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(54) **TIAL-BASED ALLOY, PROCESS FOR PRODUCTION OF THE SAME, AND ROTOR BLADE COMPRISING THE SAME**

(57) A hot-forged TiAl-based alloy having excellent oxidation resistance and high strength at high temperatures, and a process for producing such an alloy. A TiAl-based alloy comprising Al: (40+a) atomic % and Nb: b atomic %, with the remainder being Ti and unavoidable impurities, wherein a and b satisfy formulas (1) and (2) below.

$$0 \leq a \leq 2 \quad (1)$$

$$3 + a \leq b \leq 7 + a \quad (2)$$

Also, a TiAl-based alloy comprising Al: (40+a) atomic % and Nb: b atomic %, and further comprising one or more elements selected from the group consisting of V: c atomic %, Cr: d atomic % and Mo: e atomic %, with the remainder being Ti and unavoidable impurities, wherein a to e satisfy formulas (3) to (9) shown below.

$$0 \leq a \leq 2 \quad (3)$$

$$3 + a \leq b + 1.0c + 1.8d + 3.8e \leq 7 + a \quad (4)$$

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$$b \geq 2 \quad (5)$$

$$c \geq 0 \quad (6)$$

$$d \geq 0 \quad (7)$$

$$e \geq 0 \quad (8)$$

$$c+d+e > 0 \quad (9)$$

Description

Technical Field

5 **[0001]** The present invention relates to a TiAl-based alloy, a process for producing the alloy, and a rotor blade that uses the alloy.

Background Art

10 **[0002]** TiAl-based alloys, which are lightweight (with a specific gravity of approximately 4) and exhibit excellent heat resistance, are attracting considerable attention as potential materials for the rotor blades used within gas turbines and Turbo-chargers. Particularly in the case of very large rotor blades, the lighter the weight of the members that constitute the rotor blade, the smaller the centrifugal stress becomes, which enables an increase in the maximum rate of revolution, an increase in the surface area of the rotor blade, and a reduction in the load stress applied to the disc portion.

15 **[0003]** TiAl-based alloys are alloys that are composed mainly of intermetallic compounds such as TiAl and Ti₃Al, which exhibit excellent high-temperature strength, and these alloys therefore have excellent heat resistance. However, TiAl-based alloys have poor casting properties, and because the production of large components by casting is extremely difficult, molding processes that use forging are being researched. Forging processes include isothermal forging using superplastic working, and hot forging. Isothermal forging is a process in which a cast alloy ingot is worked at low speed while being heated at a high temperature. Hot forging is a process in which a cast alloy ingot is heated to a high temperature, and is then worked at high speed while it cools. In the case of hot forging, in order to improve the forgeability of the TiAl-based alloy, a β -phase-stabilizing element such as Cr, V or Mn or the like is added as a third element to generate an elemental composition that precipitates a β -phase that exhibits excellent deformability at high temperature.

20 **[0004]** Patent citation 1 discloses the superplastic working (isothermal forging) of a TiAl-based alloy comprising 43 to 47 atomic % of Al and containing added Cr as a third element. A TiAl-based alloy of this composition is subjected to deformation at a low strain speed that promotes dynamic recrystallization using a plastic working apparatus fitted with a heat retention device, thereby yielding a TiAl-based alloy having a microstructure in which a β -phase has been precipitated at the γ -phase crystal grain boundaries.

25 **[0005]** Patent citation 2 discloses a TiAl-based alloy comprising 40 to 48 atomic % of Al and containing one or more elements selected from among Cr and V as an added third element, and also discloses a TiAl-based alloy comprising 38 to 48 atomic % of Al and containing added Mn as a third element. TiAl-based alloys of the above compositions are subjected to high-speed plastic working (hot forging) to form lamellar grain structures in which an α_2 -phase and a γ -phase are stacked in an alternating manner, thereby improving the high-temperature strength of the TiAl-based alloy.

35 Patent Citation 1: US Patent Publication No. 5,370,839

Patent Citation 2: Japanese Unexamined Patent Application, Publication No. 2001-316743

Disclosure of Invention

40 **[0006]** The superplastic working disclosed in patent citation 1 involves performing plastic working at a low strain speed while maintaining a high temperature, and therefore suffers from poor productivity and has minimal industrial applicability.

