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London WC1R 5JJ (GB)**(54) **TITANIUM ALLOY AND METHOD OF MANUFACTURING TITANIUM ALLOY MATERIAL**

(57) Titanium alloys with a sufficient cold workability and excellent superplasticity characteristics as shown in the (1) and (2) below, and a method for manufacturing a titanium alloy material as shown in the (3) below are provided.

(1) A titanium alloy consisting of, by mass %, Al of 2.0 to 4.0%, V of 4.0 to 9.0%, Zr of 0 to 2.0%, Sn of 0 to 3.0% and the balance being Ti and impurities.

(2) A titanium alloy consisting of, by mass %, Al of 2.0 to 4.0%, V of 4.0 to 9.0%, Zr of 0 to 2.0%, Sn of 0 to 3.0%, further one or more elements selected from Fe of 0.20 to 1.0%, Cr of 0.01 to 1.0%, Cu of 0.01 to 1.0% and Ni of 0.01 to 1.0%, and the balance being Ti and impurities, wherein V_{eq} obtained by the following equation (1) is in a range of 4.0 to 9.5:

$$V_{eq} = V + 1.9Cr + 3.75Fe \quad \cdots (1)$$

where a symbol on a right side of the equation (1) means a content of each element.

(3) A method for manufacturing titanium alloy materials, wherein the titanium alloy described in (1) or (2) is subjected to a cold working at a cross-section reduction rate of 40% or more.

EP 1 772 528 A1

Description

Technical Field of the Invention

[0001] The present invention relates to titanium alloys in use in chemical industry members such as machine structure members and heat exchanger members and consumer goods members such as golf clubs, and a method for manufacturing titanium alloy materials. The present invention particularly relates to titanium alloys with an excellent cold workability and superplasticity characteristics, and a method for manufacturing the titanium alloy materials.

Background Art

[0002] Heat exchangers are instruments capable of transmitting thermal energy between different fluids. The heat exchangers are used in, for example, air conditioners, refrigerators, air preheating equipment of burners, radiators in automobiles, parts for the chemical industry, parts for seawater and the like. In particular, heat exchangers made of titanium are used in fields requiring excellent corrosion resistance such as in the chemical industry or in salt water. In order to reduce the size of heat exchangers, it is necessary to increase the strength of the parts being used and that is why titanium alloy which are light and strong are used as a material for such heat exchangers.

[0003] A Ti-6Al-4V alloy has been widely used as the heat exchanger material due to its excellent superplasticity characteristics as described in, for example, Non-patent document 1. However, this alloy has poor cold workability. For example, when thin plates are manufactured by cold rolling the Ti-6Al-4V alloy plate which is wrapped around a coil, there is a drawback that the number of intermediate annealing needs to be increased.

[0004] Non-patent document 2 shows that a Ti-9V-2Mo-3Al alloy is a titanium alloy which has an excellent cold workability and also an excellent superplasticity workability. However, this alloy contains Mo as an essential element, which results in a high cost of raw materials. Also, because of a high melting point of Mo, there is a higher incidence of unmelted portions or solidification segregation in melting.

[0005] Patent document 1 describes a titanium alloy with excellent superplasticity workability containing, by mass %, Al of 5.5 to 6.5%, V of 3.5 to 4.5%, O of 0.2% or less, Fe of 0.15 to 3.0%, Cr of 0.15 to 3.0% and Mo of 0.85 to 3.15%, in which Fe, Cr and Mo are within a range represented by a specific equation and an average grain diameter of an α crystal is $6\mu\text{m}$ or less. This alloy can be said to be superior to the Ti-6Al-4V alloy in the superplasticity workability, but the cold workability is not considered. Namely, this alloy has a high content of Al which is 5.5% or more, which results in high deformation resistance in the cold rolling and a high possibility of cracks occurring in the edges of a plate if this alloy is subjected to cold rolling process at a cross-section reduction rate of 50%.

