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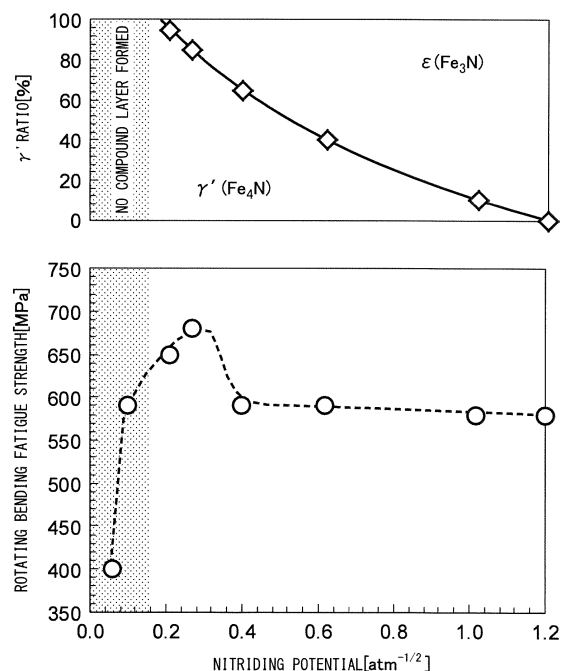
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(54) **NITRIDED COMPONENT AND METHOD FOR PRODUCING SAME**

(57) A nitrided part excellent in contact fatigue strength plus rotating bending fatigue strength, the nitrided part having a steel material having a predetermined chemical composition as a material, wherein the nitrided part comprises a compound layer formed on the surface of the steel material, the compound layer containing iron, nitrogen, and carbon, a thickness of the compound layer being 3 μm to less than 20 μm ; a phase structure in the compound layer in a range from the surface down to a depth of 5 μm contains γ' phases in an area ratio of 50% or more; a pore area ratio in a range from the surface down to a depth of 3 μm is less than 1%; and a compressive residual stress of the compound layer surface is 500 MPa or more.

FIG. 5



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Description

FIELD

5 **[0001]** The present invention relates to a gas nitrided steel part, in particular a gear, CVT sheave, or other nitrided part excellent in contact fatigue strength and bending fatigue strength and a method of production of the same.

BACKGROUND

10 **[0002]** Steel parts used in automobiles and various industrial machinery etc. are improved in fatigue strength, wear resistance, seizing resistance, and other mechanical properties by carburizing and quenching, high-frequency quenching, nitriding, nitrocarburizing, and other surface hardening heat treatment.

15 **[0003]** Nitriding and nitrocarburizing are performed in the ferrite region of the A_1 point or less. During treatment, there is no phase transformation, so it is possible to reduce the heat treatment strain. For this reason, nitriding and nitrocarburizing are often used for parts requiring high dimensional precision and large sized parts. For example, they are applied to the gears used for transmission parts in automobiles and the crankshafts used for engines.

20 **[0004]** Nitriding is a method of treatment diffusing nitrogen into the surface of a steel material. For the medium used for the nitriding, there are a gas, salt bath, plasma, etc. For the transmission parts of an automobile, gas nitriding is mainly being used since it is excellent in productivity. Due to gas nitriding, the surface of the steel material is formed with a compound layer of a thickness of 10 μm or more (layer at which Fe_3N or other nitride is formed). Furthermore, the surface layer of the steel material at the lower side of the compound layer is formed with a nitrogen diffusion layer forming a hardened layer. The compound layer is mainly comprised of $\text{Fe}_{2-3}\text{N}(\varepsilon)$ and $\text{Fe}_4\text{N}(\gamma')$. The hardness of the compound layer is extremely high compared with the steel of the base material. For this reason, the compound layer improves the wear resistance and contact fatigue strength of a steel part in the initial stage of use.

25 **[0005]** PTL 1 discloses a nitrided part in which the γ' phase ratio in the compound layer is made 30 mol% or more to thereby improve the bending fatigue resistance.

[0006] PTL 2 discloses a steel member having a low strain and excellent contact fatigue strength and bending fatigue strength obtained by forming an iron nitride compound layer having a predetermined structure on the steel member.

30 **[0007]** PTL 3 discloses a method of nitriding low alloy steel having a sufficient surface hardness and hardened layer depth by suppressing formation of a compound layer.

[0008] PTL 4 discloses a steel member having an iron nitride compound layer having a predetermined structure on its surface, having a high pitting resistance and bending fatigue strength, and having a lower strain compared with carburizing or carbonitriding.

35 [CITATION LIST]

[PATENT LITERATURE]

40 **[0009]**

[PTL 1] Japanese Unexamined Patent Publication No. 2015-117412

[PTL 2] Japanese Unexamined Patent Publication No. 2013-221203

[PTL 3] WO2015/136917A

[PTL 4] WO2013/157579A

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SUMMARY

[TECHNICAL PROBLEM]

50 **[0010]** The nitrided part of PTL 1 is gas soft nitrided using CO_2 for the atmospheric gas, so the surface layer side of the compound layer easily forms ε phases, therefore the bending fatigue strength is believed to be still not sufficient. Further, in the nitrided part of PTL 2, the atmosphere is controlled to NH_3 gas: 0.08 to 0.34, H_2 gas: 0.54 to 0.82, and N_2 gas: 0.09 to 0.18 without regard as to the constituents of the steel, so there is a possibility that, depending on the constituents of the steel, the structure or thickness of the compound layer will not become as targeted.

55 **[0011]** The nitriding method of PTL 3 is characterized by making the compound layer thinner by the two-stage nitriding of high K_N value treatment and low K_N value treatment. This method imparts the compound layer by the first-stage nitriding and breaks down the compound layer imparted by the second-stage nitriding by making N diffuse into the hardened layer to thereby deepen the effective hardened layer, but requires a complicated process of two-stage nitriding.

Further, the γ' phases become lower in ratio and easily form starting points of pitting and bending fatigue fracture.

[0012] The nitriding of PTL 4 features a broad range of control of the partial pressures of various types of gases at the time of treatment, so there is a possibility of the ratio of the γ' phases becoming lower and the porosity becoming higher.

[0013] The object of the present invention is to provide a part excellent in contact fatigue strength plus rotating bending fatigue strength and a method of production of the same.

[SOLUTION TO PROBLEM]

[0014] The inventors took note of the form of the compound layer formed on the surface of the steel material by nitriding and investigated the relationship with the fatigue strength.

[0015] As a result, the inventors discovered that by nitriding steel adjusted in constituents while controlling the nitriding potential considering the amount of C of the material, it is possible to make the vicinity of the surface a phase structure of mainly the γ' phases, suppress the formation of a porous layer, and make the compressive residual stress of the surface layer a constant value or more to thereby fabricate a nitrided part having an excellent contact fatigue strength and rotating bending fatigue strength.

[0016] The present invention was made based on this discovery and after further study. Its gist is as follows:

[0017] A nitrided part having a steel material as a material, the steel material comprising, by mass%, C: 0.05% to 0.30%, Si: 0.05% to 1.5%, Mn: 0.2% to 2.5%, P: 0.025% or less, S: 0.003% to 0.05%, Cr: over 0.5% to 2.0%, Al: 0.01% to 0.05%, N: 0.003% to 0.025%, Nb: 0% to 0.1%, B: 0% to 0.01%, Mo: 0% to less than 0.50%, V: 0% to less than 0.50%, Cu: 0% to less than 0.50%, Ni: 0% to less than 0.50%, Ti: 0% to less than 0.05% and a balance of Fe and impurities, wherein the nitrided part comprises a compound layer formed on a surface of the steel material, the compound layer containing iron, nitrogen, and carbon, a thickness of the compound layer being 3 μm to less than 15 μm ; a phase structure in the compound layer in a range from the surface down to a depth of 5 μm contains γ' phases in an area ratio of 50% or more; a pore area ratio in a range from the surface down to a depth of 3 μm is less than 10%; and a compressive residual stress of the compound layer is 500 MPa or more.

