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(54) **SINTERED ALLOY, METHOD FOR PRODUCTION THEREOF AND VALVE SHEET**

(57) To provide a sintered alloy capable of showing wear resistance and a process for producing the same as well as a valve seat of good wear resistance.

A sintered alloy comprising 4-30% by weight Mo, 0.2-3% by weight C, 1-30% by weight Ni, 0.5-10% by weight Mn, 2-40% by weight Co, and the balance of inevitable impurities and Fe when the entirety is taken as

100% by weight. A process for producing a sintered alloy in which a green compact of a raw mixture powder including hard particles is sintered, thereby producing said sintered alloy. A valve seat comprising said sintered alloy.

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DescriptionTechnical Field

5 **[0001]** The present invention relates to a sintered alloy of good wear resistance, a process for producing the same, and a valve seat comprising a sintered alloy of good wear resistance.

Background Art

10 **[0002]** Internal combustion engines applied to automotive engines and the like are provided with valves for inlet and outlet and valve seats on which the valves are seated.

[0003] It has been required for valve seats to exhibit high wear resistance. When valve seats are worn, there arises a problem that the valve seat recession occurs in which valve seats sink down upon being seated.

15 **[0004]** To valve seats of good wear resistance, sintered alloys are applied in which Co-based hard particles are dispersed in Fe-based textures. And, Japanese Unexamined Patent Publication (KOKAI) No. 9-242,516 discloses a valve seat for internal combustion engines.

[0005] The valve seat disclosed in Japanese Unexamined Patent Publication (KOKAI) No. 9-242,516 is a valve seat for internal combustion engines in which cobalt-based hard particles are dispersed in the texture of an Fe-based alloy, and is characterized in that C: 0.5-1.5% by weight; at least one element selected from the group consisting of Ni, Co and Mo: 2.0-20.0% by weight in total; and the balance: Fe are contained at least in the substrate as the texture components, and simultaneously cobalt-based hard particles are contained in an amount of from 26 to 50% by weight.

[0006] However, the valve seat has a problem in that the wear resistance is insufficient when it is applied to gas engines as the valve seats.

25 **[0007]** In engines which use liquid fuels such as gasoline and light oil, the lubricating property between the valves and valve seats are kept by the fuels or combustion products (C, for example), and the lubricating property inhibits the valve seats from being worn.

[0008] On the other hand, in engines which use gaseous fuels such as liquefied petroleum gases (LPG: Liquefied Natural Gas) and compressed natural gases (CNG: Compressed Natural Gas), the lubricating property between the valves and valve seats has not been secured sufficiently because combustion products occur less.

30 **[0009]** Moreover, in gas engines, the oxidized film which contributes to the lubrication between solids is less likely to be formed on the sliding surface of the valve seats because of the reduction action of hydrogen which is included in the fuel gases abundantly.

Disclosure of Invention

35 **[0010]** The present invention has been done in view of such circumstances. Namely, it is an object to provide a sintered alloy capable of showing sufficient wear resistance and a process for producing the same as well as a valve seat of good wear resistance.

40 **[0011]** The inventors of the present invention studied wholeheartedly in order to solve the assignment, and carried out various systematic experiments repeatedly, as a result, developed a sintered alloy and the like whose hardness is improved by enlarging the density by promoting the diffusion of Mn in sintering, and simultaneously in which Mo forms an oxidized film so that the solid lubricating property resulting from the oxidized film is secured.

[0012] A sintered alloy according to the present invention comprises: 4-30% by weight Mo; 0.2-3% by weight C; 1-30% by weight Ni; 0.5-10% by weight Mn; 2-40% by weight Co; and the balance of inevitable impurities and Fe when the entirety is taken as 100% by weight.

45 **[0013]** It can preferably have at least one member selected from the group consisting of 5% by weight or less Cr and 2% by weight or less Si when the entirety is taken as 100% by weight, i.

[0014] It can preferably have a structure in which hard phases are dispersed in the texture.

50 **[0015]** A process for producing the present sintered alloy comprises the steps of: preparing a mixture powder composed of a powder of hard particles comprising: 20-60% by weight Mo; 3% by weight or less C; 5-40% by weight Ni; 1-20% by weight Mn; 5-40% by weight Co; and the balance of inevitable impurities and Fe when the entire powder of the hard particles are taken as 100% by weight, a carbon powder, a Co powder, and an Fe powder or a low alloy steel powder, the mixture powder comprising: the powder of the hard particles in an amount of from 10 to 60% by weight; the carbon powder in an amount of from 0.2 to 2% by weight; the Co powder in an amount of 20% by weight or less; and the balance being the Fe powder or the low alloy steel powder when the entire mixture powder is taken as 100% by weight; molding the mixture powder, thereby forming a green compact; and sintering the green compact, thereby making a sintered alloy having the composition set forth in either one of claims 1 through 2.

55 **[0016]** Said mixture powder can preferably comprise an Ni powder mixed in a proportion of 10% by weight or less

when the entire mixture powder is taken as 100% by weight.

[0017] Said hard particles can preferably have at least one member selected from the group consisting of Cr in a proportion of 10% by weight or less and Si in a proportion of 4% by weight or less when the entire powder of the hard particles is taken as 100% by weight.

[0018] A valve seat according to the present invention comprises: 4-30% by weight Mo; 0.2-3% by weight C; 1-30% by weight Ni; 0.5-10% by weight Mn; 2-40% by weight Co; and the balance of inevitable impurities and Fe when the entirety is taken as 100% by weight.

[0019] It can preferably have at least one member selected from the group consisting of 5% by weight or less Cr and 2% by weight or less Si when the entirety is taken as 100% by weight.

[0020] It can preferably have a structure in which hard phases are dispersed in the texture.

[0021] Note that, in the present invention, the percentages by weight designating the compositional proportions of the respective elements are equivalent to the percentages by mass.

Brief Description of the Drawing

[0022] Fig. 1 is an explanatory diagram for illustrating the arrangement of an apparatus by which a durability test according to examples of the present invention was carried out.

Best Mode for Carrying out the Invention

[0023] Hereinafter, inventions further embodying said invention and the embodying modes of the inventions will be described.