[0007] On the other hand, the hot forging disclosed in patent citation 2 enables forge working to be performed using general-purpose equipment in substantially the same manner as typical steel materials, and therefore offers a high degree of productivity and excellent practical applicability.

45 However, although the TiAl-based alloy disclosed in patent citation 2 provides improved high-temperature strength by using hot forging to precipitate lamellar grains, the creep strength is lower than that of cast TiAl-based alloys, and the oxidation resistance also tends to be unsatisfactory. Accordingly, the usable temperature range for this TiAl-based alloy is 650°C or lower.

[0008] The present invention has an object of providing a hot-forged TiAl-based alloy having excellent oxidation resistance and high strength at high temperatures, and a process for producing such an alloy.

50 **[0009]** In order to achieve the above object, the present invention provides a TiAl-based alloy comprising Al: (40+a) atomic % and Nb: b atomic %, with the remainder being Ti and unavoidable impurities, wherein a and b satisfy formulas (1) and (2) below.

55

$$0 \leq a \leq 2 \quad (1)$$

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$$3+a \leq b \leq 7+a \quad (2)$$

5 **[0010]** Further, the present invention also provides a TiAl-based alloy comprising Al: (40+a) atomic % and Nb: b atomic %, and further comprising one or more elements selected from the group consisting of V: c atomic %, Cr: d atomic % and Mo: e atomic %, with the remainder being Ti and unavoidable impurities, wherein a to e satisfy formulas (3) to (9) shown below.

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$$0 \leq a \leq 2 \quad (3)$$

15
$$3+a \leq b+1.0c+1.8d+3.8e \leq 7+a \quad (4)$$

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$$b \geq 2 \quad (5)$$

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$$c \geq 0 \quad (6)$$

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$$d \geq 0 \quad (7)$$

35
$$e \geq 0 \quad (8)$$

40
$$c+d+e > 0 \quad (9)$$

45 **[0011]** As the Al content is increased, the high-temperature strength improve. However, if the Al content is very high, then the β -phase that exhibits excellent deformability at high temperatures either does not precipitate or only precipitates at a higher precipitation temperature range, resulting in a deterioration in the forgeability of the alloy. The TiAl-based alloy of the present invention exhibits a temperature range that yields a two-phase structure composed of an α -phase and a β -phase that can be achieved within the range of temperatures obtainable using general-purpose equipment, and hot forging of the alloy can be conducted within this temperature range. The TiAl-based alloy of the present invention comprises an amount of Nb specified above as a β -phase-stabilizing element, and by reducing the Al content to a value of not less than 40 atomic % and not more than 42 atomic %, which is lower than that used within conventional TiAl-based alloys, an alloy is obtained that exhibits a high degree of high-temperature strength while retaining favorable forgeability. Further, by adding Nb to the alloy, the oxidation resistance can be improved beyond that of conventional hot-forged TiAl-based alloys.

50 **[0012]** V, Cr and Mo, in a similar manner to Nb, are elements that facilitate the formation of a β -phase, and therefore have a significant effect in improving the forgeability of the TiAl-based alloy. By including one or more elements selected from among V, Cr and Mo in an amount specified above in addition to Nb, a TiAl-based alloy that exhibits excellent forgeability is obtained. Moreover, V also contributes to an improvement in the tensile strength at high temperatures. Cr lowers the deformation resistance of the TiAl-based alloy. Mo contributes to an improvement in the creep strength. By including one or more elements selected from among V, Cr and Mo, the alloy performance can be further enhanced.

55 **[0013]** In the present invention, the TiAl-based alloy preferably has a metal structure comprising aligned lamellar grains in which an α_2 -phase and a γ -phase are stacked in an alternating manner. A TiAl-based alloy having a metal structure comprising aligned lamellar grains exhibits a high degree of high-temperature strength.