[ADVANTAGEOUS EFFECTS OF INVENTION]

[0018] According to the present invention, it is possible to obtain a nitrided part excellent in contact fatigue strength plus rotating bending fatigue strength.

BRIEF DESCRIPTION OF DRAWINGS

[0019]

FIG. 1 is a view explaining a method of measurement of a depth of a compound layer.

FIG. 2 is one example of a structural photograph of a compound layer and diffusion layer.

FIG. 3 is a view showing a state of formation of pores in a compound layer.

FIG. 4 is one example of a structural photograph where pores are formed in a compound layer.

FIG. 5 is a view showing the relationships of nitriding potential with the phase structure of a compound layer and rotating bending fatigue strength.

FIG. 6 shows the shape of a small roller for roller pitting test use used for evaluating a contact fatigue strength.

FIG. 7 shows the shape of a large roller for roller pitting test use used for evaluating a contact fatigue strength.

FIG. 8 shows a columnar test piece for evaluating rotating bending fatigue strength.

DESCRIPTION OF EMBODIMENTS

[0020] Below, the requirements of the present invention will be explained in detail. First, the chemical composition of the steel material used as a material will be explained. Below, the "%" showing the contents of the component elements and concentrations of elements at the part surface should be deemed to mean "mass%".

C: 0.05% to 0.30%

[0021] C is an element required for securing the core hardness of a part. If the content of C is less than 0.05%, the core strength becomes too low, so the contact fatigue strength and bending fatigue strength greatly fall. Further, if the content of C exceeds 0.30%, the compound layer thickness becomes larger and the contact fatigue strength and bending resistance greatly fall. The preferable range of the C content is 0.08 to 0.25%.

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Si: 0.05 to 1.5%

5 **[0022]** Si raises the core hardness by solution strengthening. Further, it raises the temper softening resistance and raises the contact fatigue strength of the surface of the part becoming high in temperature under wear conditions. To obtain these effects, 0.05% or more is included. On the other hand, if the content of Si exceeds 1.5%, in bars and wire rods, the strength after hot forging becomes too high, so the machinability greatly falls. The preferable range of the Si content is 0.08 to 1.3%.

Mn: 0.2 to 2.5%

10 **[0023]** Mn raises the core hardness by solution strengthening. Furthermore, Mn forms fine nitrides (Mn_3N_2) in the hardened layer at the time of nitriding and improves the wear resistance and contact fatigue strength by precipitation strengthening. To obtain these effects, Mn has to be 0.2% or more. On the other hand, if the content of Mn exceeds 2.5%, not only does the effect of raising the contact fatigue strength become saturated, but also the bars and wire rods used as materials become too high in hardness after hot forging, so the machinability greatly falls. The preferable range of the Mn content is 0.4 to 2.3%.

P: 0.025% or less

20 **[0024]** P is an impurity and precipitates at the grain boundaries to make a part brittle, so the content is preferably small. If the content of P is over 0.025%, sometimes the bending straightening ability and bending fatigue strength fall. The preferable upper limit of the content of P for preventing a drop in the bending fatigue strength is 0.018%. It is difficult to make the content completely zero. The practical lower limit is 0.001%.

S: 0.003 to 0.05%

25 **[0025]** S bonds with Mn to form MnS and raise the machinability. To obtain this effect, S has to be 0.003% or more. However, if the content of S exceeds 0.05%, coarse MnS easily forms and the contact fatigue strength and bending fatigue strength greatly fall. The preferable range of the S content is 0.005 to 0.03%.

Cr: over 0.5 to 2.0%

30 **[0026]** Cr forms fine nitrides (CrN) in the hardened layer during nitriding and improves the contact fatigue strength and bending fatigue strength by precipitation strengthening. To obtain the effects, Cr has to be over 0.5%. On the other hand, if the content of Cr is over 2.0%, not only does the effect of improvement of the contact fatigue strength become saturated, but also the bars and wire rods used as materials become too high in hardness after hot forging, so the machinability remarkably falls. The preferable range of the Cr content is 0.7 to 1.8%.

Al: 0.01 to 0.05%

40 **[0027]** Al is a deoxidizing element. For sufficient deoxidation, 0.01% or more is necessary. On the other hand, Al easily forms hard oxide inclusions. If the content of Al exceeds 0.05%, the bending fatigue strength remarkably falls. Even if other requirements are met, the desired bending fatigue strength can no longer be obtained. The preferable range of the Al content is 0.02 to 0.04%.

N: 0.003% to 0.025%

50 **[0028]** N bonds with Al and V to form AlN and VN. Due to their actions of pinning austenite grains, AlN and VN have the effect of refining the structure of the steel material before nitriding and reducing the variation in mechanical characteristics of the nitrified part. If the content of N is less than 0.003%, this effect is difficult to obtain. On the other hand, if the content of N exceeds 0.025%, coarse AlN easily forms, so the above effect becomes difficult to obtain. The preferable range of the content of N is 0.005 to 0.020%.

55 **[0029]** The chemical constituents of the steel used as the material for the nitrified part of the present invention contain the above-mentioned elements and have a balance of Fe and unavoidable impurities. The "unavoidable impurities" mean constituents contained in the raw materials or entering in the process of manufacture which are not intentionally included in the steel.

[0030] However, the steel used as the material for the nitrified part of the present invention may also contain the elements shown below in place of part of the Fe.

Nb: 0% to 0.1%

5 **[0031]** Nb bonds with C or N to form NbC or NbN. Due to the pinning actions of NbC and NbN, it has the effect of suppressing coarsening of the austenite grains, refining the structure of the steel material before nitriding, and reducing variation of the mechanical characteristics of the nitrided part. This effect is obtained if adding Nb in a trace amount, but to obtain the effect more reliably, Nb is preferably made 0.01% or more. If the content of Nb exceeds 0.1%, coarse NbC and NbN are easily formed, so the above effect becomes difficult to obtain.

B: 0 to 0.01%

10 **[0032]** B has the effect of suppressing the segregation of P at the grain boundaries and improving the toughness. Further, it bonds with N to form BN and improve the machineability. These effects are obtained by adding Nb in a trace amount, but to obtain the effect more reliably, B is preferably made 0.0005% or more. If the content of B exceeds 0.01%, not only does the above effect become saturated, but also a large amount of BN segregates and sometimes cracks form in the steel material.

Mo: 0% to less than 0.50%

20 **[0033]** Mo forms fine nitrides (Mo_2N) in the hardened layer during nitriding and improves the contact fatigue strength and bending fatigue strength by precipitation strengthening. Further, Mo has the action of age hardening and improves the core hardness at the time of nitriding. The content of Mo for obtaining these effects is preferably 0.01% or more. On the other hand, if the content of Mo is 0.50% or more, the bars and wire rods used as materials become too high in hardness after hot forging, so the machinability remarkably falls. In addition, the alloy costs increase. The preferable upper limit of the Mo content for securing machinability is less than 0.40%.

V:0% to less than 0.50%

30 **[0034]** V forms fine nitrides (VN) at the time of nitriding and nitrocarburizing, improves the contact fatigue strength and bending fatigue strength by precipitation strengthening, and raises the core hardness of the parts. Further, it has the effect of refining the structure. To obtain these actions, V is preferably made 0.01% or more. On the other hand, if the content of V is 0.50% or more, the bars and wire rods used as materials become too high in hardness after hot forging, so the machinability remarkably falls. In addition, the alloy costs increase. The preferable range of the V content for securing machinability is less than 0.40%.

Cu: 0% to less than 0.50%

40 **[0035]** Cu improves the core hardness of the part and the hardness of the nitrogen diffusion layer as a solution strengthening element. To realize this action of solution strengthening of Cu, inclusion of 0.01% or more is preferable. On the other hand, if the content of Cu is 0.50% or more, the bars and wire rods used as materials become too high in hardness after hot forging, so the machinability remarkably falls. In addition, the hot ductility falls, so this causes the occurrence of surface defects at the time of hot rolling and at the time of hot forging. The preferable range of the Cu content for maintaining the hot ductility is less than 0.40%.

