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(54) **ABRASION-RESISTANT TITANIUM ALLOY MEMBER HAVING EXCELLENT FATIGUE STRENGTH**

(57) The purpose of the present invention is to provide a titanium alloy member having superior wear resistance and fatigue strength to those of conventional titanium alloys at low cost. Provided is a wear-resistant titanium alloy member having excellent fatigue strength, comprising: a matrix material which comprises, in mass%, 4.5% or more and less than 5.5% of Al, 1.3% or

more and less than 2.3% of Fe, 0.25% or more and less than 0.50% of Si, 0.08% or more and less than 0.25% of O, and a remainder made up by titanium and unavoidable impurities; and a cured layer which is formed as a surface layer of the matrix material and is composed of a solid solution of oxygen.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a wear-resistant titanium alloy member having a hardened layer in the surface layer thereof, so that it has a wear resistance when used in a part to be disposed in contact with, or in a part to be disposed in sliding contact with another member, and exhibits an excellent fatigue strength.

BACKGROUND ART

[0002] A titanium alloy, which is lightweight and has a high specific strength and an excellent corrosion resistance, is used not only in aircraft applications, but also in other wide applications such as automotive components and consumer products. Among others, a Ti-6Al-4V alloy excellent in the strength-ductility balance is a representative example thereof. On the other hand, in order to reduce the high cost thereof, as one of the factors for preventing the spread and expansion of the application thereof, an alloy having a property enabling the replacement of the Ti-6Al-4V alloy has been developed by utilizing inexpensive Fe as an alloying element.

[0003] Further, the titanium alloy may be poor in wear resistance, and this may pose a problem when it is used in a part in contact with, or in a part in sliding contact with another member. As the method to improve the wear resistance of a product used for an automotive engine component, Patent Document 1 discloses a method of forming an oxide scale on the surface of the member. However, this case may pose a problem such that the oxide scale layer of the member is readily cracked or the surface is liable to have large unevenness due to the separation or the like of the surface scale, and as compared with the case of the member which has not been subjected to such a wear resistance treatment, the fatigue strength of the treated member is greatly reduced.

[0004] In addition, a member to be used in a high-temperature environment such as that in an internal combustion engine of an automobile needs to have a good creep resistance or high fatigue strength. Each of Non-Patent Documents 1 and 2 and Patent Documents 2, 3 and 8 discloses a technique of adding Si to a titanium alloy so as to improve the creep resistance thereof. However, when Si is added thereto in a large amount, Si incapable of forming a solid solution in α phase or β phase may produce a titanium silicide, and the silicide may be coarsened during heat treatment thereof or during the use thereof at a high temperature, and become an origin of fatigue failure, so as to cause a reduction in the fatigue strength of the alloy. Si may form a solid solution of about 0.2% at 700°C in the binary system of Ti-Si, and Si may form a solid solution of only about 0.1% at 700°C in the $\alpha+\beta$ alloy of Ti-5%Al-2%Fe, although this may vary depending on the amount of constituent element and temperature. Therefore, in the application of the alloy wherein the fatigue strength thereof is required, the amount of Si to be added to the alloy may be limited, for example, to less than 0.25%.

[0005] The Ti-6Al-1.7Fe-0.1Si alloy disclosed in Non-Patent Documents 1 and 2 may be an alloy having a high strength and a high rigidity, but the amount of Al to be added thereto is large and therefore, the alloy may be disadvantageously poor in the hot workability. Further, Si is added to the alloy so as to enhance the creep resistance thereof in a high-temperature environment up to 480°C, but the amount of Si to be added to the alloy may be restricted to not more than 0.13%.

[0006] Patent Document 2 discloses an alloy composed of Al: from 4.4% to less than 5.5% and Fe: from 0.5% to less than 1.4%, as an $\alpha+\beta$ type titanium alloy having a stable and less variable fatigue strength, which is equal to that of the conventional Al-Fe-based titanium alloy, and also having a hot workability higher than that of the conventional alloy. However, this document is silent on the fatigue strength in a state of the alloy wherein a wear resistance has been imparted thereto. Further, the amount of Si to be added thereto is set to be less than 0.25% for the reason that the fatigue strength is decreased.

[0007] Patent Document discloses 3 an alloy composed of Al: from 4.4% to less than 5.5% and Fe: from 1.4% to less than 2.1%, as a titanium alloy having a fatigue strength equal to that of the conventional Al-Fe-based titanium alloy and having hot or cold workability higher than that of the conventional alloy. However, this document is silent on the fatigue strength in a state of wear resistance being imparted. Further, the amount of Si to be added thereto is set to be less than 0.25% for the reason that the fatigue strength is decreased otherwise.

[0008] Patent Document 4 discloses an alloy composed of Al: from 5.5 to 7.0%, Fe: from 0.5 to 4.0% and O: 0.5% or less, as an $\alpha+\beta$ type titanium alloy being industrially producible at a low cost and having a mechanical property equal to or greater than that of the Ti-6Al-4V alloy. However, the hot workability and cold workability thereof may be poor, because of a large amount of Al to be added thereto and further, this alloy may pose a problem such as non-uniformity of characteristics due to the Fe segregation at a high Fe concentration, and a reduction in rigidity as a member due to a decrease in the Young's modulus of the alloy.

