding and the opposite member is low, since the steel with nitriding has the microstructure as described above. As a result, the contact pressure between both sliding members is decreased. In addition, the oil is fed to the convex portions mentioned above. The scuffing can, therefore, be prevented.

[0015] The hard convex particles can attain the effects as described above, provided that they are from sub microns to a few microns in size and dispersed in an amount of 5% by area or more. In the case in which the hard particles are extremely small and case in which they are small in quantity, the mechanism according to action and effect of the convex hard particles mentioned above cannot be expected.

[0016] Meanwhile, these effects are influenced by the circumstances of the sliding surface of the opposite member. Specifically, in the case of the cast iron monolithic cylinder block having a non-uniform structure as described above, the surface of this block is liable to be roughened by the grinding. Frequently, the ferrite phase plastically flows and covers the graphite.

[0017] The sliding surface of even such cast iron is modified by appropriate sliding referred to by experts as break-in or compatibility. That is, the following phenomenon occurs. When the rough inner surface of a cylinder is smoothened during the sliding, the ferrite is removed and the covered graphite is exposed. Until the break-in is progressed, an oil film on the sliding surface is frequently liable to be absent. When the oil film is absent, friction force applied on the outer peripheral surface of a piston ring is increased. The large friction force is repeatedly applied on the outer peripheral surface of a piston ring. The nitriding layer is, therefore, repeatedly subjected to large stress resulting in initiation and enlargement of cracks in a direction perpendicular to the sliding direction. Along with the progress of the adaptability phenomenon on the inner surface of a cylinder, the stress applied is lessened, while the cracks propagate with the lapse of time. As a result, the nitriding layer may locally peel in the surface, and the inner surface of a cylinder may be damaged. The scuffing is, therefore, liable to occur in the initial period of sliding. Since the grain boundary compounds in the nitriding layer are very brittle, the presence of them promotes the initiation and propagation of cracks.

[0018] The present inventors found the following essential matters. A large number of hard particles, mainly Cr nitrides, in proper size in the nitriding layer should be uniformly dispersed in matrix in order to decrease the probability of contacts between matrix and cylinder and to prevent the initial stage scuffing. Especially the grain boundary compounds formed during nitiriding should be fine to suppress the initiation of cracks in connection with those compounds. In this fine microstructure, even if cracks initiate, the development of those can be suppressed.

[0019] When the melt of high-chromium martensitic stainless steel solidifies, the eutectic Cr carbide (η phase: $(Cr, Fe)_7C_3$) crystallizes in the grain boundaries of primary austenite (γ phase). Cr carbides exceeding 20 μ min the largest diameter are present in the high chromium martensitic stainless steel, which is solidified as above and then hot rolled, spheroidizing annealed, and finally quenched and tempered. Regarding the refining of the coarse primary eutectic Cr carbides, Tetsu and Hagane (Journal of Japan Institute of Iron and Steel), Vol., 82, No. 4. p. 309-314 (1996) reports the refinement of carbides by addition of 0.25% or more of N. According to this report, the eutectic Cr carbide in the boundaries of primary γ disappears and instead, lamellar $M_{23}C_6$ and M_2N (M: Cr, Fe) precipitate around the primary γ grain boundaries. These lamellar precipitates are finely divided in the hot rolling. In the subsequent spheroidizing annealing, fine $M_{23}C_6$ newly precipitates at sites different from those of M_2N. The Cr carbides as a whole become, therefore, fine.

[0020] Netsushori Vol. 36, No. 4, p. 234-238 (1996) reports the mechanical properties of 16.5% Cr - 0.65% C martensitic stainless steel with the addition of 0.25% of N. That is, the quenching temperature, at which the highest hardness is obtained, shifts to lower temperature with the increase in N content. The elongation also increases with the increase in N content. It is explained that the solution amount of N in the austenite phase increases and the austenite phase is stabilized with the increase in quenching temperature.

[0021] Japanese Unexamined Patent Publication Nos. 9-289053 and 9-287058 disclose the rolling bearing, in which the refining of Cr carbides due to the N addition is utilized.

[0022] The present inventors have studied the scuffing mechanisms mentioned above and the influence of relatively large lamellar grain boundary compounds on cracking in sliding surface of piston ring and applied the refining technology of Cr carbide using N addition. As a result, it is found to be desirable that a large number of nitrides dispersed uniformly in the nitriding layer and especially grain boundary compounds are fine in size. This fine microstructure provides a high chromium martensitic stainless steel piston ring with nitriding having improved scuffing, cracking and fatigue resistances even when it is used in internal combustion engines operated under high revolution and high power conditions, particularly, recent weight reduced cast iron mono-block Diesel engine, etc.

[0023] The high-chromium martensitic stainless steel piston ring with nitriding according to the present invention is characterized in that it comprises the high-chromium martensitic stainless steel, which consists, by weight %, of C: 0.3 to 1.0%; Cr: 14.0 to 21.0%, N: 0.05 to 0.50%, at least one of Mo, V, Wand Nb: 0.03 to 3.0% in total, Si: 0.1 to 1.0%, Mn 0.1 to 1.0%, P: 0.05% or less, S: 0.05% or less, the balance being Fe and unavoidable impurities; and, the high chromium martensitic stainless steel has a nitriding sliding layer, which comprises hard particles consisting of carbide, nitride and carbo-nitride, mainly nitride, and the hard particles in the surface of the nitriding layer are in a range of from 0.5 to 2.0 μm of average diameter, 7μm or less of the largest diameter, and from 5 to 30% in area %. The grain boundary compounds observed in the longitudinal cross section of the nitriding layer are 20μm or less in size (length). The nitriding surface layer having the microstructural feature mentioned above has hardness in the range of from Hv 900 to 1400 and has sufficient depth from the surface.

[0024] The method for producing the high chromium martensitic stainless steel piston ring with nitriding according to the present invention comprises: melting the steel having the above composition followed by adding nitrogen; casting the molten steel into an ingot; hot rolling; annealing; cold wire drawing; cold rolling to form an approximate cross sectional shape of the piston ring; quenching; tempering to provide the wire materials; bending the wire material into the form of the piston ring; strain-relief annealing; rough grinding of the side surfaces; nitriding; removal of surface compound layer; grinding butt ends; finish grinding of side surfaces; and lapping of the outer peripheral surfaces. Prior to the bending into the piston ring shape, quenching is carried out from the temperature of from 850 to 1000°C, which is relatively low as the quenching temperature of the high chromium martensitic stainless steel. As a result, the microstructure is fine and contains a large amount as possible of the dispersed carbides. The nitriding may be gas nitriding, ion nitriding and radical nitriding. The nitriding is carried out at in a range of 450 to 600°C for 1 to 20 hours.