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[0014] The present invention also provides a process for producing a TiAl-based alloy, the process comprising:

holding a TiAl-based alloy material, comprising Al:

5 (40+a) atomic % and Nb: b atomic %, with the remainder being Ti and unavoidable impurities, wherein a and b satisfy formulas (1) and (2) below,

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$$0 \leq a \leq 2 \quad (1)$$

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$$3 + a \leq b \leq 7 + a \quad (2)$$

at a holding temperature within an equilibrium temperature range for an ($\alpha+\beta$) phase, and subjecting the TiAl-based alloy material held at the holding temperature to high-speed plastic working while cooling to a predetermined final working temperature.

20 **[0015]** Further, the present invention also provides a process for producing a TiAl-based alloy, the process comprising:

holding a TiAl-based alloy material, comprising Al:

25 (40+a) atomic % and Nb: b atomic %, and further comprising one or more elements selected from the group consisting of V: c atomic %, Cr: d atomic % and Mo: e atomic %, with the remainder being Ti and unavoidable impurities, wherein a to e satisfy formulas (3) to (9) shown below,

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$$0 \leq a \leq 2 \quad (3)$$

35
$$3 + a \leq b + 1.0c + 1.8d + 3.8e \leq 7 + a \quad (4)$$

40
$$b \geq 2 \quad (5)$$

45
$$c \geq 0 \quad (6)$$

50
$$d \geq 0 \quad (7)$$

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$$e \geq 0 \quad (8)$$

$$c + d + e > 0 \quad (9)$$

at a holding temperature within an equilibrium temperature range for an ($\alpha+\beta$) phase, and subjecting the TiAl-based alloy material held at the holding temperature to high-speed plastic working while cooling to a predetermined final working temperature.

[0016] The TiAl-based alloy having the composition described above exhibits an ($\alpha+\beta$) phase equilibrium range at high temperature, and because the alloy also contains one or more elements selected from among V, Cr and Mo, as well as Nb, the β -phase precipitates in a stable manner. The TiAl-based alloy material is held at a temperature within the equilibrium temperature range for the ($\alpha+\beta$) phase, which ensures that the β -phase that exhibits superior high-temperature deformability exists in a stable state, while the alloy is subjected to high-speed plastic deformation, and therefore the workability of the alloy is favorable. Further, by completing the high-speed plastic working in the period during which the temperature cools from the holding temperature within the equilibrium temperature range for the ($\alpha+\beta$) phase to a final working temperature, a multitude of strains are introduced into the alloy. These strains act as origins that induce dynamic recrystallization, which eventually leads to the formation of a metal structure in which fine lamellar grains are aligned. Producing a metal structure in which these lamellar grains exist means the TiAl-based alloy exhibits a high degree of high-temperature strength.

[0017] In the present invention, provided the aforementioned holding temperature is not less than 1150°C and not more than 1350°C, an ($\alpha+\beta$) phase can be precipitated stably within the metal structure.

[0018] In the present invention, provided the final working temperature is not less than 1150°C, a high level of deformability that enables high-speed plastic working can be maintained. If the final working temperature is less than 1150°C, then the deformability tends to deteriorate, and there is a possibility that cracks may appear in the TiAl-based alloy material.

[0019] In the present invention, a forging process can be used for the aforementioned high-speed plastic working.

[0020] A rotor blade that uses the above TiAl-based alloy exhibits excellent high-temperature strength and oxidation resistance, and is capable of withstanding use at temperatures of 650°C or higher.

[0021] The present invention is able to provide a TiAl-based alloy that exhibits high levels of high-temperature strength and oxidation resistance, as well as excellent forgeability.

A rotor blade that uses the TiAl-based alloy of the present invention exhibits excellent high-temperature strength and oxidation resistance, and can therefore be used in operating environments of 650°C or higher. Further, because the TiAl-based alloy of the present invention exhibits favorable forgeability, it is able to be molded within a comparatively short time period.

Best Mode for Carrying Out the Invention

[0022] A TiAl-based alloy according to a first embodiment of the present invention comprises Al: (40+a) atomic % and Nb: b atomic %, with the remainder being Ti and unavoidable impurities, wherein a and b satisfy formulas (1) and (2) below.

$$0 \leq a \leq 2 \quad (1)$$

$$3 + a \leq b \leq 7 + a \quad (2)$$

[0023] The TiAl-based alloy of the composition described above comprises Al in a fraction of not less than 40 atomic % and not more than 42 atomic %. If the Al content is less than 40 atomic %, then the high-temperature strength deteriorates. If the Al content exceeds 42 atomic %, then the forgeability deteriorates.