[0009] Patent Document 5 discloses a titanium alloy composed of Al: from 5.0 to 7.0%, Fe+Cr+Ni: from 0.5 to 10.0% and C+N+O: from 0.01 to 0.5% and having a melting point of 1,650°C or less, and a tensile strength of 890 MPa or more

in the state of an as-cast alloy, as an $\alpha+\beta$ type titanium alloy for casting, having a strength higher than that of Ti-6Al-4V and having an excellent castability. This titanium alloy may be an alloy capable of providing a good flowability at the time of melting thereof, and an excellent strength after the solidification, but it may pose a problem that the solidification texture is liable to be coarsened and the fatigue strength thereof may be poor.

[0010] Patent Document 6 discloses a high-strength $\alpha+\beta$ type alloy composed of Al: from 4.4 to 5.5%, Fe: from 1.4 to 2.1%, Mo: from 1.5 to 5.5% and Si: less than 0.1%, and having a strength at room temperature and a fatigue strength, which are equal to or greater than those of Ti-6Al-4V. Patent Document 7 discloses an engine valve using this alloy, and a technique of forming a hard layer such as oxide layer in the surface layer of the valve, to thereby enhance the wear resistance. However, the titanium alloy disclosed in Patent Documents 6 and 7 contains a large amount of Mo, which is expensive and subject to great price fluctuation, and therefore, it may be disadvantageously difficult to stably produce the alloy at low cost. In addition, this titanium alloy contains a large amount of Mo, and accordingly the specific gravity thereof may be higher than that of the Ti-6Al-4V alloy, and the Young's modulus thereof may be also equal to that of Ti-6Al-4V alloy, which are insufficient in terms of the effect of reducing the weight of a member requiring rigidity.

[0011] Patent Document 8 discloses a process for producing a titanium alloy valve, and a method of heating a valve of Ti-6Al-4V alloy as an $\alpha+\beta$ type titanium alloy in an atmosphere of nitrogen and oxygen, to thereby oxidize and nitride the surface layer thereof. This intends to enhance the wear resistance in the face part and the surface of the edge part thereof, but the cost may be high because of the use of Ti-6Al-4V alloy and the rigidity and fatigue resistance characteristics thereof may be insufficient.

[0012] Patent Document 9 discloses an alloy having an Al equivalent of 3 to 6.5% and containing at least one complete solid solution-type β stabilizer in an amount of 2.0 to 4.5% in terms of Mo equivalent and an eutectoid β -stabilizer in an amount of 0.3 to 2% in terms of Fe equivalent, as a Ti alloy improved in the workability of the Ti-6Al-4V alloy. However, Mo, V, Ta, Nb and the like as the complete solid solution-type β -stabilizer may be expensive, and accordingly the alloy may pose a problem of high cost.

[0013] Patent Document 10 discloses a heat-resistant alloy composed of ingredients such as Al: from 5.5 to 6.5%, Sn: from 1.5 to 3.0%, Zr: from 0.7 to 5.0%, Mo: from 0.3 to 3.0% and Si: from more than 0.15% to 0.50%. The reason why Si is added to the alloy in such a large amount is to improve the creep resistance by envisaging the use thereof in a temperature region of 500 to 600°C or more. In the titanium alloy disclosed in Patent Document 8, Sn, Zr and Mo are added each in a large amount so as to obtain high-temperature strength in the temperature region stated above, and the alloy may pose a problem that, in addition to high alloy cost, the hot workability thereof is seriously poor and the production cost thereof is high. In addition, Zr is an element facilitating the formation of a silicide in the form of $(\text{Ti}\cdot\text{Zr})_x\text{Si}_y$, and the alloy may pose a problem that the fatigue strength is liable to be reduced. Further, the studies in Patent Document 8 on the wear resistance are not thoroughly made and, for example, when a hardened layer is formed as in the case of Patent Document 6 with the aim of enhancing the wear resistance, the fatigue characteristics may be greatly reduced due to the formation of a silicide as described above.

[0014] Patent Document 11 discloses a valve having a hardened layer, which has been obtained by forming a solid solution of oxygen in a low-strength Ti alloy, and also discloses an alloy of Ti-Fe: from 0.04 to 2.40%-O: from 0.08 to 0.20%, as the Ti alloy material. However, the valve may have a drawback that due to insufficient base metal strength, and the use thereof in the application requiring high strength and high fatigue strength is difficult.

