



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

(43) Date of publication:
25.05.2005 Bulletin 2005/21

(51) Int Cl.7: **C22C 14/00, C23G 1/12**

(21) Application number: **03736120.1**

(86) International application number:
PCT/JP2003/007297

(22) Date of filing: **09.06.2003**

(87) International publication number:
WO 2003/104506 (18.12.2003 Gazette 2003/51)

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT RO SE SI SK TR**
Designated Extension States:
AL LT LV MK

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(30) Priority: **11.06.2002 JP 2002169441**

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(54) **&bgr;-TYPE TITANIUM ALLOY AND PROCESS FOR PRODUCING THE SAME**

(57) The present invention provides a β type titanium alloy **characterized by** consisting of, by mass %, V: 15 to 25%, Al: 2.5 to 5%, Sn: 0.5 to 4%, O (Oxygen): not more than 0.20%, H: not more than 0.03%, Fe: not more than 0.40%, C: not more than 0.05% and N: not more than 0.02%, and the balance Ti and impurities.

The present invention also provides a method of manufacturing a β type titanium alloy **characterized by** comprising the following steps (a) to (c):

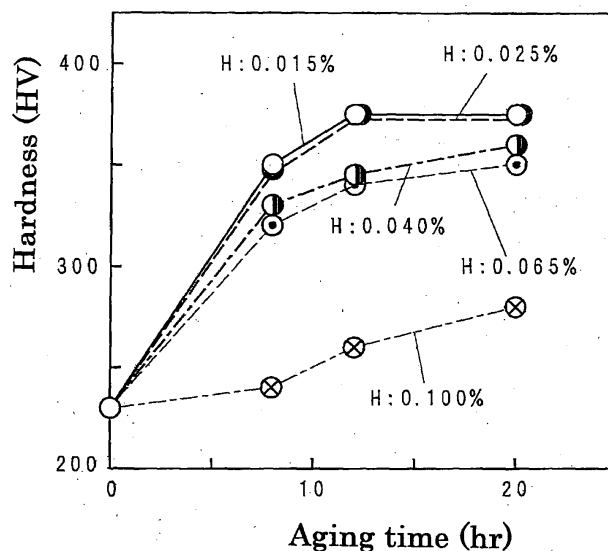
(a) Preparing a β type titanium alloy consisting of,

by mass %, V: 15 to 25%, Al: 2.5 to 5%, Sn: 0.5 to 4%, O (Oxygen): not more than 0.20%, H: not more than 0.03%, Fe: not more than 0.40%, C: not more than 0.05% and N: not more than 0.02%, and the balance Ti and impurities.

(b) Pickling the β type titanium alloy in an aqueous solution including 3 to 40 mass % of HF, and

(c) Further pickling the β type titanium alloy in an aqueous solution including 3 to 6 mass % of HF and 5 to 20 mass % of HNO_3 .

Fig. 1



Description

TECHNICAL FIELD

[0001] The present invention relates to a β type titanium alloy that has excellent deformability, in a solution-treated state, with a low deformation resistance during cold working, and also has a high strength after aging, and a method of manufacturing the alloy.

BACKGROUND ART

[0002] Titanium alloys generally have high strength at low density with the higher specific strength (strength/density) among the practical metallic materials and are excellent in corrosion resistance. Therefore, titanium alloys are used for aircraft and automobile parts, medical equipments, glass frames, golf clubs and tableware. With this extension, further improvement in property and reduction in cost are strongly demanded for the titanium alloys.

[0003] The titanium alloys are roughly classified to α type, β type and $\alpha+\beta$ type: α type has a hexagonal close packed (hcp) microstructure, β type has a body centered cubic (bcc) microstructure, and $\alpha+\beta$ type has both of hcp and bcc microstructures. A pure titanium metal and a titanium alloy with a small amount of other elements such as Al correspond to α type. A Ti-6Al-4V alloy, which is well known as a high strength alloy and used in aircrafts parts, corresponds to $\alpha+\beta$ type. A β type alloy includes elements that stabilize a β phase more than an $\alpha+\beta$ type alloy.

[0004] Since titanium alloys are generally poor in cold workability, their manufacturing cost is high. A pure titanium metal with a low oxygen content, which is relatively satisfactory in cold workability, is hardly applicable to parts requiring high specific strength, because of the insufficient strength of its molded product. On the other hand, a Ti-6Al-4V alloy with high strength that is most representative of a titanium alloy has extremely poor deformability at room temperature. Therefore, it can only be formed to an intended shape by hot working or by cutting, which causes an increased manufacturing cost.

[0005] Because of the situation described above, attention is increasingly paid to a β type titanium alloy having a body centered cubic crystalline structure. Examples of the β type titanium alloy include a Ti-3Al-8V-6Cr-4Mo-4Zr alloy and a Ti-15V-3Cr-3Al-3Sn alloy. These β type alloys have preferable characteristics, which can be used for precision parts. Because β type alloys are highly deformable in cold working when laid in a single β phase by solution treatment, they can be enhanced in strength by precipitating an α -phase by aging treatment after working.

[0006] However, conventional β type titanium alloys have satisfactory deformability but high deformation resistance. Accordingly, in cold forging, for example, a metal mold such as a die or punch is frequently cracked or chipped even when infrequently used. Further, abrasive wear of a roll is serious in cold rolling for manufacturing a work piece, and seizure is apt to occur in case of cold wire drawing.