Ni: 0% to less than 0.50%

50 **[0036]** Ni improves the core hardness and the surface layer hardness by solution strengthening. To realize this action of solution strengthening of Ni, inclusion of 0.01% or more is preferable. On the other hand, if the content of Ni is 0.50% or more, the bars and wire rods used as materials become too high in hardness after hot forging, so the machinability remarkably falls. In addition, the alloy costs increase. The preferable range of the Ni content for securing sufficient machinability is less than 0.40%.

Ti: 0% to less than 0.05%

55 **[0037]** Ti bonds with N to form TiN and improves the core hardness and surface layer hardness. To obtain this action, Ti is preferably made 0.005% or more. On the other hand, if the content of Ti is 0.05% or more, the effect of improving the core hardness and surface layer hardness becomes saturated. In addition, the alloy costs increase. The preferable range of the Ti content is 0.007 to less than 0.04%.

[0038] Next, the compound layer of the nitrided part of the present invention will be explained.

Thickness of compound layer: 3 μm to less than 15 μm

[0039] The "compound layer" is the layer of iron nitride formed by the nitriding. Its thickness affects the contact fatigue strength and bending strength of the nitrided part. If the compound layer is too thick, it easily becomes the starting point of pitting or fracture due to bending. If the compound layer is too thin, the residual stress of the surface is not sufficiently obtained and the contact fatigue strength and bending strength fall. In the nitrided part of the present invention, from the viewpoint of the contact fatigue strength and bending strength, the thickness of the compound layer is made 3 μm to less than 15 μm .

[0040] The thickness of the compound layer is found by gas nitriding then polishing the vertical cross-section of the test material, etching it, and observing it by an optical microscope. The etching is performed by a 3% Nital solution for 20 to 30 seconds. The compound layer is present at the surface layer of the low alloy steel and observed as a white uncorroded layer. Five fields of a structural photograph captured by the optical microscope by 500X (field area: $2.2 \times 10^4 \mu\text{m}^2$) are observed. In each field, four points are measured every 30 μm in the horizontal direction. The average value of the values of the 20 points measured is defined as the "compound thickness (μm)". FIG. 1 shows an outline of the method of measurement, while FIG. 2 shows one example of a structural photograph of the compound layer and diffusion layer.

 γ' phase ratio of compound layer from surface to 5 μm : 50% or more

[0041] If the ratio of the γ' phases is low and the ε phase ratio is high at the compound layer from the surface to 5 μm , the layer easily becomes the starting point of pitting or bending fatigue fracture. This is because the fracture toughness value of the ε phases is lower than the γ' phases. Further, when the phases near the surface are γ' phases, compared to when they are ε phases, the later explained compressive residual stress is easily introduced into the surface and the fatigue strength can be improved.

[0042] The γ' phase ratio in the compound layer is found by electron back scatter diffraction (EBSD). Specifically, the area of 150 μm^2 from the outermost surface of compound layer down to a depth of 5 μm is measured by EBSD and an analysis diagram for discriminating the γ' phases and ε phases is prepared. Further, the obtained EBSD analysis image is used to find the area ratio of the γ' phases using an image processing application. This is defined as the " γ' phase ratio (%)". In EBSD measurement, it is suitable to measure about 10 fields by a power of about 4000X.

[0043] The above γ' phase ratio means the ratio of the γ' phases of the "compound layer" from the surface to a depth of 5 μm . That is, if the thickness of the compound layer is less than 5 μm from the surface, the γ' phase ratio at the region of the compound layer thickness is calculated. As one example, if the thickness of the compound is 3 μm from the surface, the ratio of γ' phases of the compound layer from the surface to a depth of 3 μm becomes the γ' phase ratio.

[0044] The γ' phase ratio is preferably 60% or more, more preferably 65% or more, still more preferably 70% or more.

[0045] The γ' phase ratio may be found by the method of using X-ray diffraction. However, measurement by X-ray diffraction becomes vague in measurement region and cannot find the accurate γ' phase ratio. Therefore, in the present invention, the γ' phase ratio of the compound layer is made one found by EBSD.

Pore area ratio of compound layer of surface to 3 μm : less than 10%

[0046] If there are pores in the compound layer of the surface to 3 μm , stress concentrates and becomes starting points of pitting and bending fatigue fracture. For this reason, the pore area ratio has to be made less than 10%.

[0047] Pores are formed due to N_2 gas desorbing from the surface of the steel material along the grain boundaries from the grain boundaries and other energy stable locations at the surface of the steel material where the binding force by the matrix is small. N_2 is more easily generated the higher the later explained nitriding potential K_N . This is because as the K_N becomes higher, a $\text{bcc} \rightarrow \gamma' \rightarrow \varepsilon$ phase transformation occurs and the ε phases become larger in amount of solid solution of N_2 compared with the γ' phases and make N_2 gas become more easily generated. FIG. 3 shows an outline of formation of pores in the compound layer, while FIG. 4 shows a structural photograph of the formation of pores.

[0048] The pore area ratio can be measured by observation by an optical microscope. Specifically, the span from the surface to 3 μm at the cross-section of a test material is measured at five fields by a power of 1000X (field area: $5.6 \times 10^3 \mu\text{m}^2$). At each field, the ratio of the pores in the range from the outermost surface to a depth of 3 μm is made the "pore area ratio".

[0049] The pore area ratio is preferably less than 5%, more preferably less than 2%, still more preferably less than 1%. 0 is most preferable.

Compressive residual stress of surface of compound layer: 500 MPa or more

[0050] The nitrided part of the present invention is nitrided to harden the surface of the steel and given compressive

residual stress at the surface layer part of the steel to improve the fatigue strength and wear resistance of the part. The nitrided part of the present invention becomes one having an excellent contact fatigue strength and rotating bending fatigue strength by improving the compound layer in the above way and further introducing compressive residual stress of 500 MPa or more into the surface. The method of production for introducing such compressive residual stress into the surface of the part will be explained later.

[0051] Next, one example of a method of production of a nitrided part of the present invention will be explained.

[0052] In the method of production of a nitrided part of the present invention, a steel material having the above-mentioned constituents is gas nitrided. The treatment temperature of the gas nitriding is 550 to 620°C, while the treatment time of the gas nitriding as a whole is 1.5 to 10 hours.

Treatment temperature: 550 to 620°C

[0053] The temperature of the gas nitriding (nitriding temperature) is mainly correlated with the diffusion rate of the nitrogen and affects the surface hardness and hardened layer depth. If the nitriding temperature is too low, the diffusion rate of the nitrogen becomes slower, the surface hardness becomes lower, and the hardened surface depth becomes shallower. On the other hand, if the nitriding temperature exceeds the A_{C1} point, austenite phases (γ phases) with diffusion rates of nitrogen smaller than the ferrite phases (α phases) are formed in the steel, the surface hardness becomes lower, and the hardened layer depth becomes shallower. Therefore, in the present embodiment, the nitriding temperature is the 550 to 620°C around the ferrite temperature region. In this case, the surface hardness can be kept from becoming lower and the hardened layer depth can be kept from becoming shallower.

Treatment time of gas nitriding as whole: 1.5 to 10 hours

[0054] The gas nitriding is performed in an atmosphere containing NH_3 , H_2 , and N_2 . The time of the nitriding as a whole, that is, the time from the start to the end of the nitriding (treatment time), is correlated with formation and breakdown of the compound layer and the diffusion and cementation of nitrogen and affects the surface hardness and hardened layer depth. If the treatment time is too short, the surface hardness becomes lower and the hardened layer depth becomes shallower. On the other hand, if the treatment time is too long, denitrification and decarburization occur and the surface hardness of the steel falls. If the treatment time is too longer, further, the production cost rises. Therefore, the treatment time of the nitriding as a whole is 1.5 to 10 hours.

[0055] Note that, the atmosphere of the gas nitriding of the present embodiment includes NH_3 , H_2 , and N_2 and also unavoidably oxygen, carbon dioxide, and other impurities. The preferable atmosphere contains NH_3 , H_2 , and N_2 in a total of 99.5% (vol%) or more.