PRIOR ART DOCUMENTS

PATENT DOCUMENT

[0015]

Patent Document 1: JP-A (Japanese Unexamined Patent Publication) No. 62-256956

Patent Document 2: Japanese Patent No. 3076697

Patent Document 3: Japanese Patent No. 3076696

Patent Document 4: Japanese Patent No. 3306878

Patent Document 5: JP-A No. 2010-7166

Patent Document 6: JP-A No. 2005-320618

Patent Document 7: JP-A No. 2007-100666

Patent Document 8: JP-A No. 6-041715

Patent Document 9: JP-A No. 2000-273598

Patent Document 10: JP-A No. 2-22435

Patent Document 11: JP-A No. 7-269316

NON-PATENT DOCUMENTS

[0016]

- 5 Non-Patent Document 1: P. Bania, Metallurgy and Technology of Practical Titanium Alloys, p. 9, TMS, Warrendale, PA (1994)
 Non-Patent Document 2: F.H. FROES and I.L. CAPLAN, TITANIUM '92 SCIENCE AND TECHNOLOGY, p. 2787

SUMMARY OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0017] Heretofore, there has not been disclosed a technique satisfying both wear resistance and fatigue characteristic of a titanium alloy without the addition of Mo to the alloy.

15 In order to enhance the wear resistance of a titanium alloy member, for example, it may be considered to subject the surface layer part thereof to a wear resistance treatment of forming a hardened layer by oxidation, nitridation or carbonization. However, when such a wear resistance treatment is performed, there may be posed a problem that the fatigue strength of the member is decreased.

20 An object of the present invention is to advantageously solve the problem encountered in the prior art, and to inexpensively provide a wear-resistant titanium alloy member which is superior in fatigue strength, as compared to those of conventional titanium alloys.

MEANS FOR SOLVING THE PROBLEM

25 [0018] For achieving the above object, the present inventors have intensively examined the effect on the hot workability by adding, as a strengthening element, Fe which is more inexpensive than V and Mo, and Si exerting a high strengthening ability even when added in a small amount, and the fatigue strength of a titanium alloy, in which a hardened layer containing oxygen in a solid solution state is formed in the surface layer so as to enhance the wear resistance.

30 [0019] The present inventors have employed a β -transformation temperature of 1,000°C or less and a proportion of β phase at 900°C of 40% or more, as the indicator of hot workability for industrial production at low cost. In general, in the case of forging a billet from an ingot or hot working of a material into a member shape, the material may be heated to a β -single phase region having high deformability, and during the working the temperature may be decreased to a 2-phase region which is lower than the β transformation temperature. The reason why these are employed as the indicator is, when the heating temperature exceeds 1,000°C, this may lead to a decrease in the yield due to worsening of the surface roughness by oxidation or generation of scales or a great rise in the production cost due to an increase in the cutting time; and also, when the proportion of β phase falls below 40% resulting from temperature decrease during the working, cracking is liable to occur during the working.

35 [0020] The hardened layer containing oxygen in a solid solution state can be formed by a solid solution of oxygen or a solid solution of either one or two elements of nitrogen and carbon together with oxygen which are diffused from the surface by a thermal diffusion method, in the surface layer of a titanium alloy, after the formation thereof into a member shape.

The present inventors have employed, as the indicator of fatigue strength of a titanium alloy, the condition that when a hardened layer containing oxygen in a solid solution state is formed in the surface layer, the fatigue strength is 360 MPa or more, which is 10% larger than 330 MPa, which is the fatigue strength of conventional Ti-6Al-4V alloy.

40 As a result, it has been found that a titanium alloy excellent in fatigue strength, hot workability and wear resistance can be produced by adjusting the ranges of components Al, Fe, O and Si to appropriate amounts.

[0021] The gist of the present invention resides in the followings.

50 [1] A wear-resistant titanium alloy member excellent in fatigue strength, comprising a titanium alloy base metal comprising, in mass%, Al: 4.5% or more to less than 5.5%, Fe: 1.3% or more to less than 2.3%, Si: 0.25% or more to less than 0.50%, and O: 0.08% or more to less than 0.25%, with the balance of titanium and unavoidable impurities, and having, in the surface layer, a hardened layer containing oxygen in a solid solution state.

[2] The wear-resistant titanium alloy member excellent in fatigue strength according to [1], wherein the hardened layer has been obtained by forming a solid solution of either one or two elements of nitrogen and carbon together with oxygen, in the surface layer of the base metal.

55 [3] The wear-resistant titanium alloy member excellent in fatigue strength according to [1] or [2], wherein, in the hardened layer, the Vickers hardness of the cross-section is 450 HV or more at a depth of 10 μ m from the surface.

EFFECT OF THE INVENTION

[0022] The titanium alloy member according to the present invention has wear resistance, fatigue strength and hot workability surpassing those of the conventional titanium alloy, and is also inexpensive. Accordingly, the titanium alloy member according to the present invention can find a wider industrial application as a member in the sliding part such as engine valve and con-rod (or connecting rod) for an automobile than that of the conventional high-strength titanium alloy, and thanks to its lightweight and high-strength characteristics, it is possible to obtain an extensive effect such as improvement of fuel efficiency of an automobile and the like. Further, the titanium alloy member according to the present invention enables widespread utilization, including a member in the sliding part, and its extensive effect can be obtained, so that the industrial effect thereof may be immense.

MODES FOR CARRYING OUT THE INVENTION

[0023] Hereinbelow, the present invention will be described in detail.