[0007] As an invention which solves such problems, an alloy consisting of V: 15 to 25%, Al: 2.5 to 5%, Sn: 0.5 to 4%, oxygen: not more than 0.12%, and the balance of Ti and impurities (hereinafter referred to as "Ti-20V-4Al-1Sn alloy" for short) are disclosed in Japanese Patent No. 2669004. This alloy has not only a low deformation resistance with low strength in a solution-treated state, but also has high strength after the aging treatment, although its deformability is substantially equal to those of the conventional β type titanium alloys. However, when the alloy disclosed above is prepared and molded to various parts, the deformability in the β type alloy is not always stable, and the deformation resistance is unstable. Further, the strength after aging is largely fluctuated.

DISCLOSURE OF THE INVENTION

[0008] The first objective of the present invention is to provide a titanium alloy capable of easily and stably realizing the characteristics of excellent cold workability in a solution-treated state and high strength after an aging treatment.

[0009] The present invention also has a second objective, which is to provide a pickling method for reducing the H (hydrogen) content during manufacturing of the titanium alloy.

[0010] The β type titanium alloy has a metastable β phase that is a high temperature phase of titanium, which is quenched and kept at room temperature. The stabilizing elements for β phase are V, Mo, Nb, Ta, Cr, Fe, Mn, and the like. Among them, V and Mo are particularly given as relatively inexpensive elements, which are capable of minimizing the hardening, by solution treatment with a minimized bad effect on workability, while providing high strength by aging. However, Mo is easy to segregate because of its high melting point, and the addition of Mo leads to an increase in deformation resistance during hot or cold working. Therefore, the Ti-20V-4Al-1Sn alloy, in addition to selecting not Mo but V, is proposed to add Al in order to increase the strength in aging treatment, and also add Sn in order to suppress solid solution hardening.

[0011] In the process of preparing this alloy many times, it was found that this alloy has the problem with cold workability and age strengthenability which cannot be always stably obtained. The present inventor made various exami-

nations to determine and respond to the cause of this problem. With respect to V, Al and Sn that are the main elements of this alloy, the cold workability and the age strengthability were examined while varying the ranges of their content. However, no remarkable influence was observed on a characteristic change by the variation of the main elements of this alloy, although its effect appears close to the limit of the content ranges.

[0012] However, it was revealed in the process of the above examinations that the contents of elements O, H, Fe, C and N, which are generally regarded as impurities of titanium metal, significantly influence on the characteristics of the β type Ti-20V-4Al-1Sn alloy, particularly on the improvement in cold workability and age strengthenability. The respective contents of these impure elements are defined in the standard of a titanium metal or a titanium alloy such as JIS-H-4600, JIS-H-4605 and JIS-H-4607 according to the Japan Industrial Standard (hereinafter referred to as "JIS" for short). This definition is not intended for the β type Ti-20V-4Al-1Sn alloy to be improved by the present invention.

[0013] With respect to the effect of each of the above elements, the following facts are known.

[0014] o (Oxygen), which is a α -phase stabilizing element, which disturbs the formation of a single β -phase by a solution treatment when too much is included, and rather hardens the alloy to increase deformation resistance and also reduces the deformability. H (Hydrogen), which is a β phase stabilizing element, retards the age hardening caused by α phase precipitation, and results in disturbing the improvement in age strengthening. Fe, which is a β phase stabilizing element, enhances the strength of the solution-treated alloy and results in increasing the deformation resistance. It is not preferable to include a large amount of Fe. C forms a carbide precipitate and results in significantly reducing the deformation resistance and deformability. N, which is dissolved in β phase in an amount of about 1%, causes a significant reduction in ductility, which reduces the deformability.

[0015] However, it was found that, a β type Ti-20V-4Al-1Sn alloy includes elements that cannot be easily reduced within the ranges defined in JIS even if the impurities are restricted within these ranges; and that it includes elements whose contents have a significant influence on the characteristics of this alloy even if they are restricted within the standard. This may be because the Ti-20V-4Al-1Sn alloy is a β type, in contrast with α type titanium alloys and $\alpha+\beta$ type titanium alloys, defined in the JIS.

[0016] For example, a β type alloy absorbs hydrogen much more easily than α type or $\alpha+\beta$ type alloys. When a plate 5 mm or thinner is manufactured by cold rolling, descaling must be carried out after hot rolling in order to obtain a satisfactory surface. Although the method of mechanically grinding the surface could be adopted for the descaling, the speed and the yield are low. Accordingly, it is general to carry out a pickling with fluoric acid or nitric fluoric acid. However, a Ti-20V-4Al-1Sn alloy which is made of β type by a solution treatment for cold rolling, hydrogen is absorbed in an amount largely exceeding the upper limit of the amount defined by the JIS during the pickling. The variation of the pickling condition does not result in an effective reduction of hydrogen content. Since the above alloy includes elements that increase the oxidized scales, the absorption of hydrogen is apt to increase when the pickling time is prolonged.

[0017] A β type alloy can be improved in strength by performing an aging treatment after working into a desired shape. However, the hydrogen included in the alloy remarkably disturbs the age hardening and results in prolonging the aging treatment time or failing to produce the intended strength. Moreover, the hydrogen reduces the ductility of the alloy, which deteriorates the workability and seriously deteriorates the toughness as well. Although heating at a high temperature in a vacuum can perform dehydrogenation, this method is not practical because it requires an excessive time for treatment, which causes aging.