[0006] Patent document 2 describes a titanium alloy with excellent workability which contains, by mass %, Al of 3.0 to 5.0%, V of 2.1 to 3.7%, Mo of 0.85 to 3.15%, O of 0.15% or less, and further one or more elements of Fe, Cr, Ni and Co, in which the content of these elements is in a range represented by a specific equation. There is also described a manufacturing method of a titanium alloy material in a specific hot rolling condition, and a superplastic processing method of the titanium alloy material in the specific heat treatment condition. However, since this alloy contains Mo, there will be the same problem with the alloy described in Non-patent document 2.

[0007]

Patent document 1: Japanese Examined Patent Publication No. 1996-19502B

Patent document 2: Japanese Examined Patent Publication No.1996-23053B

Non-patent document 1: N. Furushiro and three other persons, 'Titanium' 80, 1980, pp. 993-998, published by Metallurgical Society of AIME

Non-patent document 2: T. Oka and 2 other persons, "What is being studied about titanium materials in Japan?", pp. 58-60, edited on Dec. 1, 1989 by The Iron and Steel Institute of Japan

Disclosure of the Invention

Problem to be solved by the Invention

[0008] An object of the present invention is to provide titanium alloys with the excellent cold workability and the superplasticity characteristics and a method for manufacturing the titanium alloy materials.

Means adapted to solve the problem

[0009] The present invention was accomplished as a result of repeated research made by the present inventors based on a Ti-3Al-2.5V alloy which is said to have the excellent cold workability.

[0010] The present invention is characterized by titanium alloys as shown in (1) and (2) below, and a method for manufacturing a titanium alloy materials as shown in (3) below.

[0011]

(1) A titanium alloy consisting of, by mass %, Al of 2.0 to 4.0%, V of 4.0 to 9.0%, Zr of 0 to 2.0%, Sn of 0 to 3.0% and the balance being Ti and impurities.

[0012]

(2) A titanium alloy consisting of, by mass %, Al of 2.0 to 4.0%, V of 4.0 to 9.0%, Zr of 0 to 2.0%, Sn of 0 to 3.0%, further one or more elements selected from Fe of 0.20 to 1.0%, Cr of 0.01 to 1.0%, Cu of 0.01 to 1.0% and Ni of 0.01 to 1.0%, and the balance being Ti and impurities, wherein V_{eq} obtained by the following equation (1) is in a range of 4.0 to 9.5:

$$V_{eq} = V + 1.9Cr + 3.75Fe \quad \cdots (1)$$

where a symbol on a right side of the equation (1) means a content of each element.

[0013]

(3) A method for manufacturing titanium alloy materials is characterized in that the titanium alloy described in the above (1) or (2) is subjected to the cold working at a cross-section reduction rate of 40% or more.

Effect of the Invention

[0014] A titanium alloy of the present invention has a sufficient cold workability as well as the excellent superplasticity characteristics. Therefore, it is possible to easily produce a coil by the cold rolling, and a material for a super-plastic application, having a uniform distribution in a plate thickness, can be manufactured. Therefore, it is possible to easily produce thin plates made of titanium alloy at a low cost, allowing for the expansion of an application field for the titanium alloy thin plates.

Best mode for carrying out the invention

[0015] First, chemical compositions in the titanium alloy of the present invention and the reasons for the limitation will be described. "%" in each component means "mass %" in the following explanation.

[0016] Al: 2.0 to 4.0%

Al is an element that plays a very important role in increasing the strength of the titanium alloy. Al is also an effective element for stabilizing the α phase of the titanium alloy. The superplasticity characteristics are exhibited in a temperature range in which the ratio of the α phase and the β phase is approximately 50/50. If the content of Al is low, this temperature range is narrowed, which results in difficulties obtaining stable superplasticity characteristics. The content of Al needs to be 2.0% or more so as to obtain the superplasticity characteristics in a wider temperature range. However, the cold workability reduces as the content of Al increases. In particular, if a titanium alloy in which the content of Al exceeds 4.0% is subjected to the cold working at a cross-section reduction rate of about 50%, the edge cracks occur in the edges of the plate. Therefore, the content of Al is limited to 2.0 to 4.0%.