[0025] The present invention is hereinafter described in detail.

[0026] The components of the high-chromium martensitic stainless steel according to the present invention are described.

[0027] C is an interstitial solute element in Fe and increases hardness of matrix. C is easily combined with Cr, Mo, V, W and Nb and forms carbides. The carbides are converted mainly to nitrides during the nitriding. In other words, the nitrides enhance the wear resistance and the scuffing resistance of the sliding surface of a piston ring. When the C content is less than 0.3%, the hardening and formation of carbides are not sufficient. On the other hand, when the C content is more than 1.0%, coarse eutectic Cr carbide (η phase: M_7C_3 carbide) crystallizes in large amount during the solidification of the molten steel. This carbide drastically impairs workability of the material at the subsequent production processes of wires. The carbon content is, therefore, in a range of from 0.3 to 1.0%, preferably in a range of from 0.4 to 0.9%.

[0028] Cr is a substitutional solute element in Fe. Cr not only improves the corrosion resistance but also induces the solution strengthening and hence improvement in the thermal setting resistance. Here the thermal setting is a phenomenon that sealing property is deteriorated by tension decrease due to creep during operation of a piston ring at high temperature. Cr reacts with C in steel and forms Cr carbides. These Cr carbides easily react with N, which intrudes from the surface during nitriding, and are converted to Cr nitrides. The Cr nitrides are dispersed in the nitriding layer as the hard particles. The hard particles in the nitriding layer exceedingly enhance the wear resistance and the scuffing resistance of the sliding surface of a piston ring. When the Cr content is less than 14%, the formation of Cr carbides is not sufficient. On the other hand, when the Cr content is more than 21%, the δ ferrite is formed and toughness is hence lowered. In addition, the Cr concentration in the matrix becomes so high that the Ms (the starting temperature of martensitic transformation) is so lowered such that satisfactory quenching hardness is not obtained. The Cr content is, therefore, in a range of from 14 to 21%, preferably in a range of from 16 to 19%.

[0029] N is an interstitial element in Fe, as C is. Ternary Fe - Cr - C phase diagram can be expressed by a pseudobinary phase diagram by cutting at, for example, the 17% Cr line. An eutectic reaction occurs between Fe and C, the concentration of which is given by the left end of the eutectic line. Meanwhile prior to the complete solidification, molten steel remains around the grain boundaries of primary crystals. When the temperature further falls, the molten steel undergoes the eutectic reaction. When the nitrogen is added in accordance with the present invention, the C concentration at the left side mentioned above is higher than that of the molten steel without nitrogen. Therefore, the eutectic reaction and hence the formation of η carbide are suppressed. When the temperature falls lower than the eutectic temperature, the super saturated C and N precipitate around the primary γ grains in the form of lamellar $M_{23}C_6$ and M_2N precipitates. When the N content is less than 0.05%, the η phase crystallizes. On the other hand, when the N content is more than 0.50%, the amount of M_2N precipitates in the form of a rod increases, so that the toughness is lowered. The N content is, therefore, in a range of from 0.05 to 0.50%, more preferably in a range of from 0.10 to 0.30%. The solute N in the matrix impedes the diffusion of C and also contributes to refining of the grain boundary compounds. This is first Fe_3C after casting and is finally converted to Fe_3N after nitriding treatment. Nitrogen up to 0.2% can be added under normal pressure. Nitrogen content of more than 0.2% necessitates melting under pressure N_2 atmosphere. The nitrogen content in a range of from 0.05 to 0.20% is, therefore, preferable from the viewpoint of N addition.

[0030] Any one of Mo, V, W and Nb is a carbide former and enhances wear and scuffing resistances. In addition, Mo prevents softening during the tempering and nitriding treatments and plays an important role in attaining the dimension stability of a piston ring. V promotes nitriding, and, therefore, the hardness of a nitriding layer containing V is high. Any one of these elements is effective for enhancing the properties of a piston ring. When the total content of at least one of Mo, V, W and Nb is less than 0.03%, their effects are virtually negligible. On the other hand, when the total content of these element(s) is more than 3%, the workability is seriously impaired and the toughness is lowered. The total content of at least one of Mo, V, Wand Nb is, therefore, from 0.03 to 3.0%.

[0031] Si is a deoxidizing additive. Si is also dissolved in Fe and enhances the softening resistance in tempering. The so-called thermal setting resistance can, therefore, be improved. When the Si content is less than 0.1%, its effect is slight. On the other hand, when the Si content is more than 1.0%, the toughness is impaired. The Si content is, therefore, in a range of from 0.1 to 1.0%.

[0032] Mn is also a deoxidizing additive. When the Mn content is less than 0.1%, its effect is slight. On the other hand, when the Mn content is more than 1.0%, the workability is impaired. The Mn content is, therefore, from 0.1 to 1.0%.

[0033] P forms inclusions with Mn and the like and lowers the fatigue strength and corrosion resistance. P is an impurity of steel. The less P, the better. The P content is, therefore, 0.05% or less from a practical point of view. Preferably, P is 0.03% or less.

[0034] S lowers the fatigue strength and corrosion resistance, as P does. S is an impurity of steel. The less S, the better. The S content is, therefore, 0.05% or less from a practical point of view. Preferably, S is 0.03 % or less.

[0035] The steel consisting of the composition ranges as described above is subjected to formation of a microstructure having improved scuffing resistance, that is, a number of fine nitride particles are present in the nitriding layer. More specifically, the hard particles consisting of nitrides, i.e., mainly Cr nitride, carbides and carbonitrides, present in the surface of the nitriding layer should have an average diameter in a range of from 0.2 to 2 µm, the largest diameter of 7µm or less, and area % in a range of from 5 to 30%. When the average particle diameter is less than 0.2µm, the convexities of the hard particles are not effective for preventing scuffing. On the other hand, when the average particle diameter is more than 2µm, scuffing is liable to occur when the load is high. When the largest diameter is more than 7µm, the microstructure of the nitriding layer becomes non-uniform so that scuffing is liable to occur under high load. When the area % is less than 5%, scuffing is liable to occur. On the other hand, when the area % of nitrides is more than 30%, the wire drawing and the bending into the piston ring form after melting become difficult. A preferable area % is from 10 to 25%.

[0036] The microstructure of the nitriding layer having improved cracking resistance is such that the grain boundary compounds observed in the longitudinal cross section of a piston ring are 20µm or less in size (length). When the longest length is more than 20 µm, there arises a problem that the cracking is liable to occur under high load.