(Embodying Modes of the Inventions)

[Sintered Alloy]

[0024] The present sintered alloy comprises: 4-30% by weight Mo; 0.2-3% by weight C; 1-30% by weight Ni; 0.5-10% by weight Mn; 2-40% by weight Co; and the balance of inevitable impurities and Fe when the entirety is taken as 100% by weight.

[0025] The present sintered alloy is such that the hardness is improved by enlarging the density by promoting the diffusion of Mn in sintering, and simultaneously that Mo forms an oxidized film so that the solid lubricating property resulting from the oxidized film is secured.

[0026] In the present sintered alloy, Mo is an element which forms Mo carbides to improve the hardness and wear resistance of the sintered alloy. Moreover, the present sintered alloy is such that Mo, which is dispersed and solved in the structure by sintering, and the Mo carbides form an Mo oxidized film and the resulting oxidized film improves the solid lubricating property.

[0027] And, when Mo becomes less than 4% by weight, Mo becomes insufficient so that the formation of the oxidized film becomes insufficient, and eventually the solid lubricating property cannot be obtained. Moreover, when Mo exceeds 30% by weight, the oxidized film is formed excessively so that the coming-off of the oxidized film comes to occur. The coming-off of the oxidized film lowers the hardness and wear resistance of the sintered alloy. In addition, when Mo exceeds 30% by weight, the material yield lowers in the formation of the raw material powder for forming the sintered alloy. In order to produce the raw material powder, it is possible to apply methods such as atomizing methods.

[0028] C is an element which combines with Mo to form Mo carbides and improves the hardness and wear resistance of the sintered alloy. When C becomes less than 0.2% by weight, the forming amount of Mo carbides is so less that the wear resistance becomes insufficient. Moreover, when C exceeds 3% by weight, the density of the sintered alloy lowers.

[0029] Ni is an element which increases austenitic phases increasing the solving amount of Mo. Namely, when Ni increases the solving amount of Mo, it improves the wear resistance of the sintered alloy. When Ni is less than 1% by weight, the solving amount of Mo is so less that no sufficient wear resistance can be obtained. When Ni exceeds 30% by weight, the hardness of the sintered alloy lowers.

[0030] Since Mn diffuses efficiently in sintering, it is an element which improves the adhesiveness of the structure making the sintered alloy to improve the density of the sintered alloy. Moreover, since Mn has an action of increasing austenitic phases, it improves the wear resistance by increasing the solving amount of Mo. When Mn is less than 0.5% by weight, the effect of the density increment cannot be obtained sufficiently. Moreover, when Mn exceeds 10% by weight, the aforementioned effect (the effect of the density improvement) saturates.

[0031] Co is an element which increases austenitic phases in the sintered alloy and simultaneously improves the hardness. When Co is less than 2% by weight, the effect of the Co addition cannot be observed, when Co exceeds

40% by weight, the aforementioned (austenitic-phase and hardness increment) effect saturates.

[0032] The present sintered alloy can preferably further have at least one member selected from the group consisting of 5% by weight or less chromium (Cr) and 2% by weight or less silicon (Si) when the entirety is taken as 100% by weight. Note that both 5% by weight or less for Cr and 2% by weight or less for Si designate ranges which do not include 0% by weight.

[0033] Cr is an element which inhibits from Mo forming the oxidized film in such an excessive amount that the wear resistance of the sintered alloy is lowered. Namely, on occasions such as being exposed to high temperatures, the oxidized film is formed on the sintered alloy abundantly. The generated oxidized film results in being come off so that the wear of the sintered alloy occurs. Cr has been known to exhibit a high oxidation initiation temperature. When Cr is added, the generation of oxides in the sintered alloy comes to be suppressed so that the wear resistance of the sintered alloy is inhibited from lowering. Moreover, when Cr exceeds 5% by weight, the generating amount of oxides (oxidized film) becomes so less that the solid lubricating property of the sintered alloy lowers.

[0034] Si is an element which improves the adhesiveness of the oxidized film. Moreover, when Si exceeds 2% by weight, the density lowers so that the hardness of the sintered alloy lowers.

[0035] The present sintered alloy can preferably have a structure in which hard phases are dispersed in the texture. The hard phases dispersed in the texture increase the hardness of the texture to improve the wear resistance.

[0036] The hard phases can be produced by sintering hard particles which turn into the hard phases after sintering in a mixed state. The composition of the hard phases cannot be determined explicitly due to the movement of elements which happens between hard particles and textures which occur in sintering.

[0037] Hard particles before sintering can preferably comprise 20-60% by weight Mo, 3% by weight or less C, 5-40% by weight Ni, 1-20% by weight Mn, 5-40% by weight Co, and the balance of inevitable impurities and Fe when the entire particles are taken as 100% by weight.

[Production Process of Sintered Alloy]

[0038] A production process of the present sintered alloy is a production process in which the sintered alloys set forth in claims 1 through 2 are produced by molding and sintering mixture powders which are composed of a hard-particle powder and powders of elements forming the textures.

[0039] The present production process first prepares a mixture powder which is composed of a hard-particle powder, a carbon powder, a cobalt (Co) powder and an Fe powder or a low alloy steel powder.

[0040] The hard particles make the hard phases which enhance the wear resistance in the sintered alloys produced by sintering. When the hard particles become less than 10% by weight, the amount of the hard phases becomes insufficient in the produced sintered alloys so that the effect of the wear resistance increment does not come to occur. When the hard particles exceed 60% by weight, the produced sintered alloys come short of the joining strength. Moreover, when the hard particles become excessive, the aggressiveness of the sintered alloys is enhanced with respect to mating members, and simultaneously the retention of the hard particles comes not to be secured in the produced sintered alloys.

[0041] Carbon (C) making the carbon powder diffuses or solves into the texture (Fe or low alloy steel) of the sintered alloys or the hard particles in sintering, or generates carbides (Mo carbides). As for the carbon powder, it is suitable to employ graphite powders. When the carbon powder is less than 0.2% by weight, ferritic phases exist more in the texture of the produced sintered alloys. The increment of ferritic phases lowers the hardness of the texture, thereby lowering the wear resistance of the sintered alloys. When the carbon powder exceeds 2% by weight, cementitic phases exist more in the sintered alloys so that the toughness of the sintered alloy lowers.