[0018] The absorption of hydrogen during pickling for descaling is inevitable while manufacturing a Ti-20V-4Al-1Sn alloy plate. Therefore, it is necessary to adopt a pickling method for minimizing the absorption of hydrogen, which is described later.

[0019] The inventor conceived that, even if the alloy plate after pickling might inevitably include hydrogen absorbed during pickling, the deterioration in aging speed and the reduction in workability and toughness, caused by the absorbed hydrogen during pickling, can be recovered by suppressing the amounts of other impurity elements such as O, Fe, N and C.

[0020] As a result of inspecting the influence of the contents of H, O, Fe, N and C on aging speed and workability and toughness, the inventor could stably obtain an excellent Ti-20V-4Al-1Sn alloy by limiting the respective contents of the elements O, Fe, N and C as well as H.

[0021] Based on this examination result, the inventor completed the present invention. The gist of the present invention is to provide with titanium alloys described in the following (1) to (3), and to provide with methods of manufacturing titanium alloys described in the following (4) and (5).

(1) A β type titanium alloy characterized by consisting of, by mass %, V: 15 to 25%, Al: 2.5 to 5%, Sn: 0.5 to 4%, O (Oxygen): not more than 0.20%, H: not more than 0.03%, Fe: not more than 0.40%, C: not more than 0.05% and N: not more than 0.02%, and the balance Ti and impurities.

(2) A β type titanium alloy characterized by consisting of, by mass %, V: 15 to 25%, Al: 2.5 to 5%, Sn: 0.5 to 4%, O (Oxygen): not more than 0.12%, H: not more than 0.03%, Fe: not more than 0.15%, C: not more than 0.05%

and N: not more than 0.02%, and the balance Ti and impurities.

(3) A β type titanium alloy characterized by consisting of, by mass %, V: 15 to 25%, Al: 2.5 to 5%, Sn: 0.5 to 4%, O (Oxygen): not more than 0.20%, H: not more than 0.03%, Fe: not more than 0.40%, C: not more than 0.05% and N: not more than 0.02%, and less than 3% of at least one element selected from Zr, Mo, Nb, Ta, Cr, Mn, Ni, Pd and Si, and the balance Ti and impurities.

(4) A method of manufacturing a β type titanium alloy characterized by comprising the following steps (a) to (c):

(a) Preparing a β - titanium alloy consisting of, by mass %, V: 15 to 25%, Al: 2.5 to 5%, Sn: 0.5 to 4%, O (Oxygen): not more than 0.20%, H: not more than 0.03%, Fe: not more than 0.40%, C: not more than 0.05% and N: not more than 0.02%, and the balance Ti and impurities.

(b) Pickling the β - titanium alloy in an aqueous solution including 3 to 40 mass% of HF, and

(c) Further pickling the β - titanium alloy in an aqueous solution including 3 to 6 mass% of HF and 5 to 20 mass% of HNO_3 .

(5) A method of manufacturing a β type titanium alloy characterized by comprising the following steps (a) to (c):

(a) Preparing a β type titanium alloy consisting of, by mass %, V: 15 to 25%, Al: 2.5 to 5%, Sn: 0.5 to 4%, O (Oxygen): not more than 0.20%, H: not more than 0.03%, Fe: not more than 0.40%, C: not more than 0.05% and N: not more than 0.02%, and less than 3% of at least one element selected from Zr, Mo, Nb, Ta, Cr, Mn, Ni, Pd and Si, and the balance Ti and impurities.

(b) Pickling the β - titanium alloy in an aqueous solution including 3 to 40 mass% of HF, and

(c) Further pickling the β - titanium alloy in an aqueous solution including 3 to 6 mass% of HF and 5 to 20 mass% of HNO_3 .

BRIEF DESCRIPTION OF THE DRAWING

[0022] Fig. 1 is a view showing the influence of hydrogen content on the change in hardness of a titanium alloy by aging.

BEST MODE FOR CARRYING OUT THE INVENTION

[0023] The reason of limiting the content of elements of a β type titanium alloy, according to the present invention, is as follows. The content of each component is represented by mass %.

V: 15 to 25%

[0024] V is an important element for stabilizing β phase and also making the alloy to a single β phase structure at room temperature. With less than 15% of vanadium, a martensitic structure is generated during the solution treatment by quenching, such as water-cooling from a high temperature where β phase exists, and significantly deteriorates the cold workability. When it exceeds 25%, the age hardenability of a β type alloy is deteriorated and this results in extending the time required for the aging treatment. An insufficient strength could sometimes be obtained even after the aging treatment. Moreover, the deformation resistance in cold working of the alloy is increased.

Al: 2.5 to 5%

[0025] A β type alloy is finally reinforced by the aging treatment. At that time, Al is included therein in order to attain a sufficient increase in strength. Al also effects the suppressing precipitation of ω phase that makes the alloy brittle and promotes the precipitation of α phase during the aging treatment. Such effects are insufficient with less than 2.5%, of Al. When it exceeds 5%, the hardness in β state is increased, and, consequently reduces the cold workability. Accordingly, the content of Al is set 2.5 to 5%.

Sn: 0.5 to 4%

[0026] Sn has the same effect as the above Al. Sn does not increase hardness in β state more than Al. Sn that can suppress the increase in deformation resistance can also substitute a part of Al. Since such an effect of Sn is reduced as the content of Sn is smaller, the content is set to 0.5% or more. On the other hand, since the hardness of a β type alloy is increased as the content of Sn becomes larger, the content is set up to 4%.