[0037] The microstructure of the nitriding layer as described above according to the present invention is attributable to the microstructure of stainless steel. First, no coarse eutectic Cr carbide (η phase: $(Cr, Fe)_7C_3$ carbide) is present in the steel which has been successively hot rolled, spheroidizing heat treated, cold wire drawn, quenched and tempered. This is attained by the nitrogen addition.

[0038] Second, a large number of the fine secondary carbide (ε phase, $(Cr, Fe)_{23}C_6$ carbide) precipitate when holding at the quenching temperature prior to nitriding. The Fe - Cr - C phase diagram teaches more and finer carbides precipitates as the quenching temperature is lower in the $(\gamma + \varepsilon)$ region. When the quenching is carried out from temperature as low as possible in the ($\gamma + \varepsilon$) region , fine ε carbides can be precipitated in quantity as much as possible. In addition, the growth of γ crystal grains is suppressed, so that the quenched steel is of fine grain structure. When this steel is subjected to nitriding, the grain boundary compounds becomes also fine. A preferable quenching temperature is, therefore, in a range of from 850 to 1000°C, from the viewpoints as described above. When the quenching temperature is less than 850°C, no hardening occurs and the desired hardness is not attained because of precipitation of the α phase. When the quenching temperature is more than 1000°C, the carbides coalesce in the holding step at the quenching temperature and the γ crystal grains coarsen. As a result, the coarse carbides are converted to the coarse nitrides. The grain boundary compounds, which are formed along the coarsened γ crystal grains in the subsequent nitriding treatment, become coarse.

[0039] In the present invention, high hardness of from Hv 900 to 1400 is obtained up to a satisfactory depth from the surface by the nitriding treatment for a relatively short period of time. This feature is attributable to the relatively fine γ crystal grains formed at low quenching temperature and thus to the increase of the grain boundaries which are the main diffusion passages of N during the nitriding treatment.

[0040] According to the present invention, the nitriding treatment is carried out in the temperature range of from 450 to 600°C. In the prior art, the treatment temperature of approximately 590°C, at which the nitrogen solubility in the α-Fe lattice is the greatest, has been considered to be advisable. However, since the present invention utilizes the N diffusion mainly via the grain boundaries, the treatment temperature is not limited to approximately 590°C. The lower-temperature treatment is more advisable from the viewpoint of dimension stability of a piston ring. However, from a practical point of view, the nitriding is carried out at 450 to 600°C for 1 to 20 hours.

BRIEF EXPLNATION OF DRAWINGS

[0041] Figure 1 is a photograph of back scattered electron image of surface of sliding nitriding layer observed by a scanning electron microscope. Figures 1 (a) and (b) correspond to Example 1 and Comparative Example 1, respectively.

[0042] Figure 2 is an optical microscope photograph of the cross section of a nitriding layer. Figures 2 (a) and (b) correspond to Example 1 and Comparative Example 1, respectively.

[0043] Figure 3 shows a specimen of the scuffing test.

[0044] Figure 4 shows the movement mechanism of a friction and wear tester.

[0045] Figure 5 shows the movement mechanism of a fatigue tester of a piston ring.

[0046] Figure 6 is a graph showing the fatigue limit.

[0047] Figure 7 is a photograph showing a crack formed on the sliding surface of Comparative Example 13.

BEST MODE FOR CARRYING OUT INVENTION

Examples 1 - 11 (J1 - J11) and Comparative Examples 1 - 8 (H1 -H18)

[0048] The high chromium martensitic stainless steels having a composition shown in Table 1 were melted in an amount of 10kg in a vacuum induction melting furnace. However, less than 0.2% of N was added to the steel during melting under the normal pressure, while 0.2% or more of N was added to steel during melting under pressure N_2 gas atmosphere. Wire material having 12 mm of diameter was obtained by hot working. After acid cleaning, spheroidizing annealing was carried out at 750°C for 10 hours. A wire having a rectangular cross section of 3.5 mm × 5.0mm was produced through working steps. The wire was passed through a quenching furnace (Ar protective atmosphere) and a tempering furnace (Ar protective atmosphere). The air quenching was carried out from 930°C after keeping approximately 10 minutes at that temperature. The tempering was carried out at 620°C for approximately 25 minutes. The wires were cut into 50 mm long samples for the nitriding treatment. The gas nitriding was carried out at 570°C for 4 hours. However, the quenching temperature of Comparative Example 1 (H1) was 1100°C as in the conventional method. The other conditions are the same as for the Examples and the other Comparative Examples.

Table 1 (wt%)

	C	Cr	N	Mo	V	W	Nb	Si	Mn	P	S
J1	0.65	17.5	0.13	1.5	-	-	-	0.25	0.35	0.02	0.01
J2	0.41	17.0	0.19	1.0	0.15	-	-	0.25	0.50	0.02	0.02
J3	0.83	17.8	0.23	-	0.20	-	-	0.20	0.30	0.02	0.02
J4	0.59	17.2	0.16	-	-	0.05	-	0.20	0.20	0.02	0.02

Table 1 (wt%) (continued)

	C	Cr	N	Mo	V	W	Nb	Si	Mn	P	S
J5	0.62	17.5	0.15	-	-	-	0.3	0.20	0.30	0.02	0.02
J6	0.60	14.5	0.15	1.5	0.5	0.1	0.5	0.55	0.65	0.02	0.02
J7	0.60	19.5	0.25	1.0	-	0.1	-	0.20	0.30	0.02	0.02
J8	0.35	20.3	0.28	1.0	-	-	0.3	0.20	0.30	0.02	0.02
J9	0.95	14.9	0.25	-	0.5	0.1	-	0.20	0.30	0.02	0.02
J10	0.55	16.5	0.08	-	0.5	-	0.3	0.35	0.55	0.02	0.02
J11	0.48	18.2	0.42	-	-	0.1	0.3	0.20	0.20	0.02	0.02
H1	0.81	17.5	0.03	1.0	0.3	-	-	0.25	0.25	0.02	0.02
H2	0.45	18.0	0.58	1.5	0.5	-	-	0.20	0.20	0.02	0.02
H3	0.25	17.3	0.16	1.0	0.4	-	-	0.20	0.30	0.02	0.02
H4	1.12	17.8	0.15	1.2	0.6	-	-	0.20	0.30	0.02	0.02
H5	0.69	13.2	0.21	1.1	0.5	-	-	0.20	0.30	0.02	0.02
H6	0.73	22.1	0.22	1.0	0.2	-	-	0.20	0.20	0.02	0.02
H7	0.65	17.8	0.16	-	-	-	-	0.20	0.20	0.02	0.02
H8	0.68	17.3	0.15	1.5	1.0	0.5	0.5	0.20	0.20	0.02	0.02