[0024] Because it also comprises Nb, the TiAl-based alloy of this first embodiment exhibits excellent oxidation resistance. Nb also has an effect of causing stable precipitation of a β -phase within a high-temperature range. Because the β -phase has a high degree of deformability at high temperature, stable precipitation of the β -phase results in improved forgeability. Further, precipitation of the β -phase facilitates the formation of a lamellar structure (for example, a fine lamellar structure with an average grain size of 1 to 50 μm) during the cooling step. Accordingly, the high-temperature strength of the alloy following forging, and particularly the creep strength, can be improved. If the Nb content becomes overly high, then in contrast, precipitation of a lamellar structure actually becomes less likely, and the high-temperature strength deteriorates. By ensuring that the Nb content satisfies the fraction described above, a TiAl-based alloy having excellent high-temperature strength and favorable forgeability can be obtained.

[0025] A TiAl-based alloy according to a second embodiment of the present invention comprises Al: (40+a) atomic % and Nb: b atomic %, and further comprises one or more elements selected from the group consisting of V: c atomic %, Cr: d atomic % and Mo: e atomic %, with the remainder being Ti and unavoidable impurities, wherein a to e satisfy formulas (3) to (9) shown below.

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$$0 \leq a \leq 2 \quad (3)$$

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$$3 + a \leq b + 1.0c + 1.8d + 3.8e \leq 7 + a \quad (4)$$

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$$b \geq 2 \quad (5)$$

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$$c \geq 0 \quad (6)$$

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$$d \geq 0 \quad (7)$$

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$$e \geq 0 \quad (8)$$

$$c + d + e > 0 \quad (9)$$

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[0026] V, Cr and Mo, in a similar manner to Nb, are elements that facilitate the formation of a β -phase. If the β -phase precipitating effect of Nb is defined such that a Nb equivalent is the effect provided by a Nb amount of b (atomic %), then the Nb equivalents of each of these other elements are as follows.

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$$V: b = 1.0c$$

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$$Cr: b = 1.8d$$

$$Mo: b = 3.8e$$

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In other words, the β -phase precipitating effect of V is the same as that of Nb. Further, the β -phase precipitating effects of Cr and Mo are, respectively, 1.8 times and 3.8 times that of Nb, meaning a β -phase can be precipitated stably through addition of a smaller amount of the element than Nb.

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[0027] Besides this β -phase stable precipitation effect, V also has an effect of improving the tensile strength at high temperatures. Cr has an effect of lowering the deformation resistance of the TiAl-based alloy, thereby further improving the forgeability. Mo has an effect of further improving the creep strength.

[0028] In consideration of the forgeability and the high-temperature strength, the amounts of Nb, V, Cr and Mo are preferably set within the fraction ranges described above.

[0029] A process for producing the TiAl-based alloys according to the first and second embodiments described above using hot forging is described below.

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First, a TiAl-based alloy material (such as an ingot) having a composition that satisfies one of the compositions described above is prepared by melting.

[0030] The TiAl-based alloy material is then heated in a heavy oil furnace or the like, and held for a long time at a holding temperature within the equilibrium temperature range for an (α + β) phase. This step causes the precipitation of

an α -phase and a β -phase within the metal structure. In the case of a TiAl-based alloy having a composition described above, the holding temperature is within a range from 1150 to 1350°C.

5 [0031] The TiAl-based alloy material that has been held at the holding temperature is then removed from the furnace and subjected to high-speed plastic working, using a general-purpose hydraulic press or the like, while the temperature of the alloy material is still within the (α + β) phase equilibrium temperature range. By performing high-speed plastic working during the cooling step, strains are introduced into the α -phase. Dynamic recrystallization occurs with these strains acting as origins, resulting in the formation of fine lamellar grains in which an α_2 -phase and a γ -phase are stacked in an alternating manner. The γ -phase precipitates from the β -phase during the cooling step, forming an equiaxed microstructure. In the case of a TiAl-based alloy of the composition described above, provided the final working temperature is not less than 1150°C, the plastic working can be performed in a state where the alloy contains a precipitated β -phase that exhibits superior deformability. If the final working temperature is less than 1150°C, then the deformability deteriorates, and cracking of the alloy material may occur. Furthermore, if the cooling rate is too fast, then a massive transformation may occur, preventing formation of a lamellar structure, whereas if the cooling rate is too slow, then the lamellar spacing tends to broaden, resulting in reduced material strength. The cooling rate is preferably set within a range from approximately 50 to 700°C/minute.