O (Oxygen): Not more than 0.20%

[0027] O deteriorates the deformability of the alloy causing cracking during the cold working with a strong rolling reduction and increases the deformation resistance. Although the smaller amount is better, the content of Oxygen limited to not more than 0.20%, thereby making undesirable effects inconspicuous. It is more desirably set to not more than 0.12%.

H: Not more than 0.03%

[0028] H not only retards the precipitation of α phase during aging treatment but also reduces the age strengthening.

It also deteriorates the ductility and toughness. Therefore, a smaller amount of H is preferred. However, the β type Ti-20V-4Al-1Sn alloy easily absorbs hydrogen not only during the pickling process but also outside of pickling process. Particularly when producing a thin plate of the alloy, it is difficult to reduce the content of H to an amount below 0.005%, because of descaling by pickling. Accordingly, the upper value is limited to 0.03%, which does not make a serious impact. A content of not more than 0.01% is desirable. The lower limit value is not particularly determined.

Examination examples of the influence on age hardening of the hydrogen content are shown below.

[0029] A hot rolled plate 5 mm thick of an alloy having a chemical composition consisting of V: 20.0%, Al: 3.2%, Sn: 1.0%, O: 0.11%, H: 0.015%, Fe: 0.10%, C: 0.01%, N: 0.01%, and the balance Ti and impurities was solution-treated, followed by steel shot blasting. Thereafter, the aging treatment was carried out at 450°C, where the hydrogen content varied by varying the pickling time. The solution treatment comprises heating at 850°C for 5 minutes in the atmosphere followed by cooling with water.

[0030] The examination result of the change in hardness, depending on the aging time, is shown in Fig. 1. The hardness Hv represents the Vickers hardness of a test load of 1 kgf.

[0031] When the hydrogen content is 0.015% or 0.025%, as is apparent from Fig. 1, the alloy is saturated with an intended hardness by a 12-hour aging treatment. In contrast, when the hydrogen content is 0.040% or 0.065%, the alloy does not reach a sufficient hardness even if it is treated for 20 hours. These alloys require an extended aging treatment, exceeding 20 hours, if they reach the same hardness as obtained in the alloy with a hydrogen content of 0.015% or 0.025%. When the hydrogen content is 0.100%, the alloy can be scarcely hardened as shown in Fig. 1.

[0032] From the above experimental results, the content of H in the alloy is desirably suppressed to 0.03% or less.
Fe: Not more than 0.40%

[0033] Since Fe stabilizes the β phase and retards the age hardening as well as hydrogen and further increases the deformation resistance, the smaller amount is better. Since hydrogen is inevitable included as described above, the upper limit of the content of Fe is set up to 0.40%, which never causes a remarkable increase in deformation resistance. The further desirable Fe content is not more than 0.15%.

C: Not more than 0.05%

[0034] Since C significantly reduces the ductility or deformability, the smaller amount is better. The upper limit of the content is set up to 0.05%, which never causes a remarkable reduction in deformability. The content of further desirably is not more than 0.03%.

N: Not more than 0.02%

[0035] Since N significantly reduces the deformability, a smaller amount is better. The upper limit of the content is set up to 0.02%, which never causes a remarkable reduction in deformability.

[0036] The impure elements O, Fe, C and N are derived from a sponge titanium which is a raw material, and increased in the following melting or high temperature heating processes of the alloy. Therefore, the contents of the impure elements in the alloy are never reduced to less than the level of the contents in the raw material. Accordingly, it is necessary to select a sponge titanium with smaller contents of impurities and reduce the contamination in the manufacturing process as much as possible.

Zr, Mo, Nb, Ta, Cr, Mn, Ni, Pd and Si

[0037] The alloy, according to the present invention, may contain, in addition to V, Al and Sn, less than 3% of at least one element selected from a group consisting of Zr, Mo, Nb, Ta, Cr, Mn, Ni, Pd and Si within a range that never impairs the working effect of the present invention. These elements contribute to an improvement in the strength of the alloy after aging treatment without impairing the deformability and other characteristics of the alloy of the present invention. The desirable content of each element is 0.1-1%.

[0038] The average grain size in the alloy made to β type by solution treatment is desirably 20-130 μm . With less than 20 μm , the deformation resistance is increased which makes a working difficult. With larger than 130 μm , the alloy tends to crack during working because the deformability is reduced, and this causes a lack of strength even after aging. The aging treatment is usually carried out at a temperature of 400 to 500°C. By setting the grain size of β phase to the above range, the α phase precipitated by aging can have a grain size in a preferable range of 0.02 to 0.2 μm , which provides excellent strength and toughness.

[0039] The desirable average grain size can be obtained by using the manufacturing condition described below.

[0040] The alloy plate of the present invention is manufactured by forging an alloy having a required chemical composition, hot rolling it followed by cold rolling, and then performing a solution treatment. In order to form a β alloy of the above average grain size that is excellent in cold workability or deformability with low deformation resistance, the manufacturing condition is desirably set as follows.

[0041] The heating temperature in the hot rolling is preferably set from 900 to 1050°C. If the temperature is lower than 900°C, the deformation resistance during hot working is too large a load on the working facility, and also if the temperature exceeds 1050°C, the oxidation during heating causes not only a reduction in yield but also a roughing of

the crystal grains, which affects the alloy characteristics after working. The temperature during hot working is desirably within the range of 750 to 1050°C persisting the temperature of not less than β transits, although there might be a drop in the temperature during the non-heating time between deformation works, and an increase in temperature caused by working heat.