[0042] The Co powder increases the density of the produced sintered alloys. When the Co powder exceeds 20% by weight, the effect of increasing the density of the sintered alloys saturates. Note that "the proportion of the Co powder is 20% by weight or less" designates ranges which do not include 0% by weight.

[0043] The Fe powder or low alloy steel powder forms the texture of the sintered alloys. As for the low alloy steel powder, it is possible to employ Fe-C alloy powders. For example, when the low alloy steel powder is taken as 100% by weight, it is possible to employ alloy powders having a composition comprising: 0.2-5% by weight C; and the balance of inevitable impurities and Fe.

[0044] And, the hard particles comprise: 20-60% by weight Mo; 3% by weight or less C; 5-40% by weight Ni; 1-20% by weight Mn; 5-40% by weight Co; and the balance of inevitable impurities and Fe when the entire hard particles are taken as 100% by weight.

[0045] Mo of the hard particles combines with C to form Mo carbides, thereby forming hard phases which are good in terms of the hardness and wear resistance. When Mo becomes less than 20% by weight, Mo becomes insufficient so that the formation of the oxidized film becomes insufficient and no sufficient solid lubricating property can be obtained. Moreover, when Mo exceeds 60% by weight, the oxidized film is formed excessively in the produced sintered alloys, and the oxidized film results in being come off so that the hardness and wear resistance of the sintered alloys come

to lower. Moreover, when Mo exceeds 30% by weight, the material yield comes to lower in producing, the hard-particle powder by atomizing methods and the like.

5 **[0046]** C of the hard particles combines with Mo to form Mo carbides, thereby forming hard phases which are good in terms of the hardness and wear resistance. When C exceeds 3% by weight, the density of the produced sintered alloys comes to lower. Note that even when C exists less in the hard particles, C which diffuses from the carbon powder included in the mixture powder forms Mo carbides, thereby forming hard phases. Note that, in the present production process, the hard particles contain C. Namely, 3% by weight specifying the C content in the hard particles designates a range of from more than 0% by weight to 3% by weight or less.

10 **[0047]** Ni of the hard particles increases austenitic phases which increase the solving amount of Mo, thereby forming hard phases which are good in terms of the wear resistance. When Ni is less than 5% by weight, the solving amount of Mo is insufficient so that no sufficient wear resistance can be obtained. Moreover, when Ni exceeds 40% by weight, the hardness lowers.

15 **[0048]** Since Mn of the hard particles is an element which diffuses into the texture efficiently in sintering, it improves the adhesiveness between the texture and the hard particles to improve the density of the sintered alloys. Moreover, since Mn has an action of increasing austenitic phases, it improves the wear resistance. When Mn is less than 1% by weight, the effect of the density improvement cannot be obtained sufficiently, when it exceeds 20% by weight, the aforementioned effect saturates.

20 **[0049]** Co. of the hard particles increases austenitic phases in the hard particles, and simultaneously improves the hardness. When Co is less than 5% by weight, the effect (austenitic-phase and hardness increment) of the Co addition cannot be observed, when Co exceeds 40% by weight, the aforementioned effect (austenitic-phase and hardness increment) saturates.

25 **[0050]** The mixture powder can preferably be such that an Ni powder is mixed in a proportion of 10% by weight or less when the entire mixture powder is taken as 100% by weight. Note that 10% by weight or less designates ranges which do not include 0% by weight. Namely, when an Ni powder is mixed into the mixture powder, the diffusion of elements is promoted in sintering so that the density of the sintered alloys improves. Moreover, when the proportion of an Ni powder exceeds 10% by weight, the residual austenitic phases increase in the texture so that the wear resistance of the produced sintered alloys comes to lower.

30 **[0051]** The hard particles can preferably have at least one member selected from the group consisting of Cr in a proportion of 10% by weight or less and Si in a proportion of 4% by weight or less when the entire powder of the hard particles is taken as 100% by weight. Note that both 10% by weight or less for Cr and 4% by weight for Si designate ranges which do not include 0% by weight.

35 **[0052]** Cr is an element which inhibits Mo from forming the oxidized film in such an excessive amount that the wear resistance of the sintered alloys is lowered. Namely, on occasions such as being exposed to high temperatures, the oxidized film is formed on the sintered alloy abundantly. The generated oxidized film results in being come off so that the wear of the sintered alloys occurs. Cr has been known to exhibit a high oxidation initiation temperature. When Cr is added, the generation of oxides in the sintered alloys comes to be suppressed so that the wear resistance of the sintered alloys is inhibited from lowering. Moreover, when Cr exceeds 10% by weight, the generating amount of oxides (oxidized film) becomes so less that the solid lubricating property lowers.

40 **[0053]** Si is an element which improves the adhesiveness of the oxidized film. Moreover, when Si exceeds 4% by weight, the density lowers so that the hardness of the sintered alloys lowers.

[0054] The production process of the present sintered alloy can preferably be such that a tempering treatment is performed after the green compact is sintered. Namely, when tempering is carried out onto the sintered alloy, the texture of the sintered alloy and the crystalline structure of the hard phases are stabilized.

45 **[0055]** The production process of the present sintered alloy can preferably be such that a forging treatment is performed after the green compact is sintered. When forging is carried out onto the sintered alloy, not only it is possible to make the shape of the sintered alloy into desired shapes, but also it is possible to remove pores resulting from sintering, and thereby it is possible to enhance the density and wear resistance of the sintered alloy.

50 **[0056]** The production process of the present sintered alloy is such that it is possible to intend to reduce the cost of starting materials. Moreover, it is possible to intend the compression moldability of green compacts. And, it is possible to highly densify not only the green compact but also the sintered alloy.

55 **[0057]** The production process of the present sintered alloy is such that, in the hard particles and the texture, elements included in them diffuse to the other one of them in sintering. The diffusion of elements is such that the adhesiveness between the hard particles and the texture is enhanced. In particular, since Mn included in the hard particles diffuse into the texture efficiently, the adhesiveness between the hard particles and the textures is enhanced. Thus, it is possible to intend the density improvement of the sintered alloy, the hardness improvement of the sintered alloy and the wear-resistance improvement of the sintered alloy.