[0017] V: 4.0 to 9.0%

V is an effective element for stabilizing the β phase of titanium alloys, and has an effect of increasing the ratio of the β phase in a temperature range of about 800 to 850 °C. In particular, if the content of V is 4.0% or more, the temperature range in which the ratio of the α phase and the β phase is approximately 50/50 can be increased. However, if the content of V exceeds 9.0%, oxidation resistance characteristics of the titanium alloy material are deteriorated. This is because an oxide of V has a sublimation property, so that a scale generated on the surface of the alloy is not dense but has a high permeability of oxygen if the titanium alloy in which the content of V exceeds 9.0% is exposed to a high temperature. Therefore, cracks occur more easily on the surface of the alloy, and a high temperature ductility is decreased. Accordingly, the content of V is limited to 4.0 to 9.0%.

[0018] Zr: 0 to 2.0%

Zr is an element that may not be necessarily added. If Zr is added, it contributes to strengthen the titanium alloy due to a solid solution strengthening effect thereof. If a titanium alloy containing Zr is exposed to the high temperature, a strong

Zr oxide is formed on the surface thereof to suppress oxidation inside the alloy, so that a generation of the cracks can be prevented in a deformation of the titanium alloy at the high temperature. Therefore, elongation of the titanium alloy is increased at the high temperature, and the superplasticity characteristics are improved. These effects are largely exhibited in 0.5% or more. However, Zr is an expensive element, and the oxidation suppression effect described above is saturated if the content of Zr exceeds 2.0%, leading to a cost increase. Therefore, if Zr is contained, the content is preferably limited to 2.0% or less.

[0019] Sn: 0 to 3.0%

Sn is also an element that may not be necessarily added. Although Sn does not contribute to stabilize the α phase or the β phase, it is an element that contributes to strengthen the titanium alloy. To obtain such effect of Sn, the content is preferably 0.2% or more. However, if the content of Sn exceeds 3.0%, a low melting point region is formed in solidification process, and the cracks occur from this region as a starting point. Therefore, if Sn is contained, the content is preferably 3.0% or less.

[0020] The titanium alloy of the present invention has the chemical compositions described above, and the balance being Ti and impurities. The alloy may contain one or more elements selected from Fe of 0.20 to 1.0%, Cr of 0.01 to 1.0%, Cu of 0.01 to 1.0% and Ni of 0.01 to 1.0% as substitute for a part of Ti. This is based on the following reasons.

[0021] Fe and Cr are elements contained, as impurities, in a titanium sponge which is a titanium raw material, or in an aluminum-vanadium alloy which is an additional material. Therefore, Fe of less than 0.20% and Cr of less than 0.01% are contained in the titanium alloy even if these elements are not positively added. These elements are a β -phase stabilizing element having the same effect as V, but they are cheaper than V. Accordingly, cost reduction can be realized by positively adding these elements, so that it is desirable to contain Fe of 0.20% or more and Cr of 0.01% or more. However, Fe and Cr are a eutectoid type element forming an intermetallic compound in the titanium alloy. If Fe and Cr of exceeding 1.0% are respectively contained, there will be embrittlement caused by excessive precipitations of the intermetallic compound.

[0022] Cu and Ni are a β stabilizing element in the same manner with V, and an effective element to increase the ratio of the β phase in a temperature range of 800 to 850 °C. These elements are cheaper than V, and can be added as an alternative element of V. It is desirable to contain Cu of 0.01% or more and Ni of 0.01% or more in order to obtain this effect. However, the intermetallic compound is formed and the cold workability is lowered if Cu and Ni of exceeding 1.0% are respectively added, because Cu and Ni are the eutectoid type element for titanium.

[0023] Accordingly, if one or more elements of these are contained in the titanium alloy of the present invention, the content is limited to Fe of 0.20 to 1.0%, Cr of 0.01 to 1.0%, Cu of 0.01 to 1.0% and Ni of 0.01 to 1.0%.

[0024]

$$V_{eq} (= V + 1.9Cr + 3.75Fe): 4.0 \text{ to } 9.5$$

As an index to exhibit the stability of the β phase in the titanium alloy, there is a V_{eq} represented by the following equation (1):

$$V_{eq} = V + 1.9Cr + 3.75Fe \quad \cdots (1)$$

where a symbol on the right side of the equation (1) means a content of each element.