[0042] After hot working, a quenching such as water cooling at an average cooling rate of not less than 30°C /min is preferably performed, because a slow cooling causes precipitation and hardening of α phase and makes it impossible to uncoil the coiled plate of the alloy. In order to attain sufficient softening in the following process of cold rolling or cold drawing, the alloy is solution-treated for descaling through a continuous pickling and annealing device. The solution treatment, that is β treatment, desirably comprises heating to 750-950°C followed by water-cooling, because a temperature lower than 750°C might be insufficient to form the single β phase, and a temperature exceeding 950°C might cause roughing of the crystal grains. The heating time of the solution treatment is preferably 1 to 30 minutes in order to sufficiently solution-treat the alloy and avoid useless heating.

[0043] When the hot working temperature becomes close to or lower than the β transits temperature, and the temperature in the continuous pickling and annealing device becomes close to 750°C, the average grain size becomes smaller than 20 μm , therefore, it is desirable to avoid such a temperature. When high strength after aging treatment is required, even if there is a slight sacrifice in the cold workability, the average grain size could be smaller than 20 μm , which is obtained by setting the hot working temperature to the β transits or lower and the temperature in the continuous pickling and annealing device close to 750°C. For example, the average grain size of 10 μm might be available.

[0044] For the descaling, grinding by use of a coil grinder is preferable because it involves no hydrogen absorption, but the cost is increased because of its poor productivity. Therefore, descaling by pickling should be carried out while avoiding the inclusion of hydrogen as much as possible.

[0045] It is preferred to adopt a pickling condition capable of performing not only sufficient descaling but also the removal of α case while minimizing the absorption of hydrogen to manufacture a plate having a comely surface by cold rolling. The α case means a hard and brittle oxygen rich layer formed by intrusion of oxygen to the surface of the β -titanium alloy.

[0046] A preferred example of a pickling condition is mentioned in the following of (1) to (3):

(1) Prior to pickling, shot blasting is carried out.

(2) Pickling is carried out in an aqueous solution including 3-40 mass% of HF at 20 to 70°C within 10 minutes.

(3) Pickling is carried out in an aqueous solution of nitric fluoric acid including 3-6 mass% of HF and 5-20 mass% of HNO_3 at 20-70°C within 20 minutes.

[0047] The shot blasting of item (1) above is not always necessary. However, if a light shot blasting is performed, the pickling time might be shortened because the oxidized scales are thereby cracked.

[0048] The aqueous solution of item (2) above may include, in addition to 3 to 40 mass% of HF, a reducing agent such as nitric acid and hydrogen peroxide, which suppresses absorption of hydrogen. A waste solution which is produced in a semiconductor manufacturing process is also available, which includes a reducing agent such as acetic acid in addition to fluoric acid.

[0049] The aqueous solution of item (3) above could include a reducing agent such as hydrogen peroxide and acetic acid in addition to 3 to 6 mass% of HF and 5 to 20 mass% of HNO_3 .

[0050] The pickling of item (2) above is carried out first in an aqueous solution that contains mainly fluoric acid. The pickling by fluoric acid is effective to remove the oxidized scales, but the absorption of hydrogen is excessive especially during the removal of the α case by pickling. Accordingly, the pickling of item (2) above is should be limited within 10 minutes in order to leave the α case, and then the pickling of item (3) above is successively carried out. The oxygen rich layer formed under the oxidized scales, that is the α case, can be efficiently removed by the nitric fluoric acid solution. Although the pickling by the nitric fluoric acid solution has an advantage of little absorption of hydrogen due to the reducing effect of nitric acid, the time, required for the removal is extended when the amount of oxidized scales is excessive, whereby local corrosion might progress and lead to a rough surface. Therefore, after the pickling of item (2) above by the aqueous solution mainly containing fluoric acid, the pickling of item (3) above by the nitric fluoric acid solution is carried out. However, since the absorption of hydrogen is also increased, even with the nitric fluoric acid, if the treatment is extended over a long time, the pickling is preferably carried out within 20 minutes.

[0051] In the above picklings, the temperature is set from 20 to 70°C, because, at a temperature lower than 20°C, the removal of the scales or oxygen rich layer requires too much time, and because, at a temperature exceeding 70°C, the surface is remarkably roughed and evaporation of the acid is also increased. With a concentration of HF of less than 3 mass%, the reaction speed is too slow in both the solutions of the pickling of items (2) and (3) above. On the other hand, when it exceeds 40 mass%, the reaction becomes too severe in the solution of the pickling of item (2) above, which may cause a danger, and also it is difficult to make an adjustment of corrosion quantity. In the solution of the pickling of item (3) above; if it exceeds 6 mass%, the surface roughing after pickling becomes remarkable. In

the pickling of item (3) above; if 5-20 mass% of NHO_3 is added to the solution, it is effective to suppress the hydrogen absorption. With less than 5 mass%, this effect is insufficient, and when it exceeds 20 mass%, the effect is unnecessarily saturated.

[0052] Since the hydrogen amount is suddenly increased when the dipping time in the pickling is extended, a generation of the scales in heating should be suppressed as much as possible. When the amount of scales is excessive, a mechanical scale removing method such as grinding can be used in combination.

[0053] The cold working is desirably carried out at a reduction rate of 30% or more to produce a grain size of 130 μm or less by β treatment after working. In case of the plate the rolling reduction rate is 30% or more, and in case of the bar the reduction rate of area is 30% or more. Although the reduction rate could be higher, this alloy has its own upper limit of reduction rate that is caused by its own work hardenability of the alloy.