10 [0032] A rotor blade produced using a TiAl-based alloy of one of the above embodiments exhibits excellent high-temperature strength and superior oxidation resistance at high temperatures. The rotor blade is produced using the procedure outlined below.

20 First, a TiAl-based alloy material (such as an ingot) having a composition according to the first or second embodiment described above is prepared by melting. The TiAl-based alloy material is then subjected to hot open die forging, thereby improving the forgeability during the die forging performed in a later step. Subsequently, the alloy material is cut into a rod shape, forming a rough preform for die forging of the rotor blade. In those cases where cost is a very important factor, production of the rough preform may be conducted by preparing a rod-shaped TiAl-based alloy material by melting. In order to facilitate formation of the final blade shape, the rod shape is preferably worked into a dog bone-shaped rod.

25 [0033] In the die forging step, the rod-shaped TiAl-based alloy material is heated in a heavy oil furnace or the like, and held at a holding temperature within the equilibrium temperature range for an (α + β) phase. Immediately following removal of the alloy material from the furnace, the forging preform is molded by die forging using a general-purpose hammer press. In order to prevent thermal deformation from occurring during the cooling step conducted following die forging, the cooling is conducted gradually, either inside an insulating material, or within a low-temperature oven at a temperature of approximately 600°C. Finally, the forged product is molded into the shape of the rotor blade by cutting work or the like.

30 [0034] A TiAl-based alloy according to one of the embodiments of the present invention exhibits excellent forgeability, and therefore large members such as rotor blades can be formed in a short period of time via a relatively simple process.

35 EXAMPLES

(Example 1)

40 [0035] TiAl-based alloy ingots comprising the components listed for example 1-1 to example 1-4 in Table 1 were produced by casting. Each ingot was cut to predetermined dimensions and subjected to surface machining, yielding a columnar TiAl-based alloy material having a diameter of 80 mm and a height of 60 mm.

45 [0036] Each TiAl-based alloy material was heated and held at 1300°C inside a heavy oil furnace. Following holding at this temperature, the TiAl-based alloy material was removed from the heavy oil furnace, and subjected to upset forging at a forging ratio of 3s, using a general-purpose 300-ton hydraulic press. The operation from removal of the TiAl-based alloy material from the furnace until completion of the forging was completed within 10 seconds. Following forging, the alloy material was cooled by atmospheric cooling on top of a steel trestle. A post-forging heat treatment was performed by subjecting the forged material to stress removal annealing for 24 hours at 800°C using a muffle furnace.

(Comparative example)

50 [0037] TiAl-based alloy ingots comprising the components listed for comparative example 1-1 to example 1-9 in Table 1 were produced by casting. Each ingot was cut and subjected to surface machining, yielding a columnar TiAl-based alloy material having a diameter of 80 mm and a height of 60 mm. Using the same procedure as that described for example 1, each TiAl-based alloy material was subjected to forging and post-forging stress removal annealing.

55 (Examples 2 to 5)

[0038] TiAl-based alloy ingots comprising the components listed for example 2 to example 5 in Table 1 were produced

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by casting. Each ingot was cut and subjected to surface machining, yielding a columnar TiAl-based alloy material having a diameter of 80 mm and a height of 60 mm. Using the same procedure as that described for example 1, the TiAl-based alloy material of example 2 was subjected to forging and post-forging stress removal annealing.

[0039] Each TiAl-based alloy was evaluated for forgeability, and tested for creep strength and oxidation resistance.

5 The forgeability evaluation was conducted by visually checking the forged ingot for the presence of cracks. If no cracks were observed, the forgeability was evaluated as good (o), whereas if cracks were visible, the forgeability was evaluated as poor (x).