[0056] If performing the gas nitrocarburizing in an atmosphere containing about several percent of carbon monoxide and carbon dioxide, the ϵ phases with high solid solubility limits of C are preferentially formed. The γ' phases cannot take in almost any C in solid solution, so if performing the nitrocarburizing, the compound layer becomes the single ϵ phases. Further, the growth rate of the ϵ phases is faster than the γ' phases. Thus, with gas nitrocarburizing where ϵ phases are stably formed, the compound layer is formed thicker than required. Therefore, in the present invention, rather than gas nitrocarburizing, as explained later, it is necessary to perform gas nitriding controlling the nitriding potential K_N .

Gas conditions of nitriding

[0057] In the nitriding method of the present invention, the nitriding is performed at a nitriding potential controlled considering the amount of C of the material. Due to this, it is possible to make the phase structure at the compound layer from the surface to a depth of 5 μm a γ' phase ratio of 50% or more, make the pore area ratio from the surface to a depth of 3 μm less than 10%, and make the compressive residual stress of the surface of the compound layer 500 MPa or more.

[0058] The nitriding potential K_N of the gas nitriding is defined by the following formula:

$$K_N(\text{atm}^{-1/2}) = (\text{NH}_3 \text{ partial pressure (atm)}) / [(\text{H}_2 \text{ partial pressure (atm)})^{3/2}]$$

[0059] The partial pressures of the NH_3 and H_2 of the atmosphere of the gas nitriding can be controlled by adjusting the flow rates of the gases. To form a compound layer by nitriding, it is necessary that the K_N at the time of gas nitriding be a certain value or more, but as explained above, if the K_N becomes too high, the ratio of the ϵ phases easily generating N_2 gas becomes greater and the pores become greater. Therefore, it is important to provide the condition of K_N and suppress the formation of pores.

[0060] As a result of study of the inventors, it was discovered that the nitriding potential of the gas nitriding has an

effect on the phase structure of the compound layer and the rotating bending fatigue strength of the nitrided part and that the optimal nitriding potential is determined by the C content of the steel.

5 [0061] Specifically, when making the C content of the steel (mass%) the (mass%C), it was discovered that if the nitriding potential at the time of gas nitriding continuously satisfies $0.15 \leq K_N \leq -0.17 \times \ln(\text{mass}\%C) + 0.20$ during the gas nitriding, the phase structure of the compound layer becomes one with a γ' phase ratio of 50% or more and further the nitrided part has a high rotating bending fatigue strength and contact fatigue strength.

[0062] Even if the average nitriding potential of the gas nitriding satisfies the above formula, if obtaining a nitriding potential not satisfying the above formula even temporarily, the γ' phase ratio at the compound layer will not become 50% or more.

10 [0063] FIG. 5 shows the results of investigation of the relationships of the nitriding potential with the γ' ratio of the compound layer and rotating bending fatigue strength. FIG. 5 relates to the steel "j" (Table 1) of the later described examples.

[0064] In this way, with the present nitriding method, gas nitriding is performed at a nitriding potential K_N corresponding to the amount of C of the steel used as a material. Due to this, it becomes possible to stably impart γ' phases to the surface of the steel and obtain a nitrided part having excellent contact fatigue strength and rotating bending fatigue strength, preferably a contact fatigue strength of 2000 MPa or more and a rotating bending fatigue strength of 600 MPa or more.

EXAMPLES

20 [0065] Steels "a" to "aa" having the chemical constituents shown in Table 1 were melted in 50 kg amounts in a vacuum melting furnace to produce molten steels. The molten steels were cast to produce ingots. Note that, in Table 1, "a" to "s" are steels having the chemical constituents prescribed in the present invention. On the other hand, steels "t" to "aa" are steels of comparative examples off from the chemical constituents prescribed in the present invention in at least one element.

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Table 1

Steel	Chemical composition (mass%)*1													Remarks			
	C	Si	Mn	P	S	Cr	Al	N	Mo	V	Cu	Ni	Nb		Ti	B	
a	0.19	0.80	1.50	0.015	0.010	1.50	0.028	0.011									
b	0.28	0.09	1.35	0.012	0.012	1.23	0.026	0.010	0.31								
c	0.12	1.33	0.85	0.014	0.011	1.36	0.020	0.010			0.25						
d	0.10	0.18	1.12	0.008	0.008	1.21	0.033	0.009	0.15								
e	0.20	0.41	1.14	0.019	0.032	1.27	0.022	0.018									
f	0.15	0.33	0.44	0.009	0.013	1.82	0.025	0.014					0.007				
g	0.12	0.50	0.88	0.009	0.012	1.21	0.043	0.022				0.43					
h	0.16	0.42	1.13	0.012	0.010	1.11	0.023	0.012	0.15	0.17							
i	0.15	0.43	1.20	0.009	0.006	0.87	0.028	0.011	0.20			0.15					
j	0.13	0.20	2.01	0.010	0.010	0.91	0.020	0.005	0.10								
k	0.07	0.39	1.30	0.015	0.021	0.99	0.030	0.009		0.13	0.22						
l	0.23	0.07	0.96	0.017	0.006	0.97	0.022	0.008	0.12				0.012				
m	0.25	0.29	0.38	0.012	0.010	1.35	0.025	0.008	0.35				0.008				
n	0.22	0.56	1.20	0.011	0.007	0.69	0.021	0.017	0.33	0.35	0.31			0.011			
o	0.15	0.31	1.10	0.008	0.010	1.21	0.018	0.004	0.10	0.10	0.09			0.008			
p	0.11	0.20	1.22	0.009	0.008	1.35	0.021	0.011	0.10	0.03	0.09	0.10		0.005			
q	0.06	0.05	0.39	0.017	0.007	1.98	0.023	0.010	0.25	0.04	0.22	0.25		0.035			
r	0.12	0.44	0.65	0.017	0.010	1.78	0.020	0.011	0.35	0.10		0.10	0.10	0.009			
s	0.06	0.23	0.39	0.013	0.010	0.69	0.023	0.009	0.45	0.10	0.22	0.25	0.10	0.026	0.001		

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(continued)

Steel	Chemical composition (mass%)*1													Remarks		
	C	Si	Mn	P	S	Cr	Al	N	Mo	V	Cu	Ni	Nb		Ti	B
t	<u>0.32</u>	0.33	0.65	0.011	0.012	0.71	0.023	0.009								
u	<u>0.04</u>	0.41	0.52	0.015	0.013	0.85	0.021	0.012								
v	0.21	<u>0.04</u>	0.85	0.013	0.041	1.77	0.015	0.003								
w	0.24	0.12	<u>0.18</u>	0.015	0.012	0.72	0.021	0.006								
x	0.08	0.22	0.45	<u>0.028</u>	<u>0.051</u>	0.71	0.020	0.004								
y	0.07	0.41	0.55	0.014	0.022	<u>0.48</u>	0.021	0.006						0.008		
z	0.15	1.02	0.55	0.015	0.008	0.71	<u>0.053</u>	0.003								
aa	<u>0.03</u>	0.85	<u>0.18</u>	0.012	0.009	<u>0.46</u>	0.025	0.006	0.10		0.10	0.09				

*1 Balance of chemical composition is Fe and impurities.

*2 Empty fields indicate no alloy elements intentionally added.

*3 Underlines indicate outside scope of present invention.

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[0066] The ingots were hot forged to obtain round bars of a diameter of 40 mm. Next, each round bar was annealed, then machined to fabricate small rollers for roller pitting test use shown in FIG. 6 and large rollers shown in FIG. 7 for evaluation of contact fatigue strength. Furthermore, columnar test pieces were fabricated for evaluation of the bending fatigue resistance shown in FIG. 8.

5 **[0067]** Each sampled test piece was gas nitrided under the next conditions. The test piece was loaded into a gas nitriding furnace, NH_3 , H_2 , and N_2 gases were introduced into the furnace, and nitriding was carried out under the conditions shown in Table 2. However, in Test No. 34, CO_2 gas was added to the atmosphere by a volume ratio of 3% for performing gas nitrocarburizing. Further, Test No. 35 was made two-stage nitriding with the nitriding conditions changed between the first half and the second half of the process. Test No. 36 corresponds to Example 16 in PTL 3. It
10 comprised oil cooling the gas nitrided test piece using 80°C oil.