[0025] If the V_{eq} is less than 4.0, the ratio of the β phase is lowered in a temperature range of 800 to 850 °C, and the superplasticity characteristics are hardly exhibited in this temperature range. However, if the V_{eq} exceeds 9.5, the ratio of the α phase is lowered, the superplasticity characteristics deteriorate in a temperature range of 800 to 850 °C and the specific gravity of the alloy itself increases. Accordingly, if Fe and/or Cr are contained to the titanium alloy of the present invention, it is necessary to limit V_{eq} in a range of 4.0 to 9.5.

[0026] O (oxygen), C (carbon), N (nitrogen) and H (hydrogen) are major impurities contained in the titanium alloy of the present invention. O is an impurity contained in the titanium sponge and a raw material of V, while C and N are impurities contained in the titanium sponge. Also, H is an impurity which is absorbed from an atmosphere in heating or absorbed in an acid pickling process. Impurities are preferably as low as possible in a range where O is 0.2% or less, C is 0.01% or less, N is 0.01% or less, and H is 0.01% or less.

[0027] Next, a method for manufacturing titanium alloy materials of the present invention will be explained referring to a case of manufacturing a thin plate. An ingot is prepared by an ordinary melting method such as VAR and is subjected to hot bloom forging or hot rolling so as to form a slab, after which hot rolling is conducted to prepare a hot coil, followed by the cold rolling to a target plate thickness and annealing to provide the titanium alloy material. The cold rolling is a

step that largely influences product characteristics, and a titanium alloy material with the excellent superplasticity characteristics at the high temperature can be obtained particularly by the cold working (cold rolling) at the cross-section reduction rate of 40% or more. This is based on the following reasons.

[0028] When the cross-section reduction rate is increased in the cold rolling, a crystal grain diameter in the titanium alloy, particularly a grain diameter of a pro-eutectoid α phase is decreased. Then, if the grain diameter in the titanium alloy is decreased, elongation is increased upon superplastic deformation at the high temperature, thereby the titanium alloy material with the excellent superplasticity characteristics at the high temperature is exhibited. As described above, when the cross-section reduction rate is increased in the cold rolling, the elongation upon superplastic deformation at the high temperature is sharply increased up to the cross-section reduction rate of about 40%, and less change is observed in a region of 40% or more.

[0029] Therefore, in the method for manufacturing the titanium alloy materials of the preset invention, the cold working is performed at the cross-section reduction rate of 40% or more. Although there is no particular upper limit in the cross-section reduction rate, when the cold rolling is performed at a cross-section reduction rate of exceeding 80%, the edge cracks occur in the edges of the plate. Accordingly, it is desirable in the cold working to limit the cross-section reduction rate in 80% or less. However, if the intermediate annealing is conducted for the purpose of recovering the ductility of materials, the cold working may be performed in a condition that the cross-section reduction rate exceeds 80%.

[0030] The cross-section reduction rate is obtained by the following equation (a).

$$\text{Cross-section reduction rate (\%)} = \left\{ \frac{\text{cross-section area before working} - \text{cross-section area after working}}{\text{cross-section area before working}} \right\} \times 100 \quad \dots (a)$$

Embodiment 1

[0031] Using an arc melting furnace of plasma, a button ingot with a width of 50 mm, a thickness of 15 mm and a longitude of 80 mm was prepared. After the button ingot was heated at 850 °C, it was subjected to hot rolling to prepare a hot-rolled plate with a thickness of 5 mm. After this hot-rolled plate was annealed at 750 °C for ten minutes, an oxide scale was removed by shot blast and acid pickling, and the surface was further machined to a thickness of 4mm by machining so as to prepare a material for the cold rolling. This material was subjected to the cold rolling to prepare a cold-rolled plate with a thickness of 2 mm. At this time, as an evaluation of cold-rolling property, presence of cracks in the edges on the surface of the cold-rolled plate was performed by visual observation.