10 The creep strength test was performed by cutting a test specimen from the annealed ingot, and then testing the specimen at a test temperature of 760°C and a load stress of 311 MPa. If the creep rupture time was 25 hours or longer, the high-temperature strength was evaluated as good (o), whereas if the creep rupture time was less than 25 hours, the high-temperature strength was evaluated as poor (x).

15 The oxidation resistance test was performed by cutting a cubic test specimen having a length along one side of 2.8 mm from the annealed ingot, heating the test specimen for 50 hours at 870°C, and then comparing the oxidation weight increase per unit of surface area. If the oxidation weight increase was not more than 0.01 g/mm², the oxidation resistance was evaluated as good (o), whereas if the oxidation weight increase exceeded 0.01 g/mm², the oxidation resistance was evaluated as poor (x).

[0040]

20 [Table 1]

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	Amount of added component (at%)				Evaluation and test results				Evaluations		
	Al	Nb	V	Cr	Mo	Cracking upon forging	Creep rupture time (hours)	Oxidation weight increase (g/mm ²)	Forgeability	High-temperature strength	Oxidation resistance
Example 1-1	40	3	—	—	—	No	41.6	0.0016	o	o	o
Comparative example 1-1	39	3	—	—	—	No	15.5	0.0015	o	x	o
Comparative example 1-2	40	2	—	—	—	Yes	12.8	0.0022	x	x	o
Example 1-2	40	7	—	—	—	No	85.4	0.0011	o	o	o
Comparative example 1-3	39	7	—	—	—	No	15.5	0.0012	o	x	o
Comparative example 1-4	40	8	—	—	—	No	10.2	0.00092	o	x	o
Example 1-3	42	5	—	—	—	No	65.7	0.0012	o	o	o
Comparative example 1-5	43	5	—	—	—	Yes	78.2	0.0013	x	o	o
Comparative example 1-6	42	4	—	—	—	Yes	58.6	0.0013	x	o	o
Example 1-4	42	9	—	—	—	No	94.5	0.00096	o	o	o
Comparative example 1-7	43	9	—	—	—	Yes	112.0	0.00092	x	o	o
Comparative example 1-8	42	10	—	—	—	No	20.4	0.00085	o	x	o
Comparative example 1-9	42	—	8	—	—	No	12.0	0.017	o	x	x
Example 2	42	4	4	—	—	No	94.4	0.0053	o	o	o
Example 3	42	2	6	—	—	No	40.8	0.0089	o	o	o
Example 4	42	4	—	2	—	No	25.4	0.0016	o	o	o
Example 5	42	4	—	—	0.5	No	171.0	0.0015	o	o	o

[0041] The TiAl-based alloys of examples 1-1 to 1-4 each adopted a metal structure containing precipitated lamellar grains, and exhibited a high degree of high-temperature strength. Further, compared with the TiAl-based alloys of comparative examples 1 to 9 which did not contain Nb, the oxidation resistance improved dramatically.

[0042] When the Al content was less than 40 atomic %, the creep rupture time decreased (comparative example 1-1 and comparative example 1-3). When the Al content exceeded 42 atomic %, the creep rupture time lengthened and the high-temperature strength was favorable, but cracking existed in the forged product (comparative example 1-5 and comparative example 1-7).

In those cases where the Nb content satisfied the inequality formula $b < 3 + a$, cracking existed in the forged product

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(comparative example 1-2 and comparative example 1-6). When the Nb content satisfied the inequality formula $b > 7 + a$, the creep rupture time decreased (comparative example 1-4 and comparative example 1-8).

[0043] The TiAl-based alloys of example 2 to example 5 each exhibited favorable levels of forgeability, high-temperature strength and oxidation resistance.

5 **[0044]** The results of a deformation resistance measurement, a tensile test, a creep strength test and an oxidation resistance test performed for the TiAl-based alloys of example 1-1 and examples 2 to 5 are shown in Table 2. The deformation resistance measurement was performed by cutting a circular columnar test specimen having a diameter of 7.7 mm and a length of 12 mm from the annealed ingot, and then holding the test specimen at a temperature of 1250°C using high-frequency heating, while conducting deformation at a deformation rate of 100 mm/second. The tensile test
10 was performed by cutting a test specimen having a total length of 60 mm, an evaluation section diameter of 4 mm and an evaluation section length of 20 mm from the annealed ingot, and then performing the tensile test at 700°C in an open atmosphere.