In the development, the effect of addition of Si and oxygen on the strength, Young's modulus and β transformation temperature was examined based on a Ti-5% Al-1 to 2% Fe-based alloy, which had been previously developed as a low-cost Fe-containing high-strength $\alpha+\beta$ type titanium alloy.

As a result, it has been found that both of Si and oxygen enhance the strength and Young's modulus, and that, while the addition of oxygen is greatly effective in raising the β transformation temperature, Si does not affect the β transformation temperature. Fe may decrease both of the β transformation temperature and the Young's modulus.

[0024] The method of evaluating the wear resistance is described below. While a tensile load of 300 MPa was applied in the axis direction of a round bar member, an SCM435 material was caused to collide with the member surface under the conditions of a load of 98 N (10 kgf) and a vibration frequency of 500 Hz, and the wear resistance was evaluated by the presence or absence of a crack on the surface after the application of vibration 1×10^7 times.

[0025] The fatigue strength is described below. By use of a test specimen which had been obtained by working a titanium alloy into the test specimen shape, and the specimen was subjected to a wear resistance treatment appearing hereinafter, so as to form a solid solution oxygen-containing hardened layer in the surface layer of a base metal, and then the fatigue strength was evaluated by the breaking strength in 1×10^7 cycles of an Ono's rotary bending fatigue test. As a result, there has been observed a phenomenon that where in the case of having a hardened layer in the surface layer of the base metal, as compared with the case of not having a hardened layer, when the Si content of the base metal is less than 0.25%, the fatigue strength is reduced by approximately 100 to 150 MPa, but that when the Si content of the base metal is 0.25% or more, the fatigue strength is enhanced.

[0026] In general, when a hardened layer is present in the surface layer of a base metal composed of a titanium alloy, the fatigue strength may be decreased as compared with that in the case of not having a hardened layer in the surface layer. The reason therefor is unclear, but may be presumed that a fine crack is liable to be generated in the surface layer and becomes an origin of fatigue.

In the case of having a hardened layer in the surface layer of a base metal, the mechanism of enhancing the fatigue strength with an increase in the amount of Si to be added to the base metal is not necessarily clear. However, if the reason is presumed daringly, the following mechanism may be considered. Thus, in a repeat test of about 1×10^7 cycles to be used for the evaluation of general fatigue strength, the generation of fatigue failure of a titanium alloy may originate on the surface layer. In particular, when a coarse deposit or the like of silicide is present in the surface layer, the fracture generation may be originated from such a site.

[0027] At this time, the microscopic texture of the surface layer part in the cross-section of a test specimen, where the Si content in the base metal composed of a titanium alloy is 0.25% or more was examined in detail. As a result, in the surface layer part of the base metal where the hardened layer was obtained by forming a solid solution of oxygen, a layer free from silicide was observed. The reason for this may be considered that oxygen as an α stabilizer is intruded from the outer side during an oxidation treatment for forming a hardened layer and causes an increase in the proportion of α phase and a decrease in the β phase region, and Si as a β stabilizer is transferred into a scale or into the inside of the base metal. The depth of the layer free from silicide may be smaller than the depth of the oxygenenriched hardened layer, but may be at least 3 μm or more from the surface, and this may be considered to be large enough to avoid providing an origin of fatigue crack.

[0028] Here, the silicide may be usually observed as Si enrichment by mapping analysis using EPMA. More specifically, an electron beam analysis by a transmission electron microscope should be performed. In the case of this test specimen having a hardened layer in the surface layer of a base metal composed of a titanium alloy having an Si content of 0.25% or more, the silicide present in the inside of the base metal has been confirmed to have a size of 0.1 μm or more.

[0029] As described above, when a solid solution oxygen-containing hardened layer is formed in the surface layer of a base metal composed of a titanium alloy having an Si content of 0.25% or more, Si in the surface layer may be diluted to suppress the formation of silicide in the surface layer, so as to provide no origin of fatigue failure, and on the other

hand, Si in the base metal may contribute to an enhancement of the strength. This may be considered to cause an effect that the reduction in the fatigue strength is suppressed and the fatigue strength is enhanced.

Further, when a solid solution oxygen-containing hardened layer is formed in the surface layer of a base metal composed of a titanium alloy containing Fe and having an Si content of 0.25% or more, and an increase in the proportion of α phase and a decrease in the β phase region are caused, the solid solution strengthening ability may be greatly reduced due to an extremely small amount of solid solution Fe in the α phase, whereas the amount of solid solution Si in the α phase may be larger than that of Fe and therefore, the reduction in the solid solution strengthening ability may be suppressed. This may be considered to also contribute to the enhancement of fatigue strength.

[0030] The element forming the hardened layer may not be limited to oxygen, and the hardened layer may also be obtained by forming a solid solution of either one or two elements of nitrogen and carbon together with oxygen in the surface layer of a base metal. Nitrogen and carbon are, similarly to oxygen, an α stabilizer forming a solid solution in titanium, and it may be considered that the same mechanism as that for oxygen works in the titanium alloy.

[0031] In the titanium alloy member according to the first embodiment of the present invention, the content ratio of constituent elements of the base metal and the formation of a solid solution oxygen-containing hardened layer in the surface layer of the base metal are specified.