[0032] A plate with no cracks in the cold rolling was subjected to a heat treatment in an argon atmosphere at 700 °C for 30 minutes, followed by cold rolling to a thickness of 1.5 mm, and again subjected to the heat treatment in the argon atmosphere at 700 °C for 30 minutes to provide a test specimen. From this test specimen, a plate type test piece with a thickness of 1.5 mm and a width of 12.5 mm in a parallel part was obtained so that the longitudinal direction of the test piece was in parallel to the rolling direction. The distance between gauge marks of this tensile test piece was set to be 20mm, and a tensile test was conducted at a test temperature of 800 °C and a tensile speed of 9 mm/min., so as to measure elongation at fracture.

[0033] Table 1 shows chemical compositions of the cold-rolled plate, evaluations of cold rolling property and elongation at fracture.

[0034]

[Table 1]

No.	Chemical composition (mass %, the balance being Ti and impurities)									Cold rolling property evaluation	Elongation at fracture		Remarks
	Al	V	Zr	Sn	Fe	Cr	Cu	Ni	Ve _q		Elongation (%)	Eval uation	
1	1.58*	5.08	-	-	-	-	-	-	5.5	○	180	×	Comparative example
2	2.05	4.96	-	-	-	-	-	-	5.4	○	320	○	Example of the present invention
3	3.00	4.98	-	-	-	-	-	-	5.6	○	440	○	Example of the present invention
4	3.96	4.90	-	-	-	-	-	-	5.5	○	470	○	Example of the present invention
5	4.20*	4.94	-	-	0.24	-	-	-	5.8	×	-	-	Comparative example
6	3.01	3.50*	-	-	-	-	-	-	4.1	○	160	×	Comparative example
7	3.05	4.12	-	-	-	-	-	-	4.8	○	295	○	Example of the present invention
8	3.00	7.02	-	-	-	-	-	-	7.7	○	400	○	Example of the present invention
9	2.98	8.88	-	-	-	-	-	-	9.4	○	320	○	Example of the present invention
10	3.01	5.05	-	-	0.50	-	-	-	6.9	○	355	○	Example of the present invention
11	3.03	4.98	-	-	0.98	-	-	-	8.7	○	275	○	Example of the present invention
12	3.02	5.11	-	-	1.20*	-	-	-	9.6*	○	150	×	Comparative example
13	2.99	4.97	-	-	-	0.485	-	-	6.3	○	335	○	Example of the present invention
14	2.97	4.96	-	-	-	0.95	-	-	7.2	○	300	○	Example of the present invention
15	2.99	5.00	-	-	-	2.21*	-	-	9.6*	×	-	-	Comparative example
16	3.02	5.01	-	-	0.50	1.15*	-	-	9.1	×	-	-	Comparative example
17	3.04	4.90	-	-	0.88	1.01*	-	-	10.2*	○	125	×	Comparative example
18	3.03	4.98	0.51	-	-	-	-	-	5.5	○	310	○	Example of the present invention
19	3.00	5.03	0.95	-	-	-	-	-	5.6	○	335	○	Example of the present invention

(continued)

No.	Chemical composition (mass %, the balance being Ti and impurities)								Cold rolling property evaluation	Elongation at fracture		Remarks
	Al	V	Zr	Sn	Fe	Cr	Cu	Ni		Eq	Elongation (%)	
20	3.05	4.98	1.88	-	-	-	-	-	○	5.4	340	○ Example of the present invention
21	3.00	5.01	-	-	0.98	-	-	-	○	8.7	275	○ Example of the present invention
22	3.03	5.05	-	-	-	-	0.05	-	○	5.6	420	○ Example of the present invention
23	3.01	5.02	-	-	-	-	0.98	-	○	5.6	435	○ Example of the present invention
24	3.02	4.98	-	-	-	-	1.13*	-	×	5.6	-	Comparative example
25	2.99	5.01	-	-	-	-	-	0.08	○	5.7	410	○ Example of the present invention
26	3.00	5.03	-	-	-	-	-	0.75	○○	5.7	405	○ Example of the present invention
27	2.99	5.05	-	-	-	-	-	1.28*	×	5.6	-	Comparative example
28	3.02	4.97	-	0.15	-	-	-	-	○	5.6	425	○ Example of the present invention
29	3.03	5.02	-	0.88	-	-	-	-	○	5.7	430	○ Example of the present invention
30	3.00	5.04	-	1.55	-	-	-	-	○	5.7	440	○ Example of the present invention
31	2.99	4.99	-	2.85	-	-	-	-	○	5.6	400	○ Example of the present invention
32	3.02	5.01	-	3.10*	-	-	-	-	×	5.6	-	Comparative example
33	3.01	6.51	-	-	0.90	-	-	-	○	9.9*	170	○ Comparative example
34	3.21	7.02	-	-	0.51	0.45	-	-	○	9.8*	165	○ Comparative example
35	3.11	7.55	-	-	-	0.95	-	-	○	10.0*	135	○ Comparative example