[0054] The β phase treatment after cold rolling is preferably performed by the solution treatment of heating in a temperature of 750 to 900°C and then cooling at the cooling rate of air cooling or a more rapid cooling rate, which simultaneously performs annealing. The reason why the heating temperature of 750-900°C is desirable is that the β phase treatment is insufficient when the temperature is too low, and the grain size becomes rough when the temperature is too high, similarly to the case of the heating temperature range in the above-mentioned solution treatment before cold working. Since an excessively short or long heating time similarly causes an insufficient β phase treatment or roughing of the grain size, the heating time is preferably set from 1 to 30 minutes. The heating in the solution treatment after cold rolling is desirably carried out in vacuum or in inert gas such as highly pure Ar or He. A heating in a condition causing oxidation of the surface requires removal of the oxidized film, or a pickling by nitric fluoric acid for descaling. As a result, the hydrogen content in the alloy exceeds the upper limit by intrusion of hydrogen to the alloy.

[0055] After hot rolling, the solution treatment is usually carried out prior to cold rolling. However, the alloy could be worked into the required shape in a cold rolled state and then aged. In this case, a highly strong part with minute crystal grains can be formed.

[0056] The aging treatment for reinforcing the β type alloy of the present invention is preferably carried out at 400-500°C. Although the aging precipitates a minute α phase, the age hardening requires an excessive time at a temperature lower than 400°C, and therefore, the ductility after age hardening is extremely reduced. As a result, the toughness deteriorates and the α phase becomes rough at a temperature higher than 500°C which reduces the strength.

EXAMPLES

[0057] Titanium alloys which have compositions shown in Tables 1 and 2 were melted in a vacuum arc melting furnace with a water-cooled copper crucible consumable-electrode, and produced ingots which are 140 mm in diameter. The ingots were heated to 1000°C followed by hot forging to form hot rolled materials 50mm in thickness and 150mm in width. These materials were heated to 950°C followed by hot rolling, and the rolling ended at 800°C. They were immediately cooled to 300°C at an average cooling rate of 200°C /min by a water spray cooling method, and allowed to stand cool. The resulting hot rolled plates were subjected to a solution treatment of "heating at 880°C for 10 minutes followed by water cooling".

[0058] After the solution treatment, the plates were shot blasted, dipped for 4 minutes in an aqueous solution of 30°C fluoric acid including 4 mass% of HF, and successively dipped for 10 minutes in an aqueous solution of 30°C of nitric fluoric acid including 10 mass% of NHO_3 and 4 mass% of HF in order to remove the scales and oxygen rich layers. After grinding both of the surfaces, cold rolling at a reduction rate of 80% was carried out to reduce the thickness to 3 mm.

Table 1

Test No.	Chemical Composition (mass%)								Edge cracking during cold rolling	After solution treatment		After aging	
	V	Al	Sn	O	H	Fe	C	N	others	Tensile strength (Mpa)	Grain size (μm)	Tensile strength (Mpa)	Elongation (%)
1	16.0	3.2	1.0	0.10	0.020	0.10	0.01	0.01	—	735	90	1250	12.5
2	20.0	3.2	1.0	0.11	0.015	0.11	0.01	0.01	—	700	80	1230	12.6
3	24.2	3.2	1.2	0.09	0.010	0.11	0.02	0.02	—	725	70	1220	12.9
4	20.0	2.5	1.0	0.09	0.022	0.10	0.01	0.01	—	676	80	1200	13.0
5	20.0	4.0	1.1	0.11	0.021	0.09	0.01	0.01	—	725	60	1320	10.5
6	20.0	3.0	1.9	0.10	0.018	0.09	0.01	0.01	—	720	70	1250	12.1
7	20.0	3.0	1.0	0.08	0.028	0.10	0.01	0.01	—	685	70	1230	14.5
8	20.0	3.2	1.0	0.11	0.015	0.10	0.01	0.01	—	700	60	1270	12.5
9	20.0	3.2	1.0	0.11	0.020	0.05	0.02	0.02	—	685	70	1265	12.3
10	20.2	3.4	1.0	0.10	0.006	0.11	0.02	0.01	—	700	60	1285	12.8
11	20.2	3.4	1.0	0.10	0.007	0.11	0.01	0.01	—	705	60	1285	13.0
12	20.2	3.3	1.0	0.10	0.008	0.11	0.01	0.02	—	695	70	1280	12.8
13	20.2	3.3	1.0	0.10	0.007	0.13	0.01	0.02	—	695	70	1280	12.9
14	20.2	3.3	1.0	0.10	0.020	0.11	0.01	0.02	Zr:0.3	720	65	1290	12.8
15	20.2	3.3	1.0	0.10	0.021	0.13	0.01	0.02	Cr:0.4	740	65	1290	12.9
16	20.2	3.3	1.0	0.10	0.020	0.11	0.01	0.02	Mo:0.3	730	65	1290	12.8
17	20.2	3.3	1.0	0.10	0.021	0.13	0.01	0.02	Pd:0.1	740	65	1290	12.5
18	20.2	3.3	1.0	0.10	0.020	0.11	0.01	0.02	Cr:0.4	745	65	1295	12.5
19	20.2	3.3	1.0	0.10	0.021	0.13	0.01	0.02	Zr:0.3	745	60	1300	12.3
									Cr:0.2				
									Zr:0.2				
									Cr:0.2				
									Nb:0.2				