Al is an α stabilizer and the strength of the titanium alloy member may be increased by forming a solid solution in the α phase, along with an increase in its content. However, if the base metal contains Al in an amount of 5.5% or more, the hot workability thereof may be deteriorated. For this reason, the Al content in the base metal is specified to be from 4.5% to less than 5.5%. The upper limit of the Al content may preferably be less than 5.3%. Further, the lower limit of the Al content may preferably be 4.8% or more.

[0032] Fe is an eutectoid β stabilizer and the roomtemperature strength of the titanium alloy member may be increased and the P transformation temperature may be lowered, by forming a solid solution in the P phase, along with an increase in its content. In order to secure the strength and the decrease in the P transformation temperature, the base metal should contain 1.3% or more of Fe. However, if the base metal contains Fe in an amount of 2.3% or more, the segregation may pose a problem when an ingot is intended to be produced as a large ingot. For this reason, the Fe content in the base metal is specified to be from 1.3% to less than 2.3%. The upper limit of the Fe content may preferably be less than 2.1%. Further, the lower limit of the Fe content may preferably be 1.5% or more, more preferably 1.6% or more.

[0033] Si is a β stabilizer, and the strength may be increased along with an increase in its content. In order to secure the fatigue strength when wear resistance is imparted thereto, the base metal should contain 0.25% or more of Si.

On the other hand, if the base metal contains Si in an amount of 0.50% or more, the toughness may be reduced. For this reason, the Si content in the base metal is specified to be from 0.25% to less than 0.50%. The upper limit of the Si content may preferably be less than 0.45%. Further, for the purpose of increasing the strength of the base metal, the lower limit of the Si content may preferably be 0.28% or more.

[0034] O is an element strengthening the α phase. In order to cause the effect, the O content in the base metal should be 0.05% or more. However, if the base metal contains O in an amount of 0.25% or more, the production of an α_2 phase may be promoted so as to cause brittleness, or the β transformation temperature may rise to elevate the heat treatment cost. For this reason, the O content in the base metal is specified to be from 0.05% to less than 0.25%. The content may preferably be from 0.08% to less than 0.22%, more preferably from 0.12% to less than 0.20%.

[0035] In the titanium alloy member according to the second embodiment of the present invention, the hardened layer is obtained by forming a solid solution of either one or two elements of nitrogen and carbon together with oxygen in the surface layer of a base metal.

Each of oxygen, nitrogen and carbon is an α stabilizer forming a solid solution in titanium, and it may be considered that, by forming a solid solution in the surface layer, the Si concentration in the surface layer is reduced and the production of silicide is suppressed, to thereby prevent the reduction in the fatigue strength.

[0036] In the titanium alloy member according to the third embodiment of the present invention, the Vickers hardness of the cross-section of the hardened layer is specified to be 450 HV or more at a depth of 10 μm from the surface.

As for the hardness and depth of the hardened layer, the Vickers hardness may be measured under a load of 10 gf after the mirror-polishing of the cross-section. Since oxygen may be intruded from the surface layer, the hardness of the surface may become the maximum, and as the progresses toward the inside of the base metal, the hardness may be decreased. The Vickers hardness at a depth of 10 μm from the surface of the hardened layer may preferably be HV 450 or more, more preferably HV 500 or more. When the Vickers hardness of the hardened layer is HV 450 or more, the effect of enhancing the wear resistance by providing the hardened layer in the surface layer of a base metal may be more effectively obtained.

[0037] In the titanium alloy member according to the present invention, the microscopic structure of the base metal may preferably be a acicular structure. When the microscopic structure of the base metal is an acicular structure, a titanium alloy member excellent in the creep resistance may be obtained. Further, in a case where the microscopic structure of the base metal is an acicular structure, the member may be reduced in the creep deformation, when a wear resistance treatment such as oxidation treatment to form a hardened layer so as to impart the wear resistance is performed

at a high temperature.

[0038] The titanium alloy member according to the present invention can have an excellent fatigue strength and an excellent wear resistance.

The titanium alloy member according to the present invention can be produced by a process for producing a titanium alloy and a surface treatment method, which may generally be used. The steps of a representative embodiment of the process for producing the titanium alloy member according to the present invention are as follows.

[0039] First, sponge titanium and an alloy material as raw materials are subjected a melting process wherein they are arc-melted or electron beam-melted under vacuum, and cast into a water-cooled copper mold, to thereby obtain an ingot of components for a base metal of the titanium alloy member according to the present invention. Herein, during the melting, O is added by using, for example, titanium oxide or sponge titanium having a high oxygen concentration. The thus obtained ingot is heated to an $\alpha+\beta$ region or β region of 950°C or more, then is forged into a billet shape and subjected to surface cutting, and is hot rolled at a heating temperature of 950°C or more, to thereby provide a base metal shaped as a bar material having a diameter of, for example, $\phi 12$ to 20 mm, which is an example of the shape of the titanium alloy member according to the present invention.