[0058] In the production process of the present sintered alloy, the hard particles are such that the production process is not limited in particular. As for the production process of the hard particles, for example, it is possible to name particles

which are produced by atomizing treatments by spraying molten metals, particles which are obtained by disintegrating by mechanically pulverizing solidified substances made by solidifying molten metals. As for the atomizing treatments, it is possible to employ those atomized in non-oxidizing atmospheres (inert gas atmospheres, such as the nitrogen gas and argon gas, or in vacuum).

5 **[0059]** Moreover, as for the average particle diameter of the hard particles, it is possible to select it appropriately depending on the applications, types and the like of the produced sintered alloys, however, it is preferable in general that it can be 20-250 μm approximately, 30-200 μm approximately and 40-180 μm approximately. However, the average particle diameter of the hard particles is not limited to these ranges.

10 **[0060]** In addition, the hardness of the hard particles depends on the amount of Mo carbides and the like, however, it can generally be Hv 350-750 approximately and Hv 450-700 approximately. However, the hardness of the hard particles is not limited to these ranges, and can be harder with respect to the service objects of the hard particles, like the texture of the sintered alloy and so forth.

15 **[0061]** In the production process of the present sintered alloy, as for the sintering temperature, it is possible to employ 1,050-1,250 $^{\circ}\text{C}$ approximately, in particular 1,100-1,150 $^{\circ}\text{C}$ approximately. As for the sintering time at the aforementioned sintering temperatures, it is possible to employ 30 minutes-120 minutes, in particular 45-90 minutes. Moreover, as for the sintering temperature, non-oxidizing atmospheres such as inert gas atmospheres are preferable. As for the non-oxidizing atmospheres, it is possible to name nitrogen atmospheres, argon gas atmospheres and vacuum atmospheres.

20 **[0062]** Since the production process of the present sintered alloy carries out sintering by mixing the hard particles, the carbon powder, the Co powder and the Fe alloy powder, the diffusion of the elements of the hard particles and texture is promoted in sintering, and it is possible to improve the density of the produced sintered alloys. Moreover, the diffusion of the elements is promoted, and thereby Mo is diffused abundantly. The diffused Mo forms the carbides and oxidized film, and thereby the sintered alloy is improved in terms of the wear resistance and solid lubricating property.

25 [Valve Seat]

30 **[0063]** The present valve seat comprises: 4-30% by weight Mo; 0.2-3% by weight C; 1-30% by weight Ni; 0.5-10% by weight Mn; 2-40% by weight Co; and the balance of inevitable impurities and Fe when the entirety is taken as 100% by weight.

[0064] Mo is an element which forms Mo carbides to improve the hardness and wear resistance of the valve seat. Moreover, the Mo, which is dispersed and solved in the structure by sintering, and the Mo carbides form an Mo oxidized film, and the resulting oxidized film improves the solid lubricating property of the valve seat.

35 **[0065]** When Mo becomes 4% by weight or less, Mo becomes insufficient so that the formation of the oxidized film becomes insufficient, and eventually no sufficient solid lubricating property cannot be obtained. Moreover, when Mo exceeds 30% by weight, the oxidized film is formed excessively so that it results in being come off, and the wear resistance of the valve seat lowers. In addition, when Mo exceeds 30% by weight, the material yield comes to lower in the formation of the raw material powder for forming the valve seat. As for the production of the raw material powder, there are atomizing methods and the like, for example.

40 **[0066]** C is an element which combines with Mo to form Mo carbides and improves the hardness and wear resistance. When C becomes less than 0.2% by weight, the forming amount of Mo carbides is so less that the wear resistance of the valve seat becomes insufficient. Moreover, when C exceeds 3% by weight, the density of the valve seat lowers.

45 **[0067]** Ni is an element which increases austenitic phases increasing the solving amount of Mo. When Ni increases the solving amount of Mo, the wear resistance of the valve seat improves. When Ni is less than 1% by weight, the solving amount of Mo is so less that no sufficient wear resistance can be obtained. Moreover, when Ni exceeds 30% by weight, the effect of the solving-amount increment saturates.

[0068] Since Mn diffuses efficiently in sintering, it is an element which improves the adhesiveness of the structure making the valve seat to improve the density of the valve seat. Moreover, since Mn has an action of increasing austenitic phases, it improves the wear resistance of the valve seat by increasing the solving amount of Mo. When Mn is less than 0.5% by weight, the effect of the density increment cannot be obtained sufficiently. Moreover, when Mn exceeds 10% by weight, the aforementioned effect saturates.

50 **[0069]** Co is an element which increases austenitic phases in the valve seat and simultaneously improves the hardness. When Co is less than 2% by weight, the effect of the Co addition cannot be observed, when Co exceeds 40% by weight, the aforementioned effect saturates.

55 **[0070]** The present valve seat can preferably further have at least one member selected from the group consisting of 5% by weight or less Cr and 2% by weight or less Si when the entirety is taken as 100% by weight. Note that both 5% by weight or less for Cr and 2% by weight for Si designate ranges which do not include 0% by weight.

[0071] Cr is an element which inhibits Mo from forming the oxidized film in such an excessive amount that the wear

resistance of the valve seat is lowered. Namely, on occasions such as being exposed to high temperatures, the oxidized film is formed on the valve seat abundantly. The generated oxidized film results in being come off so that the wear of the valve seat occurs. Cr has been known to exhibit a high oxidation initiation temperature. When Cr is added, the generation of oxides in the valve seat comes to be suppressed so that the wear resistance of the valve seat is inhibited from lowering. Moreover, when Cr exceeds 5% by weight, the generating amount of oxides (oxidized film) becomes so less that the solid lubricating property of the valve seat lowers.

[0072] Si is an element which improves the adhesiveness of the oxidized film. Moreover, when Si exceeds 2% by weight, the density lowers so that the hardness of the valve seat lowers.

[0073] The present valve seat can preferably have a structure in which hard phases are dispersed in the texture. The present valve seat is such that the hard phases dispersed in the texture show the wear resistance.