[0068] The H_2 partial pressure in the atmosphere was measured using a heat conduction type H_2 sensor directly attached to the gas nitriding furnace body. The difference in heat conductivities of the standard gas and measured gas was measured converted to the gas concentration. The H_2 partial pressure was measured continuously during the gas nitriding.

15 **[0069]** Further, the NH_3 partial pressure was measured by attaching a manual glass tube-type NH_3 analyzer to the outside of the furnace.

[0070] The partial pressure of the residual NH_3 was measured every 10 minutes. Simultaneously, the nitriding potential K_N was calculated. The NH_3 flow and N_2 flow were adjusted so that these converged to the target values. Every 10
20 minutes when measuring the NH_3 partial pressure, the nitriding potential K_N was calculated and the NH_3 flow and N_2 flow were adjusted so that these converged to the target values.

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Table 2

Test no.	Steel	Gas nitriding					Compound layer				Pitting strength (MPa)	Rotating bending fatigue strength (MPa)	Remarks
		Temp. (°C)	Time (h)	Nitriding potential K_N		Thickness (μm)	g' phase ratio of surface layer (%)	Pore area ratio of surface layer (%)	Residual stress (MPa)				
				Lower limit	Upper limit					Upper limit target			
1	a	590	5.0	0.22	0.39	0.48	12	55	8	-540	2050	620	
2	a	590	5.0	0.16	0.29	0.48	5	75	2	-560	2150	630	
3	a	590	5.0	0.16	0.35	0.48	8	70	5	-550	2050	630	
4	a	590	5.0	0.20	0.36	0.48	10	65	6	-540	2100	620	
5	a	570	6.0	0.18	0.35	0.48	8	65	4	-530	2100	620	
6	a	610	3.0	0.17	0.39	0.48	6	60	9	-530	2050	620	
7	a	590	5.0	0.18	0.25	0.48	4	85	1	-600	2250	630	
8	b	590	5.0	0.21	0.36	0.42	14	55	3	-530	2050	630	
9	c	590	5.0	0.20	0.35	0.56	8	60	4	-540	2150	620	
10	d	590	5.0	0.17	0.39	0.59	3	70	3	-570	2150	620	
11	e	590	5.0	0.19	0.32	0.47	4	75	2	-550	2000	610	
12	f	590	5.0	0.19	0.39	0.52	6	70	2	-530	2050	600	
13	g	590	5.0	0.20	0.43	0.56	4	70	2	-530	2050	600	
14	h	590	5.0	0.23	0.41	0.51	8	55	6	-540	2200	630	
15	i	590	5.0	0.16	0.29	0.52	4	80	2	-580	2150	630	
16	j	590	5.0	0.17	0.41	0.55	15	55	5	-510	2050	620	
17	k	590	5.0	0.21	0.50	0.65	7	70	5	-580	2050	650	
18	l	590	5.0	0.19	0.30	0.45	5	75	5	-560	2250	630	
19	m	590	5.0	0.16	0.29	0.44	4	70	3	-570	2150	620	
20	n	590	5.0	0.18	0.35	0.46	5	70	6	-550	2150	630	
21	o	590	5.0	0.21	0.38	0.52	3	60	4	-560	2100	610	

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Test no.	Steel	Gas nitriding					Compound layer				Pitting strength (MPa)	Rotating bending fatigue strength (MPa)	Remarks
		Temp. (°C)	Time (h)	Nitriding potential K_N		Thickness (µm)	g' phase ratio of surface layer (%)	Pore area ratio of surface layer (%)	Residual stress (MPa)				
				Lower limit	Upper limit					Upper limit target			
22	p	590	5.0	0.17	0.36	0.58	8	65	4	-530	2100	620	
23	q	590	5.0	0.18	0.45	0.68	6	75	4	-530	2100	610	
24	r	590	5.0	0.17	0.46	0.56	8	65	7	-570	2150	620	
25	s	590	5.0	0.22	0.45	0.68	11	65	9	-530	2050	610	
26	a	700	5.0	0.16	0.25	0.48	3	0*	25*	30*	1900*	580*	
27	a	500	5.0	0.20	0.32	0.48	0*	0*	0	-120*	1800*	520*	
28	a	590	15.0	0.38	0.47	0.48	14	50	45*	-360*	2000	580*	
29	a	590	1.0	0.22	0.35	0.48	1*	85	0	-310*	1500*	460*	
30	a	590	5.0	0.14	0.32	0.48	2*	90	0	-430*	1950*	560*	
31	a	590	5.0	0.05	0.28	0.48	0*	0*	0	-210*	1700*	500*	
32	a	590	5.0	0.22	0.49	0.48	12	50	15*	-510	2050	530*	
33	e	610	5.0	0.11	0.85	0.59	13	50	30*	-350*	1700*	520*	
34*1	a	590	5.0	0.22	0.32	0.48	11	5*	7	-80*	1800*	520*	
35*2	a	590	[1] 1.0 [2] 2.0	0.30 0.05	0.50 0.27	0.48 0.48	7	65	11*	-560	1700*	550*	Comp. ex.
36	t	590	7.0	0.23	0.37	0.39	16*	50	9	-500	1800*	590*	
37	u	590	5.0	0.21	0.43	0.75	8	70	6	-520	1900*	590*	
38	v	590	5.0	0.18	0.34	0.47	6	65	5	-540	1700*	610	
39	w	590	5.0	0.21	0.38	0.44	5	75	3	-520	1600*	580*	

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Test no.	Steel	Gas nitriding				Compound layer				Pitting strength (MPa)	Rotating bending fatigue strength	Remarks
		Temp. (°C)	Time (h)	Nitriding potential K_N ($\text{atm}^{-1/2}$)		Thickness (μm)	g' phase ratio of surface layer (%)	Pore area ratio of surface layer (%)	Residual stress (MPa)			
40	<u>x</u>	590	5.0	0.20	0.43	0.63	5	75	3	-510	1550*	530*
41	<u>y</u>	590	5.0	0.18	0.51	0.65	11	70	6	-520	1600*	490*
42	<u>z</u>	590	5.0	0.22	0.39	0.52	7	65	6	-560	2050	530*
43	<u>aa</u>	590	5.0	0.35	0.62	0.80	14	75	9	-510	1500*	470*

Underlines indicate outside scope of present invention.

* indicate not satisfying target of present invention.

*1 gas nitrocarburizing adding 3% volume ratio CO_2 gas to atmosphere.

*2 test dividing nitriding conditions into first half [1] and second half [2].

Measurement of compound layer thickness and pore area ratio

[0071] The cross-section of a gas nitrided small roller in the direction vertical to the length direction was polished to a mirror surface and etched. The etched cross-section was examined using a scanning electron microscope (SEM), measured for compound layer thickness, and checked for any pores in the surface layer part. The etching was performed by a 3% Nital solution for 20 to 30 seconds.

[0072] The compound layer can be confirmed as a white uncorroded layer present at the surface layer. The compound layer was observed from 10 fields of a structural photograph taken at 4000X (field area: $6.6 \times 10^2 \mu\text{m}^2$). The thicknesses of the compound layer at three points were respectively measured every 10 μm . The average value of the 30 points measured was defined as the compound thickness (μm).

[0073] Similarly, the ratio of the total area of the pores in an area of 90 μm^2 in a range of 3 μm depth from the outermost surface ("pore area ratio", unit: %) was found by binarization by an image processing application. Further, the average value of 10 fields measured was defined as the pore area ratio (%). Even in the case of a compound layer of less than 3 μm , the span from the surface to a depth of 3 μm was similarly measured.

Measurement of γ' phase ratio

[0074] The γ' phase ratio was found by electron back scatter diffraction (EBSD). The area of 150 μm^2 from the outermost surface of the compound layer to a depth of 5 μm was measured by EBSD to prepare an analysis diagram for discriminating between the γ' phases and ϵ phases. The obtained EBSD analysis image was measured for the γ' phase ratio (%) using an image processing application. In EBSD measurement, 10 fields were measured at 4000X power.