[0049] The wire samples mentioned above were further cut into lengths of 10 mm for observation of the microscopic structure. The specimens were embedded in resin and were mirror-finished. The observation and quantitative evaluation of the microstructure were carried out using an image analyzer. The back scattered electron image of the sliding nitriding surface was observed by a scanning electron microscope with regard to Example 1 (J1) and Comparative Example (H1). The observed images for Example 1 (J1) and Comparative Example 1 (H1) are shown in Figs. 1 (a) and (b), respectively. The cross section of the nitriding layer was observed by an optical microscope and the observed photographs are shown in Figs. 2(a) and (b), respectively, with regard to Example 1 (J1) and Comparative Example 1 (H1). The hard particles appear black in the back scattered electron image photograph and white in the optical microscope photograph. It is apparent that: the hard particles according to the present invention are extremely small in size; and, the grain boundary compounds observed in the cross section of the nitriding layer are extremely small in size. The microstructures of Example 1 through 11 (J1 - J11) and Comparative Examples 1 - 8 (H1 - H18) were quantitatively evaluated with regard to the average particle diameter, the largest particle diameter and area ratio of the hard particles in the sliding nitriding surface and the longest length of the grain boundary compounds in the cross section of the nitriding layer. These results are shown in Table 2 together with the hardness of the sliding surface of nitriding layer.

Table 2

	Hard Particles of Sliding Nitriding Layer			Longest Length of Grain Boundary Compound in Cross Section of Nitriding Layer (µm)	Vickers Hardness
	Average Particle Diameter (µm)	Largest Particle Diameter (µm)	Area % (%)		
J1	1.6	5	17.2	16	1253
J2	1.3	4	13.0	15	1050
J3	1.0	5	22.5	13	1185
J4	1.7	6	15.9	12	1120

Table 2 (continued)

	Hard Particles of Sliding Nitriding Layer			Longest Length of Grain Boundary Compound in Cross Section of Nitriding Layer (µm)	Vickers Hardness
	Average Particle Diameter (µm)	Largest Particle Diameter (µm)	Area % (%)		
J5	1.6	5	17.1	15	1148
J6	1.5	4	10.7	14	955
J7	0.9	4	21.0	12	1219
J8	1.2	6	18.0	13	1193
J9	1.3	6	13.0	12	984
J10	1.8	5	14.2	17	1031
J11	1.2	5	16.2	14	1083
H1	2.7	15	13.6	28	1065
H2	*	*	*	*	*
H3	1.5	5	7.5	15	830
H4	*	*	*	*	*
H5	1.4	5	4.0	14	920
H6	2.2	8	9.1	14	874
H7**	1.6	5	16.5	16	1109
H8	*	*	*	*	*

* Comparative Examples 2, 4 and 8 (H2, H4 and H8) could not be formed into a wire because of poor workability.

** The post-nitriding dimension was unstable in Comparative Example 7 (H7).

The yield is, therefore, low.

[0050] Referring to Fig. 3, a scuffing test sample in the form of Japanese katakana "❑" having 45 mm of the total length is shown. The wire material was shaped into scuffing test samples of two-pin integral type. The opposite material was made of FC250 and was in the form of a disc of 60 mm in diameter and 12 mm in thickness.

[0051] The sliding surface of disc 2 (Fig. 4) was adjusted to the surface roughness (Rz) of from 1 to 2 µm. The scuffing test was carried out using a friction and wear tester (Product of Riken, Trade name "Triborik I"). The front ends of the pin (reference numeral 1, Fig. 4) are convex sliding surfaces having 20 mm of radius. The front ends were subjected to gas nitriding treatment. The 5 to 20 µm thick compound layers (white layer) formed on the front ends were removed by grinding. The front ends were then mirror-finished by polishing. The surface roughness (Rz) of the sliding surface of FC250 disc (Fig.4, Reference numeral 2) used is adjusted to 1-2 µm The movement mechanism of the friction wear tester is illustrated in Fig. 4. The testing conditions of scuffing were as follows.

Sliding Speed (Disc): 8 m/sec
Pressing Load: Stepwise increase by 0.2 MPa from the initial 1.0 MPa until occurrence of scuffing
Lubricating Oil: Motor Oil (Trade Name - Nisseki Motor Oil P #20)
Temperature of Lubricating Oil: 80 °C (in the vicinity of outlet)
Oil bath: 100°C
Feeding Amount of Lubricating Oil: 40cc/min

[0052] The scuffing surface pressure was calculated from the scuffing load, and the wear area of the sliding surface. The scuffing surface pressure obtained is shown with regard to Example 1 - 11 (J1 - 11) and Comparative Examples

1 - 8 (H1 - H8)

Table 3

	Scuffing Surface Pressure (MPa)
J1	454
J2	443
J3	469
J4	428
J5	458
J6	420
J7	464
J8	430
J9	441
J10	419
J11	452
H1	376
H2	-
H3	340
H4	-
H5	328
H6	297
H7	388
H8	-

[0053] It is apparent that the scuffing resistance of Examples 1 -11 (J1 - J11) is improved over that of Comparative Examples 1, 3, 5 - 7, (H1 H3, H5 -H7).

Examples 12 - 14 (J12 - J14) and Comparative Examples 9 - 11 (H9 -H11)

[0054] The materials having the chemical composition of Example 1 were worked into a wire and air quenched from the temperature shown in Table 4. The gas nitriding treatment was carried out by the same method as in Example 1. The microstructure of the nitriding layer was quantitatively analyzed. The results are shown in Table 4.

Table 4

	Quenching Temperature (°C)	Hard Particles of Sliding Nitriding Layer			Longest Length of Grain Boundary Compound in Cross Section of Nitriding Layer (μm)
		Average Particle Diameter (μm)	Largest Particle Diameter (μm)	Area % (%)	
H9*	800	0.3	5	15.4	14
J12	870	0.5	5	19.4	11

* The hardness of the nitriding layer of Comparative Example 9 (H9) was low of Hv 860.

Table 4 (continued)

	Quenching Temperature (°C)	Hard Particles of Sliding Nitriding Layer			Longest Length of Grain Boundary Compound in Cross Section of Nitriding Layer (µm)
		Average Particle Diameter (µm)	Largest Particle Diameter (µm)	Area % (%)	
J13	920	1.3	6	18.5	15
J14	980	1.8	6	17.4	18
H10	1030	2.3	9	14.7	31
H11	1080	2.8	11	11.5	49

Example 15 and Comparative Example 12

[0055] The steel materials of Example 1 and Comparative Example 1 were subjected to working steps to form a compression ring having a rectangular cross section. The nominal diameter (d_1) was 95.0 mm, thickness (a_1) was 3.35 mm, and the width (h_1) was 2.3 mm. The quenching was carried out by means of passing through the quenching furnace at 930°C for 10 minutes and then air-cooling. The tempering was carried out by means of the tempering furnace at 620°C for approximately 25 minutes. The continuous quenching and tempering was carried out. The gas nitriding was carried out at 570°C for 4 hours. However, the quenching temperature of Comparative Example 12 was 1100°C as in the conventional method. The other conditions are the same as for the Comparative Example 15.