[0074] The present valve seat is produced by the production processes set forth in claims 3 through 5. Namely, when it is produced by carrying out mixing the hard particles, the carbon powder, the Co powder and the Fe alloy powder and sintering them, the diffusion of the elements of the hard particles and texture is promoted in sintering, and the density of the produced valve seats is improved. Moreover, the diffusion of the elements is promoted, and thereby Mo is diffused abundantly, and the diffused Mo forms the carbides and oxidized film, and thereby it becomes a valve seat which is good in terms of the wear resistance and solid lubricating property.

[0075] Since the present valve seat is such that the density is improved and simultaneously the solid lubricating action resulting from the oxidized film is improved, it has become a valve seat provided with high wear resistance so that it can show sufficient wear resistance even when it is applied to gas engines.

(Examples)

[0076] Hereinafter, the present invention will be described more specifically while naming various examples according to the present sintered alloy, production process for the same and valve seat.

(Production of Hard Particles)

[0077] In the present example, alloy powders having the compositions of Samples "A" through "R" set forth in Table 1 were produced by gas atomizing with an inert gas (nitrogen gas). Moreover, an alloy powder having the composition of Sample "S" was produced by pulverizing after melting. These alloy powders were classified to fall in a range of from 44 to 180 μm , and were used as hard particles.

[TABLE 1]

[0078] Samples "A" through "J" recited in Table 1 are powders corresponding to the hard particles of the present production process. Sample "K" corresponds to a comparative member because Mo is as less as 15% by weight. Sample "L" does not include Mn whose diffusion efficiency is good, and corresponds to a comparative member. Sample "M" corresponds to a comparative member because it includes C in a somewhat larger amount of 3.5% by weight. Sample "N" corresponds to a comparative member because it includes Ni in a somewhat larger amount of 45% by weight. Sample "O" corresponds to a comparative member because it includes Cr abundantly in an amount of 15% by weight. Sample "P" corresponds to a comparative member because it includes Si in a somewhat larger amount of 5%. Sample "Q" corresponds to a comparative member because Co is as less as 2% by weight. Sample "R" corresponds to a conventional member because it is an Ni-based alloy which does not include Mn and Co but includes Cr in a somewhat larger amount. Sample "S" is a conventional member because it is ferromolybdenum (FeMo) and does not include Ni and Mn.

[0079] Using the hard-particle powders according to these Samples "A" through "S," the respective hard-particle powders were heated in air to oxidize them, a temperature at which the weight increment accompanied by the oxidation in this instance started suddenly was surveyed, and the temperature was considered the oxidation initiation temperature. Table 1 sets forth the measured oxidation initiation temperatures altogether.

[0080] As recited in Table 1, in Samples "A" through "J" which correspond to the hard particles defined in the present production process, the oxidation initiation temperature was from 630 to 670 $^{\circ}\text{C}$ approximately, and the oxidation initiation temperatures were low. When the oxidation initiation temperature is low, it designates that the formation of the oxidized film being responsible for the solid lubricating property starts at a lower temperature range if being used as a sintered alloy. Namely, when the formation of the oxidized film is started at a lower temperature range, it means that the formation of the oxidized film is likely to occur, and designates that the oxidized film is formed in a sufficient amount for the solid lubricating property.

(Production of Sintered Alloys)

[0081] In the proportions set forth Table 2, the hard-particle powders according to aforementioned Samples "A" through "S," a graphite powder, an Ni powder whose particle diameter was from 2 to 60 μm , a Co powder whose particle diameter was from 4 to 100 μm and a pure Fe powder whose particle diameter was 150 μm or less were mixed with a mixer, thereby forming mixture powders as mixture materials. As recited in Table 2, in most of the examples, the hard-particle powders were 40% by weight, the graphite powder was 0.6% by weight, the Ni powder was 6% by weight, and the Co powder was 6% by weight.

[0082] Note that, in Example No. 11, the proportion of the hard-particle powders was reduced to 15%. In Example No. 12, the proportion of the hard-particle powders was increased to 55%. Moreover, in Example No. 13, the proportion of the graphite powder was reduced slightly to 0.3%. In Example No. 14, the proportion of the graphite powder was increased slightly to 1.5%. In Example No. 15, the Ni powder was not added. In Example No. 16, not only the Ni powder was not added, but also the proportion of the Co powder was increased slightly to 12%. In Example No. 17, the Co powder was not added. In Example No. 18, the proportion of the Co powder was increased slightly to 12%.

[TABLE 2]

[0083] And, by using a forming mold, the mixture powders mixed as described above were compression molded with a pressurizing force of 78.4×10^7 Pa (8 tonf/cm²) as a ring-shaped test piece, thereby forming green compacts. The test pieces had a valve-seat shape.

[0084] Thereafter, the respective green compacts were sintered in a 1,150°C inert atmosphere (nitrogen gas atmosphere) for 45 minutes, and tempering was carried out at 600 °C for 100 minutes, thereby forming sintered alloys (valve seats) according to the test pieces.

[0085] Note that Example No. 19 was such that forging was carried out with a pressure of 137.2×10^7 Pa (14 ton/cm²) after sintering, and thereafter tempering was carried out at 600 °C for 100 minutes. Moreover, Example No. 20 was such that sintering was carried out at a sintering temperature of 1,185 °C.

[0086] Furthermore, regarding Comparative Example No. 1 through Comparative Example No. 13 as well, a test piece having a ring shape was compression molded, thereby producing sintered alloys (valve seats) according to the test pieces.

[0087] Moreover, based on the conditions set forth in Table 3, regarding Comparative Example Nos. 14 and 15 as well, sintered alloys (valve seats) according to the test pieces were produced. Note that, in Table 3, not only the compositions of the entire sintered alloys are recited, but also the samples of the hard particles and the mixing proportions are recited.

[0088] As set forth in Table 3, Comparative Example No. 14 used Sample "S" as the hard particles, and a green compact was sintered, green compact which was made by compression molding a mixture powder mixed with 10% by weight Sample "S". Comparative Example No. 15 used Sample "R" as the hard particles, and a green compact was sintered, green compact which was made by compression molding a mixture powder mixed with 20%.