Table 2

Test No.	Chemical Composition (mass%)								Edge cracking during cold rolling	After solution treatment		After aging	
	V	Al	Sn	O	H	Fe	C	N	others	Tensile strength (Mpa)	Grain size (μm)	Tensile strength (Mpa)	Elongation (%)
20	20.0	3.2	1.0	0.11	*0.042	*0.41	*0.06	*0.05	—	small	50	1090	9.5
21	20.0	3.2	1.0	0.11	*0.060	0.10	0.02	0.01	—	no	70	905	14.8
22	20.0	3.2	1.0	0.11	0.020	*0.45	0.02	0.02	—	no	65	1100	12.1
23	20.0	3.2	1.0	0.11	0.022	0.10	*0.07	0.02	—	small	60	unmeasured	unmeasured
24	20.0	3.2	1.0	0.11	0.018	0.11	0.01	*0.12	—	small	70	unmeasured	unmeasured
25	*12.0	3.0	1.0	0.10	0.020	0.12	0.01	0.01	—	large	100	unmeasured	unmeasured
26	20.1	*6.0	1.0	0.10	0.015	0.12	0.01	0.01	—	large	60	unmeasured	unmeasured
27	20.1	3.0	*5.0	0.10	0.010	0.11	0.01	0.01	—	small	60	1250	6.5
28	20.1	3.0	1.0	*0.30	0.022	0.09	0.01	0.01	—	large	60	unmeasured	unmeasured
29	*27.1	3.0	1.0	0.10	0.021	0.11	0.02	0.02	—	no	60	1100	18.5
30	20.0	3.0	1.2	0.10	*0.060	0.11	0.02	0.02	—	no	65	900	15.0
31	20.0	3.0	1.2	0.10	0.020	0.11	0.02	0.02	*Zr:4.0	large	65	unmeasured	unmeasured
32	15.0	3.0	3.0	0.12	0.017	0.11	0.01	0.01	*Cr:3.0	no	90	1280	11.0
33	*4.0	*6.0	—	0.12	0.015	0.10	0.01	0.01	—	large	55	unmeasured	unmeasured

[notes] * shows out of scope of the present invention.

[0059] The hydrogen amounts shown in the tables are values obtained by analyzing samples after the cold rolling. The deformability of the solution treated β type alloy was determined from the state of edge cracking caused by cold rolling. Test Nos. 20, 21 and 30 were dipped for 15 minute, instead of 4 minutes, in an aqueous solution of 30°C of fluoric acid including 4 mass% of HF in order to increase the hydrogen amount.

[0060] After the cold rolling, an annealing and solution treatment of heating at 850°C in vacuum for 5 minutes followed by water cooling was carried out, and tensile test pieces of JIS No. 13B were picked from the resulting plates, and the tensile strength was measured. The deformation resistance in working can be estimated from the magnitude of this tensile strength.

[0061] Further, an aging treatment of heating at 475°C for 20 hours was performed to the plates in which a large edge cracking did not take place during the cold rolling. The tensile test pieces JIS No. 13B were picked from the aged plates, and the tensile strength and elongation were measured. The results of the measurements are also shown in Tables 1 and 2.

[0062] It is apparent from the results of Tables 1 and 2, each of Test Nos. 1 to 24 has the same main composition as that of the Ti-20V-4Al-1Sn alloy. Compared with Test Nos. 20 to 33, Test Nos. 1 to 19 are excellent in cold workability and also in strength and elongation after aging. This is the effect caused by limiting the contents of H, Fe, C and N which were not controlled in the past, showing the importance of minimizing the contents of these elements.

INDUSTRIAL APPLICABILITY

[0063] According to the present invention, a typical β -type Ti-20V-4Al-1Sn alloy can be made into an alloy which is further excellent in deformability with less deformation resistance. This can substantially reduce the manufacturing cost of a high strength titanium alloy product by extending the life of a roll or die in cold rolling and in a cold working, such as cold rolling, or extending the life of a metal mold in cold forging.

[0064] The titanium alloy according to the present invention can be suitably used as not only a material for industrial equipment, such as an automotive valve gear member or aerospace plane parts, but also as a material for daily commodities, such as a glass frame, or athlete equipment such as a golf club head.

[0065] According to the manufacturing method of the present invention, a cold rolled product of a titanium alloy, having a stable quality, can be manufactured.

Claims

1. A β type titanium alloy **characterized by** consisting of, by mass %, V: 15 to 25%, Al: 2.5 to 5%, Sn: 0.5 to 4%, O (Oxygen): not more than 0.20%, H: not more than 0.03%, Fe: not more than 0.40%, C: not more than 0.05% and N: not more than 0.02%, and the balance Ti and impurities.

2. A β type titanium alloy **characterized by** consisting of, by mass %, V: 15 to 25%, Al: 2.5 to 5%, Sn: 0.5 to 4%, O (Oxygen): not more than 0.12%, H: not more than 0.03%, Fe: not more than 0.15%, C: not more than 0.05% and N: not more than 0.02%, and the balance Ti and impurities.

3. A β type titanium alloy **characterized by** consisting of, by mass %, V: 15 to 25%, Al: 2.5 to 5%, Sn: 0.5 to 4%, O (Oxygen): not more than 0.20%, H: not more than 0.03%, Fe: not more than 0.40%, C: not more than 0.05% and N: not more than 0.02%, and less than 3% of at least one element selected from Zr, Mo, Nb, Ta, Cr, Mn, Ni, Pd and Si, and the balance Ti and impurities.