[0040] Next, the surface layer of the base metal formed in the shape of the titanium alloy member according to the present invention is subjected to a wear resistance treatment of forming a solid solution of oxygen, or a wear resistance treatment of forming a solid solution of either one or two elements of nitrogen and carbon together with oxygen. In the wear resistance treatment, for example, oxidation, carburization and nitridation by a thermal diffusion method may be used in combination as desired. As the wear resistance treatment, in the case of performing the thermal diffusion method, specifically, for example, it is preferred to use a method of performing a heat treatment where the base metal is held at 700 to 900°C for 1 to 8 hours in an oxygen-containing gas such as air for oxidation, in a nitrogen-containing gas mainly composed of nitrogen for nitridation, or in a carbon-containing gas such as carbon dioxide, carbon monoxide and methane for carburization. By performing the wear resistance treatment, the $\alpha+\beta$ type titanium alloy member according to the present invention having a solid solution oxygen-containing hardened layer in the surface layer of the base metal may be obtained.

[0041] In this embodiment, before the wear resistance treatment of forming a solid solution oxygen-containing hardened layer in the surface layer of the base metal, it is preferred that the base metal formed in the shape of the titanium alloy member is heated at a temperature not less than the P transformation temperature, and then cooled at a rate not less than that of air cooling (i.e., solution treatment). By performing the solution treatment, an α phase may be precipitated in the prior β phase of the base metal, and the microstructure of the base metal may become an acicular structure. Accordingly, by performing the solution treatment before the wear resistance treatment, the creep deformation in the member can be suppressed during the wear resistance treatment.

EXAMPLES

[0042] Hereinbelow, the present invention will be described in more detail by referring to Examples.

(Example 1)

[0043] Titanium alloys composed of components of Material Nos. 1 to 12 as shown in the following Table 1 were produced by using a vacuum arc melting method, and each of the alloys was made into an ingot of about 200 kg. Each of these ingots was forged and hot rolled to thereby obtain a round bar of 15 mm in diameter.

[0044]

[Table 1]

Material No.	Alloy Components (mass%)				Remarks
	Al	Fe	O	Si	
1	5.0	1.5	0.17	0.40	Invention
2	5.4	1.8	0.16	0.30	Invention
3	5.2	2.2	0.15	0.32	Invention
4	5.4	2.1	0.09	0.45	Invention
5	4.8	2.0	0.20	0.28	Invention
6	4.5	1.6	0.22	0.35	Invention

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(continued)

Material No.	Alloy Components (mass%)				Remarks
	Al	Fe	O	Si	
7	5.3	2.0	0.16	0.26	Invention
8	4.7	1.6	0.15	0.48	Invention
9	<u>4.0</u>	2.0	0.18	0.30	Comparative Example
10	5.0	<u>1.0</u>	0.18	0.33	Comparative Example
11	<u>6.0</u>	1.5	0.18	<u>0.13</u>	Comparative Example
12	5.4	2.0	0.15	<u>0.01</u>	Comparative Example
13	<u>6.0</u>	1.4	0.20	0.30	Comparative Example
14	5.3	1.5	<u>0.28</u>	0.45	Comparative Example
15	5.0	1.8	0.15	<u>0.60</u>	Comparative Example

[0045] Each of the Round bars of Material Nos. 1 to 15 was subjected to a solution treatment at a temperature, which was 60°C higher than the P transformation temperature as shown in Table 2, for 20 minutes, and cooling it by blowing a nitrogen gas into the furnace, to thereby form an acicular structure. Subsequently, the round bar was worked so as to obtain a base metal having a shape of the fatigue test specimen with a parallel part diameter of 4 mm, a parallel part length of 20 mm and a diameter of 15 mm. Thereafter, the thus obtained base metal was subjected to a wear resistance treatment of forming a solid solution oxygen-containing hardened layer in the surface layer of the base metal by using a heat treatment at 800°C for 1 hour in the air, to thereby obtain a fatigue test specimen.

[0046]

[Table 2]

No.	β Transformation Temperature °C	Proportion of β Phase at 900°C %	Fatigue Strength	Workability	Remarks
1	995	40	A	A	Invention
2	995	40	A	A	Invention
3	980	50	A	A	Invention
4	975	50	A	A	Invention
5	990	50	A	A	Invention
6	995	40	A	A	Invention
7	990	50	A	A	Invention
8	985	40	A	A	Invention
9	965	50	C	A	Comparative Example
10	1010	20	C	C	Comparative Example
11	1020	30	C	C	Comparative Example
12	985	50	C	A	Comparative Example
13	1040	30	A	C	Comparative Example
14	1040	30	C	C	Comparative Example
15	995	40	C	A	Comparative Example

[0047] Each of the thus obtained fatigue test specimen Nos. 1 to 15 was subjected to a fatigue test under the following conditions and evaluated in the following manner. The results obtained are shown in Table 2.

The fatigue test was performed by using an Ono's rotary bending fatigue test under the conditions of a maximum stress of 360 MPa, a stress ratio R of -1, 3,600 rpm, room temperature and 1×10^7 cycles. The test specimen was rated "A"

when it was not broken until the 1×10^7 -th cycles, and rated "C" when it was broken until that time.