[0075] Further, the average value of the γ' phase ratios of the 10 fields measured was defined as the " γ' phase ratio (%)". If the compound layer is less than 5 μm , the γ' phase ratio at the region of the compound layer thickness part was calculated.

Compound layer residual stress

[0076] The nitrided small roller contact part was measured for the residual stresses $\sigma_{\gamma'}$, σ_{ϵ} , and σ_m of the γ' phases, ϵ phases, and matrix under the conditions of Table 3 using a micro-area X-ray residual stress measurement system. Furthermore, the residual stress σ_c found by the following formula using the area ratios $V_{\gamma'}$, V_{ϵ} , and V_m of the γ' phases, ϵ phases, and matrix in the area 90 μm^2 in the range from the outermost surface to a depth of 3 μm found by EBSD was defined as the "residual stress of the surface".

$$\sigma_c = V_{\gamma'}\sigma_{\gamma'} + V_{\epsilon}\sigma_{\epsilon} + V_m\sigma_m$$

Table 3

Tester	X-ray residual stress measuring device
X-ray tube	Cr
Characteristic X-rays	$K\alpha$ rays
Measurement method	Iso-inclination method
Collimator size	$\phi 4$ mm
Counted time	30 sec
Diffraction angle 2θ	With compound layer: 135° No compound layer: 108°
Stress constant	With compound layer: $-611 \text{ MPa}/^\circ$ No compound layer: $-318 \text{ MPa}/^\circ$

Test for evaluation of contact fatigue strength

[0077] The small roller for the roller pitting test use was finished at the gripping part for the purpose of removing the heat treatment strain, then was used as a roller pitting test piece. The shape after finishing is shown in FIG. 2.

[0078] The roller pitting test was performed by combining the small roller for roller pitting test use and the large roller for roller pitting test use of the shapes shown in FIG. 3 under the conditions shown in Table 4.

[0079] Note that, in FIGS. 2 and 3, the units of the dimensions are "mm". The above large roller for roller pitting test use was fabricated using steel satisfying the standard of JIS SCM420 by a general production process, that is, a process of "normalizing→working test piece→eutectoid carburizing by a gas carburizing furnace→low temperature tempering→polishing". The Vickers hardness Hv at a position of 0.05 mm from the surface, that is, a position of a depth of 0.05 mm, was 740 to 760. Further, the depth where the Vickers hardness Hv was 550 or more was 0.8 to 1.0 mm in range.

[0080] Table 4 shows the test conditions when evaluating the contact fatigue strength. The cutoffs of the tests were made 2×10^7 cycles showing the fatigue limit of general steel. The maximum surface pressures in small roller test pieces where no pitting occurs and 2×10^7 cycles were reached were made the fatigue limits of the small roller test pieces.

Table 4

Tester	Roller pitting tester
Test piece size	Small roller: diameter 26 mm Large roller: diameter 130 mm Contact part 150 mmR
Surface pressure	1500 to 2400 MPa
No. of tests	5
Slip ratio	-40%
Small roller speed	1500 rpm
Circumferential speed	Small roller: 123 m/min
	Large roller: 172 m/min
Lubrication oil	Type: oil for automatic transmission use
	Oil temperature: 90°C

[0081] The occurrence of pitting was detected by a vibration meter provided at the test machine. After the occurrence of vibration, the rotations of both the small roller test pieces and large roller test pieces were stopped and the occurrence of pitting and rotational speeds were checked for.

[0082] In a part of the present invention, a maximum surface pressure at the fatigue limit of 2000 MPa or more was targeted.

Rotating bending fatigue resistance

[0083] Columnar test pieces used for gas nitriding were tested by an Ono-type rotating bending fatigue test. The speed was 3000 rpm, the cutoff of the test was made 1×10^7 cycles showing the fatigue limit of general steel, and the maximum stress in a rotating bending fatigue test piece when reaching 1×10^7 cycles without fracture was made the fatigue limit of the rotating bending fatigue test piece.

[0084] In a part of the present invention, a maximum stress at the fatigue limit of 600 MPa or more was targeted.

Test results

[0085] The results are shown in Table 2. In Test Nos. 1 to 25, the constituents of the steel and the conditions of gas nitriding were within the ranges of the present invention, the compound thickness was 3 to 15 μm , the γ' layer ratio of the compound layer was 50% or more, the compound layer pore area ratio was less than 10%, and the compressive residual stress of the compound layer became 500 MPa or more. As a result, good results of a contact fatigue strength of 2000 MPa or more and a rotating bending fatigue strength of 600 MPa or more were obtained.

[0086] In Test No. 26, the nitriding temperature was too high, so as a result, the γ' phase ratio of the compound layer was low, the pore area ratio was large, and the residual stress became low, so the contact fatigue strength and the rotating bending fatigue strength became low.

[0087] In Test No. 27, the nitriding temperature was too low, the compound layer was not formed, and the residual stress of the surface also became low, so the contact fatigue strength and the rotating bending fatigue strength became low.

[0088] In Test No. 28, the nitriding time was too long, the pore area ratio became large, and along with this the residual stress of the surface was released and became lower, so the rotating bending fatigue strength became low.

[0089] In Test No. 29, the nitriding time was too short, a sufficient compound layer thickness could not be obtained, and the residual stress of the surface was low, so the contact fatigue strength and the rotating bending fatigue strength became low.

[0090] In Test No. 30, the lower limit of the nitriding potential was low, a sufficient compound layer thickness could not be obtained, and the residual stress of the surface was low, so the contact fatigue strength and the rotating bending fatigue strength became low.

[0091] In Test No. 31, the lower limit of the nitriding potential was too low, the compound layer was not formed, and the residual stress of the surface was low, so the contact fatigue strength and the rotating bending fatigue strength became low.

[0092] In Test No. 32, the upper limit of the nitriding potential was high, the pore area ratio increased, and the rotating bending fatigue strength became low.

[0093] In Test No. 33, the upper and lower limits of nitriding potential were not suitable, the compound layer thickness became thick, and the pore area ratio increased, so the contact fatigue strength and the rotating bending fatigue strength became low.

[0094] In Test No. 34, the treatment was nitrocarburizing, the surface was not formed with almost any γ' phases, and the residual stress became low, so the contact fatigue strength and the rotating bending fatigue strength became low.

[0095] In Test No. 35, the average K_N was suitable and the γ' phase ratio was high, but the upper limit of the K_N during the nitriding was high and the pore area ratio increased.

[0096] In Test No. 36, the amount of C of the steel was too high and the compound layer thickness was thick, so the contact fatigue strength became low.

[0097] In Test No. 37, the amount of C of the steel was too low and a sufficient core strength was not obtained, so the part fractured early starting from the matrix.

[0098] In Test No. 38, the amount of Si of the steel was too low and a sufficient core hardness was not obtained, so the part fractured early starting from the matrix.

[0099] In Test No. 39, the amount of Mn of the steel was too low and a sufficient hardened layer hardness and core hardness were not obtained, so the part fractured early starting from the matrix.

[0100] In Test No. 40, the amounts of P and S of the steel were too high, P segregated at the grain boundaries, and coarse MnS were formed, so the part fractured early.

[0101] In Test No. 41, the amount of Cr of the steel was too low and a sufficient diffusion layer hardness and core hardness were not obtained, so the part fractured early starting from the matrix.

[0102] In Test No. 42, the amount of Al of the steel was too high and oxide inclusions were formed, so the part fractured early starting from the matrix.

[0103] In Test No. 43, the amount of C, the amount of Mn, and the amount of Cr of the steel were low and further the upper limit of the nitriding potential was high and the pore area ratio increased, so the contact fatigue strength and the rotating bending fatigue strength became low.

[0104] Above, embodiments of the present invention were explained. However, the above-mentioned embodiments are only illustrations for working the present invention. Therefore, the present invention is not limited to the above-mentioned embodiments and can be worked by suitably changing the above-mentioned embodiments within a scope not departing from the gist of the invention.