[TABLE 3]

[0089] Furthermore, regarding the sintered alloys being the respective test pieces of the examples and comparative examples, the density of the sintered alloys and the hardness of the sintered alloys were measured, respectively. The measured hardness of the sintered alloys is a macroscopic Vickers hardness (load: 10 kgf). Table 4 sets forth these measurement results.

[TABLE 4]

[0090] Next, by using a testing machine illustrated in Fig. 1, a wear test was carried out with regard to the wear resistance of the sintered alloys, thereby assessing the wear resistance.

[0091] In the wear test, as illustrated in Fig. 1, a propane gas burner 1 was used as a heating source, and the sliding portion between a ring-shaped valve seat 3, being a test piece comprising the sintered alloys of the examples and comparative examples, and a valve face 4 of a valve 1 was put in a propane gas combustion atmosphere. The valve face 4 was SUH35. The temperature of the valve seat 3 was controlled at 200 °C, a load of 18 kgf was given by a spring 6 when the valve seat 3 contacted with the valve face 4, and the valve seat 3 and the valve face 4 were contacted/ at a rate of 2,000 times/min., and thereby an 8-hour wear test was carried out.

[0092] Moreover, regarding the case where the temperature of the valve seat 3 was controlled at 300 °C as well, a wear resistance test was carried out similarly. Table 4 sets forth the wear amounts of the respective test pieces when the testing temperature was 200°C and 300 °C.

[0093] Next, regarding the processability of the sintered alloys, an assessment was carried out.

[0094] The assessment of the processability of the sintered alloys was done by cutting the ring-shaped valve seats comprising the sintered alloys of the examples and comparative examples under the conditions that the feed speed was 0.05 mm/rev., and the slitting was 0.3 mm, and by measuring the tool wear amount resulting from the cutting, and Table 4 sets forth the measurement results altogether.

[0095] The more detailed testing method was such that the valve seat was first rotated about the axial center of the ring in the peripheral direction. In this instance, a cemented carbide tool which had cutting edges comprising cemented carbide H1 was brought into contact with the inner-peripheral edge of the end surface of the ring-shaped valve seat. Thereafter, the cemented carbide tool was moved so as to move the cutting edge by 0.05 mm outward in the diametric direction, cutting edge which was brought into contact with it when the ring of the valve seat was rotated once in the peripheral direction. When the cemented carbide tool was moved in such a state that it was brought into contact with the end surface of the valve seat, the end surface of the valve seat was cut. When the cutting edge was moved outside the valve seat, it was returned back to the inner-peripheral edge of the valve seat, and the cutting was continued similarly. In this instance, the cutting edge was returned inward by 0.3 mm in the axial direction of the valve seat. When the cutting was carried out 100 times, the cutting was terminated, and the wear amount of the tool was measured.

[0096] It is apparent from Table 4 that the sintered alloys of Example Nos. 1 through 20 were good in terms of the density, hardness, wear resistance and processability.

[0097] On the other hand, the sintered alloys of Comparative Example Nos. 1 through 15 recited as well in Table 4 were inferior in terms of either one of the density, hardness, wear resistance and processability.

[0098] Next, the valve seats of Example No. 3 as well as Comparative Example Nos. 14 and 15 were incorporated into the outlet side of an engine. The engine used unleaded gasoline as a fuel, and had a displacement of 2,400 cc. And, a 180-hour durability test was carried out by using the engine.

[0099] Moreover, the valve seats of Example No. 19 and Comparative Example No. 13 were incorporated into the inlet side of an engine. The engine used CNG as a fuel, and had a displacement of 1,500 cc. And, a 300-hour durability test was carried out by using the engine.

[0100] And, the respective valve projections (mm) and valve-seat contacting-width increments (mm) were measured. As for the inlet-side condition, the valve face was SUH11 onto which a soft nitriding treatment was carried out. As for the outlet-side condition, the valve face was SUH35.

[0101] The valve projection is an amount by which the valve position is displaced (projected) outside the engine by the wear of the valve seat and the wear of the valve face when the valve was closed. The valve-seat contacting-width increment is an amount by which the width of the contacting part with the valve face of the valve seat is increased in the valve seat when the valve seat contacts with the valve seat so that the valve seat is worn. Table 5 summarizes these measurement results.

[TABLE 5]

[0102] As set forth in Table 5, it was found out that Example No. 3 incorporated into the outlet side of the gasoline engine was such that the valve projection and valve-seat contacting-width increment were reduced considerably compared with Comparative Example Nos. 14 and 15, and that it was good in terms of the wear resistance.

[0103] Moreover, it was found out that Example No. 19 incorporated into the inlet side of the gas engine was such that the valve projection and valve-seat contacting-width increment were reduced considerably compared with Comparative Example No. 13, and that it was good in terms of the wear resistance.

[0104] Namely, it is understood that the valve seats comprising the sintered alloys of the examples have high hardness and wear resistance.

[0105] Thus, since the present sintered alloy is such that not only the density is improved but also the solid lubricating property resulting from the oxidized film is improved, it has high wear resistance.

[0106] Moreover, since the production process of the present sintered alloy carries out sintering by mixing the hard particles, the carbon powder, the Co powder and the Fe alloy powder, the diffusion of the elements of the hard particles and texture is promoted in sintering so that the density of the produced sintered alloys improves. In addition, the diffusion of the elements is promoted, and thereby Mo is diffused abundantly, since the diffused Mo forms the carbides and oxidized film, the sintered alloys become good in terms of the wear resistance and solid lubricating property.

[0107] Furthermore, since the present valve seat comprises the present sintered alloy produced by the production process of the present sintered alloy, the solid lubricating property resulting from the oxidized film is improved, and accordingly it has high wear resistance.