[0056] The produced compression piston ring was tested in a fatigue tester, the movement mechanism of which is illustrated in Fig. 5. The butt ends of the compression piston ring were cut at both ends to widen the dimension of free gap. The so-treated piston ring 3 was set by an adjuster 9 in the tester in such a manner that its diameter was reduced to the nominal diameter. The eccentric cam 4 was then rotated so as to impart repeated strokes at 40 cycles per second for further reducing the diameter to less than the nominal one, until the piston ring 3 fractured. The number of stress applied at the fracture was obtained. This test was repeated, while changing the applied stress to the sample of identical specification. The so-called S-N diagram and finally fatigue limit diagram shown in Fig. 6 were obtained.

[0057] Referring to Fig. 6, it is apparent that Example 15 is outstandingly improved over Comparative Example 12.

Examples 16 - 19 and Comparative Examples 13 -14

[0058] The steel materials of Example 1 (Example 16, 17), Example 7 (Examples 18, 19) and Comparative Example 1 (Comparative Examples 13, 14) were subjected to working steps to form a compression ring (Examples 16, 18 and Comparative Example 13) and the body of a two-piece oil ring (Examples 17, 19 and Comparative Example 14). compression ring had a rectangular cross section. Its nominal diameter (d_1) was 99.2 mm, thickness (a_1) was 3.8 mm, and the width (h_1) was 2.5 mm. The body of the oil ring had a saddle-shape cross section. Its nominal diameter (d_1) was 99.2 mm, thickness (a_1) was 2.5 mm, and the width (h_1) was 3.0 mm.

[0059] The quenching, the tempering and the gas nitriding in Examples 16 - 19 were the same as in Example 15. The quenching, the tempering and the gas nitriding in Comparative Examples 13 - 14 were the same as in Comparative Example 12.

[0060] The produced compression rings and oil rings were mounted in a four-cylinder Diesel engine of 3200 cc displacement. These rings were mounted on a piston and combined with a monolithic cast-iron block and operated for 100 hours for the endurance test under the following condition.

Number of Revolutions: 3600 rpm
Power: 75kW
Load: full load
Water temperature: 110°C
Oil temperature: 130°C

[0061] Scuffing occurred after 2 hours 10 minutes in the case of Comparative Example 13 and after 7 hours 55 minutes in the case of Comparative Example 14. No trouble occurred during the test in the case of Examples 16-19. Referring to Fig. 7, the photograph of a crack on the sliding nitriding surface of Comparative Example 13 is shown.

INDUSTRIAL APPLICABLITY

[0062] According to the present invention, large amount of fine nitrides are present in the nitriding layer of the piston ring, which is made of high chromium martensitic stainless steel with nitriding. The laminar grain boundary compounds are refined, too. Such microstructure can be formed by the addition of nitrogen and the low temperature quenching. The wear resistance, scuffing resistance, cracking resistance and fatigue resistance are improved as a result of the microstructure. The piston ring according to the present invention can, therefore, he advantageously used in internal combustion engines operated under high rotation and high power conditions, particularly, the recent light-weight monolithic block Diesel engine. The piston ring according to the present invention can also be advantageously used for the piston ring of a small motor truck, in which the ring fatigue problem is likely to occur when using the exhaust brake. The piston ring according to the present invention can be appropriately embodied as the body of a two-piece oil ring and the rail of a three-piece oil ring.

Claims

1. A piston ring having improved scuffing resistance, cracking resistance and fatigue resistance, consisting of a high-chromium martensitic stainless steel and a sliding nitriding layer formed on the surface of said steel, **characterized in that** said high-chromium martensitic stainless steel consists, by weight %, of C: 0.3 to 1.0%; Cr: 14.0 to 21.0%, N: 0.05 to 0.50%, at least one of Mo, V, W and Nb: 0.03 to 3.0% in total, Si: 0.1 to 1.0%, Mn 0.1 to 1.0%, P: 0.05% or less, S: 0,05% or less, the balance being Fe and unavoidable impurities; and, further said sliding nitriding layer comprises on its surface hard particles mainly consisting of nitrides in a range of from 0.2 to 2.0 µm of average particle size, 7 µm or less of the longest diameter, and from 5 to 30% in area %

2. A piston ring according to claim 1, **characterized in that** the grain boundary nitride observed in the longitudinal cross-section of a nitriding layer is 20 µm or less in size (length).

3. A piston ring according to claim 1 or 2, wherein the N content of said high-chromium martensitic stainless steel is from 0.05 to 0.20%.

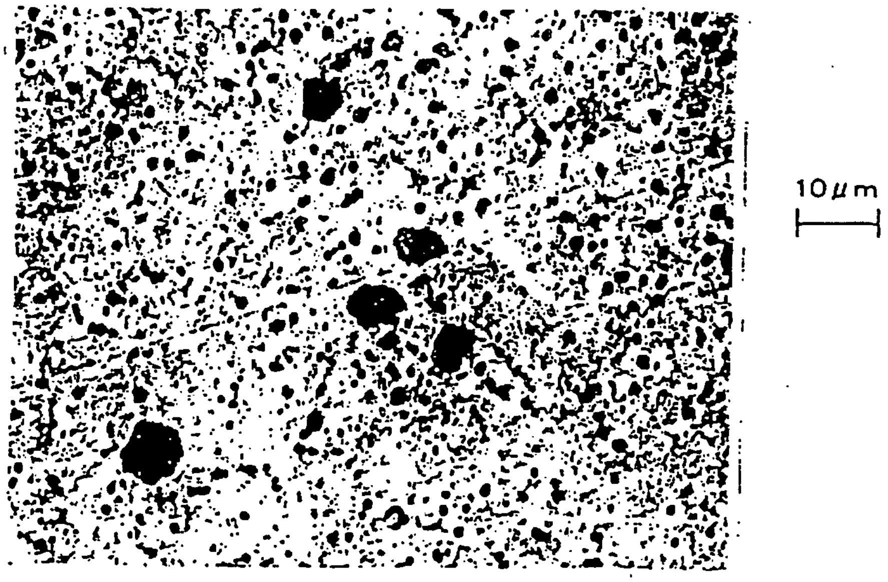
4. A piston ring according to any one of claims 1 through 3, wherein the hardness of the sliding nitriding layer is in a range of from Hv 900 to 1400.