4. A method of manufacturing a β type titanium alloy **characterized by** comprising the following steps (a) to (c):

(a) Preparing a β type titanium alloy consisting of, by mass %, V: 15 to 25%, Al: 2.5 to 5%, Sn: 0.5 to 4%, O (Oxygen): not more than 0.20%, H: not more than 0.03%, Fe: not more than 0.40%, C: not more than 0.05% and N: not more than 0.02%, and the balance Ti and impurities.

(b) Pickling the β type titanium alloy in an aqueous solution including 3 to 40 mass % of HF, and

(c) Further pickling the β type titanium alloy in an aqueous solution including 3 to 6 mass % of HF and 5 to 20 mass% of HNO_3 .

5. A method of manufacturing a β type titanium alloy **characterized by** comprising the following steps (a) to (c):

(a) Preparing a β type titanium alloy consisting of, by mass %, V: 15 to 25%, Al: 2.5 to 5%, Sn: 0.5 to 4%, O (Oxygen): not more than 0.20%, H: not more than 0.03%, Fe: not more than 0.40%, C: not more than 0.05%

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and N: not more than 0.02%, and less than 3% of at least one element selected from Zr, Mo, Nb, Ta, Cr, Mn, Ni, Pd and Si, and the balance Ti and impurities.

(b) Pickling the β type titanium alloy in an aqueous solution including 3 to 40 mass % of HF, and

(c) Further pickling the β type titanium alloy in an aqueous solution including 3 to 6 mass % of HF and 5 to 20 mass% of HNO_3 .

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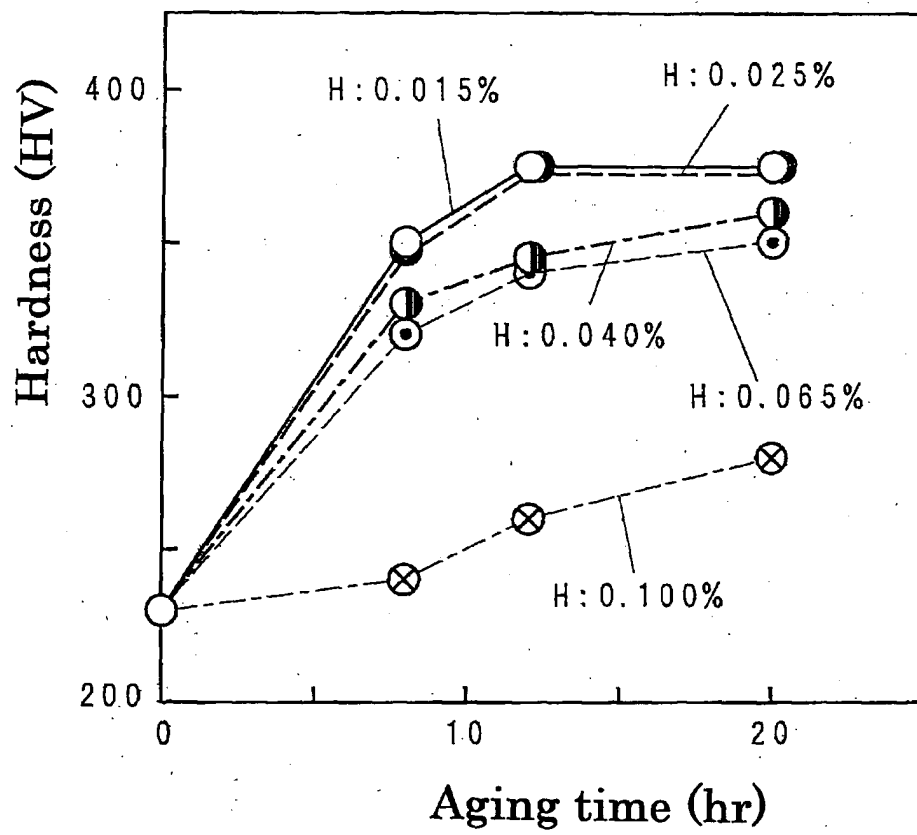
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Fig. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP03/07297

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ C22C14/00, C23G1/12		
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 C22C14/00, C23G1/12		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-2003 Kokai Jitsuyo Shinan Koho 1971-2003 Jitsuyo Shinan Toroku Koho 1996-2003		
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.
X Y	JP 2-129331 A (Sumitomo Metal Industries, Ltd.), 17 May, 1990 (17.05.90), Full text (Family: none)	1, 2 4, 5
X Y	JP 9-324247 A (The Society of Japanese Aerospace Companies (SJAC)), 16 December, 1997 (16.12.97), Full text (Family: none)	3 4, 5
X Y	JP 6-264204 A (Nippon Mining & Metals Co., Ltd.), 20 September, 1994 (20.09.94), Full text (Family: none)	1-3 4, 5
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "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) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "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 "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 "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 "&" document member of the same patent family		
Date of the actual completion of the international search 26 June, 2003 (26.06.03)		Date of mailing of the international search report 15 July, 2003 (15.07.03)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP03/07297

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6267831 B1 (Kobe Steel, Ltd.), 31 June, 2001 (31.06.01), Examples 1, 2; tables 1, 5 & JP 2000-355781 A	4, 5
A	JP 62-180091 A (Mitsubishi Metal Corp.), 07 August, 1987 (07.08.87), Claims; page 2, lower right column, line 11 to page 3, upper left column, line 10 (Family: none)	4, 5

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