TABLE 1

	Composition (% by weight)										Oxidation Initiation	
	Mo	C	Ni	Mn	Co	Cr	Si	Fe	Temp. (°C)			
A	33	0.9	10	6	30			Bal- ance	630			
B	33	0.9	10	6	30	4		Bal- ance	650			
C	33	0.9	10	6	30	4	0.8	Bal- ance	660			
D	23	0.9	10	6	30	4	0.8	Bal- ance	670			
E	60	0.9	10	6	30	4	0.8	Bal- ance	640	Present Invention		
F	33	0.9	10	1.5	30	4	0.8	Bal- ance	650			
G	33	0.9	10	18	30	4	0.8	Bal- ance	650			
H	33	2.5	10	6	30	4	0.8	Bal- ance	670			
I	33	0.9	6	6	30	4	0.8	Bal- ance	650			
J	33	0.9	35	6	15	4	0.8	Bal- ance	670			
K	15	0.9	10	6	30	4	0.8	Bal- ance	750			
L	33	0.9	10		30	4	0.8	Bal- ance	650			
M	33	3.5	10	6	30	4	0.8	Bal- ance	680			
N	33	0.9	45	6	10	4	0.8	Bal- ance	690		Comparative Member	
O	33	0.9	10	6	30	15	0.8	Bal- ance	780			
P	33	0.9	10	6	30	4	5	Bal- ance	730			
Q	34	0.8	9	6	2	4	0.8	Bal- ance	640			
R	25	3	Bal- ance			20.5	1.1	17.3	900			
S	63						1.1	Bal- ance	580			

TABLE 2

		Alloy Powder Composition (% by weight)													Graphite Powder	Fe Powder	Ni Powder	Co Powder					
		A	B	C	D	E	F	G	H	I	J	L	M	N	O	P	Q	R					
Ex. #1		40																	0.6	Balance	6	6	
Ex. #2			40																0.6	Balance	6	6	
Ex. #3				40															0.6	Balance	6	6	
Ex. #4					40														0.6	Balance	6	6	
Ex. #5						40													0.6	Balance	6	6	
Ex. #6							40												0.6	Balance	6	6	
Ex. #7								40											0.6	Balance	6	6	
Ex. #8									40										0.6	Balance	6	6	
Ex. #9										40									0.6	Balance	6	6	
Ex. #10											40								0.6	Balance	6	6	
Ex. #11				15															0.6	Balance	6	6	
Ex. #12				55															0.6	Balance	6	6	
Ex. #13				40															0.3	Balance	6	6	
Ex. #14				40															1.5	Balance	6	6	
Ex. #15				40															0.6	Balance	0	6	
Ex. #16				40															0.6	Balance	0	12	
Ex. #17				40															0.6	Balance	6	0	
Ex. #18				40															0.6	Balance	6	12	
Ex. #19				40															0.6	Balance	6	6	Forging after Sintering Temp.: 1,185 °C
Ex. #20				40															0.6	Balance	6	6	
Comp. Ex. #1											40								0.6	Balance	6	6	
Comp. Ex. #2												40							0.6	Balance	6	6	
Comp. Ex. #3													40						0.6	Balance	6	6	
Comp. Ex. #4															40				0.6	Balance	6	6	
Comp. Ex. #5																40			0.6	Balance	6	6	
Comp. Ex. #6																	40		0.6	Balance	6	6	
Comp. Ex. #7																		40	0.6	Balance	6	6	
Comp. Ex. #8				7															0.6	Balance	6	6	
Comp. Ex. #9				70															0.6	Balance	6	6	
Comp. Ex. #10				40															0.1	Balance	6	6	
Comp. Ex. #11				40															2.5	Balance	6	6	
Comp. Ex. #12				40															0.6	Balance	12	6	
Comp. Ex. #13				40															0.6	Balance	0	0	

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TABLE 3

	Composition (% by weight)								Type of Hard-particle Powder	Proportion of Hard Particles (% by weight)
	Mo	C	Ni	W	Co	Cr	Si	Fe		
Comp. #14	Ex. 6.5	0.4	9.5	0.8	9.5			Balance	S	10
Comp. #15	Ex. 9	1.5	4	2.5	4	4		Balance	R	20

TABLE 4

	Density of Sintered Body (g/cm ³)	Hardness of Sintered Body (HV10)	Wear Resistance (mm)		Wear Amount of Cutting Tool (μm)
			200 °C	300 °C	
Ex. #1	7.34	240	0.2	0.05	50
Ex. #2	7.32	250	0.15	0.045	55
Ex. #3	7.35	250	0.15	0.045	48
Ex. #4	7.32	240	0.2	0.055	46
Ex. #5	7.37	230	0.15	0.045	55
Ex. #6	7.3	235	0.22	0.065	50
Ex. #7	7.36	250	0.13	0.045	60
Ex. #8	7.3	240	0.21	0.055	55
Ex. #9	7.32	250	0.18	0.05	50
Ex. #10	7.34	230	0.2	0.055	65
Ex. #11	7.14	235	0.15	0.2	62
Ex. #12	7.3	230	0.2	0.1	50
Ex. #13	7.35	225	0.2	0.08	55
Ex. #14	7.3	270	0.2	0.1	65
Ex. #15	7.32	235	0.19	0.12	67
Ex. #16	7.35	250	0.15	0.08	72
Ex. #17	7.32	230	0.1	0.1	50
Ex. #18	7.37	260	0.15	0.04	60
Ex. #19	7.8	360	0.07	0.03	82
Ex. #20	7.38	260	0.05	0.04	52
Comp. Ex. #1	7.3	230	0.25	0.25	50
Comp. Ex. #2	7.15	240	0.3	0.2	45
Comp. Ex. #3	7.2	250	0.3	0.2	60
Comp. Ex. #4	7.3	200	0.25	0.25	55
Comp. Ex. #5	7.32	270	0.35	0.05	75
Comp. Ex. #6	7.1	230	0.3	0.2	60
Comp. Ex. #7	7.3	240	0.2	0.2	55
Comp. Ex. #8	7.05	210	0.4	0.5	57
Comp. Ex. #9	7.1	180	0.3	0.25	70
Comp. Ex. #10	7.35	200	0.35	0.15	53
Comp. Ex. #11	7.2	270	0.3	0.2	60
Comp. Ex. #12	7.44	200	0.8	0.1	44
Comp. Ex. #13	7.27	215	0.25	0.12	54
Comp. Ex. #14	7	200	0.35	0.3	219
Comp. Ex. #15	7	230	0.5	0.06	37

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TABLE 5

	Inlet		Outlet	
	Valve Projection (mm)	Seat Contacting-width Increment (mm)	Valve Projection (mm)	Seat Contacting-width Increment (mm)
Ex. #3			0.04	0.4
Comp. Ex. #14			0.08	0.6
Comp. Ex. #15			0.15	0.7
Comp. Ex. #19	0.05	0.25		
Comp. Ex. #13	0.12	0.6		

Claims

1. A sintered alloy, comprising:

- 4-30% by weight Mo;
- 0.2-3% by weight C;
- 1-30% by weight Ni;
- 0.5-10% by weight Mn;
- 2-40% by weight Co; and

the balance of inevitable impurities and Fe when the entirety is taken as 100% by weight.