[0045]

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[Table 2]

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	Amount of added component (at%)						Evaluation and test results			
	Al	Nb	V	Cr	Mo		Deformation resistance (MPa)	Tensile breaking strength (MPa)	Creep rupture time (hours)	Oxidation weight increase (g/mm ²)
Example 1-1	42	3	—	—	—		165	440	41.6	0.0016
Example 2	42	4	4	—	—		190	802	94.4	0.0053
Example 3	42	2	6	—	—		151	852	40.8	0.0089
Example 4	42	4	—	2	—		129	828	25.4	0.0016
Example 5	32	4	—	—	0.5		328	812	171	0.0015

55 **[0046]** Examples 2 and 3 which comprised V exhibited improved tensile breaking strength compared with example 1-1. Example 4 which comprised Cr exhibited reduced deformation resistance. In other words, the deformability at high temperatures improved. Example 5 which comprised Mo exhibited a significant increase in the creep strength.

Claims

1. A TiAl-based alloy comprising
 Al: (40+a) atomic % and
 Nb: b atomic %,
 with a remainder being Ti and unavoidable impurities,
 wherein
 a and b satisfy formulas (1) and (2) below:

$$0 \leq a \leq 2 \quad (1),$$

and

$$3 + a \leq b \leq 7 + a \quad (2).$$

2. A TiAl-based alloy comprising
 Al: (40+a) atomic % and
 Nb: b atomic %, and further comprising
 one or more elements selected from the group consisting of
 V: c atomic %,
 Cr: d atomic % and
 Mo: e atomic %,
 with a remainder being Ti and unavoidable impurities,
 wherein
 a to e satisfy formulas (3) to (9) shown below:

$$0 \leq a \leq 2 \quad (3),$$

$$3 + a \leq b + 1.0c + 1.8d + 3.8e \leq 7 + a \quad (4),$$

$$b \geq 2 \quad (5),$$

$$c \geq 0 \quad (6),$$

$$d \geq 0 \quad (7),$$

$$e \geq 0 \quad (8)$$

and

$$c+d+e>0 \quad (9) .$$

5 3. The TiAl-based alloy according to claim 1 or 2, having a metal structure comprising aligned lamellar grains in which an α_2 -phase and a γ -phase are stacked in an alternating manner.

4. A process for producing a TiAl-based alloy, the process comprising:

10 holding a TiAl-based alloy material, comprising
Al: (40+a) atomic % and
Nb: b atomic %,
with a remainder being Ti and unavoidable impurities, wherein a and b satisfy formulas (1) and (2) below:

$$15 \quad 0 \leq a \leq 2 \quad (1)$$

and

$$20 \quad 3+a \leq b \leq 7+a \quad (2)$$

25 at a holding temperature within an equilibrium temperature range for an ($\alpha+\beta$) phase, and
subjecting the TiAl-based alloy material held at the holding temperature to high-speed plastic working while
cooling to a predetermined final working temperature.

5. A process for producing a TiAl-based alloy, the process comprising:

30 holding a TiAl-based alloy material, comprising
Al: (40+a) atomic % and
Nb: b atomic %, and further comprising
one or more elements selected from the group consisting of
35 V: c atomic %,
Cr: d atomic % and
Mo: e atomic %,
with a remainder being Ti and unavoidable impurities, wherein a to e satisfy formulas (3) to (9) shown below:

$$40 \quad 0 \leq a \leq 2 \quad (3) ,$$

$$45 \quad 3+a \leq b+1.0c+1.8d+3.8e \leq 7+a \quad (4) ,$$

$$50 \quad b \geq 2 \quad (5) ,$$

$$c \geq 0 \quad (6) ,$$

$$55 \quad d \geq 0 \quad (7) ,$$

$$e \geq 0 \quad (8)$$

5 and

$$c+d+e > 0 \quad (9)$$

10 at a holding temperature within an equilibrium temperature range for an ($\alpha+\beta$) phase, and
subjecting the TiAl-based alloy material held at the holding temperature to high-speed plastic working while
cooling to a predetermined final working temperature.