[0048] Further, each of the fatigue test specimen Nos. 1 to 15 was subjected to a measurement for the proportion of β phase at 900°C of the base metal as follows. A sample which had been cut out from the same material was held at 900°C for 1 hour and then water-cooled, and the areas of the primary α phase and the transformed β phase in the micro-structure of the cross-section were measured, whereby the proportion was determined from the ratio therebetween. The results obtained are shown in Table 2.

[0049] Further, each of the hot rolled bar Nos. 1 to 15 was evaluated for workability during hot rolling as follows. That is, the test specimen was rated "A" when the cracking therein was not generated during hot working, and was rated "C" when the cracking therein was generated. The results are shown in Table 2.

[0050] Herein, Nos. 1 to 8 are Examples according to the present invention, and Nos. 9 to 15 are Comparative Examples, where any of material components (i.e., constituent elements of the base metal) is outside the range of the present invention. The numerical values outside the range of the present invention are underlined.

In all of Nos. 1 to 8 as Examples according to the present invention, the P transformation temperature was 1,000°C or less, the proportion of P phase at 900°C was 40% or more, the cracking did not occur during the hot working, and the fatigue strength after the wear resistance treatment was 360 MPa or more, to thereby show good hot workability and good fatigue strength.

[0051] In both No. 9 where the Al content was outside the lower limit and No. 10 where the Fe content was outside the lower limit, both of which are Comparative Examples, the fatigue strength after the wear resistance treatment was insufficient. In No. 11 as Comparative Example where the Al amount was outside the upper limit and the Si amount was outside the lower limit, the fatigue strength after the wear resistance treatment was insufficient. In No. 12 where the Si amount was outside the lower limit, the fatigue strength after the wear resistance treatment was insufficient. In No. 13 where the Al amount was outside the upper limit, the hot workability was insufficient. In No. 14 where the O amount was outside the upper limit and in Nos. 10, 11, 13 and 14 where the β transformation temperature exceeded 1,000°C and the proportion of β phase at 900°C of the base metal was less than 40%, the hot workability was insufficient. In No. 15 where the Si amount was outside the upper limit, the fatigue strength was insufficient.

(Example 2)

[0052] In Test Specimen Nos. 16 to 19, the round bar of Material No. 5 in Table 1 was used. In the test specimen No. 20, a rolled round bar of Ti-6Al-4V alloy was used for the purpose of comparison.

The round bar of Material No. 5 was subjected to the same solution treatment as that in Example 1 so as to form the microscopic structure thereof into an acicular structure, and was then worked into the same shape as that in Example 1, to thereby obtain a base metal. Thereafter, the resultant product was subjected to a wear resistance treatment so as to form, in the surface layer of the base metal, a hardened layer containing solid solution of carbon and oxygen, by applying thereto a heat treatment at 770°C for 5 hours in a carbon-containing gas atmosphere, whereby a fatigue test specimen of No. 16 was obtained.

[0053] A base metal having the same shape as in Example 1, which had been obtained in the same manner as that in the case of Test Specimen No. 16, was subjected to a wear resistance treatment for forming, in the surface layer of the base metal, a hardened layer containing solid solution of carbon and oxygen, by performing an oxynitridation treatment at 770°C for 5 hours in a nitrogen gas atmosphere containing a small amount of oxygen, whereby a fatigue test specimen of No. 17 was obtained.

[0054] The round bar of Material No. 5 was subjected to a solution treatment at a temperature, which was 30°C lower than the β transformation temperature thereof, for 60 minutes, and then was subjected to air-cooling, to thereby form the microscopic structure into a mixed structure composed of prior α phase and transformed β phase, and then was worked into the same shape as that in Example 1, to thereby obtain a base metal. Thereafter, the resultant product was subjected to a wear resistance treatment for forming a solid solution oxygen-containing hardened layer in the surface layer of the base metal, by applying thereto an oxidation treatment at 760°C for 1 hour in the air, whereby a fatigue test specimen of No. 18 was obtained.

[0055] There was provided a base metal having the same shape as that in Example 1, as a fatigue test specimen of No. 19, which had been obtained in the same manner as in the case of Test Specimen No. 18, and having an as-ground surface which had been created at the time of working the base metal into the shape of a fatigue test specimen without performing a wear resistance treatment for forming a hardened layer.

[0056] A rolled round bar of Ti-6Al-4V alloy was subjected to a solution treatment at a temperature, which was 60°C higher than the β transformation temperature thereof, for 20 minutes, and then subjected to air-cooling, and then was worked into the same shape as in the case of Example 1, to thereby obtain a base metal. Thereafter, the resultant product was subjected to a wear treatment of forming a solid solution oxygen-containing hardened layer in the surface layer of the base metal, by applying thereto an oxidation treatment at 800°C for 1 hour in the air to thereby obtain a fatigue test specimen of No. 20.

[0057] Each of Fatigue Test Specimen Nos. 16 to 20 was evaluated for the wear resistance by the evaluation method described hereinabove. The test specimen was rated "A" when the cracking was not generated, and rated "C" when the cracking was generated, and the results are shown in Table 3.