2. The sintered alloy set forth in claim 1 having at least one member selected from the group consisting of 5% by

weight or less Cr and 2% by weight or less Si when the entirety is taken as 100% by weight.

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3. The sintered alloy set forth in either one of claims 1 through 2 having a structure in which hard phases are dispersed in the texture.

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4. A process for producing a sintered alloy, comprising the steps of:

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preparing a mixture powder composed of hard particles comprising: 20-60% by weight Mo; 3% by weight or less C; 5-40% by weight Ni; 1-20% by weight Mn; 5-40% by weight Co; and the balance of inevitable impurities and Fe when the entire hard particles are taken as 100% by weight, a carbon powder, a Co powder, and an Fe powder or a low alloy steel powder, the mixture powder comprising: a powder of the hard particles in an amount of from 10 to 60% by weight; the carbon powder in an amount of from 0.2 to 2% by weight; the Co powder in an amount of 20% by weight or less; and the balance being the Fe powder or the low alloy steel powder when the entire mixture powder is taken as 100% by weight;

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molding the mixture powder, thereby forming a green compact; and
sintering the green compact, thereby making a sintered alloy having the composition set forth in either one of claims 1 through 3.

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5. The process for producing a sintered alloy set forth in claim 4, wherein said mixture powder comprises an Ni powder mixed in a proportion of 10% by weight or less when the entire mixture powder is taken as 100% by weight.

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6. The process for producing a sintered alloy set forth in either one of claims 4 through 5, wherein said hard particles have at least one member selected from the group consisting of Cr in a proportion of 10% by weight or less and Si in a proportion of 4% by weight or less when the entire powder of the hard particles is taken as 100% by weight.

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7. A valve seat, comprising:

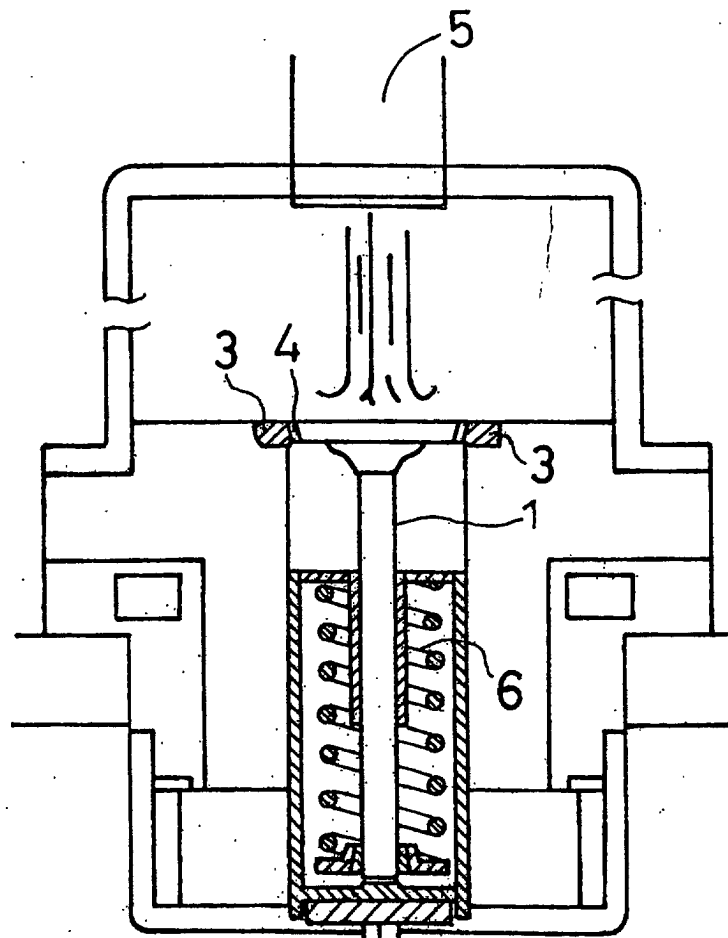
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4-30% by weight Mo;
0.2-3% by weight C;
1-30% by weight Ni;
0.5-10% by weight Mn;
2-40% by weight Co; and

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the balance of inevitable impurities and Fe when the entirety is taken as 100% by weight.

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8. The valve seat set forth in claim 7 having at least one member selected from the group consisting of 5% by weight or less Cr and 2% by weight or less Si when the entirety is taken as 100% by weight.

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9. The valve seat set forth in either one of claims 7 through 8 having a structure in which hard phases are dispersed in the texture.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/05632

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ C22C30/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁷ C22C1/04, 5/00-45/00, F01L3/02		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2002 Kokai Jitsuyo Shinan Koho 1971-2002 Jitsuyo Shinan Toroku Koho 1996-2002		
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	US 5759227 A (Nippon Piston Ring Co., Ltd.), 02 June, 1998 (02.06.98), Claims & JP 9-242516 A	7-9
P,X	EP 1108800 A (Toyota Jidosha Kabushiki Kaisha), 25 June, 2001 (25.06.01), Claims & JP 2001-181807 A & US 2001/0018852 A	1-9
X	JP 62-44556 A (Mitsubishi Materials Corp.), 26 February, 1987 (26.02.87), Claims	1-6
Y	(Family: none)	7-9
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
Date of the actual completion of the international search 10 September, 2002 (10.09.02)		Date of mailing of the international search report 24 September, 2002 (24.09.02)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

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