- 15 **6.** The process for producing a TiAl-based alloy according to claim 4 or claim 5, wherein
the holding temperature is not less than 1150°C and not more than 1350°C.
- 7.** A process for producing a TiAl-based alloy according to any one of claim 4 to claim 6, wherein
the final working temperature is not less than 1150°C.
- 20 **8.** A process for producing a TiAl-based alloy according to any one of claim 4 to claim 7, wherein
a forging process is used for the high-speed plastic working.
- 9.** A rotor blade that uses the TiAl-based alloy according to any one of claim 1 to claim 3.

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EP 2 251 445 A1

INTERNATIONAL SEARCH REPORT

International application No. PCT/JP2009/051539
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<p>A. CLASSIFICATION OF SUBJECT MATTER <i>C22C14/00</i>(2006.01)i, <i>B21J5/00</i>(2006.01)i, <i>B21K3/04</i>(2006.01)i, <i>C22F1/18</i>(2006.01)i, <i>F01D5/28</i>(2006.01)i, <i>F02C7/00</i>(2006.01)i, <i>C22F1/00</i>(2006.01)n</p> <p>According to International Patent Classification (IPC) or to both national classification and IPC</p>																				
<p>B. FIELDS SEARCHED</p> <p>Minimum documentation searched (classification system followed by classification symbols) <i>C22C1/00-49/14</i>, <i>C22F1/00-3/02</i>, <i>B21J5/00</i>, <i>B21K3/04</i>, <i>F01D5/28</i>, <i>F02C7/00</i>, <i>C22F1/00</i></p> <p>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 1996-2009 Kokai Jitsuyo Shinan Koho 1971-2009 Toroku Jitsuyo Shinan Koho 1994-2009</p> <p>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)</p>																				
<p>C. DOCUMENTS CONSIDERED TO BE RELEVANT</p> <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X A</td> <td>JP 6-116691 A (Mitsubishi Materials Corp.), 26 April, 1994 (26.04.94), Claims; Par. Nos. [0002], [0031] (Family: none)</td> <td>2, 9 1, 3-8</td> </tr> <tr> <td>A</td> <td>JP 6-33172 A (Sumitomo Light Metal Industries, Ltd.), 08 February, 1994 (08.02.94), Full text & US 5451366 A & EP 580081 A1</td> <td>1-9</td> </tr> <tr> <td>A</td> <td>JP 5-320791 A (Mitsubishi Heavy Industries, Ltd.), 03 December, 1993 (03.12.93), Full text (Family: none)</td> <td>1-9</td> </tr> </tbody> </table> <p><input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.</p> <p>* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "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 "E" earlier application or patent but published on or after the international filing date "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 "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) "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 "O" document referring to an oral disclosure, use, exhibition or other means "&" document member of the same patent family "P" document published prior to the international filing date but later than the priority date claimed</p> <table border="1"> <tr> <td>Date of the actual completion of the international search 02 April, 2009 (02.04.09)</td> <td>Date of mailing of the international search report 14 April, 2009 (14.04.09)</td> </tr> <tr> <td>Name and mailing address of the ISA/ Japanese Patent Office</td> <td>Authorized officer</td> </tr> <tr> <td>Facsimile No.</td> <td>Telephone No.</td> </tr> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X A	JP 6-116691 A (Mitsubishi Materials Corp.), 26 April, 1994 (26.04.94), Claims; Par. Nos. [0002], [0031] (Family: none)	2, 9 1, 3-8	A	JP 6-33172 A (Sumitomo Light Metal Industries, Ltd.), 08 February, 1994 (08.02.94), Full text & US 5451366 A & EP 580081 A1	1-9	A	JP 5-320791 A (Mitsubishi Heavy Industries, Ltd.), 03 December, 1993 (03.12.93), Full text (Family: none)	1-9	Date of the actual completion of the international search 02 April, 2009 (02.04.09)	Date of mailing of the international search report 14 April, 2009 (14.04.09)	Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer	Facsimile No.	Telephone No.
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Patent documents cited in the description

- US 5370839 A [0005]
- JP 2001316743 A [0005]