Claims

1. A nitrided part having a steel material as a material, the steel material comprising, by mass%,

C: 0.05% to 0.30%,

Si: 0.05% to 1.5%,

Mn: 0.2% to 2.5%,

P: 0.025% or less,

S: 0.003% to 0.05%,

Cr: over 0.5% to 2.0%,

Al: 0.01% to 0.05%,

N: 0.003% to 0.025%,

Nb: 0% to 0.1%,

B: 0% to 0.01%,

Mo: 0% to less than 0.50%,

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V: 0% to less than 0.50%,
Cu: 0% to less than 0.50%,
Ni: 0% to less than 0.50%,
Ti: 0% to less than 0.05% and
a balance of Fe and impurities,

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wherein

the nitrided part comprises a compound layer formed on a surface of the steel material, the compound layer containing iron, nitrogen, and carbon, a thickness of the compound layer being 3 μm to less than 15 μm ;
a phase structure in the compound layer in a range from the surface down to a depth of 5 μm contains γ' phases in an area ratio of 50% or more;
a pore area ratio in a range from the surface down to a depth of 3 μm is less than 10%; and
a compressive residual stress of the compound layer is 500 MPa or more.

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FIG. 1

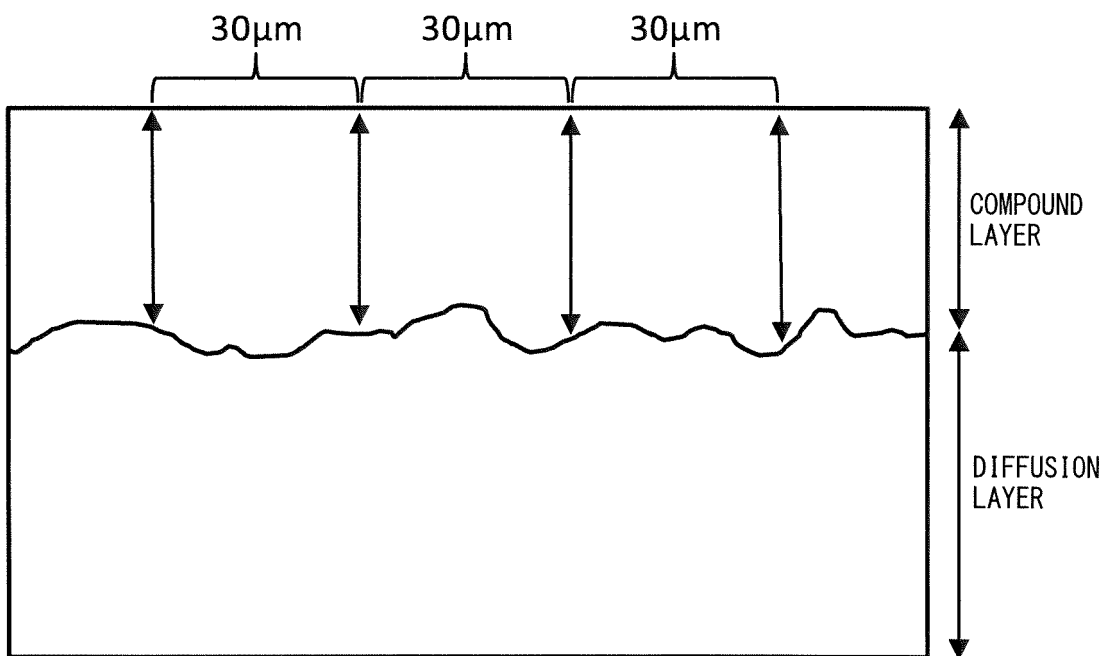


FIG. 2

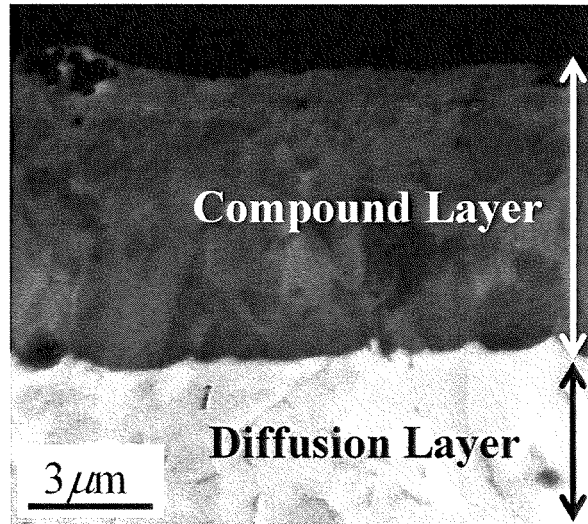


FIG. 3

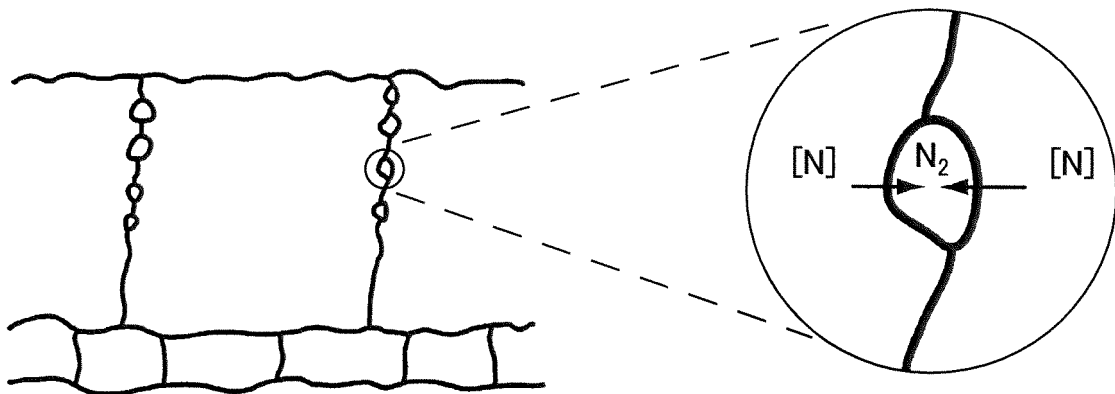


FIG. 4

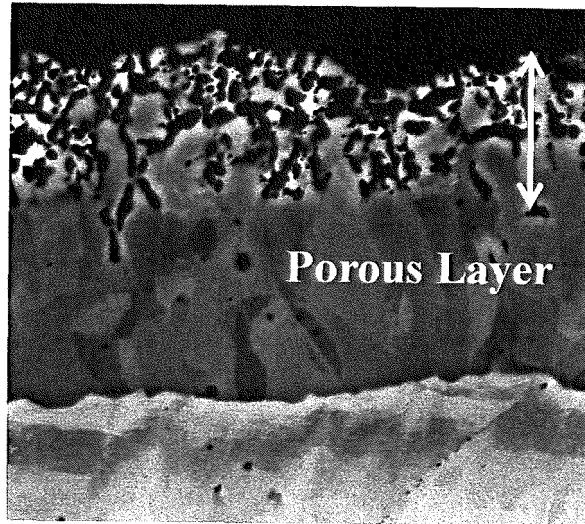


FIG. 5

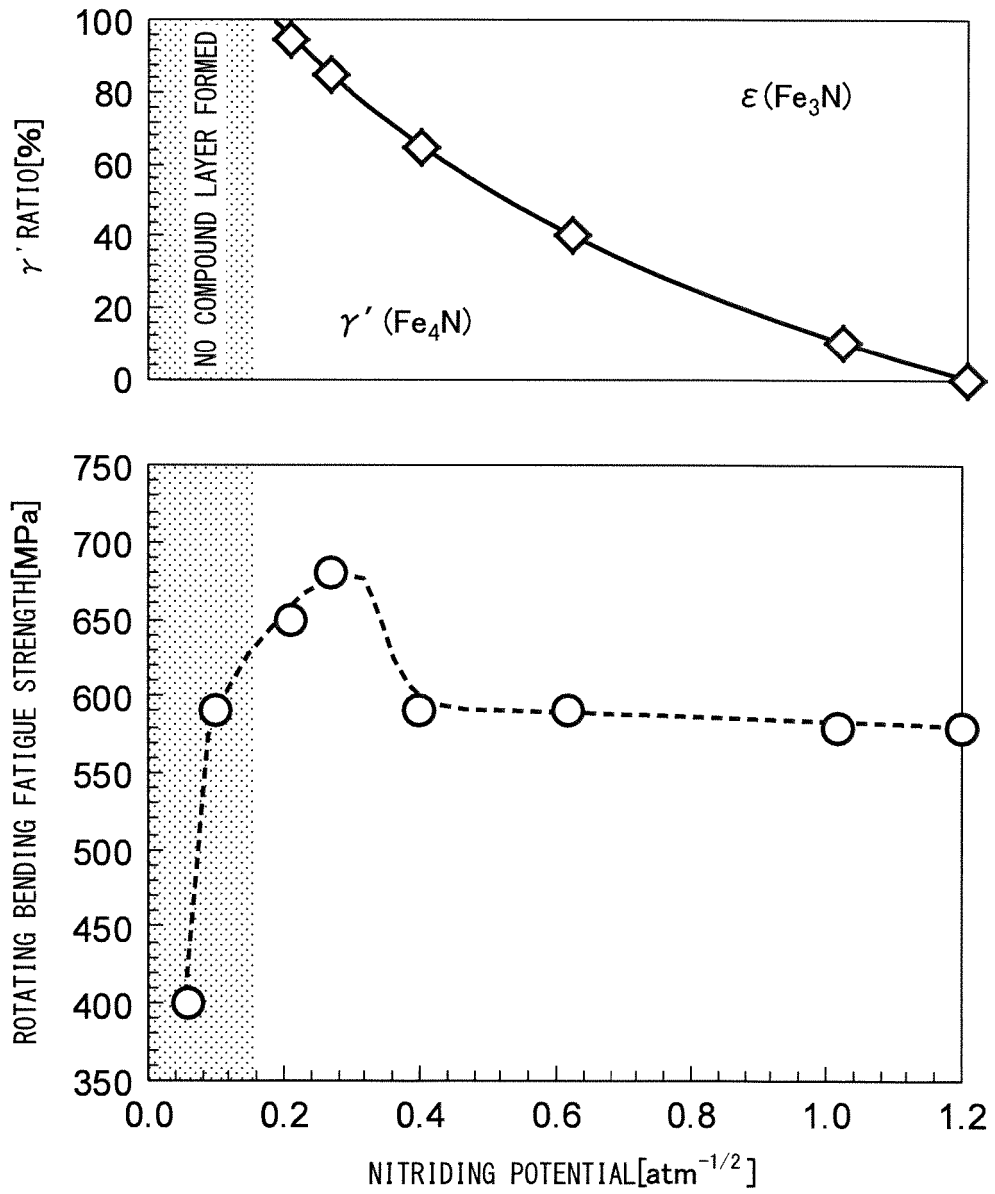


FIG. 6

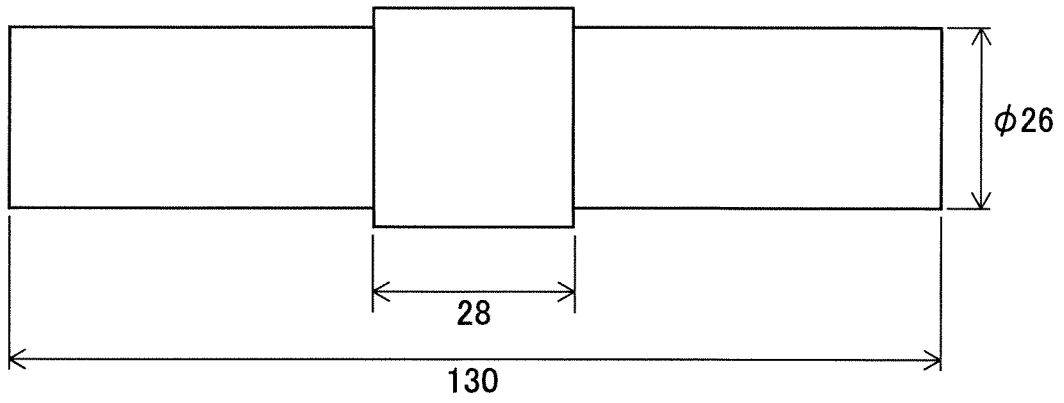


FIG. 7

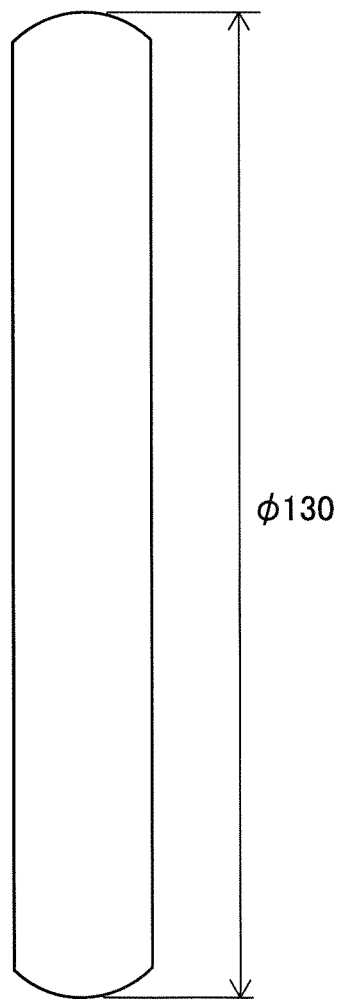
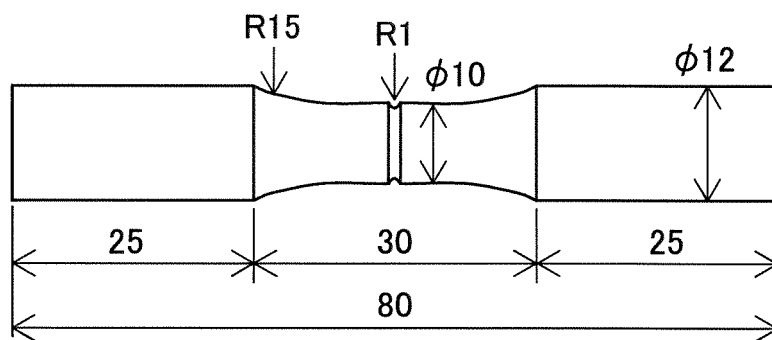


FIG. 8



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/036373