5. A method for producing a piston ring having improved scuffing resistance, cracking resistance and fatigue resistance, by means of subjecting the high-chromium martensitic stainless steel to nitriding treatment, **characterized in that** the high-chromium martensitic stainless steel consists, by weight %, of C: 0.3 to 1.0%; Cr: 14.0 to 21.0%, N: 0.05 to 0.50%, at least one of Mo, V, W and Nb: 0.03 to 3.0% in total, Si: 0.1 to 1.0%, Mn: 0.1 to 1.0%, P: 0.05% or less, S: 0.05% or less, the balance being Fe and unavoidable impurities; and, further the quenching of said high-chromium martensitic stainless steel prior to bending it into a ring shape is carried out from a temperature in a range of from 850 to 1000°C.

6. A combination of the piston ring according to any one of the claims 1 through 4, and a cast-iron monoltihic cylinder.

Fig. 1

(a)



(b)

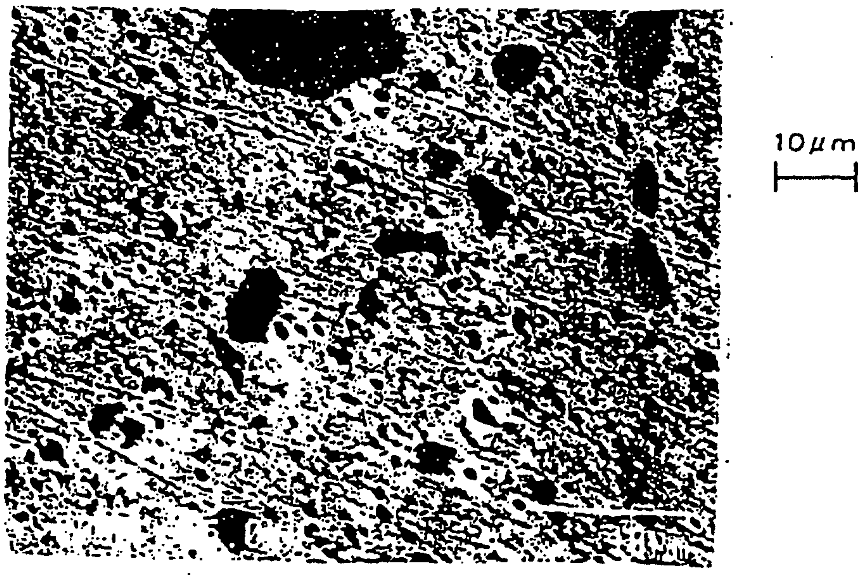
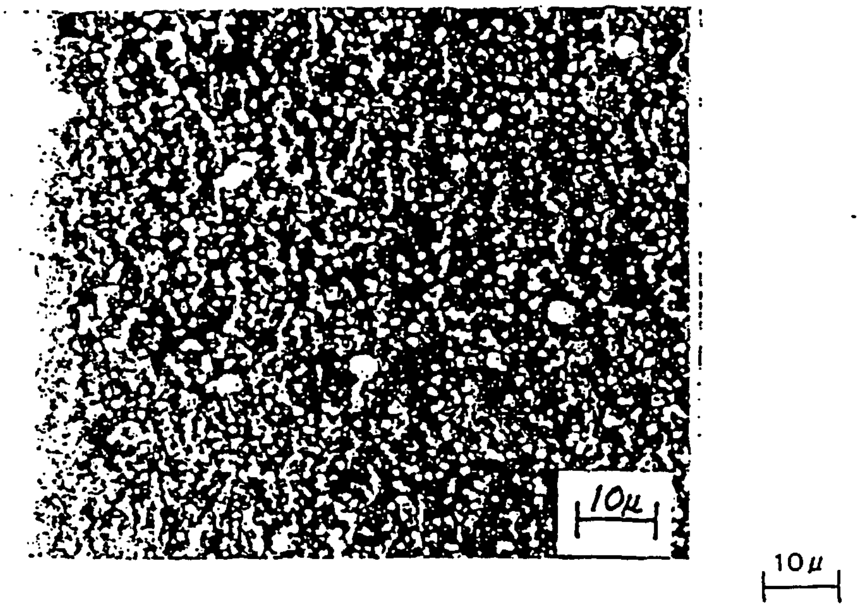