(1) [*] means outside of the range specified in the present invention
(2) [-] in the chemical composition means an impurity level, in which Fe is less than 0.20% and other than Fe is less than 0.01%.
(3) Examples with [×] in the cold rolling property had no tensile test conducted.

[0035] In the cold rolling property evaluation, a plate with no cracks is indicated as [○] and a plate with cracks is indicated as [×] when a cold-rolled plate with a thickness of 2 mm was prepared. Also, in the elongation at fracture, a plate of exceeding 200% in elongation at fracture is indicated as [○], and a plate of 200% or less in elongation at fracture is indicated as [×] when a tensile test was conducted at 800 °C.

[0036] As shown in Table 1, alloys satisfying the chemical compositions specified in the present invention are capable of being cold rolled to obtain an excellent superplastic elongation.

Embodiment 2

[0037] A material for cold rolling containing Al of 3.0%, V of 5.0% and the balance being Ti and impurities was prepared with a thickness of 4 mm in the same manner with Example 1.

[0038] The material for cold rolling was subjected to a cold rolling in different cross-section reduction rates to prepare cold-rolled plates with thicknesses of 3.5 mm, 3.0 mm, 2.5 mm, 2.0 mm and 1.5 mm. After these cold-rolled plates were subjected to the heat treatment in the argon atmosphere at 700 °C for 30 minutes, a plate type test piece with a thickness of 1.0 mm and a width of 12.5 mm in a parallel part was obtained so that the longitudinal direction of the test piece was in parallel with the rolling direction. The distance between the gauge marks in this tensile test piece was set to 20 mm, and the tensile test was conducted at the test temperature of 800 °C and a tensile speed of 9 mm/min., so as to measure the elongation at fracture.

[0039] Further, in order to examine the influence of a cross-section reduction rate to the superplasticity characteristics in the cold rolling after the intermediate annealing, the cold-rolled plate with a thickness of 2.0 mm was subjected to the heat treatment in the argon atmosphere at 700 °C for 30 minutes, followed by the cold rolling to a thickness of 1.5 mm or 1.0 mm, and again subjected to the hot treatment in the argon atmosphere at 700 °C for 30 minutes so as to prepare a test specimen. From this test specimen, the plate type test piece with the thickness of 1.0 mm and the width of 12.5mm in the parallel part was obtained, and the same tensile test as described above was conducted to measure the elongation at fracture. Table 2 shows the cross-section reduction rate and the elongations at fracture.

[0040]

[Table 2]

No.	Before intermediate annealing		After intermediate annealing		Elongation rate at fracture (%)
	Plate thickness after cold rolling (mm)	Cross-section reduction rate (%)	Plate thickness after cold rolling (mm)	Cross-section reduction rate (%)	
36	3.50	12.5	-	-	210
37	3.02	24.5	-	-	240
38	2.47	38.3	-	-	360
39	1.99	50.3	-	-	470
40	1.51	62.3	-	-	485
41	2.02	49.5	1.52	24.8	440
42	2.03	49.3	1.05	48.3	425

As shown in Table 2, since all the examples are within a range of the chemical compositions specified in the present invention, the elongation at fracture exceeds 200% and the excellent superplasticity characteristics have been obtained. In particular, the elongation at fracture is increased in accordance with the increase of the cross-section reduction rate, and there is almost no change in the elongation at fracture under a condition that the cross-section reduction rate is 40% or more. Also, from the results of No. 39 and No. 40, it is understood that an excellent elongation at fracture is observed if the cross-section reduction rate before the intermediate annealing is 40% or more, even though the cold rolling rate after the intermediate annealing is low.