[0058]

[Table 3]

Test Specimen No.	Wear Resistance	Fatigue Strength	Remarks
16	A	A	Invention
17	A	A	Invention
18	A	A	Invention
19	C	-	Comparative Example
20	C	-	Comparative Example

[0059] In Test Specimen Nos. 16 to 18 according to the present invention, the cracking was not generated. On the other hand, in Test No. 19 having no hardened layer in the surface and in Test Specimen No. 20 where the components of the base metal were outside the range of the present invention, the cracking was generated.

Further, each of Fatigue Test Specimen Nos. 16 to 18 was subjected to a fatigue test and evaluated in the same manner as in Example 1. The results obtained are shown in Table 3.

In all of Test Specimen Nos. 16 to 18, the fatigue strength after the wear resistance treatment was 360 MPa or more, so as to show good fatigue strength.

(Example 3)

[0060] In Test Specimen Nos. 21 to 23, the round bar of Material No. 5 in Table 1 was used.

The round bar of Material No. 5 was subjected to the same solution treatment as in the case of Example 1 so as to make form microscopic structure into an acicular structure, and was worked into the same shape as in the case of Example 1, to thereby obtain a base metal. Thereafter, the resultant product was subjected to a wear resistance treatment for forming a solid solution oxygen-containing hardened layer in the surface layer of the base metal, by applying thereto a heat treatment at the following temperature for the following time in the air.

[0061] In Test Specimen No. 21 where the heat treatment was performed at 740°C for 1 hour, as shown in Table 4 appearing hereinafter, the Vickers hardness at a depth of 10 μm was 420 HV. In Test Specimen No. 22 where the heat treatment was performed at 770°C for 1 hour, the Vickers hardness at a depth of 10 μm was 470 HV. In Test Specimen No. 23 where the heat treatment was performed at 800°C for 1 hour, the Vickers hardness at a depth of 10 μm was 530 HV. Herein, the Vickers hardness of Test Specimen Nos. 21 to 23 was measured under the condition of a load of 10 gf after the mirror-polishing of the cross-section of the test specimen.

[0062]

[Table 4]

Test Specimen No.	Hardness	Wear Resistance	Amount of wear μm	Fatigue Strength	Remarks
21	420	A	>50	A	Invention
22	470	A	<50	A	Invention
23	530	A	<20	A	Invention

[0063] Each of Test Specimen Nos. 21 to 23 was evaluated for the wear resistance by the above-described evaluation method. Further, each of Test Specimen Nos. 21 to 23 was measured for the amount of wear before and after the evaluation of wear resistance. Further, each of Test Specimen Nos. 21 to 23 was subjected to a fatigue test and evaluated in the same manner as in Example 1. The results obtained are shown in Table 4.

As a result of the evaluation of the wear resistance, in all of Test Specimen Nos. 21 to 23, the cracking was not generated, but the amount of wear was more than 50 μm in No. 21, from 20 to less than 50 μm in No. 22, and less than 20 μm in No. 23. In all test specimens, the fatigue strength was 360 MPa or more, so as to show good fatigue strength.

Claims

1. A wear-resistant titanium alloy member excellent in fatigue strength, comprising a titanium alloy base metal comprising, in mass%, Al: 4.5% or more to less than 5.5%, Fe: 1.3% or more to less than 2.3%, Si: 0.25% or more to less than 0.50%, and O: 0.08% or more to less than 0.25%, with the balance of titanium and unavoidable impurities, and having, in the surface layer, a hardened layer containing oxygen in a solid solution state.
2. The wear-resistant titanium alloy member excellent in fatigue strength according to claim 1, wherein the hardened layer has been obtained by forming a solid solution of either one or two elements of nitrogen and carbon together with oxygen, in the surface layer of the base metal.
3. The wear-resistant titanium alloy member excellent in fatigue strength according to claim 1 or 2, wherein, in the hardened layer, the Vickers hardness of the cross-section is 450 HV or more at a depth of 10 μm from the surface.

INTERNATIONAL SEARCH REPORT

International application No.

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A. CLASSIFICATION OF SUBJECT MATTER

C22C14/00(2006.01)i, C22F1/18(2006.01)i, C22F1/00(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)

C22C1/00-49/14, C22F1/00-3/02

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

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	JP 7-62474 A (Nippon Steel Corp.), 07 March 1995 (07.03.1995), (Family: none)	1-3
A	JP 7-70676 A (Nippon Steel Corp.), 14 March 1995 (14.03.1995), (Family: none)	1-3
A	JP 2005-89834 A (Nippon Steel Corp.), 07 April 2005 (07.04.2005), (Family: none)	1-3
A	JP 11-50227 A (Mitsubishi Materials Corp.), 23 February 1999 (23.02.1999), (Family: none)	1-3

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

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Date of the actual completion of the international search
16 April, 2012 (16.04.12)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/052265

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	JP 2007-100666 A (Nippon Steel Corp.), 19 April 2007 (19.04.2007), (Family: none)	1-3

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REFERENCES CITED IN THE DESCRIPTION

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