Fig. 2



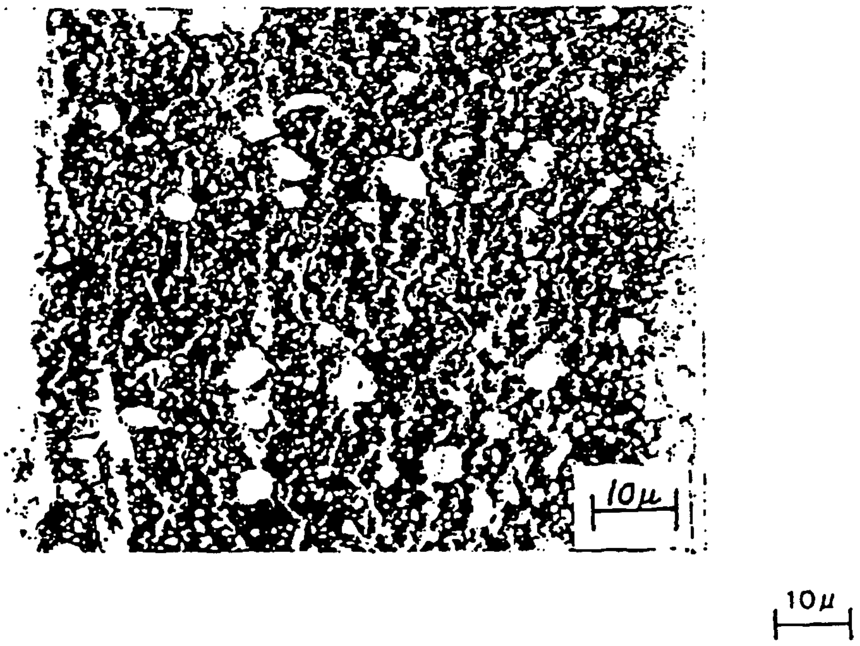


Fig. 3

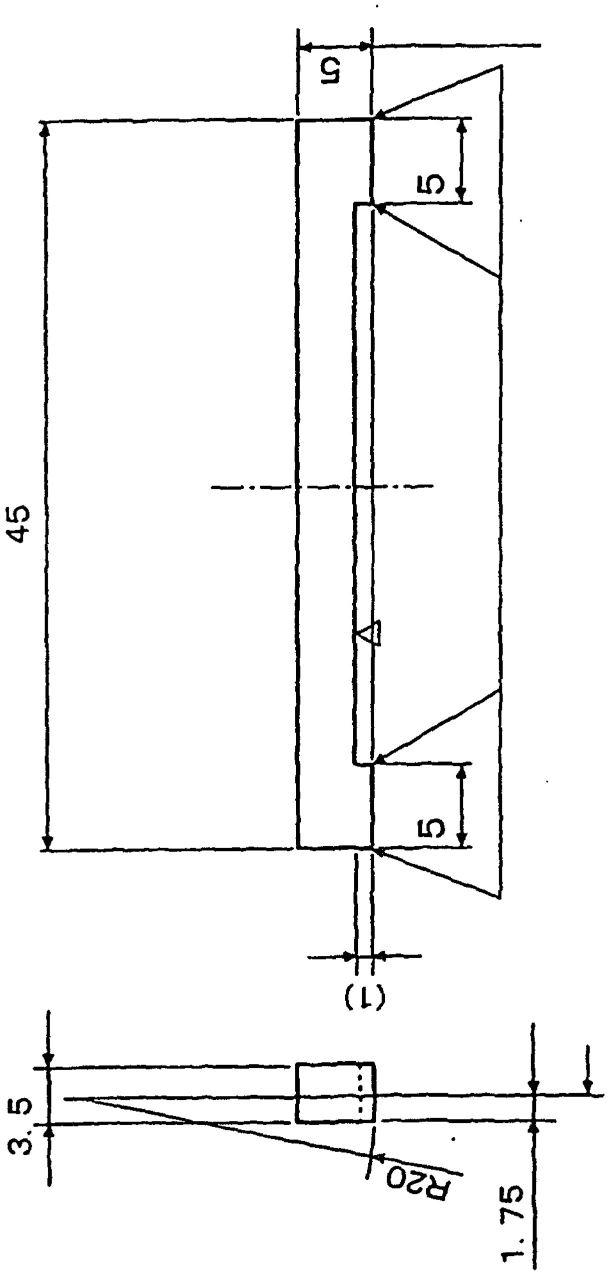


Fig. 4

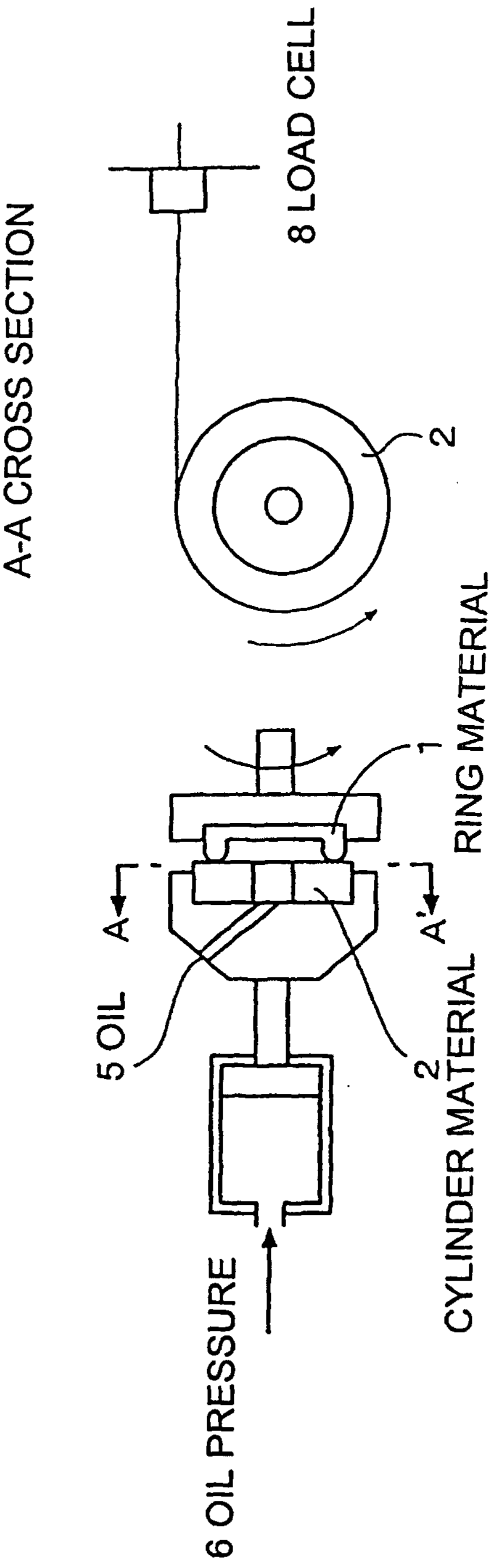

A-A CROSS SECTION
8 LOAD CELL
2
RING MATERIAL
1
A
A'
5 OIL
2
CYLINDER MATERIAL
6 OIL PRESSURE

Fig. 5

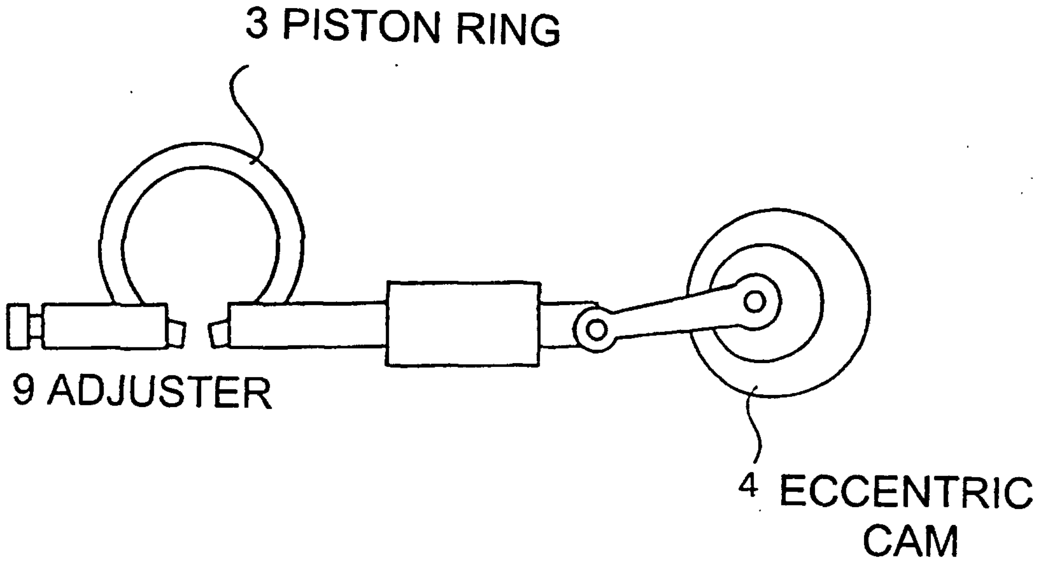


Fig. 6

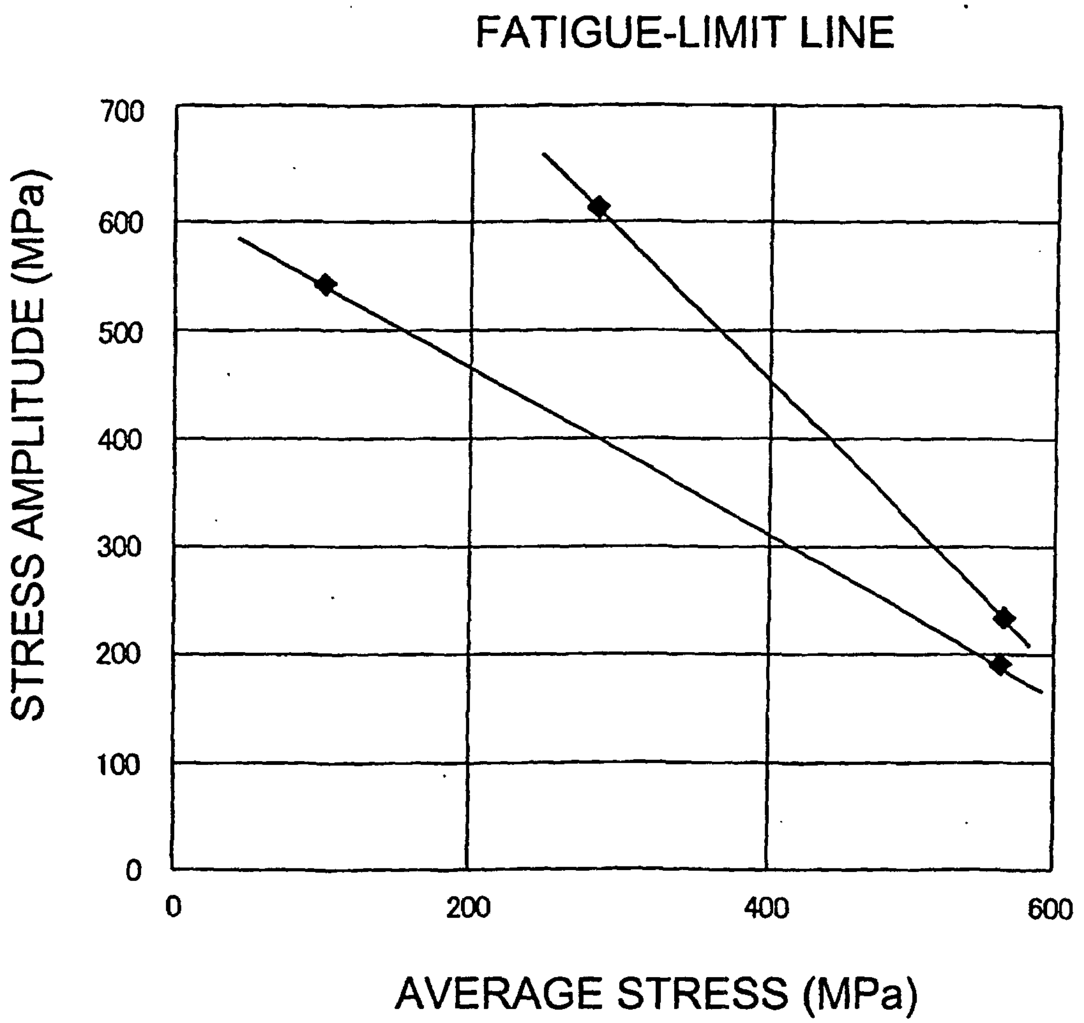
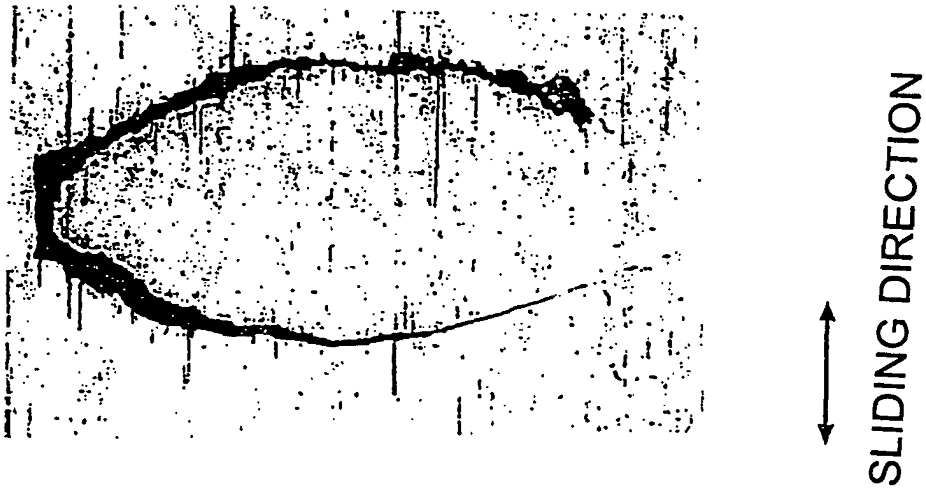

FATIGUE-LIMIT LINE
STRESS AMPLITUDE (MPa)
700
600
500
400
300
200
100
0
0
200
400
600
AVERAGE STRESS (MPa)

Fig. 7



(x200)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP01/06127

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl^7 C22C38/00, 38/34, F16J9/26

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 C22C38/00-38/60, F16J9/26

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

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 8-134596 A (Nippon Steel Corporation), 28 May, 1996 (28.05.96) (Family: none)	1-6
A	JP 7-278758 A (Nippon Steel Corporation), 24 October, 1995 (24.10.95) (Family: none)	1-6
A	JP 1-205063 A (Daido Steel Co., Ltd.), 17 August, 1989 (17.08.89) (Family: none)	1-6
A	JP 11-294584 A (Riken Corporation), 29 October, 1999 (29.10.99) (Family: none)	1-6
A	JP 5-148593 A (Hiroyuki KANAI), 15 June, 1993 (15.06.93) (Family: none)	1-6
A	JP 61-144470 A (Riken Corporation), 02 July, 1986 (02.07.86) (Family: none)	1-6
A	JP 59-162346 A (Hitachi Metals, Ltd.), 13 September, 1984 (13.09.84) (Family: none)	1-6

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

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"&" document member of the same patent family

Date of the actual completion of the international search 27 August, 2001 (27.08.01)	Date of mailing of the international search report 11 September, 2001 (11.09.01)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)