Industrial Applicability

[0041] The titanium alloy of the present invention has the sufficient cold workability as well as the excellent superplasticity characteristics. Accordingly, it is possible to easily prepare the coil by the cold rolling, and also to manufacture a material for a super-plastic application having a uniform distribution in a plate thickness. Therefore, the titanium alloy thin plates can be easily manufactured at a low cost, allowing the expansion of the application field for the titanium alloy thin plates.

Claims

1. A titanium alloy consisting of, by mass %, Al of 2.0 to 4.0%, V of 4.0 to 9.0%, Zr of 0 to 2.0%, Sn of 0 to 3.0% and the balance being Ti and impurities.

2. A titanium alloy consisting of, by mass %, Al of 2.0 to 4.0%, V of 4.0 to 9.0%, Zr of 0 to 2.0%, Sn of 0 to 3.0%, further one or more elements selected from Fe of 0.20 to 1.0%, Cr of 0.01 to 1.0%, Cu of 0.01 to 1.0% and Ni of 0.01 to 1.0%, and the balance being Ti and impurities, wherein V_{eq} obtained by the following equation (1) is in a range of 4.0 to 9.5:

$$V_{eq} = V + 1.9Cr + 3.75Fe \quad \cdots (1)$$

where a symbol of element on a right side of the equation (1) means a content of the element by mass %.

3. A method for manufacturing a titanium alloy material consisting of, by mass %, Al of 2.0 to 4.0%, V of 4.0 to 9.0%, Zr of 0 to 2.0%, Sn of 0 to 3.0% and the balance being Ti and impurities, wherein the titanium alloy is subjected to a cold working at a cross-section reduction rate of 40% or more.

4. A method for manufacturing the titanium alloy material consisting of, by mass %, Al of 2.0 to 4.0%, V of 4.0 to 9.0%, Zr of 0 to 2.0%, Sn of 0 to 3.0%, further one or more elements selected from Fe of 0.20 to 1.0%, Cr of 0.01 to 1.0%, Cu of 0.01 to 1.0% and Ni of 0.01 to 1.0%, and the balance being Ti and impurities, wherein the titanium alloy with the V_{eq} obtained by the following equation (1) being in the range of 4.0 to 9.5 is subjected to the cold working at the cross-section reduction rate of 40% or more:

$$V_{eq} = V + 1.9Cr + 3.75Fe \quad \cdots (1)$$

where a symbol of element on the right side of the equation (1) means a content of the element by mass %.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2004/007614

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ C22C14/00, C22F1/18, C22F1/00		
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 C22C14/00		
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 1996-2004 Kokai Jitsuyo Shinan Koho 1971-2004 Toroku Jitsuyo Shinan Koho 1994-2004		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 5-117791 A (Sumitomo Metal Industries, Ltd.), 14 May, 1993 (14.05.93), Full text (Family: none)	1-4
A	JP 4-301044 A (Sumitomo Metal Industries, Ltd.), 23 October, 1992 (23.10.92), Full text (Family: none)	1-4
E, X	JP 2004-183079 A (Sumitomo Metal Industries, Ltd.), 02 July, 2004 (02.07.04), Full text (Family: none)	1-4
☐ 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 application or patent 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 06 July, 2004 (06.07.04)		Date of mailing of the international search report 27 July, 2004 (27.07.04)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 8019502 B [0007]
- JP 8023053 B [0007]

Non-patent literature cited in the description

- **N. FURUSHIRO.** Titanium. Metallurgical Society of AIME, 1980, vol. 80, 993-998 [0007]
- **T. OKA.** What is being studied about titanium materials in Japan?. Iron and Steel Institute of Japan, 01 December 1989, 58-60 [0007]