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A. CLASSIFICATION OF SUBJECT MATTER C23C8/26(2006.01)i, C21D1/06(2006.01)i, C22C38/00(2006.01)i, C22C38/60(2006.01)i, C21D1/76(2006.01)n, C21D9/30(2006.01)n, C21D9/32(2006.01)n		
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) C23C8/26, C21D1/06, C22C38/00, C22C38/60, C21D1/76, C21D9/30, C21D9/32		
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 1996-2017 Kokai Jitsuyo Shinan Koho 1971-2017 Toroku Jitsuyo Shinan Koho 1994-2017		
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.
Y	JP 2013-221203 A (Dowa Thermotech Co., Ltd.), 28 October 2013 (28.10.2013), claims; paragraphs [0001] to [0093] & US 2015/0053311 A1 claims; paragraphs [0001] to [0134] & WO 2013/157579 A1 & CN 104334766 A & MX 2014012432 A	1
Y	WO 2015/136917 A1 (Nippon Steel & Sumitomo Metal Corp.), 17 September 2015 (17.09.2015), paragraph [0046] & US 2017/0016107 A1 paragraphs [0065] to [0066] & EP 3118346 A1 & CN 105874094 A & KR 10-2016-0098336 A	1
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
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Date of the actual completion of the international search 06 November 2017 (06.11.17)		Date of mailing of the international search report 14 November 2017 (14.11.17)
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/036373

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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.
Y	Heinz-Joachim Spies, "Nitriding and Nitrocarburizing on Iron Materials", 1st edition, 1st print, AGNE Gijutsu Center Inc., 30 August 2011 (30.08.2011), pages 75 to 79	1

REFERENCES CITED IN THE DESCRIPTION

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